A COMPARISON OF SOIL NITROGEN AVAILABILITY ALONG HILLSLOPES FOR A PREVIOUSLY MINED RECLAIMED WETLAND AND TWO NATURAL WETLANDS IN FORT MCMURRAY, ALBERTA

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements for the Degree Master of Science

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Abstract

In situ measurements of soil nitrogen dynamics is a potential method for evaluating the health of constructed wetlands following oil sands mining. The objective of this study is to measure and compare the soil nitrogen availability of a reclaimed fen (Sandhill fen) with a nutrient-rich reference fen (Poplar fen) and a nutrient-poor reference fen (Pauciflora fen) in the Athabasca oil sands region of northern Alberta. Total Nitrogen (TN), Nitrate (NO₃⁻) and Ammonium (NH₄⁺) supply rates were determined along wetland hillslope transects using Western Ag Innovations Plant Root Simulator (PRSTM) probes at all three sites in 2014. Net N mineralization, net nitrification and net ammonification were determined simultaneously using the buried polyethylene bag sampling method. Overall, TN supply rates were greatest at the poor fen and least at the constructed Sandhill fen. In contrast, mineralization was greatest at the rich fen but again least at the Sandhill fen. Mineralization at the Sandhill fen was controlled evenly by ammonification and nitrification, whereas the two natural sites were controlled by ammonification. Relatively low N supply rates and mineralization at the Sandhill fen were likely due to lower soil organic matter and limited soil moisture in these newly constructed substrates. Spatial differences along the hillslopes also varied among sites. The Sandhill fen had higher TN supply rates at the upslope positions but no significant differences in net N mineralization rates along the hillslopes. The rich fen also had higher TN supply rates at the upslope but greatest mineralization rates downslope. These results highlight the importance of N storage and transport processes and offer insight into the N status of a constructed fen.

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SECTION 1 – INTRODUCTION

The Athabasca oil sands deposit in northern Alberta is economically significant to Canada as it is one of the largest reserves of recoverable oil in the world. An estimated 52.5 billion barrels of heavy crude oil out of a total 1897 billion barrels can be extracted through open pit mining (Bellows & Bohme, 1963; Brandt et al., 2013). While this is beneficial to Canada's economy, open pit mining threatens many aspects of the environment such as species habitats, ecosystem integrity and water quality. Recognizing the consequences of such widespread disturbance, the Alberta government legally requires companies participating in oil extraction to restore landscapes to equivalent land capability (Alberta Regulation 115/1993).

As of 2013, only 0.1 % of the total disturbed area is undergoing active reclamation (Alberta Government, 2012). The majority of these projects involve the reforestation of terrestrial environments in an effort to rebuild specific upland boreal ecosystems. In recent years, however, reclamation has begun focussing on wetland reconstruction due to the abundance and importance of these systems to the boreal forest. Wetland environments offer many important ecosystem services such as carbon sequestration and diverse species habitat. Certain wetlands have the unique ability to accumulate organic soil through time, called peat. This accumulation is very slow, taking thousands of years to reach depths of only several meters (Hugron et al., 2013). Therefore recreating these peatlands is challenging and requires extensive research and monitoring.

Syncrude Canada Ltd. (SCL) initiated one of the first wetland reclamation projects of its kind, called the Sandhill Fen Watershed (called simply Sandhill in this

document; see Wytrykush et al., 2012 and Vitt and Bhatti, 2012 for details). Tailings sand was used to build small hills surrounding wetland peat soil, which was imported from elsewhere on Syncrude property. The purpose for this design was to encourage the natural subsurface flow of pore water consisting of both tailings and fresh water. Since commissioning in 2012, this site has undergone extensive monitoring in an effort to understand the functionality of a reconstructed wetland.

Soil biogeochemistry is one of many important factors that must be considered when determining the success of Sandhill. Both plants and microbes rely on an adequate supply of soil nutrients for survival, thus an understanding of nutrient availability offers insight into organism productivity. The majority of plants are outcompeted by soil microbes for access to important macronutrients such as Nitrogen (N). N enters the soil in its organic form, which is unavailable to plants until converted through microbial enzymatic processes into plant-available inorganic N: nitrate (NO₃⁻) and ammonium (NH₄⁺). This process is called mineralization and is considered one of the most important pathways of N conversion for plant uptake. Conversely, immobilization occurs when microbes are N limited and must use plant-available inorganic N, thus rendering this N unavailable to plants (Schlesinger and Bernhardt, 2013). Since N is required for metabolic pathways, enzymes, proteins and chlorophyll, it is widely considered the most growth-limiting nutrient to plants, particularly in boreal ecosystems (McMillan et al., 2007; Hanselman et al., 2004; Hemstock et al., 2010; Harrison and Maynard, 2014).

Plant root exposure to NO_3^- and NH_4^+ is often quantified as a supply rate within the rhizosphere (Harrison and Maynard, 2014; Qian and Schoenau, 2002). Patterns of N supply rates are informative about the health and functionality of the soil; yet are difficult

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to measure. There is a method involving ion exchange resins that adsorb nutrients as a dynamic flux rather than a cumulative static quantity. Plant Root Simulator (PRS) probes were developed as a commercial product by Western Ag. Innovations for application of this method. The probes are widely used in agricultural studies (e.g. Davenport and Schiffhauer, 2007; Qian and Schoeanau, 2007; Thavarajah et al., 2003), but so far there has been minimal application in reclaimed wetland environments.

The objective of this study was to measure soil N (TN, NO_3^- , and NH_4^+) availability along the surrounding wetland hillslopes at the Sandhill Fen and compare with two natural boreal fens: a nutrient rich fen (Poplar Fen) and nutrient poor fen (Pauciflora Fen). Within this broad scope of analysis the following questions are addressed:

- 1. Is there seasonality associated with soil N availability throughout the growing months (May August) at the three sites?
- 2. How does the N availability at the dry upslopes, transitional midslopes, and wet downslopes compare within and among the three sites?
- 3. What is the relationship between N availability and soil properties at each site, and do these relationships differ among sites?

Warmer temperatures increase plant and microbial activity, which generally occurs in the middle of the growing season. Therefore, it is hypothesized that all sites will have experienced similar patterns of seasonality (i.e. the highest net N mineralization and supply rates occurring mid-summer). Typically, nutrient rich fens experience greater nutrient supply and mineralization rates, particularly in the wetter lowland regions. Soils at the Sandhill fen have undergone disturbances that have likely interrupted N recycling

processes and therefore may have exhibited patterns commonly associated with nutrient poor sites or other types of disturbed environments. Thus, it is hypothesized that N availability and transformations will have differed between Sandhill and the two natural wetlands. Finally, it is expected that mineralization will have been greater in the wet lowland regions for all three sites given that this hillslope position demonstrates characteristics conducive for N production (i.e. high soil moisture and organic content).

Ultimately, the purpose of this study was to better understand the biogeochemical properties of a reconstructed wetland for the benefit of future oil sands reclamation projects. A special focus on the soil N status is necessary because it is one of the most important soil nutrients for plant and microbial growth. To date, however, there is a limited understanding of the efficacy of oil sands reclamation in terms of N cycling. Furthermore, incorporating natural reference sites into this reclamation study is critical for contextualization. The N status of natural boreal wetlands has been well researched, especially since the commencement of open pit oil sands mining (Bridgham et al., 1996; Bridgham et al., 1998; Jonasson and Shaver, 1999; Nordbakken et a., 2003; Weedon et al., 2012; Wieder and Vitt, 2006; Wray and Bayley, 2007). However, N supply and mineralization rates are variable over time due to climate change and landscape disturbance (Hemstock et al., 2010; Weedon et al., 2012). This region in particular is vulnerable to such variability due to oil sands disturbances and therefore requires continuing attention. As a result, this study not only benefits the Sandhill Fen pilot study and reclamation practices in general, but also offers additional insight into the N status of natural boreal fens.

SECTION 2 - LITERATURE REVIEW

2.1 Boreal Wetlands

Wetland ecosystems have a relatively small global area of $12.8 \times 10^6 \text{ km}^2$ or <0.1 % of Earth's total land surface area (Mitsch and Gosselink, 2000). In the 1980's it was estimated that 18 % of Canadian landscapes were classified as wetland ecosystems (Zoltai and Pollet, 1983). Unfortunately, due to human impact and climate change, this number has been reduced to approximately 14 % by 2010 (Environment Canada, 2010). Despite this overall decrease in area, wetlands still supply up to 15 % of terrestrial productivity and store over half of Earth's soil carbon (Roulet, 2000).

Wetlands can be defined as systems that support hydrophilic vegetation, maintain wet soils with a water table at or above the mineral soil during the growing season, and have areas of open water (Roulet, 2000; Zoltai and Pollet, 1983). A wetland is a term used to describe a broad spectrum of ecosystems that offer a variety of different services. Peatlands are a subset of wetland environments where detritus of hydrophilic vegetation accumulates in anoxic conditions below the surface. The accumulation of organic detritus must be at least 40 cm in depth to be considered a peatland and may reach up to 2 meters depending on climate and geography (Gorham, 1991; Zoltai and Pollet, 1983). The rate of decomposition of organic material is less than plant growth, thus boreal peatlands are net sinks of carbon dioxide (CO₂) and therefore a critical component in the global carbon cycle. In the last 12 000 years approximately 500 x 10^{15} g of organic carbon (Gorham, 1991, M. Waddington, personal communication 2015) has accumulated in these northern peatlands (Moore et al., 1998).

There are four basic classes of wetlands that involve variations of peat abundance and water tables: bogs, fens, marshes, and swamps. Bogs have water tables below the surface throughout the majority of the year with a rise in water level to the surface during the spring thaw (Zoltai and Pollet, 1983). They are acidic ombrotrophic (rain-fed) peatlands dominated by *Sphagnum* mosses with low alkalinity and low availability of important base cations in surface waters (Bedford et al., 1999). Bogs have closed drainage thus only experience recharge through precipitation and runoff (Schlesinger and Bernhardt, 2013).

Fens are wetlands that have water tables at or below the surface. Fens produce and decompose peat at different rates depending on acidity and amount of minerotrophic drainage (Bedford et al., 1999). Nutrient poor fens are similar to bogs in that they are *Sphagnum* dominated, acidic peatlands whereas nutrient rich fens are dominated by brown mosses and sedges and receive relatively more groundwater and surface water inputs (Trites and Bayley, 2009). Rich fens are alkaline and have more base cations than bogs and poor fens, likely due to increased recharge (Bedford et al., 1999). However fens usually exist where drainage is relatively restrictive and therefore demonstrate low rates of oxygen saturation. Drainage and nutrient transport across most fens are slow due to low slope gradients of approximately 1-3° (Zoltai and Pollet, 1983). Fens and bogs are the only wetland classes that provide appropriate conditions for substantial peat accumulation (Vitt, 2006; Zoltai and Vitt, 1995). Maintaining an active understanding of fens and bogs is especially important for boreal regions because of their relatively large surface area and biodiversity (Vitt and Bhatti, 2012).

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Swamps and marshes develop on shallow peat or mineral soils and are not regarded as significant peat-accumulating ecosystems (Vitt, 2006; Zoltai and Vitt, 1995). Swamps may have standing water that persists longer than the growing season and may allow channels of flowing water showing subsurface water flow. Oxygen saturation and nutrient availability is enhanced due to increased transport and mixing (Zoltai and Pollet, 1983). Out of all the wetland classes, marshes sustain the highest and most prolonged standing water. The substrate comprises of organic soils and negligible peat accumulation. Due to the gravitational water table and interchanging channels of flowing water, these soils have high counts of mineral nutrients and oxygen saturation (Zoltai and Pollet, 1983).

2.2 Nitrogen

2.2.1 Nitrogen cycle

The atmosphere holds the greatest portion of Earth's nitrogen content (Trenberth and Guillemot, 1994). Soil organic matter (SOM) up to 1 m depth can hold as much as 1.4×10^{17} g of N, whereas terrestrial biomass only holds an averaged 3.8×10^{15} g (Batjes 2014; Post et al., 1985). Atmospheric N₂ is unavailable to plants because of its inert triple bond, which requires a considerable amount of energy (226 kcal/mole) to break (Davies, 1972; Schlesinger and Bernhardt, 2013).

Approximately 15 % of plant available N is provided by fixation from the atmosphere, and the rest from internal recycling and decomposition (Schlesinger and Bernhardt, 2013). Soil microorganisms decompose organic residue and metabolize organic N to produce inorganic N in the form of NH_4^+ ; a process called ammonification.

This involves an enzymatic breakdown of large C—H and C—NH₂ bonds through deaminases and hydrolases occurring both intra- and extra-cellularly (Brady and Weil, 2008). There are three types of microorganisms that function simultaneously to metabolize N in the soil: aerobic microorganisms, anaerobic microorganisms and facultative bacteria (which are both aerobic and anaerobic) (Brady and Weil, 2008). This newly available NH₄⁺ is either taken up by plants, lost through leaching or volatilization, or oxidized by chemoautotrophic bacteria (called *Nitrosomonas* and *Nitrobacter*) to form NO₃⁻; a process called nitrification (Meyer, 1994; Pedersen et al., 1999).

Ammonification and nitrification can be grouped together as a single process called mineralization (1):

$$R \longrightarrow ^{+2H_2O} OH^- + R \longrightarrow OH + NH_4^+ \rightarrow 4H^+ + energy + NO_2^- \rightarrow energy + NO_3^-$$
(1)

Mineralization rates have been widely studied in many different soil types because it provides a frequency at which organic nutrients are converted into plant available nutrients (Braskerud, 2002; Fellman and D'Amore, 2007; Harrison and Maynard, 2014; McMillan et al., 2007; Qian and Schoenau, 1995). Optimal decomposition and mineralization conditions maintain near neutral pH, warm temperatures (+25°C), sufficient aeration, adequate soil moisture (pore space consisting of ~60 % water), and low C/N ratio in organic residue (Booth et al., 2005; Brady and Weil, 2008; Bramley and White 1990; Hartley and Schlesinger, 2000; Perakis and Sinkhorn, 2011; Robertson, 1982; Rosswall, 1982; Wetselaar, 1968). If the organic material has a C/N ratio greater than 25:1, microbes are forced to use soil N to metabolize the carbon from the organic matter, which ultimately affects the amount of N available for plant uptake (Brady and Weil, 2008).

Disturbances, such forest fires, harvests or soil replacement, have a major effect on mineralization rates (Vitousek et al., 1982). When soil is bare, moisture and temperatures are relatively higher which accelerates mineralization (Schlesinger and Bernhardt, 2013). As the bare soil begins to generate vegetation, the abundance of inorganic N in the soil decreases (Robertson and Vitousek, 1981). NO₃⁻ losses through microbial immobilization and stream water transport are also accelerated in these disturbed soils further lowering NO₃⁻ concentrations.

Some environments promote N removal through denitrification (2) or N retention through microbial immobilization. In this instance, N in anoxic soils may advance through a denitrification process where bacteria from the genus *Pseudomonas* transform NO_3^- to NO, N₂O, and finally N₂ (Knowles, 1982).

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 7H_2O$$
 (2)

Microbial immobilization converts soil NO₃⁻ and NH₄⁺ into organic N thus rendering it unavailable to plants. Microbes compete with plants by accumulating and retaining nutrients from the soil into their cells. Similar to plants, N is a limiting nutrient in microbes so immobilization is higher in nutrient poor environments (Federer, 1983; Manzoni et al., 2008; Staaf and Berg, 1982). Immobilization effects net mineralization because both processes occur simultaneously in the soil and therefore both equally important in N availability.

