University of Alberta

Ecological Response of Atmospheric Nitrogen Deposition on Reconstructed Soils in the Athabasca Oil Sands Region

by

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Abstract

Oil and gas extraction in the Athabasca oil sands region has increased anthropogenic nitrogen (N) emissions over the past two decades. This study quantified atmospheric N deposition and assessed the potential implications of increased N deposition in aspen (*Populus tremuloides* Michx.) and jack pine (*Pinus banksiana* Lamb.) stands located on reclaimed sites. Nitrogen deposition was significant on these sites, and in all cases was dominated by ammonium. Bulk precipitation was significantly greater than throughfall, which indicates canopy uptake of N in both stand types. In aspen stands, positive relationships were found between ammonium deposition, and N isotope signature in forest floor, foliage, and roots, suggesting that biocycling of N was taking place between soil and plants. However, in pine, the lack of similar relations together with high soil nitrate concentrations indicated that the N cycle was more open, potentially leading to leaching losses.

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List of Symbols and Abbreviations

δ	Delta
ε	Enrichment factor
AIC	Akaike's information criterion
Al^{+3}	Aluminum
ANOVA	Analysis of variance
AOSR	Athabasca oil sands region
C	Carbon
Ca^{+2}	Calcium
CaCl	Calcium chloride
DBH	Diameter at breast height
F	Fibric forest floor horizon
H^+	Hydrogen
^2H	Deuterium (heavy hydrogen)
ha	hectare
K^+	Potassium
KCl	Potassium chloride
L	Litter forest floor horizon
HCl	Hydrogen chloride
HNO_3	Nitric acid
Mg^{+2}	Magnesium
MgO	Magnesium oxide
N	Nitrogen
Na^+	Sodium
NaCl	Sodium chloride
NH_4^+	Ammonium
NH_3	Ammonia
NH_4NO_3	Ammonium nitrate
NITREX	Nitrogen saturation experiments
NO	Nitric oxide
NO_2	Nitrous dioxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_x	Nitrogen oxides
P	Phosphorous
PRS	Plant root simulator
PVC	Polyvinyl chloride
USDA	United States Department of Agriculture

CHAPTER 1

Introduction

1.1 Background

The increase in atmospheric nitrogen (N) deposition is an issue of global concern (Vitousek et al. 1997, Galloway 1998). It is an important issue to consider for the ecology of many forests as it has the ability to change their community structure and function (Aber et al. 1989, Zottl 1990, Aber et al. 1998, Fenn et al. 1998). Recently there have been questions raised in regards to atmospheric N deposition in the Athabasca Oil Sands Region (AOSR), since anthropogenic N emissions are expected to increase in this region due to oil and gas extraction (Aherne and Shaw 2010). Production of oil sands began in the 1960's, and approximately 663 km^2 of land have been disturbed today (Government of Alberta 2011). Oil reserves in northern Alberta have been confirmed to have 1.7 trillion barrels of oil (Kean 2009) and are reported to be second in size globally to those in Saudi Arabia. Current production is 1.5 million barrels per day, which will increase to about 3.2 million barrels per day by 2019 (Government of Alberta 2011).

Reactive N compounds most commonly deposited on landscapes are nitric acid (HNO_3), nitrous dioxide (NO_2), nitric oxide (NO), ammonia (NH_3), particulate nitrate (NO_3^-), and particulate ammonium (NH_4^+) (Hanson and Lindberg 1991). In Europe, and the United States, industrial emissions and fossil fuel combustion are the two main anthropogenic sources for nitrogen oxide (NO_x)

pollutants (Hanson and Lindberg 1991, Bytnerowicz and Fenn 1996, Vitousek et al. 1997). Whereas NH_3 emissions in Europe and the United States may originate from agricultural practices, such as feedlots or inefficient fertilizer use in the agricultural industry (Hanson and Lindberg 1991, Bytnerowicz and Fenn 1996). In the AOSR, potential sources for NO_x emissions may originate from fossil fuel combustion from vehicles or exhaust from other industrial machinery (Bytnerowicz et al. 2010). Total NO_x emissions are predicted to increase from 140 tonnes per day in 2000 to 360 tonnes per day in 2032 (Doram and Rawlings 2006). Ammonia emissions from industrial activities may originate from bitumen extraction and processing (Farwell et al. 2009, Whitfield et al. 2010a), and volatilization from urea fertilizers that are utilized on lands ongoing reclamation (Bytnerowicz et al. 2010). During bitumen extraction and processing, some N can undergo volatilization in the second stage of bitumen upgrading called hydrotreating. Another potential source of NH_3 from industrial activities may be tailings ponds, since they contain high concentrations of NH_4^+ (Bytnerowicz et al. 2010).

Atmospheric N can be deposited by two processes; dry and wet. Dry deposition is defined as the transfer of gasses and particles to land surfaces via atmospheric turbulence and diffusion without the intervention of precipitation. Wet deposition is defined as the removal of gases or aerosols from the atmosphere via precipitation (Böhm 1992). Nitrogen oxides are typically deposited from the atmosphere to terrestrial ecosystems by direct dry deposition whereas HNO_3 can be deposited by dry deposition or within rainfall due to the reaction with alkaline aerosols (Hanson and Lindberg 1991). Ammonia is water soluble and considered to be highly reactive (Nihlgard 1985, Lindberg et al. 1986, Hanson and Lindberg 1991), thus it can be removed by both dry and wet deposition. In the atmosphere, NH_3 can react with HNO_3 to form fine ammonium nitrate (NH_4NO_3) aerosols or with acidic aerosols to form nitrate salts (Hanson and Lindberg 1991). Ammonia and HNO_3 are the two major drivers for atmospheric dry deposition in forests (Lovett 1994), while NH_4^+ and NO_3^- are the dominant forms of N in wet deposition (Hanson and Lindberg 1991, Bytnerowicz and Fenn 1996).

Atmospheric N deposition from anthropogenic processes is a potentially important source of N to ecosystems (Kochy and Wilson 1997), as has been shown to be the case in North America (Fenn et al. 1998) and Europe (Zottl 1990). Nitrogen deposition rates vary with location ranging from 10-80 kg N ha^{-1} yr^{-1} in Europe, with highest values near industrial activities (Zottl 1990, Krupa 2003, Nilsson et al. 2006). In the United States, typical total N deposition rates vary from 7-27 kg N ha^{-1} yr^{-1} (Lovett 1992, Fenn et al. 1996, Tomaszewski et al. 2003), but can range from 35-53 kg N ha^{-1} yr^{-1} in highly polluted regions (Fenn et al. 1996, Fenn and Poth 1999). In southern Ontario (Toronto-Montreal corridor), total N deposition can be up to 15 kg N ha^{-1} yr^{-1} (Houle et al. 1999, Watmough 2010), while in National Parks across the Great Plains (Alberta, Saskatchewan and Manitoba) wet N deposition rates range from 5-11 kg N ha^{-1} yr^{-1} (Kochy and Wilson 2001).

1.2 Impact of N deposition on forest ecosystems

Nitrogen is one of the most limiting nutrients in forest ecosystems (Aber et al. 1989, Tamm 1991). Forests ecosystems can receive N from atmospheric deposition (Fenn et al. 1998), biological fixation (Galloway et al. 1995) and fertilization (Figure 1). Human activities have induced major changes to the global N cycle and currently we produce twice as much total reactive N as natural processes (Galloway et al. 2004, Galloway et al. 2008). Nitrogen input from anthropogenic processes has increased to ~210 Tg N yr^{-1} globally in terrestrial ecosystems (Galloway et al. 2008).

The majority of N in the atmosphere is in the form of N_2 (g), which is not readily available for biological uptake in forest ecosystems (Galloway 1998). Two natural processes, biological fixation (~107 Tg N yr^{-1}) and lightning (<10 Tg N yr^{-1}) are responsible for converting N from the atmosphere to biologically available forms (Galloway et al. 1995, Vitousek et al. 1997, Galloway et al. 2004). The main processes for the internal N cycle include: mineralization, nitrification, microbial immobilization, and plant uptake. Plants and microbes obtain N from mineralization of the soil organic matter (Tamm 1991). In N limited systems there is competition for mineral N between plants and microbes that may suppress nitrifier populations, thus inorganic N in soil solution is typically dominated by ammonium rather than nitrate (Gundersen 1991). The conversion of ammonium to nitrate can lead to losses by leaching or denitrification. However, in forests, losses due to denitrification and leaching are typically minimal as most forest ecosystems are efficient in retaining N (Gundersen 1991, Tamm 1991, Krupa

2003). Increases in anthropogenic emissions of N have caused an imbalance between inputs to the ecosystem and uptake by either microbes or plant communities (Fenn et al. 1998, Allen and Bayley 2004) leading to a new ecological status in which some forest ecosystems are being identified as N saturated (Aber et al. 1989, Zottl 1990).

Nitrogen saturation has been defined in the literature as the condition where N availability exceeds the capacity of plants and microbes to retain N (Aber et al. 1989). Recent research suggests the need to distinguish between kinetic N saturation and capacity N saturation (Lovett and Goodale 2011). Kinetic N saturation is reached when the rate of N inputs exceeds the rate of N retention by vegetation and soil. During kinetic N saturation, both soil and vegetation are still actively accumulating N, however N losses are occurring simultaneously to N retention. Capacity N saturation is attained when soils and vegetation have accumulated N to the extent that N retention cannot occur anymore; in that case, inputs equal outputs (Lovett and Goodale 2011).

Three stages of N saturation have been identified that encompass several biogeochemical, physiological, and ecological responses of forest ecosystems to N deposition (Figure 2). Stage 1 or the production phase, represents the initial effects of chronic N deposition, where N added via wet and dry deposition is absorbed by vegetation, microbes and soil. Overall, internal N cycling increases during this stage and provides a positive effect in forest productivity (Aber et al. 1989, Gundersen 1991, Bytnerowicz and Fenn 1996). Plants respond to additional N by expanding canopies, increasing plant biomass and N content in foliage

(Gundersen 1991, Aber et al. 1998, Fenn et al. 1998). Increases in foliage N can result in increases in N:nutrient ratios, such as N:Mg and N:P, while causing decreases in Ca:Al ratios in foliage (Aber et al. 1998, Fenn et al. 1998). The increased organic N inputs through litter in turn can affect forest soil N cycle (Gundersen 1991, Tamm 1991, Aber et al. 1998). The soil N cycle is accelerated through increases in litter production, reduced C:N ratio in litter, and accelerated decomposition (Gundersen 1991, Aber et al. 1998), all of which further increase soil N availability.

Nitrogen availability is mainly controlled by net mineralization rates (Fenn et al. 1998). Increases in net mineralization and nitrification can contribute to greater amounts of nitrate present in the soil solution (Fenn et al. 1998). By adding more N to the system through atmospheric N deposition, the production of nitrate can increase leading to increased N leaching (Gundersen 1991, Fenn et al. 1998). Therefore, increases in N deposition may increase N availability, foliar and root N concentrations, net primary productivity, decomposition of roots and foliage, N cycling between soils and vegetation, nitrification, and nitrate availability to roots, but also denitrification and leaching (Nadelhoffer 2007).

Forest ecosystems have a finite ability to assimilate and retain N, since the availability of other essential nutrients for growth may ultimately become limited (Aber et al. 1989). Stage 2, N saturation, also called the destabilization phase, is reached when forest vegetation is unable to retain and assimilate N from mineralization and atmospheric N deposition (Figure 2) (Aber et al. 1989, Gundersen 1991). N saturation is not controlled, but accelerated by N deposition

(Bytnerowicz and Fenn 1996). Over time N retention in mineral soils and forest floor increases, causing the N uptake from plants to be limited by the availability of other nutrients like phosphorus, or other growth limiting factors like water (Aber et al. 1989, Fenn et al. 1998). As plant N uptake declines, microbes may have additional N substrate to utilize for N mineralization and nitrification. Nitrification can produce large amounts of NO_3^- that may leach to lower depths, since NO_3^- is highly mobile. Nitrate production can be enhanced from chronic N deposition, since it may maintain high nitrifier populations, which will increases nitrification (Fenn et al. 1998).

Nitrification can have negative effects on forest ecosystem function and structure (Aber et al. 1989). The process of nitrification causes a release in H^+ into the soil, which can cause acidification. In addition, nitrate leaching is typically accompanied by leaching of base cations such as Mg^{+2}, K^+, Na^{+3} and Ca^{+2}, which can result in more exchange sites being occupied by H^+ and Al^{+3} (Aber et al. 1989, Wallace et al. 2007). This will cause an imbalance in plant nutrients, which may affect plant nutrient uptake (Driscoll et al. 2003, Wallace et al. 2007), and causes nutrient deficiencies (Aber et al. 1989, Gundersen 1991).

Stage 3, the decline phase (Figure 2) is hypothesized, because it is more difficult to assess, but in recent studies in Europe and the United States, researchers have observed forest decline through manipulated fertilizer experiments (Aber et al. 1989, Gundersen 1991, McNulty et al. 1996, Aber et al. 1998, Wallace et al. 2007). Forest growth and decline can potentially be induced by relatively low but chronic additions of N (McNulty et al. 1996). Soil acidification may decrease fine root biomass, which can minimize the amount of nutrients and water plants can take up (Aber et al. 1989). Over time, these sites will have reduced fertility and nutrient deficiencies causing trees to be more susceptible to physical and pathogen stressors, such as frost damage (Aber et al. 1989, Gundersen 1991, Fenn et al. 1998). Forest decline was found to be correlated to foliar nutrient imbalances, such as N:P and Ca:Al (McNulty et al. 1996, Fenn et al. 1998). In addition, tree mortality and decreases in live basal area have been shown to increase when the soil Ca:Al ratio is below one (Wallace et al. 2007). Finally, tree mortality may be species-specific. Conifers are more sensitive to N saturation, while less sensitive trees, such as some deciduous species, may benefit from the additional N (Aber et al. 1998, Wallace et al. 2007).

1.3 Nitrogen critical loads

Nitrogen critical loads are hard to assess as these vary among forest ecosystems due to differences in their N cycle, forest productivity and in the type and degree of biotic and abiotic interactions within their soils (Gundersen 1991, Fenn et al. 1998, Ferm 1998). The critical load of N is defined as a value that when exceeded causes significant harmful effects to sensitive biotic components of an ecosystem (Nilsson and Grennfelt 1988). Young or disturbed soils with reduced carbon and N pools have the ability to retain more N than older forests (Fenn et al. 1998).

Research in North America and Europe has provided ranges for critical N loads for different forest ecosystems. In heath and bogs, the critical load can range from 5 to 10 kg N ha^{-1} yr^{-1}, whereas in forests it typically ranges between 10 and 20 kg N ha^{-1} yr^{-1} (Krupa 2003). The range in forests also varies as a function of the dominant vegetation. A range from 5 to 20 kg N ha^{-1} yr^{-1} has been estimated for deciduous forests, while in coniferous forests it is on average lower, from 3 to 15 kg N ha^{-1} yr^{-1} (Ferm 1998). Recent studies have suggested that the critical N load in boreal forests may be lower than in temperate and tropical forests, and may be as low as 6 kg N ha^{-1} yr^{-1} (Nordin et al. 2005). At 6 kg N ha^{-1} yr^{-1}, observed changes in biotic interactions include changes in plant species composition and increased pathogen damage to trees (Nordin et al. 2005, Bobbink et al. 2010).

1.4 Potential indicators of N saturation

The effects of N deposition depend on the duration, amount and form of N being deposited, the ecosystem storage capacity, the sensitivity of the vegetation present and abiotic conditions, such as climate and soil type (Gundersen 1991, Bobbink et al. 2010). These factors also play a role in determining the amount of soil N availability, which may increase with N deposition. However, the use of soil N availability to assess N saturation is not effective, since soil N availability is difficult to quantify (Pardo et al. 2007). Therefore, alternate N indicators are necessary to monitor and identify forest ecosystems at risk of becoming N saturated (Fenn and Poth 1996).

Over the years, researchers in Europe and North America have identified a series of potential indicators of N saturation (Table 1). These indicators were established from vegetation and soil responses to N deposition studies across a gradient of N deposition, as well as through field manipulation experiments (Fenn and Poth 1996, Fenn et al. 1996, Koopmans et al. 1997, Emmett et al. 1998, Gundersen et al. 1998b, Pardo et al. 2006, Nadelhoffer 2007, Templer et al. 2007, Watmough 2010, Fang et al. 2011). Nitrogen indicators based on vegetative responses are more accurate as they incorporate interactions between plants and their environment; thus, plants may act as biomonitors, since they respond more quickly (Fenn and Poth 1996). On the other hand, soil-based indicators can take longer to show a response to N deposition, since soils can store large quantities of N (Emmett et al. 1998).

Multiple complementary N indicators should be used in order to gain a better understanding of the forest N status, i.e.; its degree of N limitation, sufficiency, or excess (Fenn and Poth 1996). The following indicators have been proposed: foliar N:P, soil C:N, soil solution NO_3^-, potential mineralization and nitrification rates, $\delta^{15}N$ enrichment factors, and $\delta^{15}N$ natural abundance (Table 1). Foliar nutrient ratios, especially N:P, have been found to increase with N deposition (Bytnerowicz and Fenn 1996, Fenn et al. 1996). A N:P ratio of 8.5 was reported in highly polluted areas of California, while in low polluted areas the ratio was 6.4 (Fenn et al. 1996).

Potential mineralization and nitrification rates have been found to increase with N deposition (Aber et al. 1989, Van Miegroet et al. 1992, Fenn and Poth 1996). Increases in mineralization and nitrification can potentially increase the amount of available soil N (Fenn et al. 1998) and the amount of NO_3^- in soil solution (Fenn et al. 1996). Forest floor C:N ratios can also be a good indicator of potential NO_3^- leaching. Sites with C:N ratios below 25-27 may have higher amounts of NO_3^- leaching than sites with C:N ratios above 27 (Gundersen et al. 1998a, Gundersen et al. 1998b). In younger forest ecosystems where the forest floor is not as developed, the mineral soil C:N can alternatively be used as an indicator of NO_3^- leaching (Gundersen et al. 1998a, Gundersen et al. 2009). An important point to remember when using C:N ratios as an indicator of potential NO_3^- leaching is that once NO_3^- forms in the forest floor the likelihood of it leaching is high, as NO_3^- immobilization is low even at high C:N ratios (Vitousek 1982, Gundersen et al. 1998a).

The $\delta^{15}N$ enrichment factor ($\varepsilon_{foliar\text{-}soil} = \delta^{15}N_{foliar} - \delta^{15}N_{soil}$) is a good indicator of the N status of forest ecosystems, since it normalizes for spatial heterogeneity and reflects differences in N fluxes and rates of N cycling (Emmett et al. 1998, Pardo et al. 2006). As systems become more N-rich, the enrichment factor becomes more positive (Garten and Van Miegroet 1994, Fang et al. 2011). Also in N rich systems, positive relationships have been observed between soil N availability, foliar ^{15}N and enrichment factors (Garten and Van Miegroet 1994, Garten et al. 2007).

Root and foliar ^{15}N natural abundance can be used to provide additional information with regards to forest N status and may be used to identify forest ecosystems that are influenced by N deposition (Emmett et al. 1998, Pardo et al. 2006). Root $\delta^{15}N$ may be a better indicator than foliar $\delta^{15}N$, since there is little potential for direct root uptake of N deposition, as opposed to the canopy (Pardo et al. 2006). The $\delta^{15}N$ natural abundance values from all potential sources need to be considered, and integrated when using N saturation indicators (Koopmans et al. 1997, Koba et al. 2003, Pardo et al. 2006, Templer et al. 2007, Fang et al. 2011). To increase the value of the $\delta^{15}N$ natural abundance method, data on $\delta^{15}N$ natural abundance from vegetation, soil, bulk precipitation, throughfall, and soil inorganic N should be incorporated together (Koopmans et al. 1997).

1.5 ^{15}N Natural abundance

The use of ^{15}N natural abundance has been used in ecology and soil science for several decades to study N sources and transformations (Handley and Raven 1992, Nadelhoffer and Fry 1994, Högberg 1997, Robinson 2001, Dawson et al. 2002, Makarov 2009). The $\delta^{15}N$ of atmospheric N_2 is 0‰, thus if plants were to mainly use atmospheric N_2, their $\delta^{15}N$ should be close to 0‰. However, plants have access to more readily available N pools, such as NH_4^+, NO_3^- and dissolved organic N from atmospheric deposition and from the soil solution; all of these can change the $\delta^{15}N$ of plants (Robinson 2001). Issues may arise with using ^{15}N natural abundance as a tracer when different sources of N pools mix, or fractionation between the ^{15}N and ^{14}N isotopes occurs during biological or physicochemical processes. Thus, ^{15}N natural abundance as an indicator of the source of N may only be used when there are large differences between all potential N sources. Alternatively, plant $\delta^{15}N$ value can be used as a natural integrator that encompasses both fractionations of ^{15}N and ^{14}N and mixing of N pools (Robinson 2001, Dawson et al. 2002).

