University of Alberta

Assessing the long-term impact of acid deposition and the risk of soil acidification in boreal forests in the Athabasca oil sands region in Alberta, Canada

by

Kangho Jung

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Abstract

Significant amounts of SO_2 and NO_x have been emitted from the Athabasca oil sands region (AOSR) in Alberta, Canada, in the past several decades. The impact of acid deposition on forest ecosystems and the risk of soil acidification were assessed in jack pine (*Pinus banksiana*) and trembling aspen (aspen) (*Populus tremuloides*) stands in acid-sensitive watersheds (NE7 and SM8) in the AOSR. NE7 has been exposed to greater rates of deposition. A simulated N and S deposition experiment was also conducted. Nitrogen deposition increased N availability in NE7, indicated by increasing Diff_N (Diff_x: the difference of parameter x in tree rings between NE7 and SM8) and decreasing Diff_δ^{15}N over time in aspen stands. Sulfur deposition increased in stemflow due to interception deposition, which decreased pH and base cations in soil towards jack pine but not towards aspen releasing enough base cations through canopy leaching. The Ca/Al ratio did not reach the critical limits of 1.0 for soil solution (range: 1.0 to 4.1) or 0.5 for fine roots (range: 0.7 to 7.9) while Al concentrations in soil solutions (range: 0.1 to 8.5 mg L^{-1}) achieved the level inhibiting seedling growth of aspen and *Picea glauca* (a common species succeeding aspen). Critical loads of S deposition ranged from 223 to 711 $mol_c\ ha^{-1}\ yr^{-1}$, and S deposition did not exceed critical loads; N deposition was not considered due to N limitation in boreal forests. Exceedances were underestimated when only bulk deposition was considered as compared to those that use total deposition because intercepted SO_4^{2-} deposition made up approximately 60% of total deposition. The H^+ budgets of soils were negative in NE7 and SM8, implying that soils were recovering from previous acidification, reflecting the reducing trends of S emission. Simulated N deposition provided beneficial effects on tree growth but not for understory. Simulated S deposition increased leaching loss of base cations and reduced exchangeable base cations in the surface soil. I concluded that acid deposition has changed soil and tree chemistry, and tree growth in the AOSR, which could give adverse effects on understory plants sensitive to Al toxicity and cationic nutrient deficiency.

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List of Symbols and Abbreviations

$\delta^{13}C$: carbon isotope composition

$\delta^{15}N$: nitrogen isotope composition

+N: nitrogen addition treatment

+NS: nitrogen and sulfur addition treatment

+S: sulfur addition treatment

AOSR: Athabasca oil sands region

BC: base cations

BD: bulk deposition

Ca/Al: a molar ratio of calcium to aluminum

CE: canopy exchange

CK: control

CL: critical load of soil acidification

CU: canopy uptake

Diff_x: a parameter x of tree ring in watershed NE7 minus that that in watershed SM8

EX: exceedance of acid deposition to critical load

ID: interception deposition

JP: *Pinus banksiana* (jack pine)

LE: canopy leaching

MBC: soil microbial biomass carbon

MBN: soil microbial biomass nitrogen

SF: stemflow

SMB: simple mass balance

TA: *Populus tremuloides* (trembling aspen)

TF: throughfall

WA: weak acid anions

Chapter 1. General introduction

1. Background

Acid emission and subsequent deposition caused by industrial activities have been demonstrated to affect forest ecosystems (Ulrich, 1983). The earliest use of the term “acid rain” reported changes in precipitation chemistry that coincided with large-scale industrialization in Europe (Smith, 1872). Currently, the term acid deposition is preferred to acid rain because acid materials reach earth through both wet and dry depositions. In the 1950’s and 1960’s, the impacts of acid deposition started to be studied in North America and Europe, which discovered that acid causing materials were produced by fossil fuel combustion and acid deposition affected soil, vegetation, and lake water even far from the emission sources (e.g., Gorham, 1955; Oden, 1968).