2.2.2 Nitrogen availability in wetlands

Wetlands have inherently hydric soils and therefore perform a series of reductions to maintain adequate nutrient supply for plants and microbes. Aerobic bacterial

respiration depletes oxidants in a predictable order ($O_2 \rightarrow NO_3^- \rightarrow Mn^{4+} \rightarrow Fe^{3+} \rightarrow SO_4^{2-}$ \rightarrow CH₄) according to redox reactions through a succession of fermentations (Schlesinger and Bernhardt, 2013). These fermentations are a result of the unique ability of wetland microbes to exploit anaerobic metabolic pathways after the oxygen supply has been depleted. The "redox ladder" functions solely from microbial competition in order to gain an alternative electron acceptor for metabolism (Stumm and Morgan, 1996). Each successional oxidant supports a lower energy yield for metabolic pathways and thus microbes exhaust each oxidant fully before advancing to the following (Stumm and Morgan, 1996; McLatchey and Reddy, 1998). In a closed system, like many boreal peatlands, these processes have the ability to advance down the redox ladder. However systems that experience external sources of recharge – such as groundwater flow, seasonal flooding, and precipitation – may receive sufficient oxidation.

Some types of wetlands (i.e. fens) that receive intermittent flooding events as opposed to permanent inundation can support high net primary production (NPP) (Megonigal et al., 1997). Soil drainage promotes decomposition and nutrient mineralization, which increases the concentration of bioavailable nutrients for plants, while periodic flooding offers nutrient recharge (Choi et al., 2007; Megonigal et al., 1997). However many boreal peatlands are closed systems (i.e. bogs) and often limiting in N supply. These environments have decelerated rates of decomposition and accumulate unavailable forms of N in the soil equating to a net accumulation of SOM (Damman, 1988).

2.2.3 Soil properties and Nitrogen availability

Nitrogen dynamics in wetlands are largely controlled by soil moisture content. Soil moisture below 50 % affects microorganisms by reducing mobility, cellular water potential, and diffusion of soluble substrates (Agehara and Warncke, 2005; Csonka, 1989; Griffin, 1981; Killham et al., 1993; Schjønning et al., 2003; Stark and Firestone, 1995). Microbial mineralization is responsible for most new plant-available forms of N, thus it is important to consider soil moisture and other soil properties influencing microbial activity.

N mineralization processes favour soil moisture conditions of between 50 - 78 % (Agehara and Warncke, 2005; Sleutel et al., 2008). Excess soil moisture slows mineralization rates because the nitrification process is limited to oxidized soil. Prolonged periods of flooding reduce the supply of oxygen in the soil and force organisms to rely on alternate election acceptors (Schlesinger and Bernhardt, 2013). Studies show that the drying of wetlands significantly increases the nitrification process, and in turn mineralization as well (Agehara and Warncke, 2005; Chen, et al., 2012; Geurts et al., 2010; Sleutel et al., 2008). Interestingly, Yu and Ehrenfeld (2009) found that long term wetland drying fundamentally increased N mineralization rates by changing labile pools of N, plant communities and the quality of SOM. However, extensive wetland draining permanently alters the soil properties and landscape classification.

Wetland soils contain high contents of organic matter, which is important because this directly affects many soil properties. SOM has a high water holding capacity (WHC) of 200 - 400 times the mass of its dry weight relative to mineral soil that holds 20 - 40

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%. Soils with high contents of organic matter have a relatively large cation exchange capacity (CEC) of up to 300 cmol_c/kg due to increased organic acid and phenolic groups, which are major sources of CEC in soils (Brady and Weil, 2008; Schlesinger and Bernhardt, 2013; Stevenson, 1986). This is important because large CEC's indicate that there are many potential exchangeable cations in the soil; such as NH_4^+ . Studies have shown coextensive patterns of soil N and SOM, likely because SOM consists of ~5 % organic N (Brady and Weil, 2008; Geurts et al., 2010; He et al., 2012; Qian and Schoenau, 1995). Therefore organic matter is an important factor to consider when determining soil N availability.

Soil structure affects mineralization especially with high moisture content because microbial processes depend on diffusion of substrate and oxygen which are a function of tortuosity, porosity, and bulk density (Skopp et al., 1990; Sleutel et al., 2008). Bridgeham et al. (1998) found strong correlations between N mineralization and bulk density in ombrotrophic and minerotrophic wetlands. This study determined that the size of nutrient pools available for microbial mineralization and plant uptake is a function of bulk density. Laboratory studies suggest that bulk densities above 1.7 g/cm³ start to have negative effects on mineralization (Beylich et al., 2010).

Due to the nature of organic soil having a very small mass per unit area, wetland soils have a high porosity. Breland and Hansen (1996) found that organic matter, N mineralization, and microbial biomass were negatively affected when soil compaction increased. More specifically, soil compaction caused N loss through microbial immobilization and increased gaseous N₂O, which lead to 18 % less mineralization in the soil. Therefore, higher porosities are favoured for microbial mineralization.

2.3 Techniques for Measuring Nutrient Availability

2.3.1 PRS Probes: Background and origin

PRS probes originated from ion exchange theories that began in the mid 1800's and have since become useful tools in many fields. Ion exchange resins consist of spherical porous polymers with large surface areas allowing them to adsorb and release ions simultaneous; a process that occurs naturally in the cells of organisms. The first practical application of ion exchange theories for measuring soil quality and health began in agriculture using early versions of ion exchange beads (Converse et al., 1943; Schlenker, 1942). Following which Pratt (1951) and Amer et al. (1955) applied this concept to assess nutrient availability and release rates. Sibbesen (1977) improved the method by using netted polyester bags to encase the resin beads during incubation. Ion exchange resins were then used in a variety of contexts with a focus on the bioavailability of soil nutrients (Sagger et al., 1990).

Early versions of this method involved shaking a mixed solution of soil, water, and resin beads following an incubation period. Unfortunately this did not account for vertical diffusion, showed evidence of rupturing and loss of resin beads in the field, and posed issues of increased trapped materials like roots and soil particles (Qian and Schoenau, 2002; Sagger et al., 1990). Since the resin beads proved to be too sensitive for both field and lab testing, ion exchange resin strips or membranes were introduced. Saunders (1964) first discovered that the beads and membranes behaved similarly prompting many researchers to switch to membranes. The resin membrane generally consists of some structure that permanently supports and protects the resin, such as polytetrafluorethylene (PTEE) (Qian and Schoenau, 2002). When the resin is inserted

into the soil solution it acts as a dynamic exchanger of ions (except in cases where the soil ion exchange capacity is very large, in which case it becomes a sink) (Qian and Schoenau, 2002).

Western Ag Innovations was one of the first companies to create a commercially available ion exchange product called the Plant Root Simulator or PRSTM probe. The probes follow traditional preparation where anion probes are saturated with bicarbonate (HCO_3^-) and the cation probes with Sodium (Na^+) , which are readily displaced by soil ions upon burial. Part of the reason HCO_3^- and Na^+ are used as counter ions are to simulate the HCO_3^- released during plant excretion of CO_2 in the rhizosphere and because Na^+ has a relatively low affinity (Qian and Schoenau, 2002). The amount of ions remaining on the probes at the end of the incubation period represents nutrient supply rate as a result of the biological, chemical, and physical soil properties. (Western Ag Innovations Saskatoon, SK, Canada)

2.3.2 PRS Probes: Environmental reclamation

PRS probes have been applied in a variety of fields such as agriculture (Davenport and Schiffhauer, 2007; Qian and Schoenau, 2005; Thavarajah et al., 2003), ecology and climate change (Concilio and Loik, 2013; Liancourt et al., 2012), forestry (Brais and Drouin, 2012; Brockett and Prescott, 2012), and environmental reclamation (Harrison and Maynard 2014; Hemstock et al., 2010; McMillin et al., 2007; Rowland et al., 2009; Yan et al., 2012). Much of the popularity towards PRS probes is due to their ability to consider important soil properties when measuring nutrient availability (Drohan, 2005; Qian and Schoenau, 2002; Sagger et al., 1990).

Over the last decade the probes have become more popular in oil sands reclamation research in northern Alberta because they are simple, available in large quantities, and can be analyzed quickly. Additionally the probes provide a timeintegrated indication, rather than instantaneous sample. Rowland et al. (2009) used the PRS probes to compare nutrient availability between different combinations of reclaimed peat soil overlying mined surfaces, and an array of natural boreal forest ecosystems. It was determined that the reclaimed soil types facilitated higher NO_3^- , while the natural sites generated higher NH_4^+ . Additionally, the use of an intermediate subsoil capping layer between the overburden and the reclaimed peat in combination with a single application of fertilizers led to conditions within the range of a natural forest ecosystem in a 15 year trajectory.

Hemstock et al. (2010) conducted a comprehensive study on the effectiveness of different kinds of peat amendments and their ability to produce ideal conditions for bioavailable N. It was discovered that there were large seasonal variabilities in net N mineralization rates peaking in the fall, but without reference to a control this information is difficult to contextualize. Similarly, Yan et al. (2012) used PRS probes to show the relationship between growth parameters of natural jack pine forests and indices of soil N availability in the oil sands region, but without reference to reclaimed sites. To date there has been little research comparing N availability of reclaimed peat soils with natural sites especially in terms of wetland reclamation in the oil sands region.

One of the challenges with the PRS probes is that the ion exchange is highly affected by competition with microbes and plants. Subler et al. (1995) found that resin strips installed in N-immobilizing soils showed considerably less NO_3^- . However since

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plant roots would encounter the same limitations this accurately describes the plant available N for that soil. Binkley (1984) and Huang and Schoenau (1996) demonstrate that in some soils the ion exchange resins do not compete well with plants for N adsorption. This indicates that the PRS probes measure the nutrient supply rate after plants and microbes have satisfied their nutrient requirements.

2.3.3 Polyethylene buried bag method

A common practice in studies of nutrient bioavailability is to couple ion exchange resins with a more direct measurement of bioavailable N achieved through chemical extractions. Exchange resins measure pools of inorganic nutrients and capture their highly variable turnover rates. However, because they represent supply rate and not a quantity of ions, it becomes difficult to determine the immobilization period (Booth et al., 2005; Fisher and Binkley 2000; Harrison and Maynard, 2014). Chemical extractions from soil samples provide a quantity of inorganic nutrients, which is applied to a simple equation to evaluate the rate at which nutrients are becoming bioavailable or immobilized (Maynard & Kalra, 1993). These complementary techniques report different soil functions and ultimately strengthen the understanding of nutrient availability.

The method most commonly used to collect chemical extractions from the soil is termed the buried polyethylene bag method (Eno, 1960; Fellman and D'Amore, 2007; Hanselman et al., 2004; Sleutel et al., 2008). At the beginning of the experiment, two "paired" soil samples are collected and placed in separate polyethylene bags. One of the bags (incubated sample) is placed back in the ground in the location from which that sample was taken (and subsequently incubated), and the second sample (initial sample) is

immediately processed for chemical analyses (i.e. extractable nutrients). After a predetermined amount of time (usually from days to weeks) the bag left in the ground (incubated sample) is removed and also processed and analyzed (extractable nutrients). The difference between the quantity of ions at the beginning (initial sample) and end of the incubation period (incubated sample) provides an estimate of net mineralization or net immobilization (Eno, 1960; Fellman and D'Amore, 2007; Hanselman et al., 2004; McMillan et al., 2007).

Chemical extractions and soil incubations are some of the earliest methods for determining net mineralization rates and, while widely used, have some disadvantages. The bags can be easily damaged in the field therefore suffering N loss through mass flow and diffusion. The dynamic properties of soil water quality are difficult to capture with the buried bags (Hansel et al., 2004). While the bags allow for external exchange of oxygen and CO_2 to eliminate the potential of anaerobic conditions affecting mineralization within the bag, this is difficult to monitor and control (Bridgham et al., 1998; Eno, 1960). Consequentially, denitrification may occur if CO_2 and NO_3 ⁻ levels become too high (Eno, 1960; Subler et al., 1995). However Zou et al. (1992), Schmidt et al. (2002), and Hanselman et al. (2004) all report that the most effective method of evaluating soil nutrient availability is through the combination of both buried bags and ion exchange resin (e.g. PRS probes) since each technique addresses the other's disadvantages.

SECTION 3 – SITE DESCRIPTION, MATERIALS AND METHODS

3.1 Site Description

All sites are located on the Athabasca oil sands deposit of the boreal region in North-eastern Alberta (Figure 3.1). This continental humid to sub-humid ecoclimate can be defined by short warm summers, cold winters, and an average annual temperature of +0.5°C (Turchenek and Lindsay, 1982; Natural Regions Committee, 2006). Precipitation is moderately variable with a mean of 480 mm, which is generally highest in July. Growing season is typically May – September, but may be as short as June – August in higher latitudes (Turchenek and Lindsay, 1982).

The modal soil type for this region are orthic gray luvisols although organic cryosols, gleysols, eluviated eutric brunisols, degraded dystric brunisols, and gray luvisols are also native to this area (Syncrude Canada Ltd., 1984; Turchenek and Lindsay, 1982). Surficial deposits of till, lacustrine and fluvial plains, and sand dunes from glacial activity are the parent materials from which the soils have formed (Crown and Twardy, 1970). Soil moisture ranges from very dry and drought resistant xeric regimes to sub-hydric or aquic soils with water tables at or near the surface for prolonged periods of time. These conditions support *Picea glauca* (white spruce) and *Populus* (aspen) forests as well as *Abies balsamea* (balsam fir), *Populus balsamifera* (balsam poplar), *Pinus banksiana* (jack pine) and *Betula papyrifera* (paper birch) (Turchenek and Lindsay, 1982).

3.1.1 Sandhill Fen

The Sandhill Fen Watershed (57°2'22.31"N, 111°35'20.40"W), located on SCL

property, is approximately 35.2 km north of the city of Fort McMurray and is considered part of the Central Mixedwood subregion of the boreal forest in Alberta. Previously this site functioned as a 60 metre deep open-pit mine site called East-In-Pit (EIP). The reclamation project began in 2008 as an attempt to cover tailings sands and composite tailings with a functioning wetland watershed. The total area of the watershed is 57 hectares (0.57 km²) with 17 hectares (0.17 km²) dedicated to a groundwater-fed fen. Construction began with 35 m of layered tailings sands and composite tailings followed by a 10 m cap of tailings sand. A 0.5 m clay-till cap was applied over the tailings sands and overlain with 0.5 m of peat soil that had been recently reclaimed from a natural site on SCL property. The soil was applied over oil sands burden specifically to support fen vegetation and to allow hydrologic manipulations to determine optimal substrate conditions (Vitt and Bhatti, 2012). A mixture of tailings sand and mineral soil was used to construct the surrounding upland areas in an effort to support native wetland tree species.

Following site construction and soil application, the Sandhill Fen Watershed was officially commissioned in 2012 (Figure 3.2). The site was vegetated with native upland and wetland species in the first two growing seasons (i.e. 2012 and 2013) including *Picea glauca/mariana* (white and black spruce), *Populus tremuloides* (trembling aspen), and *carex spp.* (sedge species). To minimize disturbance during the instrumentation and monitoring process, extensive boardwalks were built throughout the wetland.