Fractionation of N isotopes occurs during several biological and physicochemical processes of the N cycle (e.g.; mineralization, nitrification, denitrification, assimilation by microbes and plants, volatilization and ion exchange). These processes discriminate against the heavier N isotope, ^{15}N (Handley and Raven 1992, Nadelhoffer and Fry 1994, Högberg 1997, Robinson 2001, Dawson et al. 2002, Makarov 2009). Variations in $\delta^{15}N$ reflect the N isotope fractionations that occur, due to the energy required to break or form chemical bonds with ^{15}N. It is difficult to measure *in situ* fractionation for most soil processes, therefore the observed discrimination (ε) between substrate and product ($\varepsilon_{substrate-product}$) are used. The observed discrimination reflects variations in individual transformations where the reaction product will be depleted in ^{15}N relative to the substrate (Table 2) (Robinson 2001, Garten et al. 2007). The fractionation occurring during ion exchange and diffusion is small compared to other fractionations, but over time, it has the potential to affect the vertical distribution of $\delta^{15}N$ within the soil profile (Nadelhoffer and Fry 1994, Högberg 1997). Fractionation due to ammonification is also considered to be small, approximately 5‰ (Heaton 1986, Robinson 2001). Larger fractionations occur during nitrification especially in the first, rate-limiting step of the nitrification reaction, $NH_4^+ \rightarrow NO_2^-$ (Heaton 1986, Högberg 1997). The second step in the reaction, $NO_2^- \rightarrow NO_3^-$ is not rate limiting, hence it does not cause further fractionation (Högberg 1997). The NO_3^- formed is strongly depleted in ^{15}N compared to NH_4^+ (Table 2). This is especially true in situations where NH_4^+ concentrations are significantly (>4 times) higher than NO_3^- (Makarov 2009).

However, if all the substrate for nitrification (i.e.; NH_4^+) were to be exhausted, $^{15}N\text{-}NO_3^-$ would not differ from $^{15}N\text{-}NH_4^+$ (Nadelhoffer and Fry 1994). When little NH_4^+ is available, $^{15}N\text{-}NO_3^-$ has a N signature similar to organic N (Heaton 1986).

Fractionation also occurs during ammonia volatilization and denitrification. Ammonia volatilization involves several steps where isotope fractionation can occur, depending on the rate limiting step and pH of the substrate. These steps are: equilibrium of $NH_4^+ \leftrightarrow NH_3$ in solution; diffusion of NH_3 to the location of volatilization; the volatilization of NH_3 itself; and the diffusion of NH_3 away from the location of volatilization (Högberg 1997). Isotopic fractionation from NH_3 volatilization produces depleted $\delta^{15}N\text{-}NH_3$ gas and enriched $\delta^{15}N\text{-}NH_4^+$ pools. Ammonia volatilization in forest ecosystems may be unimportant because most forest soils are acidic enough to prevent NH_3 losses (Nadelhoffer and Fry 1994). Fractionation caused from denitrification is highly variable and occurs in conjunction with nitrification (Högberg 1997), which may enrich the remaining nitrate pools in ^{15}N (Garten et al. 2007). Denitrification may constitute an important flux in forest soils with elevated N inputs from throughfall or periodic moisture saturation (Nadelhoffer and Fry 1994).

The abundance of $\delta^{15}N$ in plants represents the net effect of a range of N processes. The difference found between $\delta^{15}N$ of plants and N source(s) is due to enzyme-mediated reactions that discriminate against ^{15}N. Plant $\delta^{15}N$ will resemble the $\delta^{15}N$ of the external source when the entire N pool is converted from the substrate to the product (Dawson et al. 2002). This would explain why discrimination by plants in N-limited systems is negligible (Nadelhoffer and Fry 1994). On the other hand, in situations where N availability is high compared to plant demand, discrimination against ^{15}N will occur (Högberg 1997). Plant tissues may become depleted in ^{15}N due to exudation of ^{15}N enriched NH_4^+ or dissolved organic N from roots (Dawson et al. 2002). In N-rich systems with high nitrification rates, the resulting NH_4^+ enrichment may drive foliar N enrichment (Pardo et al. 2006); foliar ^{15}N appears to be positively related to soil nitrification rates (Garten et al. 2007). In addition, NH_4^+ enrichment may lead to enrichment of the NO_3^-produced through nitrification processes (Feigin et al. 1974, Pardo et al. 2006). An important point to remember is that plants can change their preference between NO_3^- and NH_4^+ when environmental conditions change, causing a depletion in foliar ^{15}N (Marshall et al. 2007)

Metabolism of N within plants can create variations in the $\delta^{15}N$ which may confound the interpretations of N source (Högberg 1997). Typically, within plant variation is between 2 and 3‰ (Dawson et al. 2002), where roots are typically enriched compared to foliage (Pardo et al. 2006). Foliar $\delta^{15}N$ values also vary among trees species. Conifer foliar $\delta^{15}N$ is usually lower than deciduous trees, which may be attributed to a more tight N cycle (Pardo et al. 2006, Fang et al. 2011).

Overall, in forest ecosystems plants and litter are depleted in ^{15}N relative to soils (plant $^{15}N<$ litter $^{15}N<$ organic soil $^{15}N<$ mineral soil ^{15}N). In forests, $\delta^{15}N$ in soil typically ranges from 4 to 9‰ (Heaton 1986) with a mean value of +6.1‰ (Makarov 2009). In organic soils mostly comprised of peat, ^{15}N values range from

-3 to 2‰ (Heaton 1986). Organic horizon (L,F,H) δ^{15}N values of upland forest soils may be close to those of fresh plant litter, but these increase with depth and mineral horizons resulting in higher δ^{15}N values (Nadelhoffer and Fry 1994). The most common explanation for ^{15}N depletion of soil available N and corresponding ^{15}N enrichment of soil organic matter is microbial discrimination against the heavier N isotope (Nadelhoffer and Fry 1994, Makarov 2009). Heterotrophs become enriched in ^{15}N as they excrete depleted ^{15}N-NH_4^+. In turn, this lowers the δ^{15}N value of exchangeable NH_4^+ while the δ^{15}N of the remaining soil organic N increases *via* microbial biomass incorporation and turnover (Nadelhoffer and Fry 1994). Plant δ^{15}N values usually range from -5 to +2‰ (Nadelhoffer and Fry 1994), but on occasion values can be found outside this range varying from -10 to 10‰ (Dawson et al. 2002).

Many studies have been conducted to gain a better understanding of soil N dynamics controlling the isotopic patterns of soil inorganic N (Koopmans et al. 1997, Miller and Bowman 2002, Choi and Ro 2003, Koba et al. 2003, Sah and Brumme 2003, Cheng et al. 2010, Koba et al. 2010, Takebayashi et al. 2010). In most forest soils, the products of N mineralization tend to be depleted in δ^{15}N relative to substrates ($\delta^{15}N_{organic} \geq \delta^{15}N\text{-}NH_4^+ > \delta^{15}N\text{-}NO_3^- > \delta^{15}N_2O$) (Nadelhoffer and Fry 1994, Makarov 2009, Cheng et al. 2010). However, in N rich ecosystems, which consist of high rates of nitrification and large losses of ^{14}N-NO_3^-, there may be a significant enrichment of inorganic NH_4^+ (Makarov 2009). A study in Japan reported the following order of ^{15}N enrichment in the soil: $\delta^{15}N\text{-}NH_4^+ > \delta^{15}N_{organic} > \delta^{15}N\text{-}NO_3^-$ (Koba et al. 1998). These sites were found to be N rich sites with high rates of nitrification (Koba et al. 2003).

Lastly, when interpreting soil inorganic $\delta^{15}N$ values, one should not forget that both NH_4^+ and NO_3^- turn over quickly. Studies that look at soil inorganic N at one point in time may not represent the long-term average signal (Hobbie and Ouimette 2009). Therefore, a simple analysis of a soil solution or soil extract may not conclusively determine the source of N, but it may be used to determine the relative preference of NH_4^+ vs NO_3^- for plant uptake (Marshall et al. 2007).

1.6 Research objectives

Studies have been conducted outside the active mine area of the AOSR to determine critical N loads (Whitfield et al. 2010b) and to assess the impact of N deposition on surrounding natural forest ecosystems (Laxton et al. 2010, Wieder et al. 2010, Laxton et al. 2011). However, there are limited data on atmospheric N deposition on reconstructed soils closer to the active mines. Previous studies on reconstructed soils have found high amounts of soil NO_3^- (Rowland et al. 2009, Hemstock et al. 2010, MacKenzie and Quideau 2010), raising concerns about elevated N deposition. The two main objectives of this study were to:

1) Determine seasonal amounts of wet N deposition and soil N availability, and their potential relationships in jack pine and trembling aspen dominated stands of varying canopy cover classes located on reconstructed soils in the AOSR; and

2) Assess the ecological response and potential implications of atmospheric N deposition on reconstructed soils in the AOSR by investigating N status indicators such as foliar N, soil NO_3^- concentrations, and $\delta^{15}N$ values in different plant and soil pools.

Table 1-1 Soil and plant potential indicators of N saturation, including their potential response times.

POTENTIAL INDICATORS	*RESPONSE TIME*	*REFERENCE*
Plant N Indicators		
Foliar N:P	2-4 years	(Bytnerowicz and Fenn 1996, Fenn et al. 1996, Fenn et al. 1998, Gundersen et al. 1998b, Tessier and Raynal 2003)
^{15}N enrichment factor	unknown	(Emmett et al. 1998, Gundersen et al. 1998b)
^{15}N natural abundance	unknown	(Koopmans et al. 1997, Emmett et al. 1998, Pardo et al. 2006, Pardo et al. 2007, Fang et al. 2011)
Soil N Indicators		
C:N ratio- forest floor & mineral soil	>5 years	(Bytnerowicz and Fenn 1996, Fenn and Poth 1996, Fenn et al. 1996, Gundersen et al. 1998a, Gundersen et al. 1998b, Nadelhoffer 2007, Gundersen et al. 2009)
Soil NO_3^-	1 year	(Bytnerowicz and Fenn 1996, Fenn et al. 1996, Fenn et al. 1998, Gundersen et al. 1998b)
Flux rates of NO and N_2O gaseous emissions from soils	2-4 years > 5 years	(Fenn and Poth 1996, Fenn et al. 1998, Gundersen et al. 1998b)
NO_3^- leaching	1 year	(Gundersen 1991, Dise and Wright 1995, Aber et al. 1998, Gundersen et al. 1998a, Gundersen et al. 1998b)
Potential N mineralization & nitrification rates	2-4 years	(Fenn and Poth 1996, Watmough 2010)

Table 1-2 Fractionations ($\varepsilon_{substrate\text{-}product}$) of N isotopes determined for major processes within the N cycle (Robinson 2001).

N Cycle Processes	ε(‰)
N fixation	0-6
Ammonia volatilization	40-60
Ammonification	0-5
Ammonium assimilation by plants	9-18
Nitrification	35-60
Nitrate assimilation by plants	0-19
Nitrate or organic N assimilation by microbes	13
Denitrification	28-33

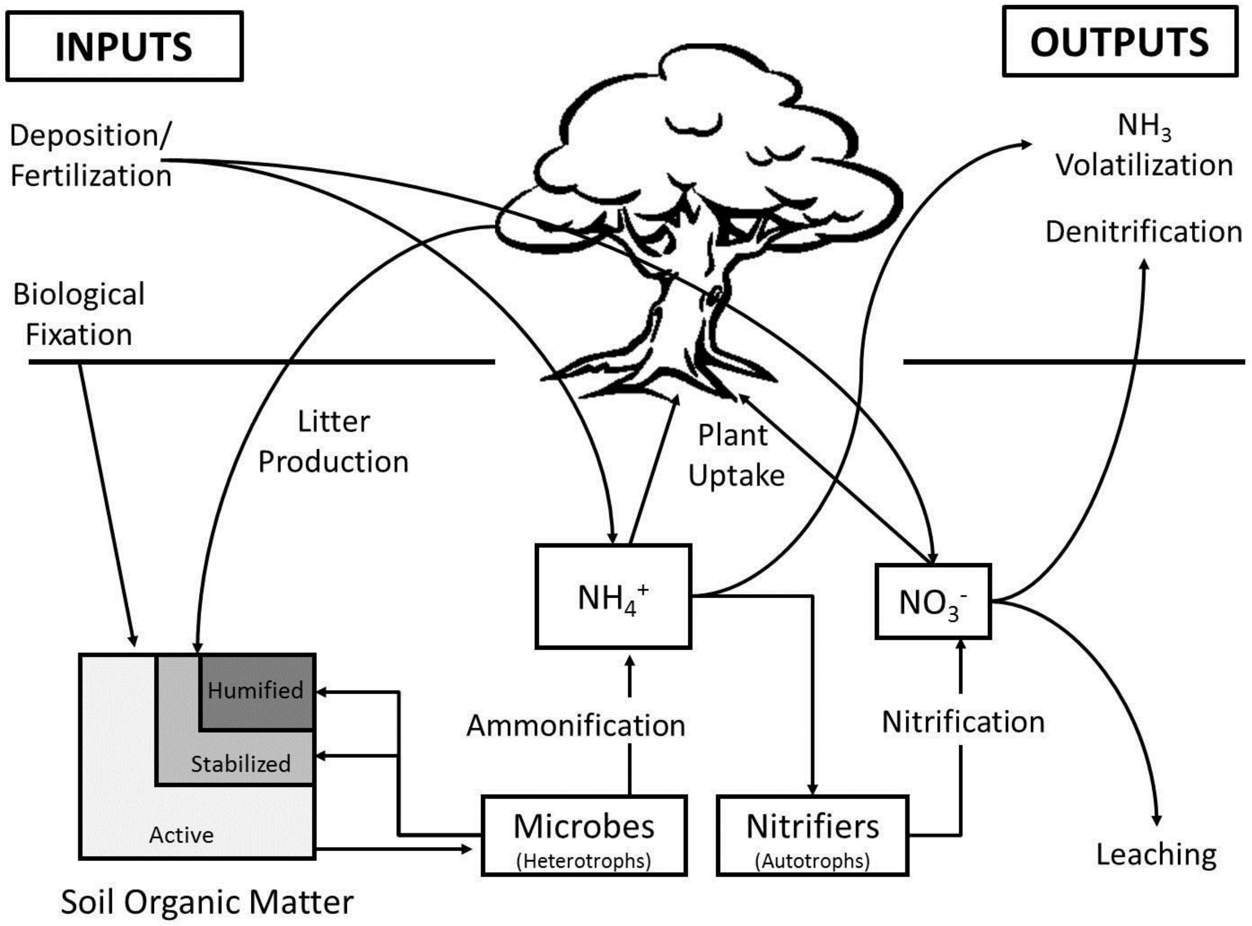

Figure 1-1 A simplified model of the forest N cycle consisting of N inputs, internal N cycle and N outputs from the ecosystem.

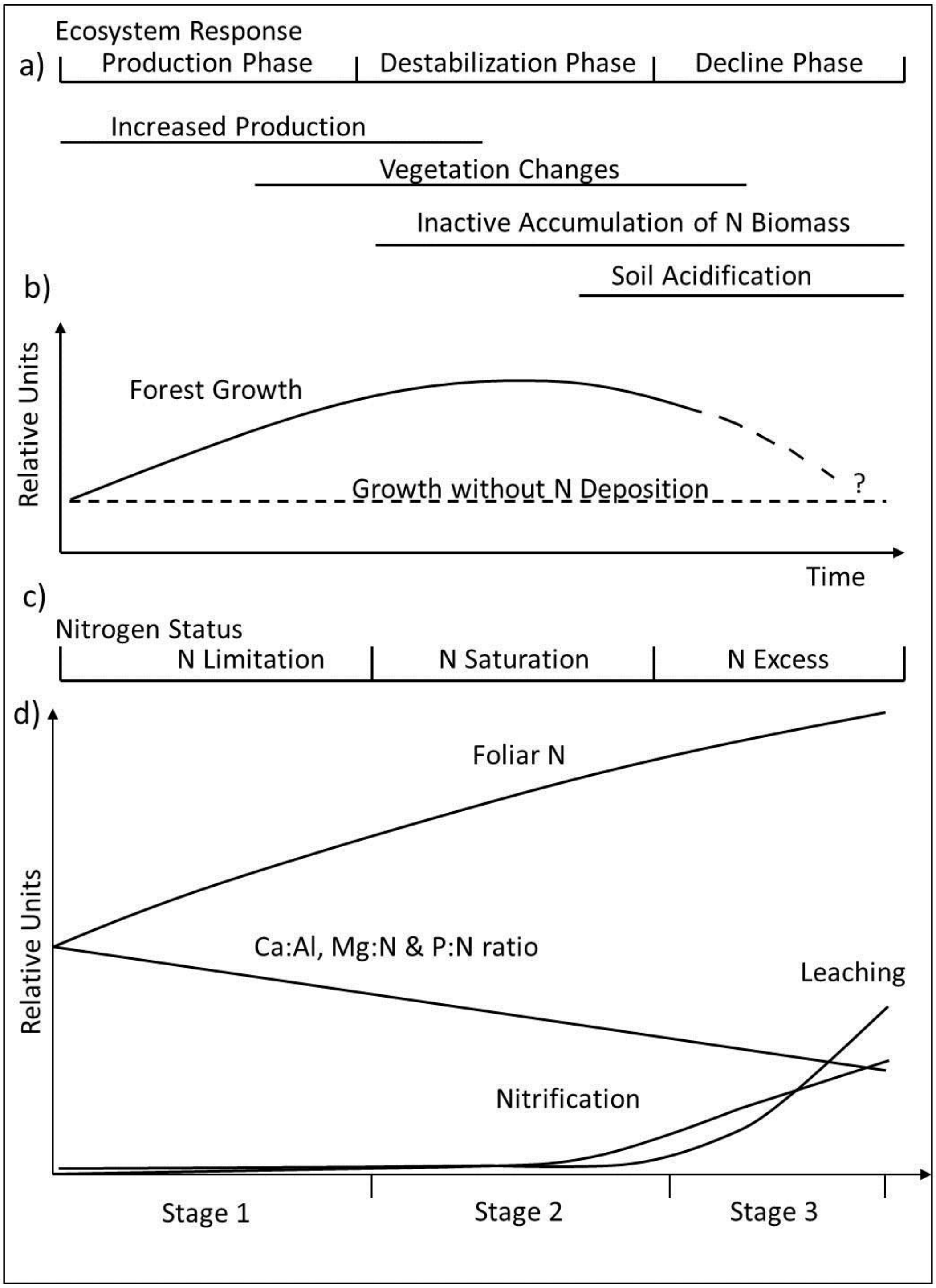

Figure 1-2 Hypothesized responses of forest ecosystems to increased atmospheric N deposition (adapted from Aber, Nadelhoffer et al. 1989; Gundersen 1991; Aber, McDowell et al. 1998; Fenn, Poth et al. 1998). a) ecosystem response; b) net productivity production with and without N deposition; c) soil N status; d) foliar nutrient response, soil nitrification and N leaching changes over time.

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CHAPTER 2

Atmospheric Nitrogen Deposition on Reconstructed Boreal Forest Soils in the Athabasca Oil Sands Region

2.1 Introduction

Nitrogen (N) is one of the most frequently limiting nutrients in many terrestrial ecosystems (Aber et al. 1989, Tamm 1991), which may receive N from atmospheric N deposition (Fenn et al. 1998) and biological fixation (Galloway et al. 1995). Over the past century, the total amount of N input from atmospheric N deposition due to human activities has doubled the amount produced by natural processes in terrestrial ecosystems (Galloway et al. 2004, Galloway et al. 2008). The increase in atmospheric N deposition is an issue of global significance (Vitousek et al. 1997, Galloway 1998) and one that causes ecological concern with the ability to change plant community structure and function (Aber et al. 1989, Zottl 1990, Fenn et al. 1998).

Recently there have been questions raised concerning atmospheric N deposition in the Athabasca Oil Sands Region (AOSR), since anthropogenic N emissions are expected to increase in this region due to oil and gas extraction (Vitt et al. 2003, Laxton et al. 2010). Production of oil sands began in the 1960's, and approximately 663 km^2 of land has been disturbed today. Oil reserves in northern Alberta have been confirmed to have 1.7 trillion barrels of oil (Kean 2009) and are reported to be second in size to those in Saudi Arabia. Current production is

1.5 million barrels per day, which will increase to about 3.2 million barrels per day by 2019 (Government of Alberta 2011).