The major acid causing materials from industrial practices are sulphur dioxide (SO_2) and nitrogen oxides (NO_x) that are deposited as sulfuric acid (H_2SO_4) and nitric acid (HNO_3), respectively, after they reacted with water in the atmosphere or on wet surface. Long-term atmospheric sulfur (S) and nitrogen (N) depositions have been shown to cause changes in elemental biogeochemical cycles, soil acidification, and nutrient deficiency or imbalance in forest ecosystems (Aber et al., 1989; Johnson and Siccama, 1983). When sulfate (SO_4^{2-}) is deposited to the soil, it can be retained in the ecosystems in a variety of forms, e.g., as sulfate ions in the soil solution, as adsorbed sulfate on soil particles, and as organic sulfur (S) in soil and plants (Reuss and Johnson, 1986). It also can be lost from the soil through leaching. Leaching of sulfate ions would lead to the leaching of cationic elements from the soil, which accelerates soil acidification and finally induces detrimental effects on plants such as calcium (Ca) deficiencies and aluminum (Al) toxicity. Therefore, impacts of S deposition are various with S storage capacity of ecosystems, mainly sulfate adsorption by soil (Barton et al., 1999) and base cation supply by weathering and through atmospheric deposition.

The major pool of N in forest ecosystems is organic N while that of S is adsorbed S in soil (Reuss and Johnson, 1986). The N status of forest ecosystems can be divided into different stages with relation to responses of ecosystems to chronic N deposition: N limitation, alleviation of N limitation, and N saturation (Aber et al., 1998). In boreal forests, the initial phase has been known to be N-limited followed by alleviation of N limitation as N availability increases through chronic N deposition (Hari and Kulmala, 2008). In the second stage, external N input may be taken up by plants and thus provide a beneficial effect on tree growth. However, N leaching and N emissions from the soil occur as the ecosystem becomes N saturated (Aber et al., 1998; Matson et al., 2002). While the deposited N plays the role of a fertilizer in N-limited forests, cationic nutrient leaching along with nitrate in combination with excessive uptake cations may cause cationic nutrient deficiencies or nutrient imbalances for trees, which may eventually cause forest degradation (Erisman and De Vries, 2000; Skeffington and Wilson, 1988).

The emission of SO_2 has decreased globally, and NO_x emissions in industrialized regions remain elevated (Galloway et al., 2004). In eastern Canada and U.S., with technical development and political efforts such as the Eastern Acid Rain Program in Canada and the US Clean Air Act (Morrison, 2005), the emission of SO_2 has decreased since the 1970s, and NO_x emission plateaued between 1985 and 1990 and decreased thereafter (Niemi, 2005). However, acid causing materials remain or even increase in other industrially developing areas, e.g., western Canada (Aherne and Shaw, 2010) and China (Lu et al., 2010).

The Athabasca oil sands region (AOSR) is the world's second largest reservoir of recoverable oil (> 130 billion barrels) in the form of bitumen and the largest area for open-pit oil sands mining in Alberta, Canada (Humphries, 2008). Bitumen is heavy crude petroleum bound to sand particles that has high carbon-to-hydrogen ratio (C/H) and S concentration compared to light crude oil. In order to produce synthetic crude oil suitable for transportation by pipeline and further refinement into lighter petroleum products, the processes of extracting and upgrading (reducing C/H and S concentration) bitumen to synthetic crude oil need to occur. Those processes intensively consume energy and resources such as fuel (approximately 30 million m^3 day^{-1} of natural gas) and water (approximately 0.5 million m^3 day^{-1}) (Griffiths et al., 2006; Millington and Mei, 2011). As a result, a large amount of air pollutants has been released from the oil sands region in the past several decades. The SO_2 emission peaked at approximately 400 Mg day^{-1} in the 1980s followed by a substantial reduction in the mid-1990s and remained between 250 and 300 Mg day^{-1} in 2000s (Hazewinkel et al., 2008). Meanwhile, NO_x production increased continuously from 20 Mg day^{-1} in 1970 to approximately 300 Mg day^{-1} in the mid-2000s, with increased fossil fuel combustion for upstream oil and gas activities and transportation (Hazewinkel et al., 2008). With the increased oil sands mining activities that are already occurring and those that have been planned for the near future, the rate of NO_x emission is expected to increase while that of SO_2 is expected to remain stable through increased recovery of S in the upgrading process (Niemi, 2005).