3.1.2 Poplar Fen

The Poplar Fen (56°56'25.24"N, 111°33'0.89"W), located on Crown land, is 23.8

km north of Fort McMurray and 11.2 km south of the Sandhill Fen and is also part of the Central Mixedwood subregion of Alberta. The study took place on the northwest half of this 25 km² fen. Poplar Fen can be classified as a medium-rich treed fen with a surrounding upland dominated by a coniferous forest (Figure 3.3). The main vegetation species in the wetland are *Larix laricina* (tamarack), *Betula pumila* (dwarf birch), *Carex* (sedges), *Tomenthypnum nitens* (golden moss), and *Sphagnum* (peat moss), whereas *Pinus banksiana* (jack pine), *Picea mariana/glauca* (black and white spruce), *Ledum groenlandicum* (Labrador tea), *Equisetum* (horsetail) and feather moss occupy the majority of the uplands. The wetland soil has a relatively high organic content with sub-xeric moisture regimes (Table 1).

3.1.3 Pauciflora Fen

The Pauciflora Fen (56°22'37.45"N, 111°14'12.17"W), also situated on Crown land, is approximately 41.6 km south of Fort McMurray (~77 km south of the Sandhill Fen) and considered part of the Lower Boreal Highlands subregion of the boreal forest in Alberta. This region receives more precipitation and has characteristically higher elevations and lower temperatures in comparison to the Central Mixedwood subregion (Figure 3.4).

The fen is approximately 22 km² ranging from nutrient poor conditions in the north to almost bog-like characteristics in the south. The vegetation is very similar to that at the Poplar Fen however with the addition of certain bog species such as *Rubus chamaemorus* (cloudberry) and bog cranberry (Figure 3.5). Wetland soils are a

peat/mineral mix and thus have lower organic content than Poplar Fen (Table 1).

3.1.4 Fieldwork design

A total of twenty representative transects among the three sites were established along the hillslopes at the beginning of the 2014 growing season. Ten transects were established at Sandhill, six at Pauciflora and four at Poplar, all of which consisted of three sub-locations: upslope, midslope, and downslope. The number of transects that were established at each site were relative to the size of the study area. PRS probes were installed at every hillslope position along all transects whereas mineralization was measured at only half the transects. The soil samples collected for mineralization were also used to determine soil properties such as soil type, degree of peat humification, soil moisture, soil organic matter, porosity, and bulk density (Table 1).

3.2 Materials and Methods:

3.2.1 PRS probes

PRS probes were installed at each sub-location of all transects at the three sites. Each sub-location consisted of 3 sets of coupled cation and anion probes for improved precision and accuracy (Figure 3.6). An additional experiment was conducted at one of the sites to test the accuracy and precision of the probes. This involved the comparison of mean values from sets of one, two, and three coupled probes over a burial period. Results from this experiment did not indicate any significant difference among values; but, for better accuracy 3 sets of probes were used at each hillslope position.

The probes contain a sensitive resin that begins to actively exchange ions at room

temperature and when exposed to light, so they were refrigerated in the dark until immediately before installation. On installation days the probes were removed from the refrigerator and transported to the sites in coolers filled with cold packs. The tops of the probes have a small hole ideal for tying flagging tape for easy detection during removal.

As recommended by Western Ag. Innovations, probes remained in the soil for 26 days before being replaced. This amount of time allowed the flux of nutrients to the probes to become stable and representative (Drohan et al., 2005). Therefore the study spanned over three burial periods marking the beginning (Burial Period 1), middle (Burial Period 2) and end (Burial Period 3) of the growing season:

Burial Period 1: 27 May 2014 – 21 June 2014 Burial Period 2: 21 June 2014 – 17 July 2014 Burial Period 3: 16 July 2014 – 10 August 2014

Great care was taken during probe removal. First, as a probe was removed from the soil a new probe of the same type (i.e. cation or anion) was installed in exactly the same location. This consecutive burial technique would determine seasonal changes in N supply rates. The only exception was the final removal at the end of the summer, at which no new probes were installed. The removed probes were then cleaned with deionized (DI) water and gently scrubbed with a toothbrush. It was imperative that all soil was removed from the probes before sending to the lab, to prevent any further exchange of ions with solids. Finally, all three cation and anion probes at each sub-location were placed in one sealable polyethylene bag labeled with the sample ID, date, locations, burial duration, and location type. This process was repeated at all sites until removal/installation was complete. All bags were kept in a cold cooler or refrigerator until shipped to Western Ag,'s laboratory in Saskatoon, Saskatchewan for analysis.

3.2.2 Polyethylene buried bag method

At each site, half of the PRS transects were selected for the buried bag sampling of extractable nitrogen. A cylindrical bulb corer (11 cm x 6 cm) with a fixed volume was used for the collection of each soil sample (Figure 3.7). During the initial installation two soil samples were collected with the bulb corer at each sub-location of the selected transects. The first was placed into a labeled polyethylene bag, which was then sealed and placed in a cooler (t₀). The second was also placed in a polyethylene bag however instead of sealing the bag the end was twisted several times. This is to restrict the flow of water while allowing the soil to experience oxygen exchange with the atmosphere. The bag was then inserted back into the soil in the location it was originally taken (t₁). This was repeated until all soil samples were collected and buried bags installed. During PRS removal, the buried bags that were left in the soil were also removed, sealed, and placed in a cooler. The buried bag sampling process described above was then repeated. The two sampling methods (i.e. PRS probes and buried bags) were conducted simultaneously.

3.2.3 Chemical extractions and soil analyses

Soil samples were immediately taken back to the lab for preliminary chemical extractions before being sent to the University of Waterloo. Soil cores were sufficiently mixed (homogenized) to ensure that a representative sample was obtained. Approximately 10 g of soil was then taken from each bag (via quartering) and weighed (W₁) in individual sterile plastic cups labeled with sample ID and soil weight. Next, 50 ml of a 2M KCl solution (150 ml of potassium chloride for every 1000 ml of DI water) was added to each cup. The cups were capped and placed on a table shaker for one hour.

During this time, GE Healthcare Life Sciences Whatman 42 Ashless 125 mm diameter filters papers were folded into cones and placed on new sterile cups labeled with the same sample IDs and soil weight. After an hour, the samples were removed from the shaker and passed through the filters into cups with corresponding IDs until 15 ml of clear liquid was obtained. Depending on soil type the rate of gravity filtration varied between 30 minutes (course grained material) and 6 hours (fine grained material). Finally, the clear liquid was transferred into labeled sterile centrifuge tubes and frozen until the end of the season. Samples were packed on ice and shipped to the Biogeochemistry Lab at the University of Waterloo for analyses of nitrogen species via colorimetry (Bran Luebbe AA3, Seal Analytical, Seattle, U.S.A., Methods G-102-93 (NH₄⁻), G-109-94 (NO₃⁻⁺+NO₂⁻)). It is important to note that the extractions were done on moist field samples because drying samples can inflate extractable nutrients (Binkley and Hart, 1989; Macrae et al., 2013).

All soil samples were transported to McMaster University for supplementary soil quality analyses. Soil moisture was determined using the direct, standard gravimetric method (g water⁻¹ g soil). Approximately 6-7 g of each soil sample was weighed, dried at 103°C for 24 hours, then re-weighed to calculate soil moisture. Gravimetric water content (GWC) can be expressed as:

$$GWC = (weight of water)/(weight of dry soil)$$
(3)

When NO_3^{-N} and NH_4^{+N} concentrations were obtained from the University of Waterloo, nitrification, ammonification and N mineralization for each burial period was calculated for every hillslope position through the following steps:

Step 1:

$$V_w = (W_1 \times GWC) + V_{KCl}$$
(4)

$$V_{w} = Volume \text{ of water in sample (mL)}$$

$$W_{1} = weight \text{ of initial soil subsample}$$

$$GWC = Gravimetric \text{ water content}$$

$$V_{KCl} = Volume \text{ of KCl solution (i.e. 50 mL)}$$
Step 2:

$$W_d = W_1 \times (1-GWC) \tag{5}$$

 $W_d = Dry$ weight of sample (g)

Step 3a:

$$NO_3^{-N}_{solution} = NO_3^{-N}_{conc} \times (V_w/1000)$$
(6)

$$NO_3^{-N}_{solution} = Amount of NO_3^{-N} in solution (mg)$$

 $NO_3^{-N}_{conc} = NO_3^{-N}$ concentration from subsample (mg/L)

Step 3b:

$$NH_4^{+N}_{solution} = NH_4^{+N}_{conc} \times (V_w/1000)$$
⁽⁷⁾

 $NH_4^{+N}_{solution} = Amount of NH_4^{+N} in solution (mg)$ $NH_4^{+N}_{conc} = NH_4^{+N}$ concentration from subsample (mg/L)

Step 4a:

$$NO_{3}^{-N}/W_{d} = (NO_{3}^{+N}_{\text{solution}} \times 1000)/W_{d}$$
 (8)

 $NO_3^{-N}/W_d = Extractable NO_3^{-N}$ per dry weight of sample (ug/g dwt)

Step 4b:

$$NH_4^{+N}/W_d = (NH_4^{+N}_{solution} \times 1000)/W_d$$
 (9)

 $NH_4^{+N}/W_d = Extractable NH_4^{+N}$ per dry weight of sample (ug/g dwt)

Step 5:

$$TN/W_d = NO_3^{-N}/W_d + NH_4^{+N}/W_d$$
 (10)

 TN/W_d = Total nitrogen per dry weight of sample (ug/g dwt)

Step 6:

$$Nitrification = NO_3^{-N} / W_d (t_1 - t_0)$$
(11)

 t_0 = Beginning of burial period t_1 = End of burial period

Ammonification =
$$NH_4^{+N} / W_d (t_1 - t_0)$$

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N Mineralization = nitrification + ammonification

Availability of nutrients for plant uptake is partially a function of soil quality therefore soil organic matter (SOM), bulk density (ρ_b), and porosity (Φ) were calculated, which also aided in identifying soil types. A loss on ignition (LOI) test was used to determine SOM content. Representative 10-15 g subsamples were weighed, heated at 103°C for 24 hours (dry weight), and reweighed in the absence of liquid water. Then, subsamples were heated to 550°C (ash dry weight) for 5 hours and reweighed. The calculation for SOM (%) from LOI is:

$$SOM(\%) = (W_a)/(W_d)$$
 (12)

 W_d = Dry weight of sample (g) at 103°C W_a = Ash dry weight of sample (g) at 550°C

To determine ρ_b the full weight of the sample must be known as well as the volume of the corer:

$$\rho_b = W_{dry \ full} \ / \ V_c \tag{13}$$

$$\rho_b = \text{Bulk density (g/cm^3)}$$
 $W_{dry \, full} = \text{Dry weight of full sample (g) at 103°C}$
 $V_c = \text{Volume of corer}$

$$V_c = \mathbf{r}^2 \times \mathbf{h} \tag{14}$$

Porosity (Φ) was calculated from the following particle density (ρ_s) values taken from the Redding and Devito (2005): treed fen 1.51 g/cm³; open fen 1.57 g/cm³; and mineral soil 2.65 g/cm³:

$$\Phi = (1 - (\rho_b / \rho_s)) \times 100\%$$
(15)

3.3 Statistical Analyses

All statistics were computed in the program R (R Development Core Team, 2014).

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All variables from PRS probes (NO₃⁻, NH₄⁺, and TN), buried bags (nitrification, ammonification, and mineralization) and soil properties (GWC, SOM, ρ_b , and Φ) were first tested for normality. The Shapiro-Wilk test is more appropriate than other normality tests as it offers better power (i.e. the detection capacity of a sample's distribution) (Thode, 2002; Steinskog, 2007). Datasets were also tested for skewness and kurtosis to better identify normality of the samples (Thode, 2002; Oztuna et al. 2006). All datasets, except ρ_b , and Φ , were not normally distributed and therefore transformed using the natural logarithm. Homogeneity of variances were determined for most variables using Levene's test as it is less sensitive to departures of normality and therefore considered more suitable when datasets that were normally distributed were tested for equal variances with the Bartlett's test (Sokal and Rohlf, 1969).

Once all assumptions were met, statistical significances were determined using a traditional one-way analysis of variances (ANOVA), which is robust and less prone to increase type I error rates (Shaw and Mitchell-olds, 1993, Miller, 1997). Tukey's Honestly Significant Difference (HSD) *post hoc* test is considered the best method when dealing with unequal sample sizes and therefore chosen to further interpret the results from the one-way ANOVA tests (Dunnett, 1980; Brophy, 1984). Significances were justified with a 95 % confidence level (p > 0.05). Comparative tests were organized based on burial period, site, and location along slope.

The Spearman's Rank Correlation or Spearman's ρ (rho) was selected to compare relationships between variables because it deals with nonparametric datasets. The Spearman Correlation uses a monotonic instead of a linear function to measure

relationship strengths. Correlations values range from -1 (perfect negative relationship) to +1 (perfect positive relationship) with 0 reflecting no relationship (Zar, 1998). Each variable (NO₃⁻, NH₄⁺, TN, nitrification, ammonification, mineralization, GWC, SOM, ρ_{b} , and Φ) was correlated with all others within sites, totalling 36 correlations per site. All ρ and associated p-values were then compiled into tables organized by site (Table 11 – 13).

SECTION 4 - RESULTS

All results are summarized by site (Sandhill, Pauciflora, and Poplar), hillslope position (upslope, midslope, and downslope), and burial period (1, 2, and 3). The general transition from upslope to down slope can be defined as a shift from dry uplands to wet fen environments. Each results section will include a description of the statistical significances achieved from the one-way ANOVA and Tukey HSD post-hoc multiple comparison tests.

Results for each parameter will begin with a general description and comparison among the three sites as whole followed by mean and standard deviation values for all hillslope positions at each site as well as the statistical significances. The description of statistical significances attained from the above-described tests will first illustrate differences among hillslope position within each site. Then, comparisons of corresponding hillslope position between sites will reveal site differences. Finally, an explanation of the temporal characteristics for every site will conclude each parameter's section. This includes a description of the mean values and statistical significance between burial periods within each site. Statistical testing for temporal differences only compared means within each individual site, as opposed to across sites.

Bulk density and porosity was only measured once and therefore temporal characteristics will not be described for these parameters. SOM was not expected to change over the short study period and will also not include a seasonality component. Additional parameter information for each site such as max, min, 1st and 3rd quartile and median values can be found in the Appendix (Table 10).

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4.1 Soil Properties

4.1.1 Gravimetric water content

4.1.1.1 Spatial characteristics

Gravimetric water content (GWC) varied within and among sites (Figure 4.1; Table 2). Poplar had the highest total average GWC ($\bar{x} = 3.532$ g/g) and standard deviation ($\sigma = 2.605$ g/g) followed by Pauciflora ($\bar{x} = 1.242$ g/g, $\sigma = 2.416$ g/g) and finally Sandhill ($\bar{x} = 0.876$ g/g, $\sigma = 0.952$ g/g) (Table 2). The site comparison tests revealed significantly higher GWC at the Poplar Fen in comparisons to both other sites (Table 6).