Reactive N compounds most commonly deposited on landscapes are nitric acid (HNO_3), nitrous dioxide (NO_2), nitric oxide (NO), ammonia (NH_3), particulate nitrate (NO_3^-) and ammonium (NH_4^+) (Hanson and Lindberg 1991). Nitrogen oxides (NO_x) emissions in the AOSR may originate from vehicle emissions or exhaust from industrial machinery (Bytnerowicz et al. 2010). Total NO_x emissions are predicted to increase from 140 tonnes per day in 2000 to 360 tonnes per day in 2032 (Doram and Rawlings 2006). Ammonia emissions from industrial activities may originate from bitumen extracton and processing (Farwell et al. 2009, Whitfield et al. 2010a) and volatilization from fertilizers used in land reclamation (Bytnerowicz et al. 2010). There are two forms of N deposition: dry deposition, defined as the transfer of gases and particles to land surfaces without the intervention of precipitation, and the removal of gases and aerosols via precipitation, better known as wet deposition (Böhm 1992, Bytnerowicz and Fenn 1996). Dry deposition is difficult to measure in the forests compared to wet deposition. Therefore, established ratios may be used to estimate dry deposition from wet deposition (Lovett 1992, Fenn et al. 1998). Wet deposition is measured as bulk precipitation in open areas (Fenn et al. 1996) or throughfall, which is found under tree canopies (Lovett 1992, Bytnerowicz and Fenn 1996). The dominant N forms for wet deposition are NH_4^+ and NO_3^- (Hanson and Lindberg 1991, Bytnerowicz and Fenn 1996).

There are different stages of N accumulation in terrestrial ecosystems that explain impacts and responses to N deposition from a N limiting system to N saturation (Aber et al. 1989, Gundersen 1991, Aber et al. 1998). Increased N deposition is a concern in terrestrial ecosystems of the AOSR, since even low amounts of N deposition may alter the forest N cycle (Aber et al. 1989, Dise and Wright 1995, Laxton et al. 2010, Laxton et al. 2011). Plants may expand their canopies, increase plant biomass and N content in roots and foliage (Gundersen 1991, Aber et al. 1998, Fenn et al. 1998). The internal N cycle may be accelerated through increases in litter production, decomposition, and soil mineralization, all which increase soil N availability (Aber et al. 1989, Gundersen 1991, Tamm 1991, Bytnerowicz and Fenn 1996, Aber et al. 1998). This may cause an imbalance between inputs to the ecosystem and uptake by either microbes or plant communities (Fenn et al. 1998, Allen and Bayley 2004), resulting in more available N for the production of nitrate (NO_3^-) *via* nitrification (Aber et al. 1989, Bytnerowicz and Fenn 1996, Aber et al. 1998, Emmett et al. 1998). Increases in nitrification may create negative effects in forest ecosystems, such as soil acidification (Aber et al. 1989, Wallace et al. 2007).

Studies have been conducted outside the active mine areas in the AOSR to assess the impact of N deposition on natural forest ecosystems (Vitt et al. 2003, Laxton et al. 2010, Wieder et al. 2010, Laxton et al. 2011) and to determine critical N loads (Whitfield et al. 2010b). However, little data are available on atmospheric N deposition on reconstructed soils close to active mine sites. Modeled N deposition rates in the oil sands are estimated to be up to 65 kg N ha^{-1}

yr^{-1} near emissions sources (Allen and Bayley 2004). In addition, previous studies on reconstructed soils have found high amounts of NO_3^- in the soil (Rowland et al. 2009, Hemstock et al. 2010, MacKenzie and Quideau 2010). Our first objective was to quantify the amount of wet N deposition being received on reconstructed soils with differing stand types and canopy density. Due to the industrial activity in the area and increased N emissions (Laxton et al. 2011) we hypothesized that deposition rates would be greater than background levels. In addition, we hypothesized that bulk precipitation would be the same regardless of stand type, but that differences in throughfall between stand types would increase with increasing canopy cover. Our second objective was to examine how seasonality affected N deposition and soil N availability.

2.2 Methods

2.2.1 Study area

The study area was located approximately 40 km north of Fort McMurray, north-eastern Alberta (56°39’12N, 111°13’24W), in the Central Mixedwood Natural Subregion of the Canadian boreal forest (Natural Regions Committee 2006). The climate in this region is dominated by long cold winters (average -18.8 °C) with short summers (average +16.8 °C) and a mean annual temperature of +0.2°C. The annual precipitation is 455 mm in which 342 mm falls as rain during the growing season between May to September (Environment Canada 2011). The dominant tree species in upland forests are trembling aspen (*Populus tremuloides* Michx.), white spruce (*Picea glauca* (Moench) Voss) and jack pine (*Pinus* *banakasina* Lamb.), while black spruce (*Picea mariana* (Mill.) BSP) is found mainly in lowland positions. Gray Luvisols are found on medium to fine-textured calcareous parent material, while Dystric Brunisols have developed on coarser more acidic parent material (Turchenek and Lindsay 1982). Organic soils have developed on poorly drained lowlands (Natural Regions Committee 2006).

Sites used in this study were located on two different mine leases, Syncrude Canada Ltd. and Suncor Energy. Soil reconstruction (0-1 m) following oil sands mining is accomplished by using a range of materials, including mineral and organic soils salvaged prior to mining, overburden or industrial by-products such as tailings sand (Sorenson et al. 2011). The topsoil amendment used for soil reconstruction consisted of peat salvaged from lowland areas mixed with mineral soil (peat mineral mix). The most common shrubs planted on site were wild rose (*Rosa acicularis* Lindl.), common blueberry (*Vacciuium angustifolium* Aiton), red osier dogwood (*Cornus stolonifera* Michx.), saskatoon berry (*Amelanchier alnifolia* Nutt.), green alder (*Alnus crispa* (Chaix.) D.C.) and various willow species (*Salix* spp.) (Personal comm. Francis Salifu, Suncor Energy & Marty Yarmuch, Syncrude Canada Ltd., 2010). Reconstructed soils were fertilized with varying N-P-K-S regimes established by the different lease holders. Syncrude Canada Ltd. fertilizes in the first year following planting with rates of 350 kg/ha (10-30-15-4), while sites at Suncor Energy receive fertilization annually for the first 5 years at a rate of 300 kg/ha (23.5-25-8-0) in the first year and 250 kg/ha (31.5-16-5-0) in the following years (Lanoue 2003). The dominant form of fertilizer used on these reconstructed soils was granular urea (Personal comm.

Francis Salifu, Suncor Energy & Marty Yarmuch, Syncrude Canada Ltd., Doris Clark Sturgeon Valley Fertilizers 2010).

2.2.2 Site selection and stand characteristics

In fall 2008, 20 sites were selected covering three canopy density classes (0-30%, 31-65%, and 66-100%) over two different stand types, which were trembling aspen (n=3, 3, 4) and jack pine (n=3, 4, 3). In July 2009 seven sites were added to the study, increasing the number of replicates for both aspen (n=5, 4, 6) and jack pine (n=3, 4, 5). Sites were selected from long-term soil and vegetation monitoring plots (Oil Sands Vegetation Reclamation Committee 1998) and a previous forest floor development study (Sorenson et al. 2011). Criteria for site selection were based on the topsoil amendment used (peat mineral mix), site availability, tree species, age and canopy cover. The three canopy cover classes (0-30%, 31-65%, and 66-100%) were selected based on findings from previous work conducted in the AOSR on reconstructed soils (Sorenson et al. 2011). In Sorenson et al. (2011), the authors found significant differences in soil microbial populations at 30% and at 64% canopy cover in both aspen and pine stands. This resulted in a limited number of sites available on both mine leases, such that the majority of the sites, in this study, was located around tailings ponds (Appendix 1a).

In July 2010, stand characteristics (Appendix 1b), tree height, crown thickness, canopy cover, tree density, and dbh were measured at all 27 sites. Five 10 m^2 fixed plots were established on each site to measure tree height and crown thickness (Vertex III, Haglöf Sweden AB, Langsele Sweden), canopy cover (Spherical Model-A densitometer, Forest Densitometers, Bartlesville, OK) and tree density. In each plot, three of the largest trees were selected for tree height, height to live crown and dbh, while canopy cover was measured once in each cardinal direction at the intersection of the circular plot. Canopy cover was measured once for jack pine, but twice for aspen to quantify both summer (July 2010) and winter (October 2010) canopy cover. Stand characteristics from each fixed plot were then averaged for each site. Distance to emission point source (stack) was determined from each sample site to the closest stack emission source found on each mine lease. Precipitation data were obtained from weather stations located in the study area from Syncrude and Suncor.

2.2.3 Atmospheric wet N deposition

At each site, five atmospheric deposition collectors were set up following a similar design as Fenn and Poth (2004). Each collector was composed of a snow tube (75 cm x 22.5 cm), a plastic funnel (23 cm diameter) with a PVC filter, and a resin column (2.5 cm x 30 cm) containing 50 ml mixed bed resin (IONAC ® NM-60 H^+/OH^-, J.T. Baker, Phillipsburg, NJ) that permitted water flow via percolation. Glass wool was inserted in the top and bottom of the resin column to minimize contamination. A field blank resin column was installed at every site, which was constructed the same way as the other resin columns, but was capped at both ends. All collectors were cleaned with 0.5M HCl and rinsed with distilled water prior to installation. Once installed, the total collector height was about 1.6

m. Consequently, collectors captured bulk precipitation at the 0-30% canopy cover class, but throughfall at the >30% canopy cover classes. At the beginning of every spring (May) and fall (October) resin columns were exchanged, except for the first set of resin columns that were installed at the end of July 2008 and removed at the end of October 2008. At each collection period, funnels and filters were cleaned with distilled water and replaced if broken.

After deployment, NH_4^+ and NO_3^- were extracted from resin columns with four rinses of 40 ml 2M KCl. The eluent was analyzed for NH_4^+ and NO_3^- by segmented flow colorimetry (SmartChem™ 200 Discrete Analyzer, Mandel Scientific Company Inc., Guelph Ont) using the nitro-prusside/salicylate method and the cadmium reduction method, respectively (Mulvaney 1996). Extraction efficiency was tested by completing two more rinses of 40 ml KCl to eight randomly selected resin columns. After four extractions of field-exposed columns the average percent removed for NH_4^+ was 99.8%, compared to 98% for NO_3^-. Thus, it was apparent that the fifth and sixth rinses were insignificant, which is similar to what Fenn et al. (2002) found for extraction efficiency. Total deposition has been measured to be about twice as large as wet deposition in low elevation forests, as the following equation would suggest (Lovett 1992). Total N deposition, which includes both dry and wet, was estimated using total N deposition=wet N deposition*1/0.56 (Fenn et al. 1998).

Resin columns were washed and recharged before being deployed again following the method established by Thiffault et al. (2000). Resin columns were rinsed with two 50 ml additions of 2N NaCl, followed by a 50 ml de-ionized water rinse and then two 50 ml rinses of 0.1 N NaOH. Resin columns were rinsed again with 50 ml de-ionized water before reinstallation. If a resin column was found to be contaminated with sediments, all resin columns on the site were rebuilt with new mixed bed resin.

2.2.4 Soil N availability

Plant root simulator (PRS^{TM}) probes (Western Ag Innovations Inc., Saskatoon, SK, Canada) were used to measure soil N availability *in situ*. Probes were comprised of 10 cm^2 of anion or cation exchange membrane (215 meq of exchange capacity) fused to a plastic frame that use Na^+ and HCO_3^- as counter ions (Qian and Schoenau 2002, Johnson et al. 2005). Four probes, two anion and two cation, were installed horizontally under the forest floor at each atmospheric deposition collector and in the mineral soil. Probes were installed for four time periods, fall 2008 (August to November), winter 2008-2009 (November to May), spring 2009 (May to mid-July) and summer 2009 (mid-July to October). After each sampling period, probes were removed, washed with deionized water, and returned for extraction and analysis. Probes were extracted with 0.5M HCl and analysed colorimetrically for NH_4^+ and NO_3^- by a segmented flow Autoanalyzer III (Bran and Lubbe, Inc., Buffalo, NY), following the methods above.

Resin capsules (Unibest PST-1, Unibest International Walla Walla WA) were installed instead of probes in winter 2009-2010 and summer 2010. Capsules were installed at 7 cm below the soil surface to measure N availability. Capsules (2 cm diameter) consist of 1 g mixed-bed exchange resin encapsulated in a nylon mesh (Johnson et al. 2005). Two capsules were installed in the mineral soil at each atmospheric collector using a one inch diameter soil core. For the winter 2009-2010 installation only, an additional four probes, two cation and two anion, were installed near a capsule in the mineral soil at one atmospheric collector per site. After each sampling period, capsules were removed, washed with deionized water, and extracted for NH_4^+ and NO_3^- with three sequential 20 ml rinses of 2M KCl. The effluent was analyzed for NH_4^+ and NO_3^- by segmented flow colorimetry (SmartChem™ 200 Discrete Analyzer, Mandel Scientific Company Inc., Guelph Ont), with the methods above.

2.2.5 Statistical analysis

Pearson's correlations were performed using R (version 2.12.2, The R Foundation for Statistical Computing). Soil N availability in forest floor and mineral soil, as estimated by PRS probes were highly correlated (Pearson's correlation R= 0.87 p= 7.2x 10^{-07}), therefore we combined the two values for total soil N availability. Soil capsule data was compared to the probe data from the winter 2009-2010 sampling period. The data was log transformed to meet the assumptions of normality and homogeneity of variances for Pearson`s correlation. Total inorganic N (R=0.72, p=1.996 x 10^{-5}) and inorganic NO_3^- (R=0.74, p= 9.124 x 10^{-6}) were highly correlated between capsule data and probe data, therefore equations (1) and (2) were used to derive soil N amounts in probe equivalents from capsules for inter-annual comparisons. Ammonium was calculated as the difference between equations (1) and (2).

$$PRS^{TM}\ Total\ Inorganic\ N = \left[\frac{Resin\ Capsule\ Total\ Inorganic\ N}{0.03}\right]^{\left[\frac{1}{1.50}\right]} \tag{1}$$

$$PRS^{TM}\ Inorganic\ NO_3^- = \left[\frac{Resin\ Capsule\ Inorganic\ NO_3^-}{0.03}\right]^{\left[\frac{1}{1.54}\right]} \tag{2}$$

$$PRS^{TM}\ Inorganic\ NH_4^+ = (1) - (2) \tag{3}$$

Two-way ANOVA and multiple regressions were performed using R, while repeated measures ANOVA was completed using SAS software (version 9.2, SAS Institute Inc., 2002, Cary, NC). Data was log transformed for aspen and pine when required to meet the assumptions of homogeneity of variances and normality. Repeated measures ANOVA were used to compare atmospheric N deposition and soil N availability within density classes for aspen and pine stands. Aspen and pine stands were analyzed individually. Repeated measures ANOVA examines variation between density classes over time as well as the variation within density classes across time, which produces interactions with time and density class (Vittinghoff 2005). Multiple comparisons were completed with a bonferroni adjustment. A two-way ANOVA was used to compare the difference between years for atmospheric wet N deposition and soil N availability. Multiple regressions were completed for each season, for total wet N deposition and total soil N availability. The best fit model was selected using the AIC (Akaike Information Criterion) and adjusted R^2 values (Steel and Torrie 1980).

2.3 Results

2.3.1 Atmospheric N deposition

Over two years, the average wet N deposition in aspen was 12.9 ± 7.6 kg N ha^{-1} yr^{-1} (mean±SD) while in jack pine it was 15.6 ±13.0 kg N ha^{-1} yr^{-}, the majority of which was in the form of NH_4^+ (Figure 2-1). Estimated total N deposition ranged from was 20.2 ± 11.9 kg N ha^{-1} yr^{-1} in aspen and 24.3 ± 20.0 kg N ha^{-1} yr^{-1} in jack pine (Figure 2-2).

Nitrogen deposition in both aspen and pine varied significantly among seasons and was lower in winter (Figure 2-3 & 2-4). Results also indicated that the interactions between canopy density categories and season were significant, where differences were found between 0-30% and 66-100% canopy cover categories in fall 2008 and summer 2010 in aspen (Table 2-1; Figure 2-3 & 2-4). Comparisons between years showed that year two (October 2009-2010) had significantly more N deposition. In year two, the canopy density categories 0-30% and 31-65% had significantly more N than 66-100% (Table 2-1; Figure 2-5). Pine had similar results to aspen except only the 0-30% canopy density category was significantly different in all summer measurements and winter 2009. There was no difference found between years in pine (Table 2-1; Figure 2-4 & 2-5).

Differences found in N deposition rates between canopy classes for both aspen and pine may be attributed to canopy cover. Multiple regressions illustrated that canopy cover, precipitation and distance to emission source (stack) were the three most important factors influencing N deposition rates in aspen and pine. Canopy cover appears to be the most important factor that influences deposition rates for both aspen and pine across the majority of seasons. As canopy cover increases, the amount of wet N deposition found under the canopy decreases (Table 2-2; Figure 2-3 & 2-4).

2.3.2 Soil N availability

Total soil available N in both pine and aspen stands varied by season, but did not vary with canopy cover class, or the interaction between canopy cover class and season (Table 2-1). Summer 2009 had significantly more soil inorganic N available for plant uptake than all other seasons in aspen and pine (Figure 2-3 & 2-4; Table 2-1). Winter 2009 had significantly more soil available inorganic N than summer 2010 in aspen (Figure 2-3). Nitrate dominants the soil available N pool in aspen 0-30% canopy density and all canopy density categories in pine (Figure 2-3, 2-4 & 2-5). In addition, soil N availability appears to be lower in aspen than in pine (Figure 2-5). Soil N availability was influenced by N deposition, precipitation, and tree density in aspen and pine, depending on the season and year (Table 2-3). In aspen, N deposition and precipitation significantly influenced soil N availability, while in pine, forest stand conditions, and precipitation affected soil N availability (Table 2-3).

2.4 Discussion

2.4.1 Atmospheric N deposition

The atmospheric N deposition rates found in this study were above the natural background levels of approximately <1 kg N ha^{-1} yr^{-1} in the AOSR (Vitt et al. 2003). Nitrogen deposition on reconstructed soils appears to be greater than other regions in Canada and seems to be on par with industrial areas in Europe and the United States (Zottl 1990, Lovett 1992, Houle et al. 1999, Köchy and Wilson 2001, Nilsson et al. 2006, Watmough 2010). A recent study conducted in natural forests from the AOSR found wet N deposition averaged 0.95 kg ha^{-1} yr^{-1} with total N deposition rates ranging from 7 to 13 kg ha^{-1} yr^{-1} (Laxton et al. 2010). The wet N deposition values from this study were calculated using a model, while dry deposition values were estimated using different deposition velocities. In southern Ontario (Toronto-Montreal corridor) total N deposition rates are up to 15 kg N ha^{-1} yr^{-1} (Houle et al. 1999, Watmough 2010), while in National Parks across the Great Plains (Alberta, Saskatchewan and Manitoba) wet N deposition values range from 5 to 11 kg N ha^{-1} yr^{-1} (Kochy and Wilson 2001). In Europe, total N deposition rates vary from to 10-80 kg N ha^{-1} yr^{-1} (Zottl 1990, Nilsson et al. 2006), while in the United States (California and the northeast) rates are from 7-53 kg N ha^{-1} yr^{-1}, with highest annual amounts located near industrial or populated regions ((Johnson and Lindberg 1992, Lovett 1992, Fenn et al. 1996, Fenn and Poth 1999, Tomaszewski et al. 2003).

The dominant form of wet N deposition in our study was NH_4^+ (Figure 2-1). Ammonium was also the dominant form in wet N deposition on undisturbed sites in the AOSR (Wieder et al. 2010, Laxton et al. 2011). This corroborates other studies that have found greater concentrations of NH_3 in the atmosphere when compared to HNO_3 and NO_2 in the AOSR (Bytnerowicz et al. 2010, Laxton et al. 2010). Potential sources for NH_3 are industrial activities (Farwell et al. 2009, Bytnerowicz et al. 2010, Laxton et al. 2010) and fertilization used in land reclamation (Bytnerowicz et al. 2010). Ammonia emissions from industrial activities can include the aqueous mixture used to separate and recover bitumen from tar, volatilization of NH_3 during upgrading by hydrotreating, and tailings ponds contaminated with NH_3 (Bytnerowicz et al. 2010, Laxton et al. 2010). Ammonia volatilization in water is greatest when pH is high, when NH_4^+ concentrations are high and during windstorms that cause turbulence and wave formation (Boyd and Tucker 1998). Thus, ammonia volatilization from tailing ponds may be high due to high pH (8 to 8.4) and high NH_4^+ concentrations (14 mg/L)(Allen 2008) and seasonal storms in the region. Another potential source is the urea fertilizer applied as a granular medium to the surface of reconstructed soils. Studies have found 10 to 20 percent of surface applied urea fertilizer to volatilize into the atmosphere (Nihlgard 1985, Schlesinger and Hartley 1992, Rawluk et al. 2001), particularly when soil conditions stimulate rapid granular dissolution with little infiltration into the soil (Rawluk et al. 2001). Further work examining N isotope signatures might reveal the other potential sources.