In order to assess the impact of air pollution by mining activities on forest ecosystems in the AOSR, a number of projects have been conducted. Wood Buffalo Environmental Association founded in 1997 has been monitoring air quality, terrestrial ecosystem quality, acid deposition, and so on since 1998 as the official Clean Air Strategic Alliance (CASA) representing the Regional Municipality of Wood Buffalo (WBEA, 1999). Based on their work, concentrations of acid materials in the air have been found to range from 4.8 to 29.7 ppb for NO_2 and from 1.1 to 2.9 ppb for SO_2 in mining areas in 2009; while those in less-polluted areas such as Anzac and Fort Chepewyan were lower than in mining areas, with values of 1.1 to 2.5 ppb for NO_2 and 0.3 to 0.7 ppb for SO_2 (WBEA, 2010). Concentrations of NO_2 or gaseous HNO_3 have increased with increasing NO_2 emission with spatial and temporal variation while SO_2 remained at a similar level throughout the 2000s (WBEA, 2010; Bytnerowicz et al., 2010). Bulk depositions of NO_3^- and SO_4^{2-} on the ten ecosystems selected in the AOSR were 0.9 kg ha^{-1} y^{-1} and 3.4 kg ha^{-1} y^{-1}, on average, between 2005 and 2008 (Wieder et al., 2010), which are relatively low compared with values of greater than 10 kg ha^{-1} yr^{-1} each for SO_4^{2-} and NO_3^- in areas affected by air pollution in eastern North America (Vet et al., 2005; WMO, 2005), Europe (e.g., Vanguelova et al., 2007b), and eastern Asia (e.g., Fujii et al., 2008).

A significant portion of soils in the AOSR was evaluated to be acid-sensitive in the mid-1980s based on soil depth, soil texture, base cation content, soil drainage, and parent material (Holowaychuk and Fessenden, 1987). These acid sensitive soils include soil series of Firebag, Mildred, Marguerite, and Kinosis. The average pH of these soils was 4.4 for both forest floor and in the 0-25 cm mineral soil (0-25 cm) and average cation exchange capacity (CEC) was only 1.7 $\mathrm{cmol_c\ kg^{-1}}$ for the 0-25 cm mineral soil layer (AMEC, 2009). The sulfate adsorption capacity of sensitive soils in the AOSR ranged from 50 to 500 mg SO_4^{2-} $\mathrm{kg^{-1}}$ (Whitfield et al., 2010a; Jung et al., 2011b), suggesting that the ability of the soils in the AOSR to retain SO_4^{2-} was relatively low as compared to other soils in North America, such as glaciated acid-sensitive soils in northeastern United States (Macdonald and Hart Jr, 1990; Nodvin et al., 1986; Nodvin et al., 1986) and eastern Canada (Bhatti et al., 1997; Neary et al., 1987), and in northern Europe (Barton et al., 1999; Martinson and Alveteg, 2004). Therefore, long-term impacts of acid deposition on ecosystems are of concern in the AOSR to all levels of the government, the industry and the general public due to the expected increase in rates of acid emission and acid-sensitive nature of soils in the oil sands region.

With general concerns of NO_x and SO_2 emissions in the AOSR, the NO_x-SO_2 Management Working Group (NSMWG) (currently Air Working Group (AWG)) of the Cumulative Environmental Management Association (CEMA) in

Alberta was formed with the objective of developing and recommending a plan for NO_x and SO_2 emission management in the oil sands region. A number of studies have been conducted to evaluate air quality and deposition. However, changes in the forest ecosystems caused by air pollution are poorly understood in the AOSR. Hence, this thesis research has been performed as a part of the larger project funded by NSMWG in order to evaluate the risk of soil acidification and assess the impact of acid deposition on forest ecosystems in the AOSR.