Gravimetric water content generally increased from the upslope position to the downslope position at all sites. GWC in the downslope position at the Pauciflora site ($\bar{x} = 3.960 \text{ g/g}$) were considerably greater than the upslope ($\bar{x} = 0.359 \text{ g/g}$) and midslope ($\bar{x} = 0.314 \text{ g/g}$) positions. The increase in GWC was more gradual at Poplar (upslope $\bar{x} = 1.463 \text{ g/g}$; midslope $\bar{x} = 3.124 \text{ g/g}$; downslope $\bar{x} = 5.664 \text{ g/g}$) and Sandhill (upslope $\bar{x} = 0.080 \text{ g/g}$; midslope $\bar{x} = 0.802 \text{ g/g}$; downslope $\bar{x} = 1.806 \text{ g/g}$) sites.

A one-way ANOVA comparing hillslope locations at Pauciflora Fen indicate that downslopes had significantly greater GWC than both midslopes and upslopes (Table 7). Poplar's downslopes had significantly larger GWC in comparison to its upslope positions but differences between the midslope and adjacent positions (upslope, downslope) were not significant. Lastly, all hillslope positions at the Sandhill Fen were significantly different in terms of GWC (Table 7).

A comparison of hillslope differences across sites found that the upslope positions at Sandhill were significantly drier than upslope positions at the other two sites. (Table

8). Poplar midslopes had greater GWC than midslopes at both sites and Sandhill midslopes had greater GWC than Pauciflora midslopes. Finally, Poplar downslopes had greater GWC than Sandhill's downslope.

4.1.1.2 Temporal characteristics

GWC at Pauciflora began with lower mean values in the first burial period ($\bar{x} = 0.365 \text{ g/g}$), peaked in the second ($\bar{x} = 1.616 \text{ g/g}$), and then decreased slightly in the third burial period ($\bar{x} = 1.454 \text{ g/g}$) (Figure 4.2; Table 5). Mean and standard deviation ($\sigma = 0.152 \text{ g/g}$) for GWC in the first burial period at Pauciflora was the lowest across all sites and burial periods. Poplar had an opposing pattern with the highest mean values during the first ($\bar{x} = 4.643 \text{ g/g}$) and third ($\bar{x} = 3.250 \text{ g/g}$), and a slight decrease in the second ($\bar{x} = 2.888 \text{ g/g}$). Poplar's GWC in the first burial period had the largest mean and standard deviation ($\sigma = 3.921 \text{ g/g}$) across all sites and burial periods. Sandhill had a similar pattern where the highest GWC occurred during the first burial period ($\bar{x} = 1.153 \text{ g/g}$), lowest during the second ($\bar{x} = 0.676 \text{ g/g}$), and increased during the third ($\bar{x} = 0.816 \text{ g/g}$). No significant differences were found for GWC across burial periods at any of the sites (Table 9).

4.1.2 Soil organic matter

Similar to GWC, Poplar had the highest average SOM ($\bar{x} = 58.6$ %) and standard deviation ($\sigma = 28.7$ %) (Table 2; Figure 4.1). Sandhill had a lower site average ($\bar{x} = 25.1$ %) followed by Pauciflora with the least SOM of the three sites ($\bar{x} = 15.9$ %). Both

Sandhill and Pauciflora had very similar standard deviations. ($\sigma = 23$ %). Similar to GWC, Poplar had significantly more SOM than both other sites (Table 6).

Pauciflora downslopes had the highest average SOM and standard deviation ($\bar{x} = 33.4 \%$, $\sigma = 33.3 \%$), followed by the midslopes ($\bar{x} = 7.3 \%$, $\sigma = 5.6 \%$) and upslopes ($\bar{x} = 7.1 \%$, $\sigma = 3.6 \%$). Poplar had similar SOM values at the downslopes ($\bar{x} = 66.0 \%$) and midslopes ($\bar{x} = 68.2 \%$), whereas the upslopes had the least SOM ($\bar{x} = 41.7 \%$), and the highest standard deviation ($\sigma = 41.6 \%$) out of all hillslope locations across the three sites. Sandhill had a gradual decrease in SOM from downslopes ($\bar{x} = 42.4 \%$) to midslopes ($\bar{x} = 28.7 \%$) to upslopes ($\bar{x} = 4.1 \%$). Standard deviations were similar for the midslopes ($\sigma = 21.6 \%$) and downslopes ($\sigma = 19.3 \%$) whereas upslopes had the lowest standard deviation ($\sigma = 0.9 \%$) out of all sites.

Pauciflora's downslopes had significantly more SOM than both midslope and upslope positions (Table 7). Poplar showed no significant difference between the SOM content along the hillslope. SOM content at Sandhill, however, was significantly different at all slope positions.

There were significantly larger SOM values at Poplar upslopes compared to Sandhill upslopes (Table 8). All midslopes were significantly different with Poplar having the most SOM and Pauciflora having the least. Similarly, SOM content was significantly higher at Poplar downslopes than at Pauciflora downslopes.

4.1.3 Bulk density

Pauciflora had the highest average bulk density (ρ_b) ($\bar{x} = 0.58 \text{ g/cm}^3$) followed by Sandhill ($\bar{x} = 0.52 \text{ g/cm}^3$) and then Poplar ($\bar{x} = 0.36 \text{ g/cm}^3$) (Table 2; Figure 4.3).

Standard deviations were inversely related to the mean values for ρ_b . The one-way ANOVA tests did not reveal any significant differences between sites for ρ_b (Table 6; Table 8).

There was little variation in ρ_b at Pauciflora, but there was a gradual decrease in mean values from upslope ($\bar{x} = 0.61 \text{ g/cm}^3$) to downslope ($\bar{x} = 0.54 \text{ g/cm}^3$). Pauciflora midslopes had the lowest standard deviation ($\sigma = 0.08$) out of all sites. Average ρ_b at Poplar downslopes ($\bar{x} = 0.23 \text{ g/cm}^3$) and midslopes ($\bar{x} = 0.20 \text{ g/cm}^3$) were much lower than the upslopes ($\bar{x} = 0.66 \text{ g/cm}^3$). Additionally, Poplar upslopes had the highest standard deviation across all sites ($\sigma = 0.66 \text{ g/cm}^3$). Sandhill demonstrates a gradual increase in bulk density from downslopes ($\bar{x} = 0.28 \text{ g/cm}^3$) to upslopes ($\bar{x} = 0.74 \text{ g/cm}^3$). The difference between ρ_b at Sandhill's upslopes and downslopes was the only statistically significant finding for this parameter (Table 7).

4.1.4 Porosity

Porosity (Φ) has an inverse relationship to ρ_b , for example Pauciflora had the lowest mean porosity ($\bar{x} = 78.1$ %) and standard deviation ($\sigma = 7.8$ %), Sandhill had the second lowest ($\bar{x} = 78.9$ %, $\sigma = 10.2$ %) and Poplar the highest ($\bar{x} = 82.8$ %, $\sigma = 12.7$ %) (Table 2; Figure 4.3).

Pauciflora's midslope ($\bar{x} = 78.3$ %) and downslope ($\bar{x} = 79.0$ %) positions had slightly lower Φ than the upslopes ($\bar{x} = 76.3$ %). Poplar's midslope position had the highest average Φ ($\bar{x} = 90.6$ %) and standard deviation ($\sigma = 0.7$ %) across all sites. Upslopes at Poplar had the lowest mean Φ ($\bar{x} = 72.5$ %) as well as the largest standard deviation ($\sigma = 21.3$ %) across all sites. Sandhill exhibited a gradual decrease in Φ from

downslope ($\bar{x} = 84.9$ %) to upslope ($\bar{x} = 72.1$ %). There were no significant differences between any of the sites or between positions along hillslope (Table 6, Table 7 and Table 8).

4.1 Nitrogen Supply Rates

4.2.1 TN supply rates

4.2.1.1 Spatial characteristics

Poplar had the highest average TN supply rate ($\bar{x} = 7.5 \ \mu g/10 \text{cm}^2/\text{month}$) and the lowest standard deviation ($\sigma = 4.6 \ \mu g/10 \text{cm}^2/\text{month}$) compared to the other sites (Table 3; Figure 4.4). Conversely, Sandhill had the lowest TN supply rate ($\bar{x} = 5.7 \ \mu g/10 \text{cm}^2/\text{month}$) and the highest standard deviation ($\sigma = 8.0 \ \mu g/10 \text{cm}^2/\text{month}$). Poplar and Pauciflora had significantly greater TN supply rates than Sandhill (Table 6).

Pauciflora's downslopes had the highest average TN supply rate ($\bar{x} = 10.8 \ \mu g/10 \text{cm}^2/\text{month}$) and standard deviation ($\sigma = 12.5 \ \mu g/10 \text{cm}^2/\text{month}$) across all slope positions at every site. The midslopes ($\bar{x} = 4.5 \ \mu g/10 \text{cm}^2/\text{month}$) and upslopes ($\bar{x} = 4.23 \ \mu g/10 \text{cm}^2/\text{month}$) at Pauciflora had similar mean supply rates. TN supply rates at Poplar were different from Pauciflora increasing from downslope ($\bar{x} = 5.4 \ \mu g/10 \text{cm}^2/\text{month}$) to upslopes ($\bar{x} = 9.5 \ \mu g/10 \text{cm}^2/\text{month}$). Similarly, Sandhill's largest supply rate occurred at the upslopes ($\bar{x} = 8.9 \ \mu g/10 \text{cm}^2/\text{month}$) while the midslopes ($\bar{x} = 3.6 \ \mu g/10 \text{cm}^2/\text{month}$) showed the lowest mean supply rates and standard deviation ($\sigma = 2.0 \ \mu g/10 \text{cm}^2/\text{month}$) out of all hillslope locations across all sites.

In terms of the differences between hillslope positions at Sandhill the upslopes had significantly greater TN supply rates than both midslopes and downslopes (Table 7).

The only significant differences for the other two sites were between downslopes and midslopes at Pauciflora and between downslopes and upslopes at Poplar.

None of the upslopes at the three sites were significantly different from each other. The midslopes at the Sandhill Fen, however, had significantly lower TN supply rates than midslopes at the other two sites (Table 7). Lastly, downslopes at Pauciflora Fen had significantly greater supply rates compared to both other sites.

4.2.1.2 Temporal characteristics

TN supply rate during the first burial period at Pauciflora had the largest mean (\bar{x} = 12.3 µg/10cm²/month) and standard deviation (σ = 10.3 µg/10cm²/month) out of all burial periods at every site (Figure 4.5; Table 5). The average TN supply rates declined during the second period (\bar{x} = 7.2 µg/10cm²/month) and then increased slightly during the third (\bar{x} = 7.9 µg/10cm²/month). Poplar's TN supply rates decreased from the first (\bar{x} = 7.4 µg/10cm²/month) to the second (\bar{x} = 5.7 µg/10cm²/month) before climbing to a peak mean of 9.3 µg/10cm²/month during the third burial period. Sandhill demonstrated a similar pattern with a decline in supply rates from the first (\bar{x} = 4.7 µg/10cm²/month) to the second (\bar{x} = 3.6 µg/10cm²/month), and then increasing again in the third (\bar{x} = 6.0 µg/10cm²/month) burial period. No significant differences were found for TN supply rate across burial periods (Table 9).

4.2.2 NO₃ supply rates

4.2.2.1 Spatial characteristics

Poplar and Sandhill had the highest NO₃⁻ supply rates with means of 4.3 μ g/10cm²/month and 4.1 μ g/10cm²/month, respectively (Table 3; Figure 4.4). Sandhill also had the largest standard deviation ($\sigma = 7.90 \mu$ g/10cm²/month). Pauciflora had the lowest average supply rates ($\bar{x} = 1.3 \mu$ g/10cm²/month) and standard deviation ($\sigma = 1.1 \mu$ g/10cm²/month). However, the three sites did not demonstrate significant differences in NO₃⁻ supply rates (Table 6).

Pauciflora's highest NO₃⁻ supply rates occurred at the midslopes ($\bar{x} = 1.5 \ \mu g/10 \text{cm}^2/\text{month}$), which also had the lowest standard deviation ($\sigma = 1.0 \ \mu g/10 \text{cm}^2/\text{month}$) across all sites. The upslopes then had the second highest rates ($\bar{x} = 1.2 \ \mu g/10 \text{cm}^2/\text{month}$) at Pauciflora followed by downslope ($\bar{x} = 1.0 \ \mu g/10 \text{cm}^2/\text{month}$). Poplar showed a gradual increase in NO₃⁻ supply rates from downslope ($\bar{x} = 2.3 \ \mu g/10 \text{cm}^2/\text{month}$) to upslope ($\bar{x} = 6.0 \ \mu g/10 \text{cm}^2/\text{month}$). Supply rates at Sandhill were lowest at the midslopes ($\bar{x} = 1.9 \ \mu g/10 \text{cm}^2/\text{month}$) and highest at the upslopes ($\bar{x} = 7.3 \ \mu g/10 \text{cm}^2/\text{month}$). Sandhill's upslopes had the highest mean NO₃⁻ supply rates and standard deviation ($\sigma = 11.5 \ \mu g/10 \text{cm}^2/\text{month}$) across all sites.

There were no significant differences among hillslope positions at both Sandhill and Pauciflora (Table 7). Poplar upslopes, however, had significantly higher NO_3^- supply rates than downslopes, which was the only significant difference among slope positions.

The comparisons for hillslope position across sites revealed no significant difference for the upslopes and the downslopes (Table 8). However the midslopes at Poplar did have significantly higher supply rates than the midslopes at Sandhill.

4.2.2.2 Temporal characteristics

Pauciflora had the largest mean NO₃⁻ supply rate during the first burial period (\bar{x} = 3.7 µg/10cm²/month) (Figure 4.5; Table 5). Rates declined during the second period (\bar{x} = 1.4 µg/10cm²/month) followed by a slight increase in the third (\bar{x} = 1.7 µg/10cm²/month). Poplar's average NO₃⁻ supply rate decreased from first (\bar{x} = 4.8 µg/10cm²/month) to second (\bar{x} = 3.1 µg/10cm²/month) burial periods and reached maximum supply rates during the third (\bar{x} = 5.2 µg/10cm²/month). Likewise, Sandhill's largest mean NO₃⁻ supply rates occurred during the third burial period (\bar{x} = 4.6 µg/10cm²/month) following a decline in rates from the first (\bar{x} = 3.6 µg/10cm²/month) to the second period (\bar{x} = 1.5 µg/10cm²/month). There were no significant differences in NO₃⁻ supply rates between burial periods for any site (Table 9).

4.2.3 NH₄⁺ supply rates

4.2.3.1 Spatial characteristics

Mean NH₄⁺ supply rates ($\bar{x} = 4.5 \ \mu g/10 \text{cm}^2/\text{month}$) and standard deviation ($\sigma = 6.5 \ \mu g/10 \text{cm}^2/\text{month}$) were greatest at Pauciflora (Table 3; Figure 4.4), whereas the lowest mean rates ($\bar{x} = 1.5 \ \mu g/10 \text{cm}^2/\text{burial}$ duration) and standard deviation ($\sigma = 1.1 \ \mu g/10 \text{cm}^2/\text{month}$) were found at the Sandhill Fen. One-way ANOVA tests revealed significantly greater NH₄⁺ supply rates at Pauciflora in comparison to both other sites (Table 6). Additionally, Poplar had significantly greater rates than Sandhill.