Nitrogen deposition rates were influenced by a number of factors also, found in literature including: distance to emission point source (Bytnerowicz and Fenn 1996, Fenn and Poth 1999, Metcalfe et al. 1999, Kochy and Wilson 2001, Bytnerowicz et al. 2010, Laxton et al. 2010), canopy cover (Gundersen 1991, Fenn and Poth 1999) and precipitation (Lindberg et al. 1986, Kochy and Wilson 2001, Tomaszewski et al. 2003) (Table 2-2). Distance to emission point source (stack) explained some of the variation in our wet N deposition rates. Ammonia has a short residence time in the atmosphere (Metcalfe et al. 1999, Krupa 2003), thus it travels less distance prior to interception in precipitation (Asman et al. 1998, Metcalfe et al. 1999, Harrison et al. 2000). In addition, measured bulk precipitation at the pine sites was greater than at the aspen sites, which may be linked to their position on the mine leases. Pine stands were located on the southeast quadrant, while aspen stands were located on the northeast quadrant of the mine leases. The dominant wind direction in the AOSR is east to southeast (Wieder et al. 2010), which may explain why the pine stands received more N deposition. Precipitation positively influences the amount of wet N deposition received on a landscape (Lindberg et al. 1986, Kochy and Wilson 2001, Tomaszewski et al. 2003). We know that NH_4^+ levels are greater in summer than winter, which is most likely due to increased precipitation and therefore, increased interception of NH_3 in the atmosphere (Figure 2-3 & 2-4).

In our study canopy cover was an important factor that influenced the amount of wet N deposition received by reconstructed soils (Table 2-2). We found sites with <30% canopy cover (bulk precipitation) to have more N deposition than sites with >30% canopy cover (throughfall). In sites with >30% canopy cover, canopy N uptake may occur in both deciduous and coniferous forests in foliage (Lindberg et al. 1986, Böhm 1992, Lovett and Lindberg 1993), or *via* canopy lichens (Reiners and Olson 1984) and microorganisms that live on canopy surfaces (Parker 1983, Reiners and Olson 1984, Lovett et al. 1989, Lovett 1992, Harrison et al. 2000). In addition, it appears that throughfall in aspen with a canopy cover class of 66-100% was more than in the jack pine with a canopy cover class of 66-100%. This was similar to another study in the AOSR where jack pine was found to intercept more deposition than aspen (Jung et al. 2011). Studies have found that coniferous forests, spruce, spruce-fir, and pine have higher uptake of N through canopy interception than deciduous trees in the United States (Lovett 1992, Cappellato et al. 1993, Lovett and Lindberg 1993, Neary and Gizyn 1994). In addition, needle leaf structures may have a higher efficiency to collect water droplets compared to leaf structures (Erisman and Draaijers 2003). This may explain why we observed a difference in throughfall between aspen and pine when canopy cover was >66%.

2.4.2 Soil N availability

In mature, undisturbed natural forest ecosystems, NO_3^- is rarely measured in significant amounts, since mature forests tend to have the capacity to retain and accumulate N in the plants and soil organic matter (Johnson 1992, Van Miegroet et al. 1992a, Van Miegroet et al. 1992b). Soil N availability in our study was mainly in the form of NO_3^- rather than NH_4^+. Other studies on reconstructed soils in the AOSR have found similar results, where NO_3^- is the dominant form of available N (Rowland et al. 2009, Hemstock et al. 2010). Nitrate accumulation in the soil is of concern, since NO_3^- is highly mobile, which can lead to leaching and loss of this form of N from the terrestrial environment. In this study differences were found between aspen and pine for soil N availability (Figure 2-3 &2-4). In pine higher amounts of soil total inorganic N were found in the summer, while in aspen only summer 2009 had high amounts of soil total inorganic N (Figure 2-3 &

Figure 2-4). In jack pine, greater amounts of soil NO_3^- were found in all canopy density categories, whereas in aspen this trend was not as evident. In aspen, NH_4^+ levels were similar to NO_3^- levels with canopy density >30% (Figure 2-3). After five years following clear cutting in northern Alberta, NO_3^- concentrations were low in aspen and spruce (Jerabkova and Prescott 2007). Even after 12 years following fire in jack pine stands, NO_3^- availability was low at only 2-3% of the total inorganic N (Yermakov and Rothstein 2006). In our study, the contribution of NO_3^- to soil total available N averaged 47% in aspen and 65% in pine after 30 years post reclamation. Therefore, we suggest that evidence of high NO_3^- availability in the soil during summer measurements represents a disconnect between plant uptake and soil inorganic N cycling. This is a potential concern for jack pine stands, where NO_3^- was the dominant form in all seasons regardless of canopy cover.

Differences in N availability between aspen and jack pine maybe explained by physiological differences, since stand development, age and land use history are similar. Coniferous species have a lower demand for N and are adapted to a lower supply of nutrients, particularly N (Pardo et al. 2007). Jack pine prefers NH_4^+ as a substrate for uptake, (Ste-Marie and Pare 1999, Choi et al. 2005) while aspen are highly efficient at NO_3^- uptake (Min et al. 1998, Choi et al. 2005). Aspen trees have higher fine root biomass than pine and their roots have higher root N concentrations, which may be the result of greater uptake of soil N (Yuan and Chen 2010). In addition, uptake rates of N by deciduous trees are greater than coniferous trees, due to annual requirements in new foliage growth

(Cole and Rapp 1981, Van Miegroet et al. 1992a). On average deciduous trees, require 94 kg ha^{-1} yr^{-1} of N for growth of which a third of their annual nutrient requirement was from translocation of N within the tree. Coniferous trees require on average 39 kg ha^{-1} yr^{-1} for growth, which mainly comes from the soil (Cole and Rapp 1981). These characteristics might make aspen more useful for land reclamation in high N depositional environments.

2.4.3 Relationship between N deposition and soil N

Soil inorganic N availability, particularly soil NO_3^-, was found to increase with N deposition at these sites, and this relationship has been found in the literature (Tietema and Verstraten 1991, Aber 1992, Cole et al. 1992, Bytnerowicz and Fenn 1996, Fenn et al. 1996, Kiefer and Fenn 1997, Köchy and Wilson 2001, Nilsson et al. 2006). A study in northern Alberta aspen stands found a linear relationship between soil inorganic N availability and N deposition (Kochy and Wilson 2001), however we did not find a linear relationship in either aspen or jack pine stands. Aber et al. (1998) hypothesised that studies may find non-linear responses of N deposition due to the complexity of the N cycle. However, we found that N deposition helped to explain some of the variance in soil N availability. This suggests N deposition was influencing the total amount of soil N availability on these sites. In addition, when wet N deposition levels were greatest, so was the amount of soil inorganic N in most cases. Research has shown that N deposition will positively affect soil N availability over time. This may occur *via* direct additions of inorganic N and/or an accelerated N cycle. The N cycle can be accelerated through increases in litter production, reduced C:N ratio in litter, and accelerated decomposition, all of which further increase soil N availability (Gundersen 1991, Cole et al. 1992, Aber et al. 1998).

2.4.4 Critical N load and N saturation

An ecosystem`s threshold for retaining N is referred to as its critical N load, which can vary with soil types. Surpassing this critical load may result in negative effects, such as changes in species composition, and increased susceptibility to plant pathogens or insects (Hornung and Langan 1999, Bobbink et al. 2010). In heath lands and bogs, the critical N load ranges from 5 to 10 kg N ha^{-1} yr^{-1}, whereas in forests it can be 10 to 20 kg N ha^{-1} yr^{-1} (Krupa 2003). Recent studies have suggested that the critical N load may be as low as 6 kg N ha^{-1} yr^{-1} in boreal forests (Nordin et al. 2005, Whitfield et al. 2010b). However, critical N loads do not include the amount of N forest canopies take up, even though it enters the ecosystem (Harrison et al. 2000).

The effects of N deposition are complex and the time to N saturation is different for each ecosystem (Van Miegroet et al. 1992b). However, there is potential concern that these reconstructed soils may be in the initial stage of N saturation. Studies have found that even with low N deposition, sites may eventually become saturated unless nitrogen is periodically removed from the ecosystem (Dise and Wright 1995). Furthermore Laxton et al. (2010) found natural jack pine sites closest to industrial activity in the AOSR may be in the early stages of N saturation. Sites used in our study have greater than the critical

N load for boreal forests, which may cause shifts in vegetation leading to decreases in key ecosystem species that maintain the boreal forest biodiversity (Nordin et al. 2005).

Forest management practices should try to make use of the additional atmospheric N by utilizing specific fertilization schemes. Studies have found that phosphorus (P) a limiting nutrient in the AOSR (Rowland et al. 2009), thus if fertilizers are used Syncrude and Suncor could focus on P additions more than N. In addition, reforestation in the AOSR could use tree species that are more N demanding, like aspen, to accumulate this additional N and to minimize losses. Further research is required on these sites to determine the fate of N deposition and to investigate the ecological response of this increased N deposition, as N saturation may be a concern.

Table 2-1 ANOVA tables for N deposition and soil N availability within aspen and jack pine over two seasons for two years. A) Repeated measures ANOVA table across each season for the duration of the two years; B) Two-way ANOVA comparing year one (October 2008 to October 2009) to year two (October 2009 to October 2010).

Stand Type	Data Source	Nitrogen Form	Factor	p-value
A)				
Aspen	Wet Deposition	Total Inorganic N	Canopy Cover	0.0038
			Season	<0.0001
			Canopy Cover*Season	0.0013
	Soil Availability	Total Inorganic N	Canopy Cover	0.3799
			Season	0.0045
			Canopy Cover*Season	0.3327
Pine	Wet Deposition	Total Inorganic N	Canopy Cover	<0.0001
			Season	<0.0001
			Canopy Cover*Season	0.0370
	Soil Availability	Total Inorganic N	Canopy Cover	0.1510
			Season	0.0020
			Canopy Cover*Season	0.1666
B)				
Aspen	Wet Deposition	Total Inorganic N	Canopy Cover	0.003
			Year	0.01
			Canopy Cover*Year	0.002
	Soil Availability	Total Inorganic N	Canopy Cover	0.15364
			Year	0.0020
			Canopy Cover*Year	0.08461
Pine	Wet Deposition	Total Inorganic N	Canopy Cover	<0.0001
			Year	0.5777
			Canopy Cover*Year	0.5947
	Soil Availability	Total Inorganic N	Canopy Cover	0.01473
			Year	0.07815
			Canopy*Year	0.43061

Table 2-2 Multiple regression parameters for relationships between dependent variables (total inorganic nitrogen wet deposition) and independent variables (canopy cover (%), age, elevation (m), distance to closest point source (m), precipitation (mm), slope (%), crown thickness (m), and height of tree (m)) in trembling aspen, and jack pine across different seasons on reclaimed sites previously disturbed by oil sands mining.

Season	Dependent Variable(s)	Stand Type	Independent Variable(s)	R^2	p-value
Fall 2008	Total Wet N Deposition	Aspen	Canopy Cover	0.63	0.006
		Pine	Canopy Cover, Distance, Elevation	0.97	<0.0001
Winter 2008-2009	Total Wet N Deposition	Aspen	Canopy Cover, Tree Height, Elevation	0.85	0.007
		Pine	Canopy Cover, Tree Height, Slope	0.42	0.32
Summer 2009	Total Wet N Deposition	Aspen	Age, Distance, Tree Height	0.52	0.19
		Pine	Canopy Cover, Precipitation	0.75	0.008
Winter 2009-2010	Total Wet N Deposition	Aspen	Canopy Cover, Distance, Precipitation, Slope	0.77	0.003
		Pine	Canopy Cover, Distance, Precipitation, Slope, Age	0.81	0.03
Summer 2010	Total Wet N Deposition	Aspen	Canopy Cover, Precipitation	0.47	0.0219
		Pine	Canopy Cover, Distance, Elevation	0.83	0.002

Table 2-3 Multiple regression parameters for relationships between dependent variables (total soil inorganic nitrogen availability) and independent variables (total inorganic nitrogen wet deposition, age, canopy cover (%), elevation (m), tree density, precipitation (mm), slope (%), crown thickness (m), and height of tree (m)) in trembling aspen, and jack pine across different seasons on reclaimed sites previously disturbed by oil sands mining.

Season	Dependent Variable(s)	Treatment	Independent Variable (s)	R^2	p-value
Fall 2008	Total Inorganic Soil N	Aspen	Total Wet N Deposition, Canopy Cover	0.62	0.033
		Pine	Slope, Tree Density	0.378	0.19
Winter 2008-2009	Total Inorganic Soil N	Aspen	Tree Density	0.55	0.015
		Pine	Total Wet N Deposition, Slope	0.41	0.16
Summer 2009	Total Inorganic Soil N	Aspen	Total Wet N Deposition, Precipitation, Slope, Elevation	0.89	0.013
		Pine	Precipitation, Tree Density	0.63	0.031
Winter 2009-2010	Total Inorganic Soil N	Aspen	Total Wet N Deposition, Precipitation	0.60	0.004
		Pine	Tree Density	0.26	0.09
Summer 2010	Total Inorganic Soil N	Aspen	Precipitation	0.28	0.04
		Pine	Precipitation, Age, Tree Height, Slope, Elevation	0.90	0.006

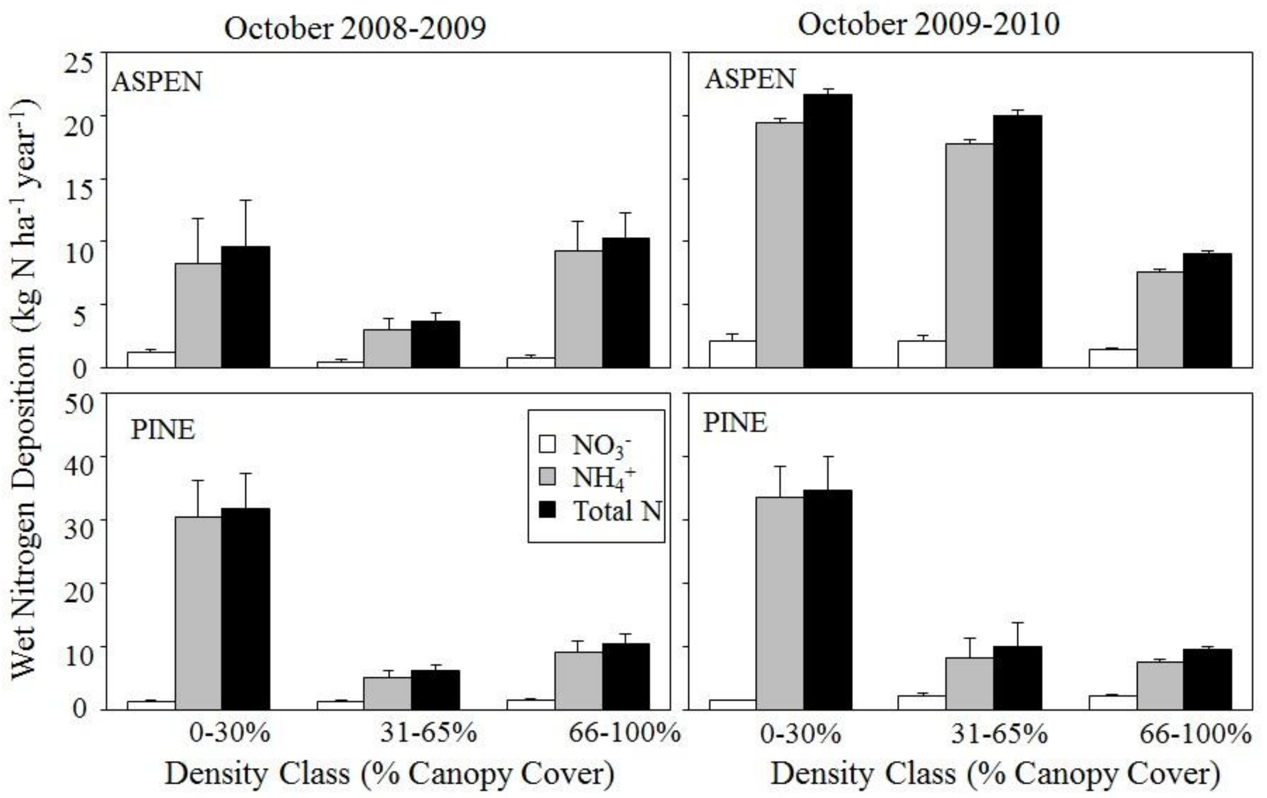

Figure 2-1 Yearly atmospheric wet nitrogen deposition (mean ± SE) (kg N ha^{-1} yr^{-1}) (October 2008 to October 2009 (n=20) and October 2009 to October 2010 (n=27)) in aspen and jack pine stands across three density classes, 0 to 30%, 31 to 65% and 66% to 100%.

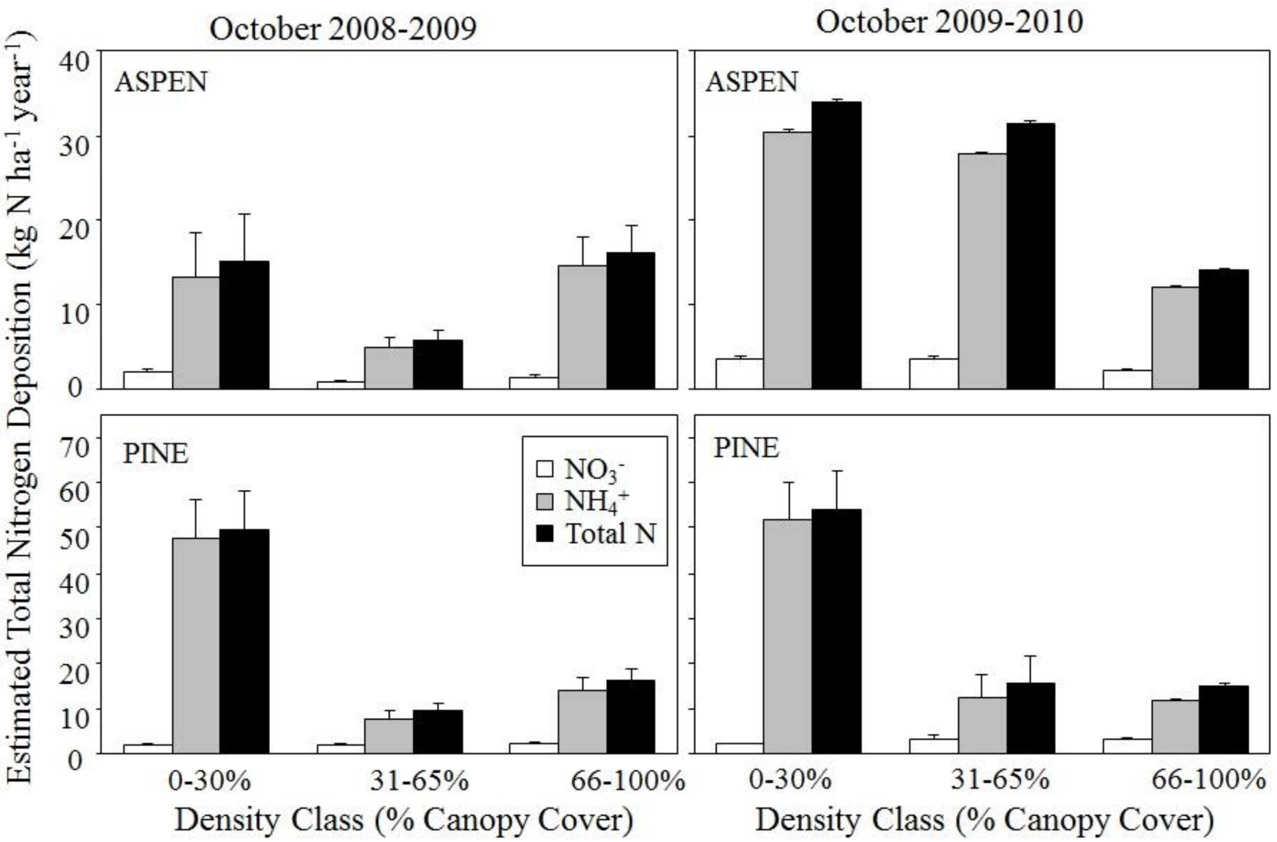

Figure 2-2 Estimated wet nitrogen deposition (mean ± SE) (kg N ha^{-1} yr^{-1}) (October 2008 to October 2009 (n=20) and October 2009 to October 2010 (n=27)) in aspen and jack pine stands across three density classes, 0 to 30%, 31 to 65% and 66% to 100%. Ratio 0.56 (Johnson and Lindberg 1992) was used to determine total amount of deposition (wet +dry).