2. Study overview

2.1 Current uncertainties in the impact of acid deposition on boreal forests

2.1.1 Chronological impacts of air pollution on forest ecosystems

The boreal forests in the AOSR have been exposed to air pollution for several decades. Air quality and atmospheric deposition have been monitored by several projects while historical changes of forest ecosystems caused by air pollution are poorly understood in the AOSR. Because the effects of air pollution on forest ecosystems are the results of long-term chronic exposure, time-integrating indicators may be useful in understanding how air pollution has affected tree and soil chemistry (Legge et al., 1984). Tree ring chemistry such as isotope ratios of C and N ($\delta^{13}C$ and $\delta^{15}N$, respectively) and nutrient concentration has been used as a datable archive of historical, environmental changes as such tree ring chemistries are susceptible to the growth condition in the year when the specific growth ring formed (Kwak et al., 2009; Martin and Sutherland, 1990; Watmough et al., 1999).

For example, as pollutants emissions are generally associated with fossil fuel combustion that releases ^{13}C-depleted CO_2, tree rings formed in ecosystems under severer air pollution may have more negative $\delta^{13}C$ unless other factors such as water and nutrient availability are limited (Bert et al., 1997; Choi et al., 2005; Farmer and Baxter, 1974). Meanwhile, air pollutants such as SO_2 and NO_x that are co-emitted with CO_2 have been shown to cause stomatal closure, leading to less negative $\delta^{13}C$ (Savard, 2010). Therefore, $\delta^{13}C$ of tree rings is likely to be determined by the balance between ^{13}C-depleted CO_2 effect and pollutants-induced stomatal closure. The $\delta^{15}N$ of tree rings can serve as another indicator of atmospheric-environmental changes (Savard et al., 2009; Norby, 1998) as anthropogenic NO_x, which is one of the N sources for tree uptake in forests, emitted from fuel combustion consistently has lower $\delta^{15}N$ than available soil N (Nadelhoffer and Fry, 1994). Due to the reason, several studies reported that tree ring $\delta^{15}N$ was correlated with NO_x emission and deposition history (Kwak et al., 2009; Poulson et al., 1995). The N concentration and/or content seems to be another indicator of atmospheric N deposition in N-limited forest ecosystems as atmospheric N supply increases N availability in the ecosystems, which induces increasing N uptake (Aber et al., 1998). However, N concentration in tree ring may not provide reliable information on historical changes in N availability of the ecosystems due to inter-translocation of N to newer tissues (Poulson et al., 1995; Bukata and Kyser, 2005; Sheppard and Thompson, 2000).

2.1.2 Cumulative impacts of acid deposition and current acid stress

Soil acidification caused by chronic acid deposition is of concern in boreal forests in the AOSR with acid-sensitive soils having coarse texture and a low capacity of sulfate adsorption, as mentioned in section 1. Acid deposition and subsequent leaching of strong acid anions such as SO_4^{2-} increase soil acidity and reduce concentrations of base cations such as Ca^{2+} in ecosystems (Likens and Bormann, 1995). Increasing soil acidity raises Al solubility and Al concentrations (particularly in the forms of Al^{3+} and $AlOH^{2+}$) in soils (Marion et al., 1976). In acidic soils, dominant forms of Al ions such as Al^{3+} and $AlOH^{2+}$ are toxic to plants (Delhaize and Ryan, 1995). Therefore, Al toxicity and Ca deficiency are common strains in acidic soils (Clark and Baligar, 1995). As Al toxicity and Ca deficiency are closely interwoven with each other due to antagonism between Al and Ca uptake (Delhaize and Ryan, 1995), Ca/Al ratios of soil solution and plant tissues have been suggested as sensitive indicators presenting current acidity stress and cumulative impacts of acid stress under elevated levels of acid deposition (Cronan and Grigal, 1995; Hirano et al., 2007; Innes, 1995; Shortle and Smith, 1988; Vanguelova et al., 2007a). Recently, chemical properties such as pH, CEC, exchangeable cation concentrations of acid-sensitive soils have measured in the AOSR by several projects (WBEA, 2010; AMEC, 2009). Meanwhile, Ca/Al ratios of soil solution and plant tissues have not been examined in the AOSR although Ca/Al ratio is so far the most practical indicator of acidity stress (Vanguelova et al., 2007a). Therefore, investigating Ca/Al ratios of soil solution and plant tissues may allow better understanding of acid stress of trees in the AOSR.