The hillslopes at Pauciflora increased in average NH₄⁺ supply rate from upslope $(\bar{x} = 2.4 \text{ }\mu\text{g}/10\text{cm}^2/\text{month})$ to downslope $(\bar{x} = 9.8 \text{ }\mu\text{g}/10\text{cm}^2/\text{month})$. The downslopes at Pauciflora had the highest average supply rate out of all the sites. NH₄⁺ supply rates along Poplar hillslopes were very similar, decreasing only slightly from upslope $(\bar{x} = 3.4 \text{ }\mu\text{g}/10\text{cm}^2/\text{month})$.

 $\mu g/10 \text{cm}^2/\text{month}$) to midslope ($\bar{x} = 3.2 \ \mu g/10 \text{cm}^2/\text{month}$) to downslope ($\bar{x} = 3.2 \ \mu g/10 \text{cm}^2/\text{month}$). Additionally, Poplar's downslope had the largest standard deviation ($\sigma = 11.6 \ \mu g/10 \text{cm}^2/\text{month}$). Likewise, Sandhill's hillslopes only differed slightly with the lowest mean rates ($\bar{x} = 1.3 \ \mu g/10 \text{cm}^2/\text{month}$) and standard deviation ($\sigma = 0.8 \ \mu g/10 \text{cm}^2/\text{month}$) occurring at the downslopes and highest mean rates occurring at the midslopes ($\bar{x} = 1.70 \ \mu g/10 \text{cm}^2/\text{month}$). Sandhill downslopes had the lowest mean NH₄⁺ supply rate across all sites.

Location along hillslope did not play a significant role for NH_4^+ supply rates at Poplar and Sandhill fens as no significant differences were found from the one-way ANOVA tests (Table 7). Conversely, NH_4^+ supply rates varied significantly across all hillslope positions at Pauciflora with downslopes having significantly higher rates than both midslopes and upslopes. The midslopes at Pauciflora also had significantly higher supply rates than upslopes.

Upslopes at Poplar had significantly higher NH_4^+ supply rates than upslopes at Pauciflora, which were significantly larger than upslopes at Sandhill (Table 8). Sandhill's midslopes had significantly lower rates in comparison to both Pauciflora and Poplar midslopes. Lastly, downslopes at Poplar had significantly greater NH_4^+ supply rates than Sandhill while Pauciflora had significantly greater rates in comparison to both sites.

4.2.3.2 Temporal characteristics

Pauciflora's highest average NH_4^+ supply rate occurred during the first burial period ($\bar{x} = 8.6 \ \mu g/10 \text{cm}^2/\text{month}$) (Figure 4.5; Table 5). This mean and standard deviation ($\sigma = 8.8 \ \mu g/10 \text{cm}^2/\text{month}$) was the largest of all burial periods at every site. NH_4^+ supply

rates at Pauciflora declined during the second burial period ($\bar{x} = 5.4 \ \mu g/10 \text{cm}^2/\text{month}$) before increasing slightly during the third ($\bar{x} = 6.2 \ \mu g/10 \text{cm}^2/\text{month}$). Poplar's NH₄⁺ supply rates were comparable in the first ($\bar{x} = 2.6 \ \mu g/10 \text{cm}^2/\text{month}$) and second ($\bar{x} = 2.6 \ \mu g/10 \text{cm}^2/\text{month}$) burial periods and increased during the third ($\bar{x} = 4.0 \ \mu g/10 \text{cm}^2/\text{month}$). NH₄⁺ supply rates at Sandhill were lowest during the first ($\bar{x} = 1.2 \ \mu g/10 \text{cm}^2/\text{month}$) and third ($\bar{x} = 1.4 \ \mu g/10 \text{cm}^2/\text{month}$) burial periods and peaked during the second period ($\bar{x} = 2.1 \ \mu g/10 \text{cm}^2/\text{month}$). Statistical tests revealed that the second burial period had significantly larger NH₄⁺ supply rates at the Sandhill Fen (Table 9). Additionally, Sandhill's first burial periods for every site.

4.3 Nitrogen Mineralization

4.3.1 N Mineralization

4.3.1.1 Spatial characteristics

N mineralization at Poplar had the highest mean ($\bar{x} = 17.5 \ \mu g \ N/g \ dry \ soil/month$) and standard deviation ($\sigma = 25.5 \ \mu g \ N/g \ dry \ soil/month$), followed by Sandhill ($\bar{x} = 7.4 \ \mu g \ N/g \ dry \ soil/burial \ duration$) and finally Pauciflora ($\bar{x} = 3.03 \ \mu g \ N/g \ dry \ soil/burial \ duration$) (Table 4; Figure 4.6). Poplar had significantly more mineralization than both Sandhill and Pauciflora (Table 6).

At Pauciflora the downslope positions had the most mineralization ($\bar{x} = 11.8 \ \mu g$ N/g dry soil/month), whereas both midslope and upslope positions had much lower mineralization with means of 0.02 μg N/g dry soil/month and 0.20 μg N/g dry soil/month, respectively. Additionally, these two positions had the lowest mean and standard

deviation across all sites. Poplar exhibited a gradual decrease in mineralization from downslope ($\bar{x} = 32.7 \ \mu g \ N/g \ dry \ soil/month$) to upslope ($\bar{x} = 1.4 \ \mu g \ N/g \ dry \ soil/month$). Poplar's downslope had the highest mean and standard deviation across all sites. Finally, Sandhill's highest average mineralization occurred at the midslopes ($\bar{x} = 10.4 \ \mu g \ N/g \ dry$ soil/month), followed by the downslopes ($\bar{x} = 7.5 \ \mu g \ N/g \ dry \ soil/month$), and then upslopes ($\bar{x} = 4.2 \ \mu g \ N/g \ dry \ soil/month$).

Pauciflora's downslopes had significantly more mineralization in comparison to both other hillslope positions (Table 7). The one-way ANOVA tests for Poplar and Sandhill revealed no significant difference in mineralization along hillslopes.

While no significant differences were found between the upslopes of all sites (Table 8), the mean mineralization value at Poplar midslopes was significantly greater than Pauciflora midslopes. Lastly, Poplar downslopes had significantly more mineralization that Sandhill downslopes.

4.3.1.2 Temporal characteristics

Pauciflora's first burial period had the lowest mean and standard deviation for mineralization out of all other sites (Figure 4.7; Table 5). Pauciflora started with negative mineralization in the first burial period ($\bar{x} = -0.42 \ \mu g \ N/g \ dry \ soil/month$), increasing to positive values in the second ($\bar{x} = 3.66 \ \mu g \ N/g \ dry \ soil/month$), and further increasing in the third ($\bar{x} = 4.70 \ \mu g \ N/g \ dry \ soil/month$). Poplar had an opposing trend with the highest average mineralization in the first period ($\bar{x} = 23.12 \ \mu g \ N/g \ dry \ soil/month$) and declining in second ($\bar{x} = 16.78 \ \mu g \ N/g \ dry \ soil/month$) and third ($\bar{x} = 13.59 \ \mu g \ N/g \ dry \ soil/month$) burial periods. Mean mineralization and standard deviation were greatest in the first

burial period at Poplar compared to all other burial periods at every site. Likewise, Sandhill had a gradual decrease from the first ($\bar{x} = 7.95 \ \mu g \ N/g \ dry \ soil/month$) to the second ($\bar{x} = 7.52 \ \mu g \ N/g \ dry \ soil/month$) to the third ($\bar{x} = 6.61 \ \mu g \ N/g \ dry \ soil/month$) burial period. No significant differences were identified for any burial period comparison for any site (Table 9).

4.3.2 Nitrification

4.3.2.1 Spatial characteristics

Sandhill had the largest average nitrification ($\bar{x} = 3.49 \ \mu g \ N/g \ dry \ soil/month$) and standard deviation ($\sigma = 8.83 \ \mu g \ N/g \ dry \ soil/month$) and Pauciflora had the lowest average nitrification ($\bar{x} = 0.54 \ \mu g \ N/g \ dry \ soil/month$) and standard deviation ($\sigma = 1.92 \ \mu g \ N/g \ dry \ soil/month$) (Table 4, Figure 4.6). However none of the sites were significantly different (Table 6).

Pauciflora's downslope had the most nitrification ($\bar{x} = 1.89 \ \mu g \ N/g \ dry$ soil/month) at the site followed by upslope ($\bar{x} = 0.14 \ \mu g \ N/g \ dry$ soil/month) and midslope ($\bar{x} = 0.05 \ \mu g \ N/g \ dry$ soil/month). Poplar had a gradual decrease in nitrification from upslope ($\bar{x} = 4.30 \ \mu g \ N/g \ dry$ soil/month) to midslope ($\bar{x} = -0.77 \ \mu g \ N/g \ dry$ soil/month) to downslope ($\bar{x} = -6.74 \ \mu g \ N/g \ dry$ soil/month). Poplar's downslope had the lowest nitrification across all sites. Sandhill had the highest mean nitrification and standard deviation ($\sigma = 12.37$) across all sites at the midslopes ($\bar{x} = 5.83 \ \mu g \ N/g \ dry$ soil/month). Sandhill's lowest nitrification occurred at the upslopes ($\bar{x} = 0.96 \ \mu g \ N/g \ dry$ soil/month). There were no significant differences found for any comparison tests within or between sites for nitrification (Table 7 and Table 8).

4.3.2.2 Temporal characteristics

Pauciflora had the lowest mean nitrification values during the first ($\bar{x} = -0.27 \ \mu g$ N/g dry soil/month) and third ($\bar{x} = -0.01 \ \mu g$ N/g dry soil/month) burial periods, and peaked during the second ($\bar{x} = 1.63 \ \mu g$ N/g dry soil/month) (Figure 4.7; Table 5). Poplar had the lowest nitrification across all sites during the first burial period ($\bar{x} = -10.45 \ \mu g$ N/g dry soil/month). Mean nitrification increased in the second ($\bar{x} = 1.01 \ \mu g$ N/g dry soil/month) and further in the third ($\bar{x} = 3.03 \ \mu g$ N/g dry soil/month) burial period at Poplar. Similar to Pauciflora, Sandhill's nitrification peaked during the second burial period ($\bar{x} = 5.82 \ \mu g$ N/g dry soil/month) with lower mean values occurring in the first (\bar{x} = 2.97 μg N/g dry soil/month) and third ($\bar{x} = 1.66 \ \mu g$ N/g dry soil/month) periods. Sandhill had the highest mean nitrification for all burial periods and sites occurring during the second period. Results from the one-way ANOVA test show a significant increase in nitrification at Pauciflora from burial periods 1 to 2 (Table 9). In addition, there was a significant increase in nitrification at Poplar in both second and third burial periods compared to the first burial period.

4.3.3 Ammonification

4.3.3.1 Spatial characteristics

Poplar had the highest mean ammonification ($\bar{x} = 19.17 \ \mu g \ N/g \ dry \ soil/month$) whereas Sandhill ($\bar{x} = 3.85 \ \mu g \ N/g \ dry \ soil/month$) and Pauciflora ($\bar{x} = 2.49 \ \mu g \ N/g \ dry \ soil/month$) had significantly lower mean ammonification values (Table 3 and Table 6; Figure 4.6).

Ammonification at Pauciflora was greatest at the downslope position ($\bar{x} = 9.90 \ \mu g$ N/g dry soil/month). Minimal ammonification occurred at the midslopes ($\bar{x} = -0.03 \ \mu g$ N/g dry soil/month) and upslopes ($\bar{x} = 0.06 \ \mu g$ N/g dry soil/month). Additionally, Pauciflora's midslope position had the lowest average ammonification across all sites. The highest mean ($\bar{x} = 39.42 \ \mu g$ N/g dry soil/month) and standard deviation ($\sigma = 31.42 \ \mu g$ N/g dry soil/month) across all sites occurred at Poplar's downslopes. Ammonification at Poplar demonstrates a gradual decrease from downslope to midslope ($\bar{x} = 16.60 \ \mu g$ N/g dry soil/month) to upslope ($\bar{x} = -2.05 \ \mu g$ N/g dry soil/month). Sandhill's average ammonification values were comparable along hillslope positions. The midslopes ($\bar{x} = 4.53 \ \mu g$ N/g dry soil/month) were only slightly larger than the upslopes and downslopes ($\bar{x} = 3.3 \ \mu g$ N/g dry soil/month).

Pauciflora's downslopes had significantly more ammonification than both midslope and upslope positions (Table 7). Poplar's upslopes had significantly less ammonification than both midslope and downslope positions. Sandhill Fen showed no significant difference in ammonification along hillslopes.

Among the three sites, the upslope positions did not have significantly different mean ammonification values (Table 8). Midslopes were only significantly different between Pauciflora ($\bar{x} = -0.03 \ \mu g \ N/g \ dry \ soil/month$) and Poplar ($\bar{x} = 16.60 \ \mu g \ N/g \ dry \ soil/month$). Finally, Poplar downslopes had significantly more ammonification than Sandhill downslopes.

4.3.3.2 Temporal characteristics

Mean ammonification increased gradually at Pauciflora from the first ($\bar{x} = -0.15$ µg N/g dry soil/month) to the second ($\bar{x} = 2.04$ µg N/g dry soil/month to the third ($\bar{x} = 4.70$ µg N/g dry soil/month) burial periods (Figure 4.7; Table 5). Yet, Pauciflora had the lowest mean ammonification for all burial periods across all site. Poplar had a converse trend with the largest mean ammonification in the first period ($\bar{x} = 33.58$ µg N/g dry soil/month), gradually decreasing in the second ($\bar{x} = 15.77$ µg N/g dry soil/month) and further in the third ($\bar{x} = 10.56$ µg N/g dry soil/month). Furthermore, mean ammonification during the first burial period at Poplar was greater than all other burial periods at each site. Sandhill's ammonification declined from first ($\bar{x} = 4.99$ µg N/g dry soil/month) to second ($\bar{x} = 1.69$ µg N/g dry soil/month) period, and increased in the third burial period to a mean value comparable with the first burial period ($\bar{x} = 4.94$ µg N/g dry soil/month). Significant differences between burial periods were not found for any site (Table 9).

4.4 Relationships Between Site Properties and N Availability

The Spearman Rank Correlation tests were intended to aid in the understanding of the relationship between site properties and nutrient status at each site. Relationships with moderate (rho = 0.4 - 0.59) to very strong (rho = 0.80-1) correlation strengths are considered significant. While all parameters were correlated at each site, only parameters that are directly related will be discussed in this study. These direct parameter correlations are: TN supply rate and NO₃⁻ supply rate (Figure 4.8), TN supply rate and NH₄⁺ supply rate (Figure 4.8), mineralization and nitrification (Figure 4.9), nitrification and NH₄⁺ supply rate

(Figure 4.10), NO_3^- supply rate and mineralization (Figure 4.11), ammonification and GWC (Figure 4.12), and ammonification and SOM (Figure 4.12). Spearman rho values for these and all other correlations are available in the Appendix (Tables 11-13).

TN supply rates were correlated against NO_3^- and NH_4^+ supply rates to understand which form of inorganic N controls TN (Figure 4.8). NO_3^- supply rates largely controlled TN at Sandhill and Poplar, whereas NH_4^+ controlled TN at Pauciflora. Likewise, mineralization was correlated against nitrification and ammonification at each site to identify which form of N transformation controlled TN mineralization (Figure 4.9). Poplar and Pauciflora mineralization was dominated by ammonification. Correlations for Sandhill mineralization, however, demonstrated a similar contribution by both nitrification and ammonification.