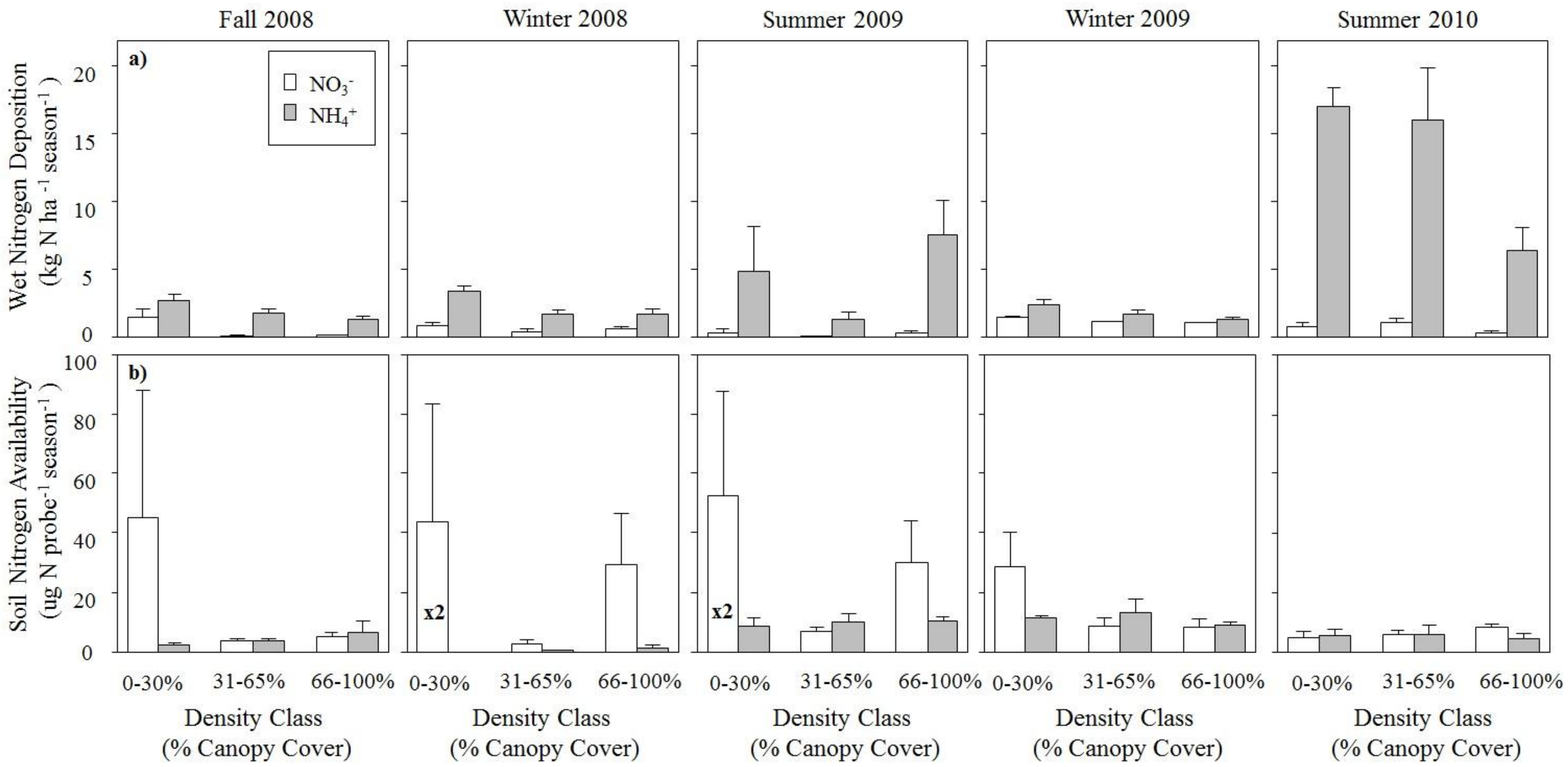

Figure 2-3 Seasonal variations in aspen stands (June 2008 to October 2010) in across three density classes, 0 to 30%, 31 to 65% and 66% to 100%; a) Seasonal atmospheric wet nitrogen deposition (mean ± SE) (kg N ha^{-1} yr^{-1}); b) Seasonal total soil inorganic N availability (µg N probe^{-1} yr^{-1}). Bar graph's with x2 mean that the value is 2 times greater than represented in graph.

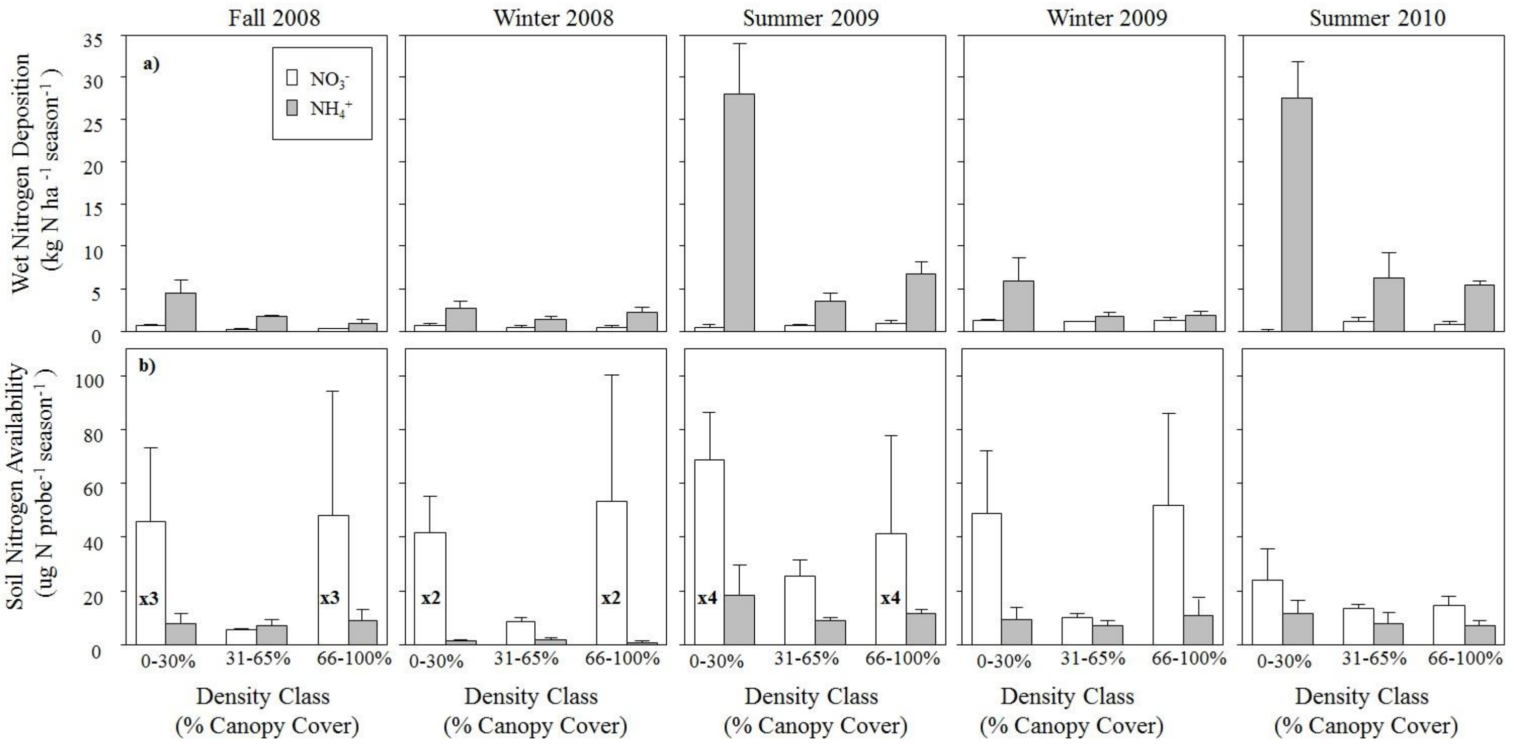

Figure 2-4 Seasonal variations in pine stands (June 2008 to October 2010) in across three density classes, 0 to 30%, 31 to 65% and 66% to 100%; a) Seasonal atmospheric wet nitrogen deposition (mean ± SE) (kg N ha^{-1} yr^{-1}); b) Seasonal total soil inorganic N availability (µg N probe^{-1} yr^{-1}). Bar graphs with x2, x3, or x4 mean that the value is 2, 3, or 4 times greater than represented in graph.

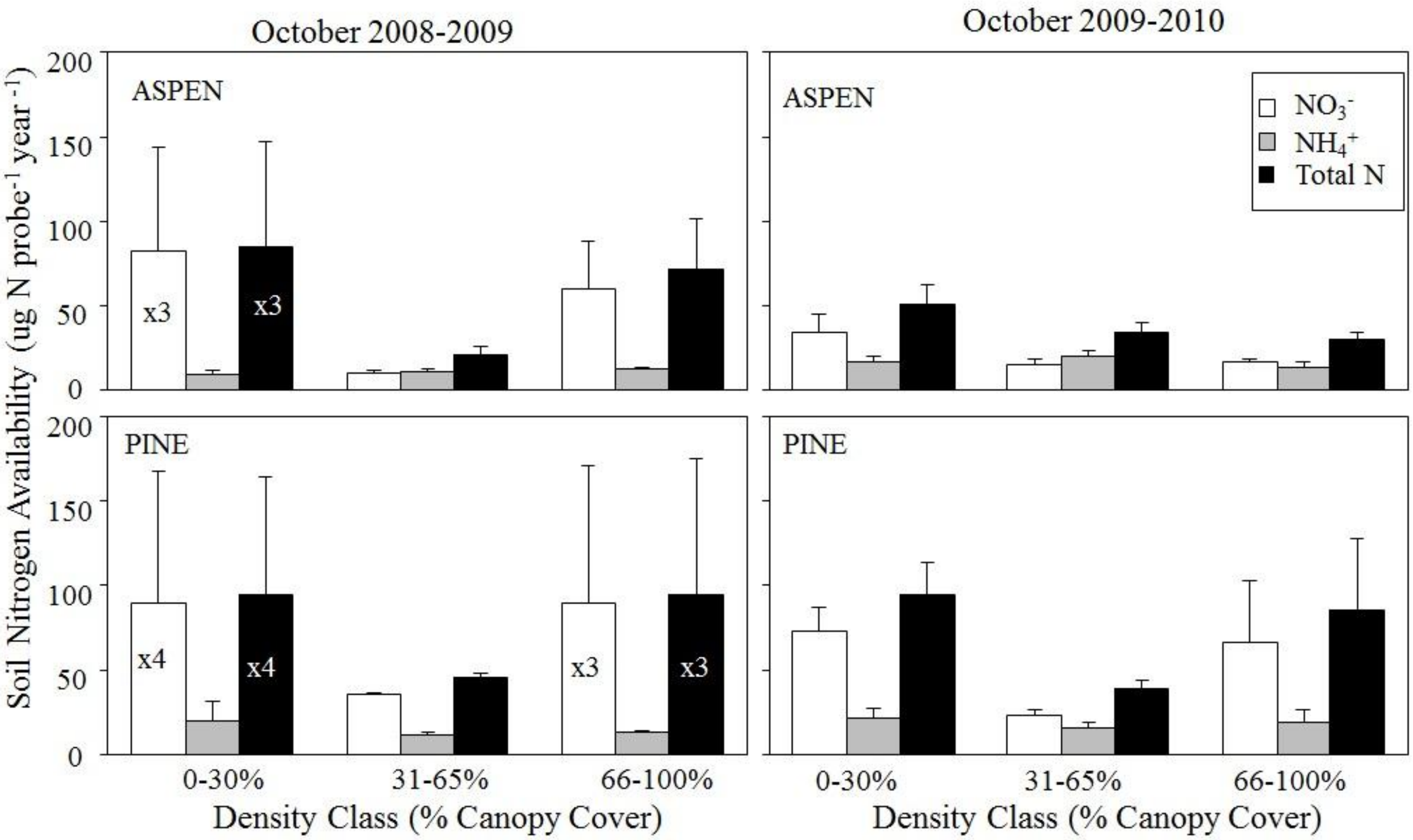

Figure 2-5 Yearly total soil inorganic N availability (mean ± SE) (µg N probe^{-1} yr^{-1}) (October 2008 to October 2009 (n=20) and October 2009 to October 2010 (n=27)) in aspen and jack pine stands across three density classes, 0 to 30%, 31 to 65% and 66% to 100%. Bar graph's with x3 or x4 means that value is 3 or 4 times greater than represented in graph.

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CHAPTER 3

Ecological Response to Atmospheric Nitrogen Deposition in the Athabasca Oil Sands Region

3.1 Introduction

The increase in atmospheric nitrogen (N) deposition linked to anthropogenic activity is an issue of global importance (Vitousek et al. 1997; Galloway 1998), and is a potential concern in the Athabasca Oil Sands Region (AOSR) of northeastern Alberta, Canada. Industrial activity linked to oil and gas extraction in the AOSR, over the past 25 years, has resulted in significant increases in nitrogen oxides (NO_x) and ammonia (NH_3) emissions (Laxton et al. 2010). Nitrogen oxides may originate from vehicle emissions or exhaust from other industrial machinery (Bytnerowicz et al. 2010), while NH_3 arises from bitumen extraction and processing (Bytnerowicz et al. 2010; Whitfield et al. 2010), and volatilization from fertilizers that are utilized on land under reclamation (Bytnerowicz et al. 2010). These atmospheric N emissions may then be deposited to the AOSR forested landscape by two processes: dry deposition, including NH_3 and nitric acid (HNO_3) (Lovett 1994), or wet deposition, for the most part comprised of ammonium (NH_4^+) and nitrate (NO_3^-) (Hanson and Lindberg 1991; Bytnerowicz and Fenn 1996).

Atmospheric N deposition is an important issue to consider for the ecology of forest ecosystems, as it has the ability to change both their community structure and function (Aber et al. 1989; Aber et al. 1998; Fenn et al. 1998). Increases in atmospheric N deposition have caused imbalances between inputs to the ecosystem and uptake by either soil microbes or plants (Fenn et al. 1998; Allen and Bayley 2004) leading to a new ecological status called N saturation (Aber et al. 1989, Aber et al. 1998). Nitrogen saturation is defined as the condition where N availability exceeds the capacity of plants and soil microbes to retain it (Aber et al. 1989). Kinetic N saturation is reached when the rate of inputs exceeds the plant and soil uptake rates, although the ecosystem is still acting as a net N sink. On the other hand, once capacity N saturation is attained, net N retention cannot occur anymore such that outputs are greater than or equal to inputs (Lovett and Goodale 2011).

The effects of N deposition on terrestrial ecosystems are dependent upon the duration, amount and form of N being deposited, the ecosystem storage capacity, sensitivity of the vegetation present and abiotic conditions such as climate and soil type (Gundersen 1991,Bobbink et al. 2010). Therefore, multiple complementary N indicators have been proposed as a tool to monitor and identify ecosystems at risk of becoming N saturated, including: extractable foliar NO_3^-, foliar N:P, foliar N, soil C:N, soil solution NO_3^-, potential mineralization and nitrification rates, $\delta^{15}N$ enrichment factors, and $\delta^{15}N$ natural abundance (Bytnerowicz and Fenn 1996, Fenn and Poth 1996, Emmett et al. 1998, Pardo et al. 2006, Nadelhoffer 2007, Templer et al. 2007).

Stable N isotopes have been used in ecology and soil science research for several decades to investigate both external N sources and internal ecosystem transformations. For instance, many processes of the internal N cycle (e.g.; nitrification, microbial and plant uptake), discriminate against the heavier N isotope, causing progressive ^{15}N enrichment of the residual pool that can be used as an indicator of the different reaction rates (Handley and Raven 1992, Nadelhoffer and Fry 1994, Högberg 1997, Robinson 2001, Dawson et al. 2002, Makarov 2009). Similarly, plant $\delta^{15}N$ values encompass the net effect of a range of N processes. In N-limited systems, plant $\delta^{15}N$ closely resembles the $\delta^{15}N$ of its sources since the entire available N pool is utilized. However, in N-rich systems, which tend to exhibit high nitrification rates and NO_3^- losses of depleted ^{15}N, enrichment of soil NH_4^+ may occur causing plants to eventually become enriched in ^{15}N (Nadelhoffer and Fry 1994; Högberg 1997; Dawson et al. 2002). Consequently, soil and plant ^{15}N abundance values may be powerful indicators of an ecosystem N status and its potential to become N saturated, especially when all potential N sources can be constrained (Koopmans et al. 1997; Koba et al. 2003; Pardo et al. 2006; Templer et al. 2007; Fang et al. 2011).

The impact of increased N emissions on natural ecosystems surrounding the active mine area of the AOSR has been previously investigated (Vitt et al. 2003; Laxton et al. 2010; Wieder et al. 2010; Laxton et al. 2011). Previous research also established that N deposition on terrestrial ecosystems currently undergoing reclamation, which are directly adjacent to the active mines, exceeds background levels (Chapter 2). The main objective of this study was to assess the potential implications of this increased atmospheric N deposition on the ecological response of reclaimed sites planted with trembling aspen (*Populus* *tremuloides* Michx.), and jack pine (*Pinus banakasina* Lamb.), two of the dominant tree species used to re-establish a forest cover in the AOSR. Several indicators of N status were investigated, including foliar N concentrations, soil NO_3^- concentrations, and $\delta^{15}N$ values of different plant and soil pools. Since the N cycle in conifers has been reported to be more vulnerable to increased N inputs than is the case for hardwoods (Pardo et al. 2006), we hypothesized that the two stand types would respond differently to the increased N deposition. We also examined two age classes, young (4 to 8 years) and old (17 to 23 years), for both aspen and pine stands, in order to explore the potential effects of chronic N deposition over time. We hypothesized that trees in the older stands under the influence of N deposition for a longer period of time would be enriched in ^{15}N relative to the younger stands.

3.2 Methods

3.2.1 Study area

The study area is located approximately 40 km north of Fort McMurray, northeastern Alberta (56°39’12N, 111°13’24W). The climate in this area is characterized by long cold winters and short summers. The mean monthly temperatures range from -18.8 °C in January to +16.8 °C in July with a mean annual temperature of +0.2°C. The mean annual precipitation averages 455 mm with 342 mm of precipitation between May and September (Environment Canada 2011). The study area is located in the Central Mixedwood Subregion of the

Canadian boreal forest (Natural Regions Committee 2006). Upland forests are dominated by trembling aspen, white spruce (*Picea glauca* (Moench) Voss) and jack pine. Gray Luvisolic soils (Haplocryalfs according to the USDA system) are typically found on imperfectly to well drained, medium to fine-textured calcareous parent material, while Dystric Brunisols (Dystrocryepts) have formed on coarser, more acidic parent material (Turchenek and Lindsay 1982). Organic soils have developed on poorly drained lowlands (Natural Regions Committee 2006).

In summer 2010, 12 sites covering two age categories, young (4 to 8 years) and old (17 to 23 years) were selected from a network of long term soil and vegetation monitoring plots (Oil Sands Vegetation Reclamation Committee 1998) and a series of sites previously used to conduct a forest floor development study (Sorenson et al. 2011). Two stand types, trembling aspen (3 young and 3 old sites) and jack pine (2 young and 4 old sites) were included as part of our study. The young stands averaged a height of 1.4 m with a tree density ranging from 3000 to 4000 trees ha^{-1}. The older aspen stands averaged 9.0 m in height, while the pine stands averaged 4.9 m. The tree density in the older stands ranged from 3500 to 4000 trees ha^{-1}. These 12 sites were located on two different mine leases, Syncrude Canada Ltd. and Suncor Energy, and were selected to contain comparable topsoil amendments. Soil reconstruction (0-1 m) following oil sands mining is completed by using a range of materials, including mineral and organic soils salvaged prior to the onset of mining, overburden or industrial by-products such as tailings sand (Sorenson et al. 2011). The topsoil amendment used for soil reconstruction at all study sites consisted of peat salvaged from lowland areas mixed with mineral soil. Sites were originally planted with either aspen or pine as the dominant tree species respectively. Shrubs most commonly planted on site included wild rose (*Rosa acicularis* Lindl.), common blueberry (*Vacciuium angustifolium* Aiton), red osier dogwood (*Cornus stolonifera* Michx.), saskatoon berry (*Amelanchier alnifolia* Nutt.), green alder (*Alnus crispa* (Chaix.) D.C.) and various willow species (*Salix* spp.) (Pers. comm. F. Salifu, Suncor and M. Yarmuch, Syncrude). Reconstructed soils were fertilized with varying N-P-K-S regimes established by the different leaseholders. Syncrude Canada Ltd. fertilizes in the first year following planting with rates of 350 kg/ha (10-30-15-4), while sites at Suncor Energy receive fertilization annually for the first 5 years at a rate of 300 kg/ha (23.5-25-8-0) in the first year and 250 kg/ha (31.5-16-5-0) in the following years (Lanoue 2003).