Spatial patterns of soil chemistry can be another indicator of cumulative effects of atmospheric deposition. In industrial areas, the decreasing patterns of soil pH and base cations of soil towards a tree bole have been reported consistently in conifer stands (Zinke, 1962; Riha et al., 1986; Skeffington, 1983). It results from increasing SO_4^{2-} and decreasing pH in throughfall and stemflow from bulk precipitation due to accumulated acid deposition and organic acid from canopy leaching (Staelens et al., 2008; Jung et al., 2011a). It implies that gradients of soil chemistry with a distance from a tree bole can reflect cumulative effects of atmospheric deposition. In deciduous stands, spatial patterns of soil chemistry have not been consistent, with both lower (Sato and Wakamatsu, 2001) and higher (Skeffington, 1983; Chang and Matzner, 2000) acidity towards a tree bole being reported. The deciduous canopy can raise pH of throughfall and stemflow through canopy exchange while it can intercept acid materials increasing acidity in throughfall. Soil acidity in deciduous stands can decrease toward tree boles in the non or less polluted areas due to canopy leaching of base cations while increasing soil acidity can be found towards deciduous tree boles in highly polluted areas due to interception deposition of acid materials. Therefore, the spatial variation of soil chemistry surrounding tree boles and in open fields may show cumulative effects of atmospheric deposition, which may allow us to compare the long-term impacts of acid deposition between watersheds with different deposition rates.

2.1.3 Tree species effects on atmospheric deposition and critical loads

Acid materials fall to ground through two different pathways: precipitation deposition (= bulk deposition) and interception deposition (Ulrich, 1983). Precipitation deposition means deposition occurring vertically by gravity. Interception deposition involves aerosols or particulate matters being intercepted by obstacles such as tree canopy in forests, especially through fogs, clouds, or dews, and the dissolution of them on wet surfaces. In forests, interception deposition is a significant portion of total atmospheric deposition and has a different chemical composition from bulk deposition. Especially, proportions of SO_4^{2-} and NO_3^- are usually greater in interception deposition than in bulk deposition because aerosol, a principal form of acid materials, is less affected by gravitational precipitation than particulate matter, a dominant form of base materials (Draaijers and Erisman, 1995; Jung et al., 2011a; Staelens et al., 2008). Interception deposition was similar to bulk deposition for base cations and more than twice of bulk deposition for SO_4^{2-} and NO_3^- in *Pseudotsuga menziesii* (Douglas-fir) stands in the Netherlands (Draaijers and Erisman, 1995). Similar trends were found in *Fagus sylvatica* L. (European beech) stands in Belgium and mixed *Acer saccharum* Marsh. (sugar maple) stands in Quebec (Staelens et al., 2008). In addition, interception deposition is influenced by tree species. For example, canopy of conifer trees can catch acid deposition more efficiently than that of deciduous trees under the same condition due to the shape of needles and higher crown density (Augusto et al., 2002; De Schrijver et al., 2004).

The concept of critical load (CL) has been used to estimate acceptable levels of acid deposition and to identify acid sensitive regions using exceedance of acid deposition to CL (EX) (Nilsson and Grennfelt, 1988; Sverdrup and De

Vries, 1994). The CLs in the AOSR and other regions in Alberta have been assessed by the simple mass balance (SMB) method (Aherne, 2008; Whitfield et al., 2010b);

$$CL = BC_{dep} – Cl_{dep} + BC_{w} – BC_{up} – N_{i} – N_{u} + N_{de} – Alk_{le,crit}$$

$$EX = \text{Deposition of S and N} - CL$$

where BC is base cations as the sum of Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}, BC_{dep} is the atmospheric deposition of BC, Cl_{dep} is the atmospheric deposition of Cl^{-}, BC_{w} is the weathering rate of BC, BC_{up} is net base cation uptake, N_{i}, N_{u}, and N_{de} are immobilization, uptake, and denitrification, respectively, of N, and $Alk_{le,crit}$ is a critical alkalinity leaching rate.