 $\rm NH_4^+$ supply rates were plotted against nitrification at the three sites (Figure 4.10). Sandhill and Pauciflora both had moderate to strong positive correlations, whereas Poplar had a weak negative correlation.

N mineralization was also plotted against NO₃⁻ supply rates for all sites (Figure 4.11). Sandhill and Pauciflora had very weak to weak positive correlations, whereas Poplar had a strong negative correlation.

Lastly, ammonification was plotted against gravimetric water content and soil organic matter (Figure 4.12). Sandhill had very weak correlations with both soil properties. Pauciflora showed moderately strong positive correlations with both soil moisture and organic content. By comparison, Poplar had a moderately strong positive correlation with soil moisture but a weak negative correlation with organic matter.

SECTION 5 - DISCUSSION

The research purpose for the Sandhill Fen was to determine the effectiveness of reclamation techniques for establishing a peatland system. Some reforestation projects on post oil sands mine sites have shown promise for success, notably Syncrude's "Gateway Hill" that received a reclamation certificate in 2008 (Davidson and Gismondi, 2011). To date, however, there have been only two attempts to established peatland ecosystems (Vitt and Bhatti, 2012).

Soil nutrient status is an important component in the overall understanding of ecosystem productivity. Nitrogen supply rates as measured by the PRS probes offer some insight into soil quality, although this method has some disadvantages in that PRS probes do not compete well with other soil organisms (Qian and Schoenau, 2002). Therefore, it is appropriate to couple these measurements with other methods of examining soil nutrient status. Here, N mineralization was determined through the buried polyethylene bag sampling method (Eno, 1960), which includes both nitrification and ammonification processes. This technique provides information about microbial immobilization and the overall efficacy of the soil to transform organic N into plant available forms (Eno, 1960; Hanselman et al., 2004; Harrison and Maynard, 2014; Zou et al., 1992).

This study focused on the N supply rates and mineralization at the Sandhill Fen in comparison to two natural reference sites: a nutrient poor fen and a nutrient rich fen. This contextualization aids in our understanding of soil nutrient dynamics. All three wetland watersheds were sampled across a topographic gradient consisting of a mineral soil

upland, transitional midslope, and organic wetland components. As hillslope position strongly influences soil properties, there are marked differences in nutrient status.

The three sites experienced variable N supply rates, mineralization and soil properties. Within each site, N availability varied along hillslope position as a function of soil structure and soil properties. Temporal factors had weak effects and were restricted to two parameters at a few locations: NH_4^+ supply rates and nitrification. Overall, time did not significantly impact supply rates and mineralization. Finally, reclamation soils had significant and unique effects on N cycling and supply.

5.1 Influence of Hillslope Position on Nutrient Status

Jordan et al. (2011) note that wetland soils have a high potential for removal of NO_3^- through denitrification. In this study, the lowest NO_3^- supply rates were found in the downslope position at all three sites (Figure 4.4). This can be explained by the relationship between NO_3^- transformation processes and soil moisture. Increasing soil moisture content in wetland soils impede NO_3^- production, particularly with lower redox potentials (Brady and Weil, 2008; Burgin et al., 2010; Malhi et al., 1990), explaining lower NO_3^- supply rates in the wet downslope positions and higher in dry upslope positions. These findings are consistent with literature that report high denitrification rates in topographically low saturated areas of boreal fens (Mewhort, 2000; Wray and Baylay, 2007). Vymazal (2007) conducted a N removal study and found that anoxic wetland conditions enhanced denitrification. Furthermore, studies that have added NO_3^- to anaerobic wetland soils found that up to 90% was removed after only a few days. This NO_3^- loss was likely due to a combination of denitrification and microbial immobilization

(Nichols, 1983). Thus, it is plausible that Poplar's anaerobic soils in the downslope positions explain the net negative nitrification. Unfortunately, the research design of this study did not include additional measurements to determine which removal process (i.e. microbial immobilization or denitrification) was responsible for the negative values, creating uncertainty in reasons behind the lack of available N. Significantly higher nitrification and NO₃⁻ supply rates at Poplar's upland are presumed due to more aerobic conditions (Figure 4.4 and Figure 4.6) (Bowden, 1987). GWC at these locations was much closer to optimal nitrification levels as reported elsewhere (Agehara and Warncke, 2005; Mahli and McGill, 1982; Sleutel et al., 2008).

Pauciflora had little variability in NO_3^- supply rates and nitrification along the hillslopes. In fact, supply of NO_3^- was the lowest across all sites and net nitrification was close to 0 µg/g dry soil/month for all hillslope positions. Pauciflora is characteristically acidic and poorly drained, which creates unfavourable conditions for NO_3^- production (Brady and Weil, 2008; Limpens et al., 2006). Poorly drained soils have higher rates of denitrification compared to well-drained soils, especially if they are acidic (Groffman et al., 2003; Seitzinger, 1994). Sphagnum mosses and vascular plants often assimilate additional inputs of NO_3^- in these types of environments before inorganic N reaches microbial levels of denitrification and immobilization (Limpens et al. 2006; Woodin and Lee, 1987).

Similar to Pauciflora, Sandhill had comparably low NO_3^- supply rates in the downslopes and midslopes (Figure 4.4). This was unexpected for the midslopes given ideal soil moisture content of 0.802 g/g (Figure 4.1), adequate organic content (~30%) and high nitrification (Figure 4.6) (Agehara and Warncke, 2005; Bowden, 1987; Sleutel

et al., 2008). Plants and microbes are excellent competitors against the PRS probes for nutrient uptake (Qian and Schoenau, 2002). In fact, Subler et al. (1995) found that cation exchange membranes accumulated significantly less NO₃⁻ under conditions of high immobilization and Binkley (1984) reported that grass roots outcompeted resin bags for inorganic N. Both hillslope positions at Sandhill were highly productive with large vascular plants (Figure 4.13). Therefore, it is possible that NO₃⁻ was produced and then lost through plant uptake before detection by the PRS probes.

Net ammonification generally controls net mineralization in most boreal peatland soils (Bayley et al., 2005), largely due to the positive association between ammonification and soil moisture (McMillan et al., 2007). Ammonification can take place in both oxic and anoxic environments, whereas nitrification is largely limited to aerobic conditions (Chen et al., 2012; Hefting et al. 2004; Pinay et al., 2002). For example, Chen et al. (2012) reported that fen soils respond to permanent flooding by increasing gross ammonification levels. Similarly Wray & Bayley (2008) found a positive correlation between gross ammonification and soil moisture content in a boreal peatland.

A study conducted on four boreal peatlands by Bayley et al. (2005) found negligible nitrification as well as almost identical net mineralization and net ammonification demonstrating the large imbalance between ammonification and nitrification in boreal wetland soils. Additionally this comparison study found higher ammonification rates in the peat fen site compared to the bog site. Net mineralization at the natural sites in this study (Pauciflora and Poplar) was consistent with the abovementioned literature. Pauciflora and Poplar were both dominated by ammonification and

furthermore the nutrient rich fen (Poplar) had significantly more net ammonification than the nutrient poor fen (Pauciflora). Poplar experienced the most ammonification out of all sites in the downslopes, which can be explained by reduced anoxic conditions (Bowden, 1987). Here, ammonification decreased gradually along the hillslope reaching negative values in the uplands as a result of increasingly aerobic conditions. Ammonification in the downslopes did not correlate with larger NH_4^+ supply rates, which suggests other forms of removal in the wetland. N transformation processes are an unlikely source of removal since nitrification and NO_3^- supply rates in the downslopes are negative and low. Therefore, plant uptake of NH_4^+ is likely the main source of N removal in the downslope positions at Poplar.

Pauciflora downslopes had the highest NH_4^+ supply rates among all sites, which dropped significantly in the midslopes, increasing again in the upslopes. This drop in NH_4^+ supply rates at the midslopes can be explained in part due to the topographic position and soil properties. Soil types were mostly sandy clay, suggesting that NH_4^+ fixation by clay minerals may be affecting N availability (Brady and Weil, 2008; Kowalenko and Cameron, 1976; Vitousek and Melillo, 1979). The midslopes at Pauciflora had a steeper slope compared to the flatter upslope and downslope positions. This convex curvature enhances runoff (Beven and Kirkby, 1979) and may consequently encourage the erosion of fine-grained material such as clays as well as any NH_4^+ that is fixed to the clays (Schlesinger and Bernhardt, 2013). Additionally, Limpens et al., (2006) states that the majority of N available for NH_4^+ production in peatland is in the organic material. Therefore, NH_4^+ production may have been limited due to lack of organic

matter at the midslopes (Figure 4.1), which is apparent from the net ammonification values (Figure 4.6).

Many natural boreal peatlands with high organic matter contents have high ammonification (Baylay et al., 2005; Geurts et al., 2010). However soil organic matter was not significantly correlated to ammonification at Sandhill (Figure 4.12), which may explain the consistently low net ammonification along the hillslopes. The downslopes at Sandhill also had significantly lower soil moisture than the downslopes at the other sites (Figure 4.1). Therefore the highly organic anaerobic conditions required for ammonification were not present at Sandhill. Low NH_4^+ levels indicate either high plant uptake or nitrification; or low ammonification (Davidson et al., 1990; Schlesinger and Bernhardt, 2013). Net nitrification was relatively high at the downslope and midslope positions, which had a significant positive correlation with low NH_4^+ supply rates (Figure 4.10). This suggests a highly transient form of NH_4^+ , transforming rapidly to NO_3^- through nitrification at Sandhill's midslopes and downslopes.

5.2 Influence of Seasonality on Nutrient Status

Microorganisms in natural boreal peatlands are vulnerable to changes in soil moisture as a result of seasonality (Williams and Silcock, 2000). Nitrifying bacteria is considerably more susceptible than heterotrophic organisms responsible for ammonification (Brady and Weil, 2008). These microorganisms are temperature sensitive, therefore nitrogen transformation processes are also subject to seasonality (Bowden, 1987).

N supply rates and soil properties at all sites were not significantly variable throughout the growing season, except for NH_4^+ at Sandhill. Hemstock et al. (2010)

found no significant difference in total labile N in natural and reclaimed peat materials in the boreal region between May and August. However concentrations increased significantly following the growing season peaking in November. It is possible that similar mechanisms occurred during this study and were not accounted for in the research design.

Nitrification at Pauciflora increased significantly from negative values in the first to positive values in the second burial period. This is likely due warmer temperatures and decreased water tables in the downslopes. Nitrification is strongly influenced by temperature, which is generally most productive between 30 and 40 °C (Agehara and Warncke, 2005; Mahli et al., 1990). However depending on the soil type the optimal temperature may be higher or lower (Macduff and White, 1985; Mahli and McGill, 1982). Mean temperatures for all sites were lowest in the first burial period (Figure 3.4). In fact, when samples were collected at the beginning of the first burial period at Pauciflora, the wetland soils had yet to thaw. Cooper et al. (1996) stated that the development of nitrifying bacteria is limited to temperatures over 4°C. Pauciflora experienced atmospheric temperatures below 5°C in the first period, which likely hindered soil warming and bacteria growth. Therefore nitrification at Pauciflora would have been reduced early in the season from the colder temperatures.

Poplar experienced a similar phenomenon, having very low net negative nitrification values in the first burial period and increasing significantly to positive nitrification values in the second and third period. Nitrification was significantly lower in the first period likely due to low temperatures (Figure 3.4), and high GWC (Figure 4.1).

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Soil moisture decreased throughout the summer, which likely allowed nitrifying bacteria to become more productive.

5.3 Influence of Oil Sands Reclamation on Nutrient Status

In natural boreal wetlands with high SOM contents, the production of NH_4^+ through the inter-cellular enzymatic breakdown of C—H and C—NH₂ bonds is very efficient (Brady and Weil, 2008). Breland and Hansen (1996), Mummey et al. (2002), Rowland et al. (2009), and Visser et al. (1983) all stated that soil microbial biomass is generally lower following some form of disturbance. The Sandhill Fen had both low SOM (Figure 4.1) and ammonification (Figure 4.6) likely leading to low NH_4^+ supply rates. Disturbance of the peat soil through removal, transportation and application may have disrupted the breakdown of organic material by microorganisms. A study conducted by Dimitriu and Grayston (2010) compared bacterial communities in natural boreal forest and reclaimed peat sites. They not only found that the disturbed sites had decreased diversity in active communities but that soil disturbance through reclamation practices may coerce shifts in bacterial communities through changes in pH and soil moisture. Therefore it is plausible that in conjunction with low SOM, Sandhill is also experiencing reduced activity from soil microbes, which in turn hinders ammonification processes.

Mineralization in typical boreal peat soils is controlled by ammonification, which was true for Pauciflora and Poplar (Carmosini et al., 2003; Jerabkova et al., 2006; Westbrook and Devito, 2004). However, Sandhill's mineralization was evenly controlled by both ammonification and nitrification processes. A similar comparison study conducted by McMillan et al. (2007) also found lower net ammonification in reclaimed

peat soils compared to natural sites. Literature indicates that this transient nature of NH_4^+ and the significance of net nitrification are typical in soils that have experienced mass disturbance such as clear cutting, but not in natural boreal soils (Carmosini et al., 2003; Jerabkova et al., 2006; Lindo and Visser, 2003; McMillan, 2005; Westbrook and Devito, 2004). Rowland et al. (2009) used PRS probes to quantify soil N availability and found lower NH_4^+ supply rates in reclaimed forested systems as well. This shows that ammonification and NH_4^+ supply are affected in several forms of reclaimed ecotypes.

Boreal wetland studies have established a positive correlation between net N mineralization and soil moisture (Kowalenko and Cameron 1976; Stottlemyer and Toczydlowski 1999; Carmosini et al. 2003). Pauciflora and Poplar both had moderately strong positive correlations between ammonification and GWC. Sandhill, on the other hand, demonstrated no such relationship. Hemstock et al. (2010) found similar results between peat amendments and natural sites. Further, this study discussed the ambiguity that more soil moisture will lead to increased net mineralization due to the control of nitrification in certain reclaimed systems. This would greatly impact internal N cycling at the Sandhill Fen and thus warrants further research.

When Sandhill was first commissioned the peat and mineral soils were completely bare. The initial lack of organic material available for decomposition and mineralization may have retarded ammonification processes as well as subsequent NH₄⁺ supply rates. Even though Sandhill is currently vegetated with different vascular plants that include some tree species, the site is too juvenile for significant canopy cover. Natural boreal peatlands benefit from canopy cover by slowing evaporation and regulating soil temperatures (McMillan et al., 2007). Sandhill's soils have more exposure

and subsequent warmer temperatures, which accelerates nitrification (Cooper et al., 1996; Vymazal, 1995; Vymazal, 2007). These relatively lower NH_4^+ supply rates at the Sandhill Fen are consistent with Rowland et al. (2009) who found lower NH_4^+ in the reclaimed peat soils and claims this is typical of these sorts of constructed environments.

Sandhill had higher overall bulk densities than Poplar. Other reclamation sites involving the stockpiling of peat soil before placement show similarly large bulk densities (Bradshaw, 1983; Grigal, 2000, McMillan et al., 2007). However, the peat soil at the Sandhill Fen was only stockpiled for a short period before transported directly to site. This demonstrates that the use of heavy machinery for peat application may affect bulk densities through soil compaction. It is also likely that mineral material was unintentionally included in the peat extraction from the donor site further contributing to higher bulk densities. This is consistent with Walczak et al. (2002) who reported higher bulk densities when mixing sand with peat soil.