3.2.2 Soil and plant sampling

In July 2010, soil, foliage and root samples were collected at each of the 12 sites. On each site, five 1 m x 1 m plots were established on a 25 m transect at 5 m intervals. Within each plot, four forest floor cores (20 cm diameter) were taken. All the live vegetation was removed prior to collection of the entire forest floor. The forest floors on these reclaimed sites consisted of a L layer, comprised of relatively fresh plant residues that retained their structure and could be easily identified, and a F layer, which was partially decomposed material where incomplete plant structures were still identifiable (Green et al. 1993). Forest floor at the young sites consisted of the L fraction only, while it included both L and F layers at the older sites. In addition, for each plot, four mineral soil cores (10 cm diameter x 7 cm depth) were sampled. For both the organic and mineral samples, the four subsamples taken per plot were composited to yield five representative samples per site. Samples were kept cool (4°C) in a refrigerator until returned to the laboratory for processing.

Foliage samples were taken from five dominant trees located near each plot for a total of 25 trees sampled per site. Foliage samples were collected from the upper half of the crown, but below the top ¼ of the crown (Carter 1992). The aspen foliage samples corresponded to current year's growth while the pine needles were second year's growth. Samples were placed in paper bags and air-dried until returned to the laboratory.

3.2.3 Atmospheric NH_4^+ *and* NO_3^- *deposition*

Five atmospheric deposition collectors were used to measure wet N deposition at each site over a 6 month period in the summer (May to October) and winter (October to May) periods for two consecutive years (winter 2008- summer 2010), following the design from Fenn and Poth (2004). Each collector was composed of a snow tube (22.5 cm diameter x 75 cm), and a plastic funnel (23 cm diameter) with a PVC filter and a resin column (2.5 cm diameter x 30 cm) containing 50 ml of mixed bed resin (IONAC ® NM-60 H^+/OH^-, J.T. Baker, Phillipsburg, NJ) that permitted flow *via* percolation. To minimize contamination, a plug of glass wool was inserted at the top and bottom of each resin column. At every site a field blank resin column was installed, which was constructed the same way as the other resin columns, but was capped at both ends. All collector snow tubes, funnels and filters were cleaned with 0.5M HCl then rinsed with distilled water prior to installation. Once installed, the total collector height was about 1.6 m, which was above the trees in the young stands, but under the tree canopy in the older stands. Consequently, collectors captured bulk precipitation at the young stands but throughfall at the old stands. Resin columns were exchanged every spring (May) and fall (October). At each collection period, funnels and filters were cleaned with distilled water and replaced if broken.

3.2.4 Soil inorganic NH_4^+ *and* NO_3^- *availability*

In October 2009, two resin capsules (Unibest PST-1, Unibest International Walla Walla, WA) were installed to capture available soil N in close proximity to each atmospheric collector. Capsules (2 cm diameter) consisted of 1 g mixed-bed exchange resin encapsulated in a nylon mesh (Johnson et al. 2005), and were installed at 7 cm below the soil surface using a one inch diameter soil core. Capsules were removed at the same time as the resin columns (May 2010), and were composited for each atmospheric collector allowing for five replicates per site. A second set of capsules was installed and left to incubate between May and October 2010, again corresponding to the same monitoring period as the atmospheric collectors.

3.2.5 Laboratory analyses

In the laboratory, foliage samples collected at each plot were composited by weight for a total of five composited samples per site. Mineral soil samples were air-dried and then sieved through 5 mm and 2 mm sieves. Roots <5 mm were collected from the mineral soil samples and washed with de-ionized water. Roots were classified and separated as woody or herbaceous, live or dead based on color, texture, and shape (Vogt and Persson 1991), so that aspen and pine roots could be isolated for further analysis. Roots and foliage were dried in a forced air oven at 65°C for 24 hours, and then mechanically ground using a Wiley Mill. The pH values were measured with a glass electrode on the mineral soil and ground forest floor samples using a 0.01 M $CaCl_2$ solution, a 4:1 solution:soil ratio for forest floor and a 2:1 ratio for mineral soil (Kalra and Maynard 1991). After ball mill grinding, subsamples from the collected mineral soil, forest floor, root and foliage were analyzed for total carbon and nitrogen concentrations by pyrolysis using a Costech ECS 4010 CHNS-O Elemental Combustion System (Costech Analytical Technologies Inc., Valencia, CA)

Resin columns were pre-rinsed with 50 ml de-ionized water prior to extraction. Ammonium and NO_3^- were extracted with four rinses of 40 ml 2M KCl via percolation. For each extraction, KCl was left in the column for 20 minutes prior to drainage to increase the removal of NH_4^+ and NO_3^-. Resin capsules were washed with deionized water, and extracted for NH_4^+ and NO_3^- with three sequential 20 ml rinses of 2M KCl. After each extraction, 15 ml of eluent was decanted leaving 5 ml in the centrifuge tube. The KCl effluent was analyzed for NH_4^+ and NO_3^- using a segmented flow colorimetry (SmartChem™ 200 Discrete Analyzer, Mandel Scientific Company Inc., Guelph Ont), using the nitro-prusside/salicylate method and the cadmium reduction method, respectively (Mulvaney 1996). The KCl effluent was kept frozen until it could be analyzed for $\delta^{15}N$.

3.2.6 *$\delta^{15}N$ values for wet N deposition and soil inorganic (available) N*

The diffusion method established by Brooks et al. (1989) was used to measure $\delta^{15}N\text{-}NH_4^+$ and $\delta^{15}N\text{-}NO_3^-$ values in the KCl effluents. For each site, five samples were composited into one sample prior to diffusion. For $\delta^{15}N\text{-}NH_4^+$, the KCl effluent was put into a 120 ml capped vial in which approximately 0.2 MgO was added, along with an acidified filter paper ($KHSO_4$) suspended above the effluent for six days. Filter disks were encapsulated for ^{15}N measurement after drying in a desiccator for 24 hours. A similar procedure was completed for $\delta^{15}N\text{-}NO_3^-$, but instead of putting the filter in with the MgO, the vial was left open for six days to allow NH_3 to volatilize. After the initial six day incubation, about 0.4 g Devarda's alloy was put into the vial with an acidified filter disk. The lids were closed and incubated for an additional six days. Again, filter disks were dried and encapsulated for ^{15}N measurements.

3.2.7 *δ^{15}N values for fertilizer N urea and tailings pond water*

Granular urea (n=2) was obtained from Sturgeon Valley Fertilizers, Legal AB for δ^{15}N analysis. Sturgeon Valley Fertilizers (SVF) is a supplier to both mine leases (Pers Comm Doris Clark SVF). Urea was ground with a ball grinder until homogenous. Tailings pond samples were obtained from six different ponds located on the two different mines, Syncrude Canada Ltd. (n=2) and Suncor Energy (n=3). At each pond, one sample was taken from the middle, and the other one near the edge of the pond, except for a pond at Syncrude in which only one sample was acquired near the edge. At the time of sampling, average concentration (n=2) for NH_4^+ was 17 mg/L ± 6 (mean ±SE), but was below detection limits for NO_3^- (Pers. Comm. T. Penner, Syncrude 2010), which is similar to other studies on tailing pond water in the AOSR (Allen 2008). Samples were put on ice (0°C) and shipped overnight to the University of Alberta, where they were filtered with a GF/A Whatman® filter (1.6 µm), then poured through a resin column. Water pH was measured on the samples with a glass electrode (Accumet®AP85 pH/conductivity meter, Fisher Scientific, Singapore). Resin columns were extracted and analyzed the same way as mentioned above, but with 5 rinses of KCl. Afterwards samples were analyzed for δ^{15}N-NH_4^+ following the same diffusion method as mentioned above

The ^{15}N natural abundance analysis for all samples was conducted using a Costech ECS 4010 CHNS-O Elemental Combustion System (Costech Analytical Technologies Inc., Valencia, CA) coupled to a Conflo III & Continuous Flow

Finnigan Delta Plus Avantage IRMS (ThermoFinnigan, Bremen, Germany). All ^{15}N values are expressed using the $\delta^{15}N$ notation (‰), which represents the difference between the sample and air:

$$\delta^{15}N\ (‰) = [(R_{sample} / R_{standard})-1]*\ 1000$$

where R_{sample} and $R_{standard}$ are the $^{15}N/^{14}N$ ratios of the sample and atmospheric $N_{2,}$ respectively. Several NIST Standard Reference Materials (IAEA N1, IAEA N2, IAEA N3) were used to calibrate and standardize the instrument between different runs and dates with a precision of ±0.21‰.

The enrichment factor is a technique for comparing $\delta^{15}N$ values from different sites by normalizing for spatial heterogeneity in order to reflect differences in soil N fluxes (Emmett et al. 1998; Pardo et al. 2006; Pardo et al. 2007a). In the case of our study, enrichment factors were used to adjust for differences in the $\delta^{15}N$ of soils and plants between sites that may be caused by different land management techniques and age of soil reconstruction. Enrichment factors (ε_{p-s}) were calculated as the difference between the substrate (mineral soil) and the product (foliage) using (Mariotti et al. 1981):

$$\varepsilon_{p-s}= \delta^{15}N_{\ foliage} - \delta^{15}N_{\ soil}$$

3.2.8 Statistical analysis

Two-way ANOVAs were used to compare differences between stands and age classes for various site properties, enrichment factors, $\delta^{15}N$ values in atmospheric NH_4^+ and NO_3^- deposition, forest floor, mineral soil, root, foliage samples, and soil NH_4^+ and NO_3^- availability. A repeated measures ANOVA was used to compare atmospheric ^{15}N deposition values by stand type and age class over time. Pearson correlation coefficients were used to determine the relationships between NH_4^+ deposition, $\delta^{15}N$ values in forest floor, root, foliage, and soil available NH_4^+ and NO_3^-. Data for Pearson's correlations all met the assumption of homogeneity except for NH_4^+ deposition in the pine stands, which required log transformation. Linear regressions were conducted between soil NO_3^- availability and the enrichment factor. Data for regressions, two-way ANOVAs and repeated measures ANOVA all met the assumptions of homogeneity and equal variances except for $\delta^{15}N$-NO_3^- deposition and root N, which required a standard log transformation. Multiple comparisons for two-way ANOVAs and the repeated measures ANOVA were completed with a Bonferroni adjustment (Steel and Torrie 1980). Significance for all statistical analyses was determined at $\alpha=0.05$. All statistical analyses were performed using SAS software (version 9.2, SAS Institute Inc., 2002, Cary, NC).

3.3 Results

3.3.1 N deposition, soil N availability and ^{15}N signatures

Total wet deposition was dominated by NH_4^+ at all sites (Table 3-1). The aspen and jack pine stands were significantly different in terms of total N and NH_4^+ atmospheric deposition received, soil NO_3^- availability, foliar N concentrations, and foliar C:N ratios. Bulk NH_4^+ deposition was significantly higher than throughfall. In addition, soils from the young stands contained significantly more available NO_3^- than soils from the older stands. While the young pine sites received significantly more NH_4^+ deposition than the young aspen, no difference was observed between the old aspen and pine stands. Foliar N concentrations were significantly higher and foliar C:N ratios significantly lower in the aspen than in the pine stands, but no difference was found for root N concentrations.

Atmospheric NH_4^+ deposition was enriched in ^{15}N relative to atmospheric NO_3^- deposition (Figure 3-1). The mean value for $\delta^{15}N\text{-}NH_4^+$ in atmospheric wet deposition was 9.6±1.2‰ (mean ± SE), while $\delta^{15}N\text{-}NO_3^-$ averaged -1.8±2.7‰ over both summers (2009 and 2010). The values for $\delta^{15}N\text{-}NH_4^+$ varied significantly among seasons ($p=0.0005$) in both aspen and pine stands, but they did not vary between stand types or age classes. Specifically, the $\delta^{15}N\text{-}NH_4^+$ values in summer 2010 were significantly enriched in ^{15}N compared to both winter periods. In addition, summer 2009 $\delta^{15}N\text{-}NH_4^+$ was significantly enriched in ^{15}N compared to winter 2008, but not winter 2009. Atmospheric $\delta^{15}N\text{-}NO_3^-$ deposition varied significantly between age classes ($p=0.03$) and seasons ($p=0.01$); Summer 2010 and young stands (bulk precipitation) were enriched in ^{15}N. The tailings ponds pH ranged from 8.2 to 8.4 ($n=6$). The average $\delta^{15}N\text{-}NH_4^+$ signatures in the pond water were 28.8 ±2.8‰. The granular urea collected in 2010 had an average $\delta^{15}N$ of -0.33± 0.04‰.

3.3.2 Vegetation and soil ^{15}N pools

The ^{15}N abundance was higher in the mineral soils, while the forest floors, roots and foliage were all depleted in ^{15}N relative to the mineral soils (Figure 3-2). Significant differences were found between age classes and stand types depending on the N pool examined. Mineral soil δ^{15}N varied significantly by stand type, but not age class, where soils under pine were enriched relative to those under aspen. Forest floor, root and foliar δ^{15}N values varied significantly by age class, but not stand type, where young stands were enriched compared to the old stands.

The yearly average values for available soil NH_4^+ were slightly depleted in ^{15}N compared to NO_3^- for both aspen ($\delta^{15}N\text{-}NH_4^+ \approx -3.6$ ‰; $\delta^{15}N\text{-}NO_3^- \approx -3.1$‰) and pine ($\delta^{15}N\text{-}NH_4^+ \approx -2.0$ ‰; $\delta^{15}N\text{-}NO_3^- \approx -1.0$‰), although differences were not statistically significant (Figure 3-2). In addition, although no statistical significant difference was observed between stand types or age classes, the available soil NH_4^+ was enriched in ^{15}N in pine compared to aspen stands.

3.3.3 Relationships between wet N deposition, vegetation and soil ^{15}N compartments

In aspen, significant positive relationships were found between NH_4^+ deposition, forest floor δ^{15}N, root δ^{15}N, and foliage δ^{15}N values (Figure 3-3a). Atmospheric NH_4^+ deposition was significantly and positively related to forest floor δ^{15}N, while root δ^{15}N was positively correlated to both forest floor and foliar δ^{15}N. Foliar N isotope signature also had a significant positive correlation to forest floor $\delta^{15}N$. A different story emerged when pine stands were examined. Significant positive correlations were observed between NH_4^+ deposition, soil $\delta^{15}N$-NH_4^+, soil $\delta^{15}N$-NO_3^-, root $\delta^{15}N$ and foliage $\delta^{15}N$ (Figure 3-3b). However, no significant correlation was found between NH_4^+ deposition and forest floor $\delta^{15}N$. Both soil $\delta^{15}N$-NH_4^+ and $\delta^{15}N$-NO_3^- values were correlated with root $\delta^{15}N$. Root $\delta^{15}N$ was also correlated to foliage $\delta^{15}N$ values, but no significant relationship was found between foliar $\delta^{15}N$ and forest floor $\delta^{15}N$. Finally, a relationship between wet NH_4^+ deposition and foliar $\delta^{15}N$ was detected at α=0.10. Enrichment factors, in the young aspen and pine were significantly greater than in the old aspen and pine stands (Table 3-1). A significant positive relationship between the enrichment factor and soil NO_3^- (R^2=0.69) was only found in the pine stands (Figure 3-4).

3.4 Discussion

3.4.1 Nitrogen sources

Our results show that atmospheric N deposition was greater than what has been reported in other studies conducted around the AOSR (Vitt et al. 2003; Wieder et al. 2010; Laxton et al. 2011), likely due to the fact that our collectors were positioned close to point and non-point sources. In areas located ≈30 km away from the active mines, N deposition in aspen and jack pine stands was <2 kg N ha^{-1} yr^{-1} for both bulk precipitation and throughfall (Laxton et al. 2011). The dominant form of N deposition in our study was NH_4^+ (≈87% of total N deposition), similarly to what has been found in other studies in the region (Wieder et al. 2010; Laxton et al. 2011). Bulk precipitation (as measured at the younger stands) averaged 24 kg N ha^{-1} yr^{-1}, while throughfall (measured at the older stands) averaged 6 kg N ha^{-1} yr^{-1} (Chapter 2). The lower amount of N deposition in throughfall may be a result of canopy uptake. Canopy uptake of N may play an important part of N retention, particularly for NH_4^+, since NH_4^+ uptake is faster than NO_3^- (Lindberg et al. 1986; Böhm 1992; Lovett and Lindberg 1993; Houle et al. 1999).

In this study, throughfall was depleted in ^{15}N relative to bulk precipitation for both NO_3^- and NH_4^+ deposition (Figure 3-2). Typically, for NO_3^-, throughfall is enriched in ^{15}N compared to bulk deposition, whereas for NH_4^+, N enrichment of ^{15}N varies depending on the study (Kendall et al. 2007). The reason for the depletion of ^{15}N for $NO3^-$ in throughfall compared to bulk deposition may be related to the low concentrations of dry NO_3^- deposition in the AOSR. Usually, NO_3^- concentrations in throughfall are greater than bulk precipitation due to inputs from dry deposition, which tend to cause an enrichment of ^{15}N (Kendall et al. 2007). However, in our study, the concentrations of NO_3^- in throughfall were small and equal to those in bulk precipitation (Table 3-1). The depletion of ^{15}N in NH_4^+ deposition in throughfall compared to bulk precipitation was also observed in other studies near Tennessee (United States) and Merlewood (U.K.) Bauer et al. 2000, Garten 1992). Theoretically, canopy uptake of NH_4^+ should have resulted in a more enriched ^{15}N value for throughfall NH_4^+ deposition than bulk precipitation, as discrimination against the heavier isotope typically occurs.

Nevertheless, the lower NH_4^+ concentrations in throughfall suggest that canopy uptake may have been occurring.

Atmospheric NH_4^+ deposition was enriched in ^{15}N (9.6 ‰ ± 1.2; mean ± SE) relative to atmospheric NO_3^- deposition (-1.8 ‰ ± 2.7; Figure 1). Both values fall within the range of -15 to +15‰ observed in other regions (Koopmans et al. 1997; Kendall et al. 2007). However, the ^{15}N enrichment in NH_4^+ compared to NO_3^- has not typically been observed near industrial settings with anthropogenic NO_x emissions (Garten 1992; Emmett et al. 1998; Kendall et al. 2007). In the AOSR region, there are high amounts of NH_3 dry deposition, which was suggested to be a consequence of upgrading processes involved in the separation and recovery of bitumen, tailing ponds containing high concentrations of NH_4^+, and fertilization of reclaimed landscapes (Bytnerowicz et al. 2010; Laxton et al. 2010). The most common type of fertilizer used in reclamation practices, granular urea, had a $\delta^{15}N$ signature of -0.33‰ (n=2), which falls within the typical range for synthetic fertilizers; i.e., -2 to 2‰ (Bateman and Kelly 2007). The NH_3 produced from volatilization of urea in soils with a pH of 4.3 to 5 would be depleted in $\delta^{15}N$ by ≈34‰ due to the fractionation from NH_4^+ to NH_3 (Nômmik et al. 1994). In soils with higher pH, the fractionation may decrease, however the $\delta^{15}N$ value would most likely still be as low as -20‰ (Kendall et al. 2007). Therefore, inputs by fertilization cannot explain the enriched ^{15}N values that were measured in our study for atmospheric NH_4^+ deposition (Figure 3-2). On the other hand, NH_3 volatilization from the ^{15}N-enriched tailing ponds ($\delta^{15}N$-NH_4^+ ≈28.8

±2.8‰) could be a significant contributor. Ammonia volatilization from water bodies is greatest when pH and NH_4^+ concentrations are high and during wind storms that cause turbulence and wave formation (Boyd and Tucker 1998). Thus, ammonia volatilization from tailing ponds may be high due to high pH (8.2 to 8.4), high NH_4^+ concentrations (17 mg/L ± 6) (Pers. Comm. T. Penner, Syncrude 2010) and seasonal storms in the summer. This may explain why our measured NH_4^+ deposition was especially enriched in ^{15}N during both summers of study, i.e., when NH_3 volatilization from the tailing ponds would be most likely to occur (Figure 3-1).