The uplands at Sandhill had significantly higher NO₃⁻ supply rates than midslopes and downslopes (Figure 4.4). Interestingly, the uplands also had the lowest net nitrification and net mineralization (Figure 4.6). This suggests that either vegetation in the uplands are underdeveloped and therefore not assimilating as much NO₃⁻ as the more productive midslope and downslope positions thus causing the probes to record larger supply rates; or Sandhill is receiving NO₃⁻ supplies from an external source. There have been concerns about the negative impacts of external supplies of N as a by-product of oil sands activities (Trites and Baylay, 2009). For example, high concentrations of NH₄⁺ found in oil sands process-affected waters have shown to be toxic to plants and indirectly slow peat accumulation through reduced productivity (Britto and Kronzucker, 2002;

Trites and Baylay, 2009). Excessive amounts of NH_4^+ can also be toxic to *Nitrobacter* and thus affect the nitrification processes as well (Brady and Weil, 2008). The oil sands region tends to have large amounts of HNO₃ as well NO₂ that is rapidly oxidized to NO₃⁻ in the atmosphere (J. Straker, personal communication 2015). In fact, a study conducted between 1994 and 1998 specifies that a significant portion of the average 303 mol_c / ha/ yr of the total N deposition in Alberta is associated with organic soils (Carou, et al., 2008). Thus the Sandhill Fen may be experiencing external sources of N as a result of oil sands activities.

5.4 Avenues for Future Research

These results provide significant acumen into the N availability of a reclaimed wetland system. However there are uncertainties around the causation of these findings as a result of the research design. It is recommended that analyses of microbial biomass and labile N pools be introduced into this study in future years. This will contribute to an understanding of microbial immobilization, as well as offer insight into the productivity of facultative bacteria and other microbial communities. It may also be beneficial to capture litter decomposition since some literature demonstrates slower decomposition in reclaimed sites (Rowland et al., 2009). Finally, it may be necessary to adjust the study period to include September and October to capture the full effects of seasonality on all parameters. It is imperative that this research continues as the Sandhill Fen matures to fully capture patterns of soil nutrient availability.

SECTION 6 - CONCLUSION

This study shows that reclamation practices affect N availability in wetland soils. The Sandhill Fen had similar overall net mineralization, net nitrification, net ammonification, and NO_3^- supply rates to Pauciflora (a poor fen), but significantly lower net mineralization, net ammonification, TN and NH_4^+ supply rates, GWC and SOM than Poplar (a rich fen). This does not imply that Sandhill is functioning as a nutrient poor fen, but rather as a disturbed system. The most significant indication of this is the prominence of net nitrification in net mineralization at Sandhill, whereas both Poplar and Pauciflora were dominated by ammonification, which is characteristic for natural boreal wetland systems. These findings are consistent with other comparison studies between different forms of reclaimed soil and natural soil (Bradshaw, 1983; Grigal, 2000, Hemstock et al., 2010; McMillan et al., 2007; Rowland et al., 2009).

In conjunction with this unnatural balance between nitrification and ammonification at the Sandhill Fen, certain conclusions can be made based on the results of this study:

1) Sandhill had lower GWC, SOM, and Φ , and higher ρ_b . These soil properties are not conducive for higher wetland N availability and likely affected the nutrient status. However these soil properties did exhibit a gradual decrease (or increase in the case of ρ_b) from downslope to upslope positions at Sandhill that would be expected in a natural fen.

2) TN supply rates at Sandhill were controlled by NO_3^- supply rates,

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which was consistent with Poplar. Sandhill TN supply was significantly less overall than both other sites, particularly in the downslope and midslope positions.

- 3) While NO₃⁻ supply rates did not vary significantly among the three sites, Sandhill's upslopes had a greater supply than both midslopes and downslopes. Since Sandhill had the lowest net nitrification at the upslopes, this discrepancy suggests an external source of N to the uplands, possibly from oil sands activities.
- 4) Sandhill had the lowest NH₄⁺ supply rates of the three sites, which is typical of reclaimed soils (Rowland et al. 2009). Both NH₄⁺ supply rates and ammonification were invariable from upslope to downslope. Generally, natural wetlands sites have correlations between ammonification and soil moisture, as exhibited at Poplar and Pauciflora but not at Sandhill (Figure 12). This disconnect between soil moisture and ammonification partially explains why these variables followed different patterns along the hillslope at the Sandhill. The lack of correlation between ammonification and soil moisture may suggest that soil disturbance has affected microbial N transformation processes.
- 5) Sandhill had significantly lower mineralization and ammonification than Poplar. However mineralization rates were slightly higher than Pauciflora. This is a function of both higher nitrification at Sandhill contributing to higher mineralization, whereas poorly drained acidic conditions at Pauciflora hindered nitrification processes. While,

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nitrification was consistently low across all sites, Sandhill exhibited the highest nitrification values at the midslopes and downslopes.

6) There was virtually no influence of seasonality on all parameters except NH₄⁺ supply rates at Sandhill and nitrification at Poplar and Pauciflora in the spring, which were likely a function of temperature.

In the construction of the Sandhill Fen, it was important to simulate the natural progression from dry mineral uplands to wet organic lowlands. This progression was captured by the soil properties along hillslope positions, which offers promise to the effectiveness of the design. However, the Sandhill Fen reflects its infancy in the supply and mineralization of N. These results also demonstrate a limited understanding of the effects of reclamation on soil nutrient regimes. While the results from this study show low net ammonification, low TN and NH_4^+ supply rates, as well as high nitrification and NO_3^- supply rates, further research is required to determine possible external sources of N and internal soil microbial activity.

In summary, oil sands mining practices involves the mass destruction of natural boreal ecosystems through forest clear cuts, stream diversions, and wetland removal. This has resulted in a cumulative disturbance of 47 832 ha from 1967 to 2006, of which only 1 % has been effectively reclaimed (Grant et al., 2008, Alberta Government, 2012). It has been estimated that by 1996 the total wetland area in Alberta had been reduced by 60% (Wilson et a., 2001). However there has been no certifiable success in reclaiming self-sustainable peat-forming wetland systems. Furthermore permanent wetland loss is expected as a result of a shift from wetland to upland ecosystems after mine closure (Grant et al., 2008). Therefore, it is absolutely essential to gain an extensive knowledge

of oil sands wetland reclamation in order to recover as much wetland space as possible. While the Sandhill Fen offers ample research opportunities in the years ahead, especially in the field of nutrient bioavailability, the lengthy trajectory of this project in combination with the uncertainty of its success should be considered during the implementation of further wetland reclamation practices.

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SECTION 8 – FIGURES AND TABLES

Figure 3.1: Map of the Sandhill fen, Pauciflora Fen and Poplar fen relative to the city of Fort McMurray, Alberta.



Figure 3.2: The Sandhill fen outlet pond facing west (a) 2012 (before boardwalks) (b) 2013 (c) 2014.



Figure 3.3: Poplar fen facing south-east.



Figure 3.4: Temperature plot from Mildred Lake airport applying to both Poplar and Sandhill fen (red) a HMP155 humidity and temperature probe at Pauciflora fen (blue). A gray dashed line delineates the burial periods.



Figure 3.5: Pauciflora fen facing south.



Figure 3.6: An anion (orange) and cation (purple) PRS probes before and after installation.



Figure 3.7: Polyethylene bag sampling method installation.





Figure 4.1: Comparative box-and-whisker plots for soil moisture and organic content for all sites (upper panel): Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray) and; b) every hillslope position (lower panel): down, mid, and up. The mean is shown with a red diamond.



Figure 4.2: Comparative box-and-whisker plots for soil moisture during all burial periods (1, 2, and 3) for all sites: Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray). The mean is shown with a red diamond.



Figure 4.3: Comparative box-and-whisker plots for bulk density and porosity for all sites (upper panel): Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray) and; b) every hillslope position (lower panel): down, mid, and up. The mean is shown with a red diamond.



Figure 4.4: Comparative box-and-whisker plots for TN supply rates for all sites (left panel): Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray) and; b) every hillslope position (right panel): down, mid, and up. The mean is shown with a red diamond.



Figure 4.5: Comparative box-and-whisker plots for TN, NO_3^- and NH_4^+ supply rates during all burial periods (1, 2, and 3) for all sites: Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray). The mean is shown with a red diamond.



Figure 4.6: Comparative box-and-whisker plots for net N mineralization, net nitrification and net ammonification for all sites (left panel): Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray); and every hillslope position (right panel): down, mid, and up. A red line delineates the boundary between net mineralization (>0) and net immobilization (<0). The mean is shown with a red diamond.



Figure 4.7: Comparative box-and-whisker plots for net N mineralization, nitrification and ammonification during all burial periods (1, 2, and 3) for all sites: Pauciflora fen (green), Poplar fen (blue), Sandhill fen (gray). A red line delineates the boundary between net mineralization (>0) and net immobilization (<0). The mean is shown with a red diamond.





Figure 4.8: Scatter plots with showing the correlation between TN supply rates and both NO_3^- supply rates (left) and NH_4^+ supply rates (right) for the three sites: a) Sandhill fen, b) Pauciflora fen, and c) Poplar fen. Trendlines are present when correlations are significant (moderate to very strong).





Figure 4.9: Scatter plots showing the correlations between TN mineralization and both nitrification (left) and ammonification (right) at the three sites: a) Sandhill fen, b) Pauciflora fen, and c) Poplar fen. Upslope locations = red circle, midslope locations = yellow triangle, downslope locations = purple diamond. Trendlines are present when correlations are significant (moderate to very strong).





Figure 4.10: Scatter plots showing the correlations between nitrification and NH_4^+ supply rates at the three sites: a) Sandhill fen, b) Pauciflora fen, and c) Poplar fen. Upslope locations = red circle, midslope locations = yellow triangle, downslope locations = purple diamond. Trendlines are present when correlations are significant (moderate to very strong).



Figure 4.11: Scatter plots showing the correlations between N mineralization and NO_3^- flux at the three sites: a) Sandhill fen, b) Pauciflora fen, and c) Poplar fen. Upslope locations = red circle, midslope locations = yellow triangle, downslope locations = purple diamond. Trendlines are present when correlations are significant (moderate to very strong).



Figure 4.12: Scatter plots showing the correlations between ammonification and both soil moisture (left) and organic matter (right) at the three sites: a) Sandhill fen, b) Pauciflora fen, and c) Poplar fen. Upslope locations = red circle, midslope locations = yellow triangle, downslope locations = purple diamond. Trendlines are present when correlations are significant (moderate to very strong).



Figure 4.13: Example of the large vascular plants that dominate the midslopes and downslopes at the Sandhill Fen.

	Transect		Degree of peat	
Site	number	Sub-location	humification	Mineral ID
Sandhill	2	Upslope		Loamy sand
Sandhill	2	Midslope		Loamy sand
Sandhill	2	Downslope	Н9	
Sandhill	4	Upslope		Loamy sand
Sandhill	4	Midslope	H7/H8	Loamy sand
Sandhill	4	Downslope	H8	Clay loam
Sandhill	6	Upslope		Sandy clay
Sandhill	6	Midslope		Loamy sand
Sandhill	6	Downslope		Loamy sand
Sandhill	8	Upslope		Loamy sand
Sandhill	8	Midslope		Loamy sand
Sandhill	8	Downslope	H8/H9	Clay
Sandhill	10	Upslope		Loamy sand
Sandhill	10	Midslope	H8	Sandy clay
Sandhill	10	Downslope	H8	Sandy clay
Pauciflora	1	Upslope		Sandy loam
Pauciflora	1	Midslope	H8	Sandy clay loam
Pauciflora	1	Downslope	H8	Clay
Pauciflora	2	Upslope		Sandy clay loam
Pauciflora	2	Midslope	H8/H9	Sandy clay
Pauciflora	2	Downslope	H8	
Pauciflora	3	Upslope		Loamy sand
Pauciflora	3	Midslope		Sandy clay
Pauciflora	3	Downslope	H8	Sandy clam loam
Poplar	1	Upslope	H7/H8	
Poplar	1	Midslope	H7/H8	
Poplar	1	Downslope	H8/H9	
Poplar	2	Upslope		Loamy sand
Poplar	2	Midslope	H7/H8	
Poplar	2	Downslope	H8/H9	

Table 1: Degree of humification and mineral identification for certain transects at all sites.

			C (g/g)	SOM (%)					Bulk Density (g/cm ³)				Porosity (%)				
			Hillslope		Hillslope			Hillslope			Hillslope			slope			
	Hillslope	S	ite	pos	ition	Si	te	posi	ion	Si	te	pos	ition	Si	ite	pos	ition
Site	position	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
	Upslope			0.359	0.183			7.1	3.6			0.61	0.18			76.83	6.64
	Midslope			0.314	0.115			7.3	5.6			0.57	0.08			78.32	3.01
Pauciflora	Downslope	1.242	2.416	3.960	3.869	15.9	22.6	33.4	33.3	0.58	0.22	0.54	0.40	78.05	7.81	78.98	13.68
	Upslope			1.463	1.717			41.7	41.6			0.66	0.66			72.48	21.26
	Midslope			3.124	1.539			68.2	20.0			0.20	0.09			90.63	0.71
Poplar	Downslope	3.532	2.605	5.664	2.657	58.6	28.8	66.0	12.6	0.36	0.38	0.23	0.04	82.81	12.72	85.31	2.82
	Upslope			0.080	0.084			4.1	0.9			0.74	0.24			72.05	8.91
	Midslope			0.802	0.571			28.7	21.6			0.53	0.25			79.86	9.27
Sandhill	Downslope	0.876	0.952	1.806	0.986	25.1	22.9	42.4	19.3	0.52	0.28	0.28	0.13	78.95	10.16	84.93	9.51

Table 2: Mean and standard deviation (σ) values for all soil properties summarized by site and hillslope location.

			TN su	pply rate			NO ₃ ⁻ su	pply rat	e	NH ₄ ⁺ supply rate				
			(µg/10c	m2/mont	1)	(µg/10cr	n2/mont	h)	(µg/10cm	2/mont	2/month)	
		~		Hills	slope			Hill	slope	~		Hillslope		
	Hillslope	S	ite	pos	tion	Site		position		Site		position		
Site	position	\bar{x}	σ	\overline{x}	σ	x	σ	x	σ	\bar{x}	σ	\bar{x}	σ	
	Upslope			4.23	4.13			1.20	1.29			2.38	3.00	
	Midslope			4.54	2.44			1.53	0.99			3.01	2.30	
Pauciflora	Downslope	6.00	7.09	10.83	12.53	1.28	1.11	1.03	1.14	4.47	6.47	9.80	2.89	
	Upslope			9.46	3.77			6.01	2.56			3.42	1.94	
	Midslope			7.95	5.55			4.78	5.21			3.17	1.80	
Poplar	Downslope	7.50	4.64	5.42	4.20	4.26	3.65	2.29	1.50	3.24	2.55	3.15	11.65	
	Upslope			8.95	11.53			7.32	11.54			1.62	1.33	
	Midslope			3.63	1.98			1.93	1.45			1.70	0.97	
Sandhill	Downslope	5.67	7.97	4.20	6.23	4.13	7.90	2.90	6.12	1.54	1.06	1.30	0.81	

Table 3: Mean and standard deviation values for all forms of N supply rates summarized by site and hillslope location.

1 able 4. Intern and standard deviation values for tv inineralization, annioinfication and intrineation rates summarized by site and infisiop												insiope ioc	ation.	
			TN Mine				Nitri	fication		Ammonification				
		(µg N/g dry	soil/month	ı)	(μ	g N/g dr	y soil/moi	nth)	(µg N/g dry soil/month)				
				Hills	slope			Hills	slope			Hills	slope	
	Hillslope	Si	ite	position		Site		position		Site		position		
Site	e position	\bar{x}	σ	x	σ	\overline{x}	σ	\bar{x}	σ	\bar{x}	σ	x	σ	
	Upslope			0.20	1.62			0.14	0.63			0.06	1.50	
	Midslope			0.02	2.03			0.05	0.51			-0.03	1.96	
Paucifl	lora Downslope	3.03	6.67	11.79	8.41	0.54	1.92	1.89	3.60	2.49	6.25	9.90	9.04	
	Upslope			1.35	7.75			3.40	7.23			-2.05	3.08	
	Midslope			15.83	24.16			-0.77	3.77			16.60	23.24	
Popla	ar Downslope	17.52	25.54	32.69	30.25	1.65	8.79	-6.74	11.56	19.17	28.00	39.42	31.80	
	Upslope			4.20	6.05			0.96	1.29			3.24	5.57	
	Midslope			10.37	18.53			5.83	12.37			4.53	13.58	
Sandh	nill Downslope	7.35	12.48	7.47	9.18	3.49	8.83	3.71	8.80	3.85	9.29	3.77	7.27	

Table 4: Mean and	standard de	viation values for 1	N mineralization,	ammonification	and nitrification	rates summ	arized by	v site and hillslop	be location.

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Table 5: Mean and standard deviation values for all parameters summarized by burial period number.

	GWC		TN sup	ply rate	NO_3 su	pply rate	NH_4 su	pply rate	TN Mine	ralization	Nitrification		Ammonification		
	Burial Period	units	s: g/g		ı	units: µg/l	0cm2/mo	nth	units: $\mu g N/g dry soil/month$						
Site Nur	Number	x	σ	x	σ	x	σ	x	σ	x	σ	x	σ	x	σ
	1	0.365	0.152	12.30	10.29	3.68	4.67	8.61	8.84	-0.42	2.71	-0.27	0.53	-0.15	2.69
	2	1.616	2.864	7.18	6.34	1.43	1.59	5.44	5.83	3.66	5.23	1.63	2.87	2.04	4.00
Pauciflora	3	1.454	2.789	7.95	8.20	1.74	1.61	6.20	7.66	4.70	9.13	0.01	0.26	4.70	8.98
	1	4.643	3.921	7.40	7.00	4.77	7.28	2.63	1.94	23.12	40.90	-10.45	10.73	33.58	42.79
	2	2.888	2.032	5.72	3.13	3.13	2.42	2.58	1.81	16.78	21.13	1.01	0.50	15.77	20.83
Poplar	3	3.250	1.860	9.25	4.80	5.20	4.97	4.03	2.49	13.59	15.89	3.03	6.52	10.56	17.32
	1	1.153	1.183	4.74	5.33	3.56	5.28	1.17	0.46	7.95	16.44	2.97	12.40	4.99	12.05
	2	0.676	0.707	3.63	1.92	1.51	1.31	2.12	1.17	7.52	8.35	5.82	8.03	1.69	2.18
Sandhill	3	0.816	0.928	6.00	9.19	4.59	9.05	1.40	0.89	6.61	12.53	1.66	4.73	4.94	10.88
Table 6: P-values for all paramet	ters from the one-way ANOV	A and Tukey HSD post-hoc multiple comparison test	ts for site differences. Data from all												
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burial periods and within site locations are grouped. $p < 0.05$ is considered significant and highlighted in red.															
	Secondar materia	Minanaliaatian	Cail anno antian												

	S	Supply rate	es		Soil properties					
Site comparisons	TN	NO ₃ ⁻	NH4 ⁺	Mineralization	Nitrification	Ammonification	SOM	GWC	ρb	Φ
Sandhill fen-Pauciflora fen	<0.05	0.71	<0.05	0.40	0.10	1.00	0.13	0.48	0.88	0.98
Sandhill fen-Poplar fen	<0.05	0.05	<0.05	<0.05	0.27	<0.05	<0.05	<0.05	0.51	0.71
Poplar fen-Pauciflora fen	0.28	0.32	<0.05	<0.05	0.95	<0.05	<0.05	<0.05	0.35	0.65

Table 7: P-values for all parameters from the one-way ANOVA and Tukey HSD post-hoc multiple comparison tests for differences in position along hillslope within each site. Data from all burial periods are grouped. p < 0.05 is considered significant and highlighted in red.

Hillslope positions	s	upply rate	es	Mineralization			Soil properties			
comparisons within each site	TN	NO ₃ -	$\mathrm{NH_4}^+$	Mineralization	Nitrification	Ammonification	SOM	GWC	ρb	Φ
				SANDHI	LL					
Midslope-Downslope	0.99	1.00	1.00	0.55	0.82	0.40	0.07	<0.05	0.17	0.67
Upslope-Downslope	<0.05	0.07	0.84	0.66	0.65	0.73	<0.05	<0.05	<0.05	0.11
Upslope-Midslope	<0.05	0.09	0.86	0.98	0.95	0.82	<0.05	<0.05	0.30	0.40
PAUCIFLORA										
Midslope-Downslope	<0.05	0.92	<0.05	<0.05	0.47	<0.05	<0.05	<0.05	0.98	1.00
Upslope-Downslope	0.30	0.09	<0.05	<0.05	0.29	<0.05	<0.05	<0.05	0.93	0.95
Upslope-Midslope	0.09	0.16	<0.05	0.97	0.96	0.97	1.00	0.96	0.98	0.98
				POPLA	R					
Midslope-Downslope	0.30	0.26	0.98	0.64	0.88	0.26	0.99	0.52	1.00	0.91
Upslope-Downslope	<0.05	<0.05	0.98	0.06	0.98	<0.05	0.31	<0.05	0.58	0.61
Upslope-Midslope	0.17	0.27	0.94	0.21	0.75	<0.05	0.25	0.05	0.54	0.42

Table 8: P-values for all parame	ters from the one-way A	NOVA and Tukey HS	D post-hoc multiple of	comparison tests fo	or differences in hill	slope position
(upslope, midslope, and downslo	ope) among sites. Data fr	from all burial periods	and upslope locations	within sites are gro	ouped. p< 0.05 is co	onsidered
significant and highlighted in re-	d					

Hillslope positions	Hillslope positions Supply rates				Mineralization				Soil properties			
comparisons across sites	TN	NO ₃ ⁻	$\mathrm{NH_4}^+$	Mineralization	Nitrification	Ammonification	SOM	GWC	ρb	Φ		
				UPSLO	РЕ							
Sandhill fen-Pauciflora fen	0.09	0.97	<0.05	0.18	0.32	0.60	0.40	<0.05	0.86	0.83		
Sandhill fen-Poplar fen	0.08	0.36	0.15	1.00	0.48	0.17	<0.05	<0.05	0.95	1.00		
Poplar fen-Pauciflora fen	lar fen-Pauciflora fen 0.96 0.58 <0.05 0.53 0.98 0.49							0.51	0.99	0.90		
MIDSLOPE												
Sandhill fen-Pauciflora fen	<0.05	0.61	<0.05	0.35	0.42	0.75	<0.05	<0.05	0.96	0.95		
Sandhill fen-Poplar fen	<0.05	<0.05	<0.05	0.16	0.97	0.05	<0.05	<0.05	0.17	0.24		
Poplar fen-Pauciflora fen	0.69	0.31	0.98	<0.05	0.66	<0.05	<0.05	<0.05	0.15	0.22		
				DOWNSL	OPE							
Sandhill fen-Pauciflora fen	<0.05	0.83	<0.05	0.39	0.66	0.26	0.08	0.36	0.34	0.72		
Sandhill fen-Poplar fen	0.14	0.72	<0.05	<0.05	0.39	<0.05	0.31	<0.05	0.97	1.00		
Poplar fen-Pauciflora fen	<0.05	0.98	<0.05	0.14	0.84	0.08	<0.05	0.25	0.38	0.79		

Burial period comparisons		Supply rat	tes		n	Soil properties					
within each site	TN	NO ₃ ⁻	$\mathrm{NH_4}^+$	Mineralization	Nitrification	Ammonification	GWC				
			SA	NDHILL							
1-2	0.82	0.35	<0.05	0.97	0.78	0.23	0.30				
2-3	0.26	0.38	<0.05	0.22	0.10	0.99	0.98				
1-3	0.56	1.00	1.00	0.38	0.44	0.20	0.23				
	PAUCIFLORA										
1-2	0.10	0.56	0.69	0.52	<0.05	0.60	0.51				
2-3	0.11	0.65	0.57	1.00	0.57	1.00	0.92				
1-3	0.98	1.00	0.96	0.50	0.29	0.59	0.72				
			P	OPLAR							
1-2	0.85	0.99	1.00	0.92	<0.05	0.56	0.93				
2-3	0.11	0.58	0.33	0.98	0.87	0.94	0.98				
1-3	0.31	0.69	0.31	0.83	<0.05	0.39	0.98				

Table 9: P-values from the one-way ANOVA and Tukey HSD post-hoc multiple comparison tests for burial period differences for all parameters at every sites (except SOM, ρb and porosity). Data from all locations within sites are grouped. p< 0.05 is considered significant and highlighted in red.

Appendix

	S	supply rate	s		Mineralization					
	(µg/	10cm2/mc	onth)	(μg	, N/g dry soil/m	onth)		Soil proper	rties	
	TN	NO ₃ -	$\mathrm{NH_4}^+$	Mineralization	Nitrification	Ammonification	SOM (%)	GWC (g/g)	$\rho b (g/cm^3)$	Φ(%)
	1			r	SAND	HILL	1	1	1	
Min.	0.00	0.00	0.00	-17.20	-4.85	-19.48	2.87	0.01	0.13	65.18
1st Qu	2.20	0.85	1.00	0.50	-0.10	0.23	4.68	0.17	0.25	69.73
Median	3.50	1.70	1.36	2.07	0.43	0.81	21.88	0.49	0.51	78.35
3rd Qu.	5.41	3.04	1.80	8.45	2.27	3.68	33.02	1.18	0.78	88.18
Max.	36.30	35.20	5.30	47.37	45.45	35.92	81.81	3.84	0.92	95.00
PAUCIFLORA										
Min.	0.00	0.00	0.00	-4.87	-1.09	-4.92	2.88	0.16	0.09	68.14
1st Qu.	2.03	0.00	1.20	0.04	-0.05	-0.11	4.23	0.25	0.49	74.05
Median	4.33	1.26	3.23	0.68	0.09	0.36	6.74	0.35	0.64	75.74
3rd Qu.	7.02	2.11	4.54	3.48	0.59	3.16	13.30	0.64	0.69	81.62
Max.	30.20	3.40	28.10	26.93	9.19	26.75	79.50	9.06	0.84	94.36
					POPL	AR				
Min.	2.10	0.96	0.80	-9.86	-24.09	-7.38	2.20	0.17	0.14	57.44
1st Qu.	3.80	1.50	1.32	-0.98	-0.37	-0.41	47.36	1.57	0.19	84.32
Median	5.78	3.60	2.30	7.22	0.21	6.59	70.94	3.34	0.23	87.41
3rd Qu.	11.20	4.80	5.30	34.68	1.12	34.71	77.40	5.33	0.26	89.48
Max.	18.40	15.10	8.90	82.12	16.30	101.01	84.41	9.73	1.13	91.14

Table 10: Additional parameter information for the Sandhill fen, Pauciflora fen, and Poplar fen from May - August 2014.

Table 11: Spearman's Rank Correlation *rho* values for comparisons between every variable at the Sandhill fen. Values that are moderate (0.40 - 0.59), strong (0.60 - 0.79), and very strong (0.80 - 1) are in bolded and values that returned a significant result (p < 0.05) are highlighted in yellow.

rho	Mineralization	NO ₃ ⁻ supply rate	Nitrification	NH4 ⁺ supply rate	Ammonification	SOM	GWC	ρb	Φ
TN supply rate	0.31	0.91	0.56	0.63	0.13	-0.23	-0.29	0.12	0.02
Mineralization		0.19	0.59	0.41	0.63	0.18	0.10	-0.44	0.42
NO ₃ ⁻ supply rate			0.43	0.36	0.04	-0.21	-0.28	0.19	-0.02
Nitrification				0.59	-0.03	-0.04	-0.19	-0.24	0.35
NH4 ⁺ supply rate					0.09	-0.01	-0.05	-0.16	0.17
Ammonification						-0.02	0.08	-0.18	0.12
SOM							0.87	-0.60	-0.43
GWC								-0.65	0.47
ρb									-0.88

Table 12: Spearman's Rank Correlation rho values for comparisons between every variable at the Pauciflora fen	. Values that are moderate $(0.40 - $
0.59), strong $(0.60 - 0.79)$, and very strong $(0.80 - 1)$ are in bolded and values that returned a significant result (p < 0.05) are highlighted in yellow.

rho	Mineralization	NO ₃ ⁻ supply rate	Nitrification	NH4 ⁺ supply rate	Ammonification	SOM	GWC	ρb	Φ
TN supply rate	0.32	0.78	0.59	0.94	0.15	0.15	0.22	0.14	-0.14
Mineralization		0.31	0.52	0.34	0.89	0.58	0.53	0.05	-0.05
NO ₃ ⁻ supply rate			0.29	0.63	0.16	-0.02	0.00	0.12	-0.12
Nitrification				0.63	0.20	0.31	0.38	-0.04	0.04
NH ₄ ⁺ supply rate					0.19	0.29	0.35	0.10	-0.10
Ammonification						0.51	0.42	0.09	-0.09
SOM							0.81	-0.38	-0.38
GWC								-0.17	0.17
ρb									-1.00

Table 13: Spearman's Rank Correlation *rho* values for comparisons between every variable at the Poplar fen. Values that are moderate (0.40 – 0.59), strong (0.60 - 0.79), and very strong (0.80 - 1) are in bolded and values that returned a significant result (p < 0.05) are highlighted in yellow.

rho	Mineralization	NO ₃ ⁻ supply rate	Nitrification	NH4 ⁺ supply rate	Ammonification	SOM	GWC	ρb	Φ
TN supply rate	-0.38	0.82	-0.08	0.63	-0.49	-0.05	-0.23	0.00	0.00
Mineralization		-0.67	0.11	0.27	0.81	-0.23	0.20	0.18	-0.04
NO ₃ ⁻ supply rate			0.18	0.16	-0.82	0.05	-0.25	-0.11	0.03
Nitrification				-0.37	-0.28	0.41	-0.12	-0.25	0.26
NH ₄ ⁺ supply rate					0.24	-0.36	-0.08	0.40	-0.27
Ammonification						-0.36	0.41	0.09	0.01
SOM							0.16	-0.81	-0.71
GWC								-0.46	0.29
ρb									-0.85