3.4.2 Plant and soil N pools

Soil available N was mainly in the form of NO_3^- rather than NH_4^+ in all stands except for the older aspen stands (Table 3-1). Other studies on reconstructed soils in the oil sands have found similar results where NO_3^- was the dominant form of inorganic soil N (Rowland et al. 2009; Hemstock et al. 2010). In mature forests, NO_3^- is rarely measured in significant amounts, except during spring melt (Johnson 1992; Van Miegroet et al. 1992; Ste-Marie and Pare 1999). Similarly, within the mine lease area, the contribution of NO_3^- to soil total available N pools averaged 10% in mature undisturbed aspen and pine stands (Rowland et al. 2009). While disturbances such as harvesting and fire may result in increased soil NO_3^- levels, this effect is typically short lived, as by 12 years post fire or 5 years post-harvest, NO_3^- concentrations were ≤2% of the total inorganic N (Yermakov and Rothstein 2006; Jerabkova and Prescott 2007). In our study, in the older (17-23 yr) stands, contribution of NO_3^- to the soil total available N pools still averaged about 47% in aspen and 65% in pine. The presence of high soil NO_3^- levels in this study after ≈20 years re-establishment is a concern as it can lead to leaching losses. Indeed, studies conducted across Europe and the United States on different soils in both deciduous and coniferous forests observed a positive relationship between N deposition and NO_3^- leaching (Van Miegroet et al. 1992; Dise and Wright 1995; Gundersen 1995; Gundersen et al. 1998): some of the forests that received > 10 kg N ha^{-1} yr^{-1} experienced NO_3^- leaching (i.e.; in cases where nitrification was enhanced); whereas at deposition rates >25 kg N ha^{-1} yr^{-1} significant leaching occurred across all sites.

Foliar N concentrations were greater in aspen than pine, while the other N pools (forest floor, mineral soil, and roots) were similar (Table 3-1). Higher foliar N in aspen than pine may be explained by species nutrient requirement and accumulation (Alban 1982; Gower et al. 2000; Ste-Marie et al. 2007). Aspen foliar N values in this study were within the range of values typically reported for the boreal forest (Gower et al. 2000; Laxton et al. 2011), whereas pine foliar N concentrations were slightly greater than what is found in undisturbed areas (Gower et al. 2000; Laxton et al. 2010). In our study, root N concentrations, even though not significantly different between stand types or age classes, were higher by twice the amount than in roots of pine trees located at natural sites ≈30 km away (Laxton et al. 2010; Laxton et al. 2011).

3.4.3 Internal cycle N fluxes

The measured ^{15}N abundance values for mineral soil, forest floor and vegetation pools (Figure 3-2) were comparable to results reported for different forest ecosystems (Heaton 1986; Nadelhoffer and Fry 1994; Pardo et al. 2006). The enrichment of ^{15}N in mineral soil relative to the forest floor and vegetation pools (mineral soil N > forest floor N > fine root N > foliar N) was also consistent with results found in other studies (Nadelhoffer and Fry 1994; Sah and Brumme 2003; Pardo et al. 2006). In addition, we were able to observe distinct differences in the N cycle processes between aspen and pine stands (Figure 3-3). In aspen ecosystems, the forest floor may be accumulating atmospheric N, as suggested by the correlation between forest floor $\delta^{15}N$ and wet NH_4^+ deposition. Forest floor has been shown to act as a major N sink, with the ability to retain up to 87% of atmospheric NH_4^+ (Johnson 1992; Fenn et al. 1998; Templer et al. 2005). The forest floor $\delta^{15}N$ values were positively correlated to root $\delta^{15}N$ (Figure 3-3), which indicates that forest floor was the primary N source for plant uptake (Gebauer and Schulze 1991; Pardo et al. 2006). The positive relationships between $\delta^{15}N$ in forest floor, root and foliage further indicated that biocycling between soil and plants was taking place in aspen stands. Aspen lose their foliage annually, thereby increasing the amount of forest floor N available for mineralization and subsequent plant uptake (Gower et al. 2000).

The N pools and fluxes in pine stands indicated very different relationships from those in aspen (Figure 3-3). For instance, NH_4^+ deposition was not related to the forest floor enrichment in ^{15}N (as it was for aspen), but instead influenced pine needle $\delta^{15}N$ values. Coniferous canopies can act as sinks for NH_4^+ deposition, and have been shown to acquire up to 40% of their total N requirements *via* canopy uptake (Lovett 1992; Piirainen et al. 1998; Houle et al. 1999; Harrison et al. 2000). In our study, concentrations of NH_4^+ deposition were less in throughfall than bulk precipitation, which may be a result of canopy uptake. Further evidence of canopy uptake in pine may be indicated by the correlation between foliar $\delta^{15}N$ and NH_4^+ deposition (Figure 3-3). However, the strong positive relationship between root and foliage $\delta^{15}N$ indicates that the soil pool remained the dominant source of N for plant uptake. Jack pine trees prefer NH_4^+ when it is the dominant source of N in the soil (Ste-Marie and Pare 1999; Choi et al. 2005), and soil $\delta^{15}N$-NH_4^+ was significantly correlated to root $\delta^{15}N$. On the other hand, when environmental conditions change, the preferred N form for plants may change (Marshall et al. 2007). The strong correlation between soil $\delta^{15}N$-NO_3^- and root $\delta^{15}N$ (Figure 3-3), as well as the abundance of soil NO_3^- in the pine stands (Table 3-1) both suggest that increased pine uptake of NO_3^- may also be occurring. In pine stands, as opposed to aspen, there was no relationship between NH_4^+ deposition and forest floor $\delta^{15}N$, forest floor $\delta^{15}N$ and foliar $\delta^{15}N$ or between forest floor and root $\delta^{15}N$. This indicates that the pine stands were not recycling N to the same extent as aspen stands did, further suggesting that their N cycle may be more open, and more prone to NO_3^- losses through leaching.

As systems become more N-rich, the enrichment factor becomes more positive (Garten and Van Miegroet 1994; Fang et al. 2011). Enrichment factors in Europe, United States, and China range from -10‰ to -1‰, with N rich sites having values from -6‰ to -1‰ (Garten 1993; Garten and Van Miegroet 1994; Emmett et al. 1998; Cheng et al. 2010; Fang et al. 2011). On sites ≈30 km away from the active oil sands mines, the enrichment factor was -9.6‰ in aspen and -8.6‰ in pine stands (Laxton et al. 2011). In our study, the enrichment factors were higher, and averaged -6.4‰ in aspen and -6.8‰ in pine. The enrichment factors observed in aspen and pine stands were similar, which suggests that the N status in these forests maybe similar (Emmett et al. 1998; Cheng et al. 2010).

In situations where N availability is high compared to plant demand, discrimination against ^{15}N will occur in plants, causing depletion in plant $\delta^{15}N$, relative to the soil pools, especially if the substrate is NH_4^+ (Högberg 1997; Högberg et al. 1999). In our study, root and foliar N concentrations in deciduous trees were depleted in ^{15}N when compared to pine stands, which does not correspond to findings in other studies. Generally, foliage in coniferous trees is depleted in ^{15}N compared to deciduous trees because of a lower plant N demand and slower N cycling (Pardo et al. 2006, Pardo et al. 2007a; Cheng et al. 2010; Fang et al. 2011). Root and foliar $\delta^{15}N$ natural abundances have been used to follow the response of forest ecosystems to increased N deposition. Increases in N deposition may cause an enrichment of ^{15}N in root and foliage due to higher rates of nitrification and NO_3^- losses of depleted ^{15}N (Högberg 1997; Pardo et al. 2006;

Pardo et al. 2007b). In this study, only the pine stands showed a positive relationship between the enrichment factor and soil NO_3^- availability (Figure 3-4).

Evidence suggests that pine stands may be at kinetic N saturation where the N inputs exceed the rate of N retention by vegetation and soil. Pine stands in this study have high root and foliar N concentrations, which suggests that N accumulation is occurring within the vegetation. However, high soil NO_3^- availability indicates a disconnect between plant uptake and soil inorganic N cycling. This may be a result of conifers being adapted to a lower supply of N, and therefore having a lower N demand than deciduous trees (Cole and Rapp 1981; Van Miegroet et al. 1992). Further evidence illustrating this disconnect in pine may be the lack of relationships between the N isotope signature in forest floor, roots and foliage. The lack of these relationships together with high soil NO_3^- concentrations indicate that the N cycle was more open, potentially leading to leaching losses. In turn, losses, due to leaching, may explain the enrichment of ^{15}N in the vegetation pools because of the preferential removal of depleted ^{14}N-NO_3^-.

The plant pools and forest floor in young stands were significantly enriched in ^{15}N compared to the older stands, even though the total N concentrations were not significantly different (Table 3-1). This corresponds to previous reports that ^{15}N abundance values are a more sensitive indicator of N deposition than total N (Koopmans et al. 1997; Fang et al. 2011). Chronic N deposition, even at low rates of N deposition, may cause forests to become N saturated, which may result in enrichment of ^{15}N in plant and soil pools

(Nadelhoffer and Fry 1994; Dise and Wright 1995). In the AOSR the old stands have been accumulating N from deposition over the past two decades, whereas young stands have only been influenced by deposition for up to 8 years. We hypothesized that in old stands the plant and soil pools would be enriched in ^{15}N relative to young stands due to the influence of N deposition. The only pool where this was the case was the mineral soil N pool (Figure 3-2), which is likely linked to the decomposition of the peat amendment used during soil reconstruction. As this organic amendment (peat) decomposes, resulting in the total soil N concentration to decrease in the older stands (Table 3-1), the residual N gradually would become enriched in ^{15}N in the older stands. On the other hand, all other pools were more enriched in the younger stands as compared to the older stands (Figure 3-2). The results suggest that NH_4^+ deposition gradually became more enriched in ^{15}N over time. Thus, when the young stands were planted they would have accumulated the more ^{15}N enriched NH_4^+ deposition. In addition, the ^{15}N enriched foliage and forest floor along with isotopic fractionation from N transformations may positively influence the δ^{15}N in the forest floor to root to foliage continuum on these young stands in the future (Fang et al. 2011). We suggest that this enrichment of ^{15}N in the plant pools may be used to further monitor the N cycle within these sites by tracing the enrichment of ^{15}N over time.

3.5 Conclusions

This study assessed the potential impact of atmospheric N deposition on reconstructed soils. Aspen and pine stands had similar enrichment factors, but differed in their internal N cycles. The pine ecosystems appeared to be more sensitive to the additional N deposition than the aspen ecosystems. Even after 20 years post reconstruction, the soil available N pool in the pine stands was still dominated by NO_3^- and the foliar and root pools were enriched in ^{15}N compared to the aspen stands. Furthermore, the pine stands had greater %N concentration in roots, and foliage than undisturbed sites located ≈30 km away in the AOSR. When $\delta^{15}N$ abundance data in vegetation, soil, bulk precipitation, throughfall, and soil solution were integrated, the N cycle was identified to be open in the pine stands, but closed in the aspen stands. This further suggests that pine stands were at kinetic N saturation; i.e., that they had reached a point where the N inputs exceed the uptake rate of the vegetation and soil N net sinks. The N cycle in aspen stands appears to be closed as indicated by the biocycling between the soil and plant pools and decreased amounts of soil NO_3^- over time. This may minimize the potential losses of NO_3^- due to leaching. The slightly increased foliar N concentrations in aspen compared to undisturbed sites located ≈30 km away in conjunction with the biocycling of N between soil and plant pools suggests that N deposition on aspen stands may have a fertilization effect. The results also show that the use of $\delta^{15}N$ signature from a range of vegetation and soil pools in conjunction with root N, foliar N and soil NO_3^- concentrations was a good indicator to follow ecosystem responses to N additions. In addition, the use of enrichment factors was a valuable tool in comparing data from different experimental areas.

Table 3-1. Site properties for aspen and jack pine stands in both age classes, young (4-8 yr) and old (17-23 yr) stands (mean±SE; α=0.05). Wet N deposition and available soil N data were from October 2009-October 2010, while all other variables were measured in July 2010. Different lower case letters indicate significant differences within each variable.

		Units	Aspen		Jack Pine	
			Young	Old	Young	Old
Atmosphere	Total N Deposition	kg ha^{-1} yr^{-1}	21.7b±2.4	9.7c±2.1	40.4a±4.0	8.2c±1.5
	NH_4^+ Deposition	kg ha^{-1} yr^{-1}	19.6b± 2.4	8.2c±1.9	39.0a±3.9	6.1c±1.4
	NO_3^- Deposition	kg ha^{-1} yr^{-1}	2.1±0.6	1.5±0.3	1.5±0.1	2.1±0.3
Soil	Forest Floor N	%	1.0±0.1	1.0±0.1	0.9±0.1	0.7±0.1
	Forest Floor C:N		29.0±1	33.0±3.2	35.0±4.6	40.0±3.8
	Mineral Soil N	%	0.5±0.1	0.4±0.2	0.3±0.1	0.2±0.1
	Mineral Soil C:N		40.4±9.7	27.4±1.9	30.2±4.0	31.5±1.6
	Available Soil Total Inorganic N	mg extraction^{-1} yr^{-1}	0.6±0.37	0.3±0.06	0.8±0.18	0.3±0.06
	Available Soil NH_4^+	mg extraction^{-1} yr^{-1}	0.1±0.04	0.2±0.05	0.2±0.15	0.1±0.01
	Available Soil NO_3^-	mg extraction^{-1} yr^{-1}	0.5a±0.34	0.1b±0.04	0.6a±0.02	0.2b±0.05
	Forest Floor pH		5.5±0.4	6.1±0.1	5.9±0.1	5.3±0.2
	Mineral Soil pH		5.4±0.8	6.4±0.1	6.8±0.1	6.5±0.4
Tree	Foliage N	%	2.3a±0.2	2.4a±0.1	1.2b±0.1	1.1b±0.1
	Foliage C:N		22.0a±1.2	19.7a±0.5	41.9b±4.3	45.6b±0.5
	Root N	%	0.9±0.1	0.8±0.1	1.0±0.2	0.7 ±0.1
	Root C:N		51.0±8.9	55.3±7.4	44.9±7.0	59.4±3.9
Enrichment Factor	$\delta^{15}N_{leaf} - \delta^{15}N_{soil}$	‰	-5.6a±0.3	-7.5b±0.5	-5.0a±0.6	-7.5b±0.5

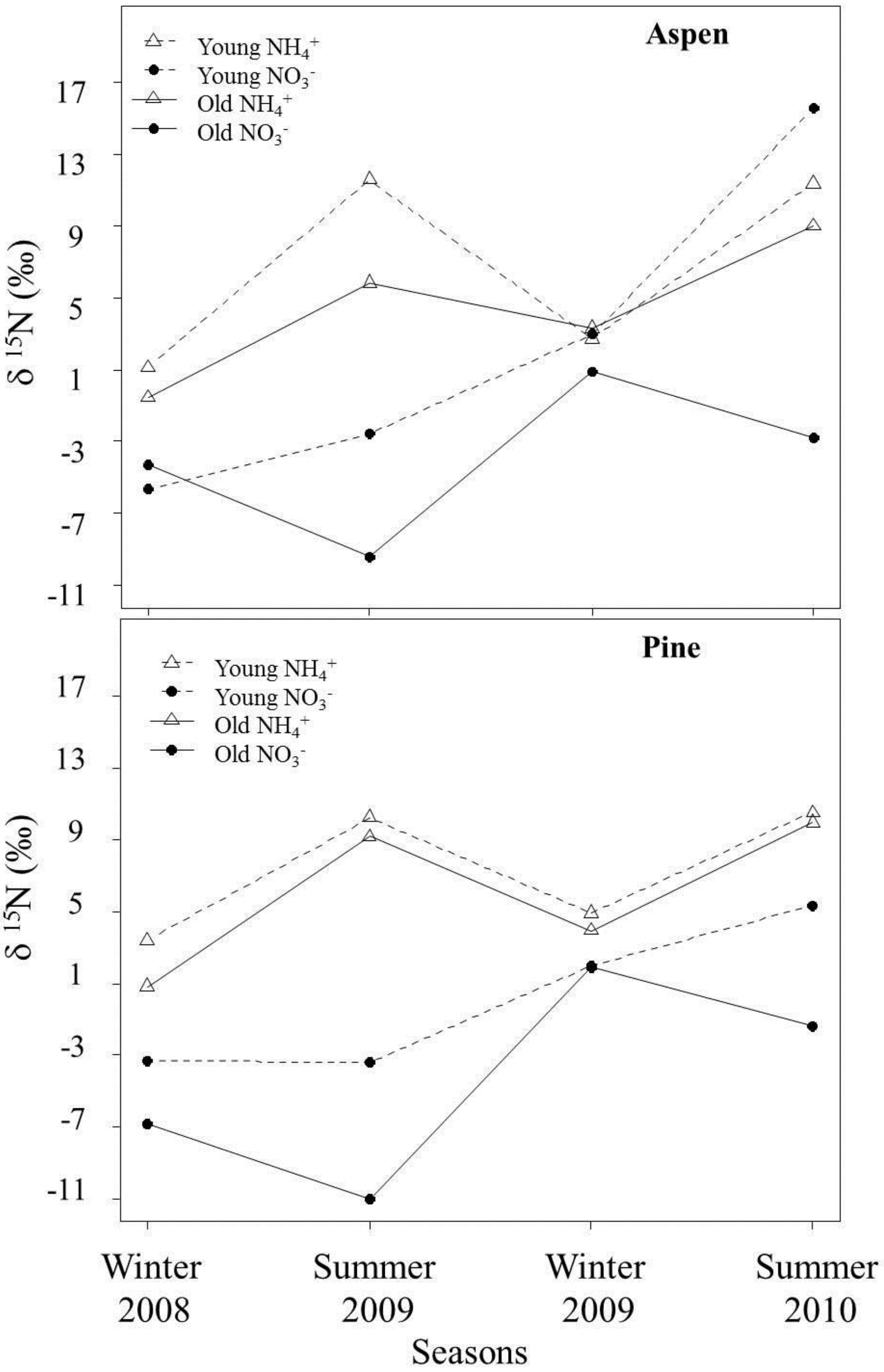

Figure 3-1. Seasonal variations of $\delta^{15}N$ (‰) in wet NH_4^+ and NO_3^- deposition in both stand types and age classes from October 2008 to October 2010.

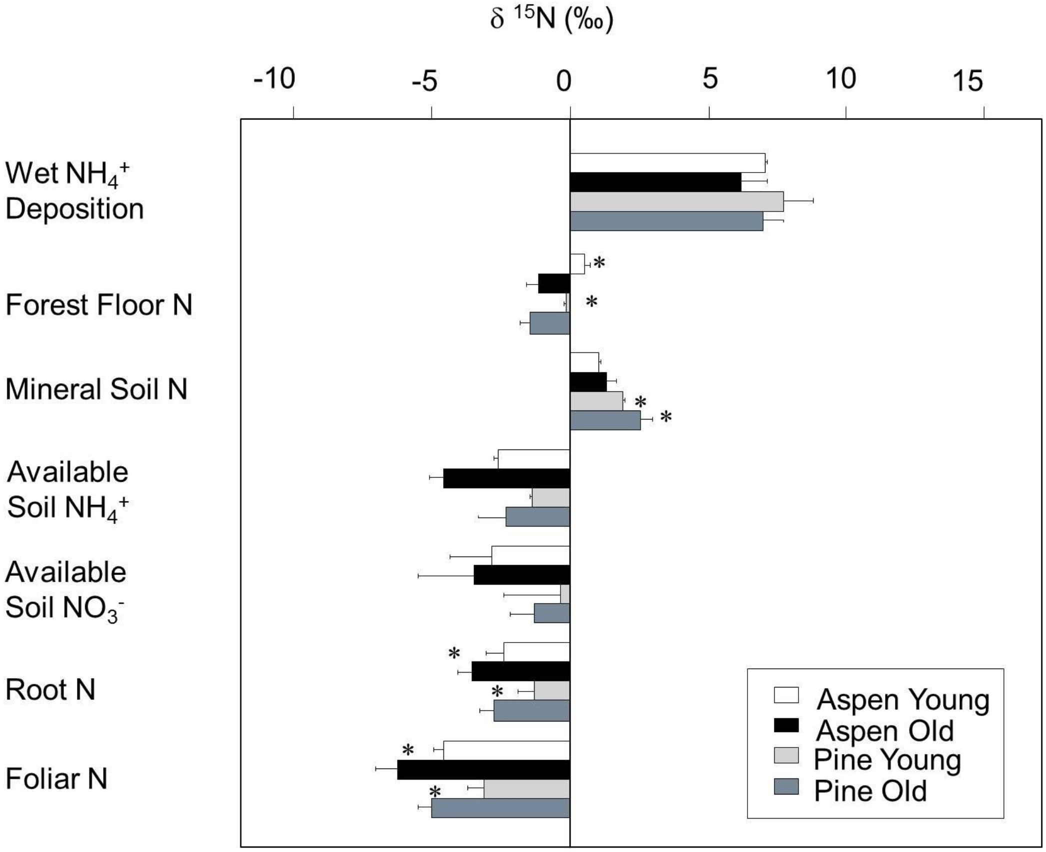

Figure 3-2. Average $\delta^{15}N$ values (‰) in different compartments of the aspen and jack pine stands (mean ±SE). Wet N deposition and available soil N data were averaged from October 2009-October 2010, while all other variables were measured in July 2010**.** Significance (α=0.05) between stand types and age classes is denoted using an asterisk (*) symbol.

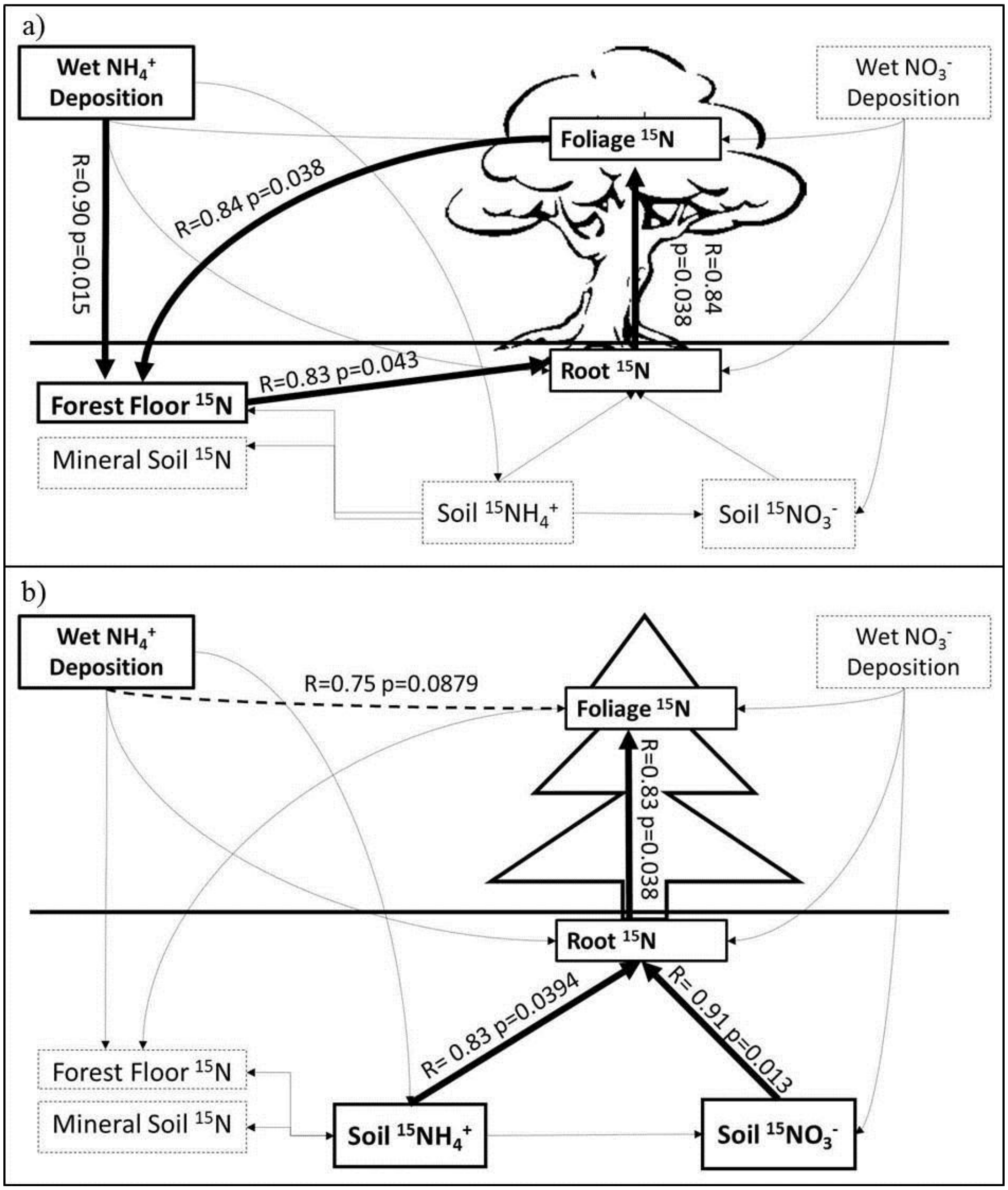

Figure 3-3. Relationships found between wet N deposition and various δ^{15}N natural abundance compartments from a) aspen (n=6) and b) jack pine stands (n=6) for summer 2010. The thick dark lines show significance at $\alpha=0.05$, while non-significant relationships were shown as faded lines. The thick dashed line in pine shows significance at $\alpha=0.1$. Arrows on the lines identify the probable direction of influence.

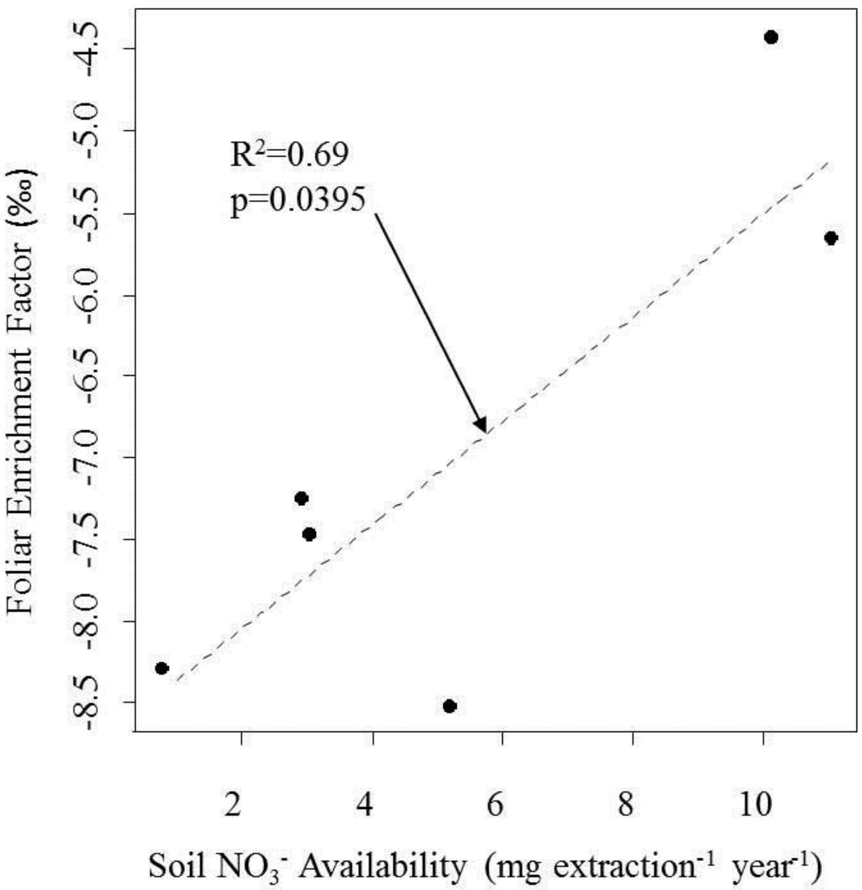

Figure 3-4. Relationships between foliar enrichment factor and available soil NO_3^- in jack pine (α=0.05).

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CHAPTER 4

Conclusions and Management Implications

4.1 Study objectives

The two main objectives of this study were to:

1) Determine seasonal amounts of wet N deposition and soil N availability, and their potential relationships in trembling aspen (*Populus tremuloides* Michx.), and jack pine (*Pinus banakasina* Lamb.) dominated stands of varying canopy cover classes located on reconstructed soils in the AOSR; and

2) Assess the ecological response and potential implications of atmospheric N deposition on reconstructed soils in the AOSR by investigating N status indicators, such as foliar N, soil NO_3^- concentrations, and $\delta^{15}N$ values in different plant and soil pools.

4.2 Atmospheric N deposition

Atmospheric N deposition rates as measured in this study were greater than in highly populated regions from Canada and seem to be *on par* with industrial areas in Europe and the United States. The dominant form of wet N deposited in this study was ammonium (NH_4^+). This was unexpected, since NO_3^- is typically the dominant form of wet N deposition in industrial areas. In addition, bulk precipitation was greater than throughfall, which suggests that canopy uptake of N occurred. Canopy uptake of N may have been greater in pine than in aspen stands as suggested by the relationship between NH_4^+ deposition and the foliar N isotope signature in pine stands.

The presence of high NH_4^+ concentrations in deposition must be linked to high concentrations of ammonia (NH_3) gas in the atmosphere. Ammonia emissions may arise from industrial activities, forest fires, and fertilizers used for land reclamation. Ammonia emissions from industrial activities may include volatilization of NH_3 from the processing of bitumen due to hydrotreating, volatilization of NH_3 from tailing ponds, and emissions from stacks. In this study, only tailings ponds and urea fertilizer were investigated as possible sources of NH_3 in the atmosphere. The average N isotope signature for NH_4^+ deposition in summer was 9.6‰, while the isotope signature for urea was -0.33‰. Since the NH_3 produced from volatilization of urea would be depleted in ^{15}N by approximately 34‰, urea fertilizer can be ruled out as a significant source for NH_4^+ deposition. In soils with high pH, this value may increase slightly. However, the $\delta^{15}N$ value would still most likely be as low as -20‰, but this would depend on pH, temperature and humidity. On the other hand, NH_3 volatilization from the ^{15}N enriched (28.8‰) tailings ponds may be a significant contributor to the positive $\delta^{15}N$ values in NH_4^+ deposition. Further research is required to identify and quantify all possible sources in the AOSR and to better trace the isotope signature from sources to NH_4^+ redeposition on the terrestrial landscape.

4.3 Forest N cycle

This study assessed the potential impact of increased N deposition on reconstructed soils. Aspen and pine stands had similar enrichment factors, which were slightly lower than N saturated sites found in Europe and the United States. In N limited forest ecosystems, enrichment factors would be approximately -10 to -8‰. In our study, enrichment factors averaged -6.4‰ in aspen and -6.8‰ in pine. Therefore, reclaimed forest ecosystems may have a higher N status than natural forest ecosystems as suggested by higher enrichment factors values. In addition, pine stands appeared to be more sensitive to the additional N deposition than aspen stands as suggested by distinct differences in N processes between aspen and pine stands. In aspen stands, the internal N cycle may be tighter than in pine, as suggested by stronger relations between the plant and soil pools, and the decreasing amounts of soil NO_3^- over time since reclamation.

Pine stands were accumulating N compared to undisturbed conditions, as suggested by the relatively high N concentrations in the roots and foliage. However, this nitrogen may not be internally recycling to the same extent as in the aspen stands. This may have explained why the soils under pine were still dominated by NO_3^- 30 years post reconstruction. The evidence of high soil NO_3^- concentrations further indicates that there was a disconnect between plant uptake and soil inorganic N. The production of nitrate *via* nitrification and losses of ^{15}N depleted NO_3^- may explain the ^{15}N enrichment of foliar and root N in pine (as compared to aspen). Therefore the N cycle in pine stands maybe more open, which could lead to leaching losses. Indeed, pine stands may have reached kinetic N saturation, where the rate of N inputs exceeds the rate of N retention.

4.4 Management implications, project limitations and future research

Forest management practices on reconstructed soils should incorporate the amount of N being deposited from atmospheric sources. For example, instead of fertilizing with 75 kg N ha^{-1} yr^{-1}, a decrease to 55 kg N ha^{-1} yr^{-1} may be more appropriate since approximately 25 kg N ha^{-1} yr^{-1} was measured in bulk precipitation. In addition, decreasing N fertilization for the jack pine stands would limit the probability of NO_3^- leaching that was identified as an area of concern based on high soil NO_3^- concentrations. Also from this study, it is apparent that aspen are better suited than pine to a N rich environment in terms of accumulating and recycling this additional N, and are a good choice for vegetation re-establishment on reconstructed soils.

This research into N deposition on reconstructed soils provides useful preliminary evidence, but it was not without its limitations. An important limitation when using ^{15}N natural abundance is that fractionation occurs during several biological and physicochemical processes of the N cycle, which may confound the results. To help overcome these issues scientists sometimes use a multi-isotope approach. Some additional isotopes that could be considered when investigating N deposition in the AOSR are oxygen for NO_3^- and deuterium for NH_4^+. By using a multi-isotope approach it may be easier to trace N through the N cycle even at low concentrations, since there are potentially less fractionations that occur with oxygen and hydrogen isotopes than with N isotopes. Another limitation in this study was that research was not simultaneously conducted on undisturbed or naturally disturbed forest ecosystems located in the AOSR (for obvious time constraints). However, I was able to compare my results with similar studies on undisturbed forest stands located 30 km away from the mine leases. Therefore, future research could be conducted to compare undisturbed, and naturally disturbed forest stands within this 30 km area to reconstructed soils. This research would help quantify the amount of N deposition emanating from the mine leases as well as the ecological response of N deposition on both undisturbed and naturally disturbed forest stands.

This study could not cover all aspects that may relate to N deposition on reconstructed soils. Therefore, here are some ideas for future work: determine all potential sources of N emissions; compare soil microbial populations in direct relation to N deposition rates; investigate plant nutrient imbalances that may arise from N saturation; measure forest growth responses to N deposition; quantify tree uptake of N; determine the critical N load, and the efflux of gases from volatilization and denitrification. Nitrogen deposition may originate from multiple sources that may mix in the atmosphere prior to being deposited onto the landscape. These other sources may include, but are not limited to ammonia volatilization from forest fires, fossil fuel combustion, and stack emissions of ammonia and nitrogen oxides. Future research on ^{15}N tracer studies ought to investigate the $\delta^{15}N$ signature of these sources in relation to the oil sands within 30 km of the mine leases, since studies have shown N deposition to return to background levels after 30 km. In addition, further research could be conducted on tailings ponds to determine the N isotope signatures from ammonia gas that may be originating from the ponds and then potentially trace this gas to wet N deposition collectors.

Future studies could also investigate the nitrifier population on reconstructed, undisturbed, and naturally disturbed soils in relation to N deposition. As NH_4^+ deposition increases, there is a concern that the microbial community may harbor a larger nitrifier population resulting in increased production of NO_3^-. Furthermore, the investigation of plant nutrient imbalances would provide further insight into which nutrients may be (and become) limiting on reconstructed soils. This would be important in determining if P (for instance) becomes a limiting factor for plant growth once N limitation is lifted, or if soil moisture is the dominant environmental stressor. Research could also investigate if tree productivity increased from N deposition on these sites by observing tree growth responses to N deposition. Finally, research into the efflux of gases from the soils due to volatilization and denitrification could be considered, since increases in N deposition have been shown to increase the amount of volatilization and denitrification losses.

APPENDIX 1- Site Map and Forest Stand Characteristics

Appendix 1a. Study site locations (57°02’31N, 111°37’15W) on Syncrude and Suncor mine leases.

Appendix 1b. Stand characteristics of aspen and pine stands on reconstructed soils. Stand characters include the site number, latitude and longitude coordinates, mine lease, year of reclamation, reclamation prescription (ptmix= peat mineral mix, OB= overburden, TSS= tailings sand, SS= secondary subsoil), elevation (m), slope (%), Canopy cover in the summer and after defoliation (%), DBH (diameter at breast height), tree height (m), height to live crown (m) and tree density ($10m^2$).

Site #	Stand type	Reclamation year	Mine lease	Reclamation prescription	Latitude and Longitude Coordinates	Elevation (m)	Slope (%)	Canopy cover (%) (Summer)	Canopy cover (%) (Defoliation)	DBH	Tree height (m)	Height to live crown	Tree density ($10\ m^2$)
1	Pine	1984	Syncrude	ptmix/TSS	N 57 02.902 W 111 39.771	326	20	95.4	95.4	10.5	8.4	3.5	3.0
2	Pine	1992	Syncrude	ptmix/TSS	N 57 03.668 W 111 39.868	324	1	88.0	88.0	7.2	5.9	1.6	3.4
3	Pine	1997	Syncrude	ptmix/TSS	N 57 04.513 W 111 40.022	323	15	0.0	0.0	4.7	1.8	0.3	1.0
4	Aspen	2003	Syncrude	ptmix/TSS	N 57 05.462 W 111 40.865	323	1	0.0	0.0	0.6	0.6	0.1	4.4
5	Aspen	1987	Syncrude	ptmix/TSS	N 57 02.858 W 111 39.395	324	23	93.1	86.7	6.2	6.2	1.3	5.8
6	Aspen	1997	Syncrude	ptmix/TSS	N 57 06.125 W 111 39.601	339	12	22.0	15.4	4.5	3.9	1.1	5.4
7	Aspen	2002	Syncrude	ptmix/SS	N 57 05.457 W 111 37.789	332	0	0.0	0.0	1.3	1.2	0.1	3.8
8	Aspen	1993	Syncrude	ptmix/SS	N 57 05.352 W 111 37.903	329	25	54.3	34.4	3.4	3.6	0.5	7.4
9	Aspen	2004	Syncrude	ptmix/SS	N 56 59.123 W 111 38.808	242	2	33.3	31.3	1.4	1.9	1.1	9.4
10	Aspen	1993	Syncrude	ptmix/OB	N 56 59.766 W 111 37.235	251	11	32.8	14.6	2.5	3.2	1.3	12.4
11	Pine	1997	Suncor	ptmix/OB	N 56 59.899 W 111 29.994	256	26	41.6	41.6	4.3	3.3	0.7	3.8
12	Pine	1991	Suncor	ptmix/OB	N 56 59.794 W 111 31.900	260	2	57.1	57.1	6.5	4.1	0.6	4.0
13	Aspen	1990	Suncor	ptmix/OB	N 56 59.903 W 111 32.438	253	26	66.0	56.2	4.6	4.5	0.4	7.6
14	Pine	1992	Suncor	ptmix/OB	N 56 58.900 W 111 30.983	337	26	69.8	69.8	8.5	5.6	0.6	3.4
15	Pine	1992	Suncor	ptmix/OB	N 56 58.902 W 111 29.976	342	28	39.1	39.1	7.0	4.1	0.6	3.0
16	Aspen	1985	Suncor	ptmix/OB	N 56 59.896 W 111 32.683	244	28	97.0	86.1	10.0	10.2	5.9	3.8
17	Pine	2006	Suncor	ptmix/OB	N 56 53.779 W 111 22.416	368	21	0.0	0.0	1.8	1.5	0.1	3.0
18	Pine	2003	Suncor	ptmix/TSS	N 57 00.636 W 111 33.140	247	32	0.0	0.0	2.1	1.3	0.2	3.0
19	Pine	1994	Syncrude	ptmix/OB	N 56 59.984 W 111 36.439	247	22	56.0	56.0	7.4	4.8	0.6	2.8
20	Aspen	1992	Syncrude	ptmix/OB	N 57 00.059 W 111 36.499	249	2	98.2	93.1	12.7	10.5	5.7	2.6
21	Aspen	1994	Syncrude	ptmix/TSS	N 57 04.898 W 111 36.731	343	10	42.5	37.0	4.9	4.2	1.0	10.6
22	Aspen	2000	Syncrude	ptmix/TSS	N 57 05.954 W 111 39.115	354	0	3.0	3.0	1.4	2.1	0.9	16.2
23	Aspen	2002	Suncor	ptmix/OB	N 56 53.986 W 111 24.391	340	2	9.9	6.6	3.0	2.2	0.8	5.0
24	Aspen	2002	Suncor	ptmix/OB	N 56 55.278 W 111 25.122	316	33	83.9	67.5	2.4	3.8	0.7	28.4
25	Pine	1983	Suncor	ptmix/OB	N 56 59.048 W 111 31.794	347	27	95.2	95.2	10.0	9.1	3.3	3.4
26	Aspen	1992	Syncrude	ptmix/OB	N 56 59.777 W 111 35.444	332	2	78.6	62.4	5.2	5.7	1.5	8.4
27	Pine	1980	Syncrude	ptmix/OB	N 56 59.458 W 111 37.013	319	32	94.2	94.2	13.1	10.2	2.9	4.0