Most areas in the AOSR that have been exposed to acid deposition had deposition rates lower than CLs (Aherne, 2008) and that acid depositions were lower than CLs in two thirds of forest stands with acid-sensitive soils (Whitfield et al., 2010b). However, interception deposition has been routinely excluded in estimating and mapping CLs and EXs in large areas (UBA, 2004) as determining interception deposition is much more complicated than determining bulk deposition (Draaijers and Erisman, 1995), even though interception deposition occupies a significant portion of total atmospheric deposition in forest ecosystems. It implies that CLs assessed with only bulk deposition may be misestimated, mainly underestimated, in forest ecosystems.

The canopy budget model was developed to calculate interception deposition and canopy exchange based on changes in chemistry of throughfall from bulk deposition (Ulrich, 1983):

$$TF_x = BD_x + ID_x + CE_x$$

$$CE_x = LE_x - CU_x$$

where TF is throughfall deposition, BD is bulk deposition, ID is interception deposition, CE is canopy exchange, LE is canopy leaching, CU is canopy uptake, and x denotes a solute.

The chemistry of throughfall can be different from that of bulk precipitation. Interception deposition and canopy exchange are two principal processes inducing changes in throughfall chemistry, through the so-called canopy-deposition interaction. Interception deposition involves aerosols or particulate matters intercepted by canopy as described in section 1. Canopy exchange, the other process of canopy-deposition interaction includes canopy uptake and canopy leaching. Canopy uptake of solutes such as NH_4^+, H^+, and NO_3^- takes place through stomatal uptake and ion exchange at the cuticle layer on a leaf surface (Draaijers et al., 1997; Zeng et al., 2005). Canopy leaching occurs through diffusion of cations and the paired anions, mostly organic anions, between the water layer covering the leaf surface and the underlying apoplast as well as a counter process of canopy uptake (Ulrich, 1983; Staelens et al., 2008; De Schrijver et al., 2007). Canopy exchange is typically greater in deciduous than in coniferous trees under similar conditions (De Schrijver et al., 2007).

The original model assumed that the only process inducing canopy leaching of base cations is the ion exchange between base cations and H^+ or NH_4^+. Later, the model was revised to include canopy leaching of base cations paired with canopy leaching of weak acid anions such as organic anions and bicarbonate (Draaijers and Erisman, 1995; Staelens et al., 2008). However, canopy leaching of H^+ with organic anions is still not clearly accounted for in the model, even though organic acids have been regarded as a possible source of H^+ in throughfall (Chiwa et al., 2008; Inagaki et al., 1995). Inclusion of canopy leaching of H^+ with organic anions in the model would improve our understanding of the role of canopy characteristics in the canopy-deposition interaction.

2.1.4 Soil acidification or recovery from acidification in the AOSR

As boreal forests in the AOSR have acid-sensitive soils with low sulfate adsorption capacity and are expected to be N-limited ecosystems (and thus N deposition would first used to meet the N requirement of the forest vegetation), S deposition has been regarded as a fundamental problem causing soil acidification. It implies that changes in soil acidity caused by acid deposition reflect trends of SO_2 emission rather than NO_x emission. In the AOSR, SO_2 emission peaked in 1980s, substantially decreased in 1990s, and remained in 2000s described in section 1. Therefore, two scenarios could be suggested with the assumption that soil acidification has followed changes in SO_2 emission: a soil acidification rate peaked in the 1980s and 1) soil acidification continues with a reduced soil acidification rate or 2) soil is recovered from previous acidification.

The H^+ budget model has been used to investigate the progress of soil acidification or recovery influenced by changes in environmental conditions such as atmospheric deposition (Marcos and Lancho, 2002; van Breemen et al., 1983). Soil acidity, represented as exchangeable acidity measured in pH units, seems to be the most appropriate indicator to describe soil acidification and recovery, whereas it does not always respond sensitively to H^+ gain or loss of soils because of the pH buffering capacity of soils (van Breemen et al., 1983; Fisher and Binkley, 2000). The H^+ budget model can assess soil acidification or recovery because the H^+ budget is influenced directly by addition or depletion of H^+ in soil and reflects the current conditions of an ecosystem. The H^+ budget model can quantify soil acidification or alkalinization rate in calculating sources and sinks of H^+ (Fujii et al., 2008; Marcos and Lancho, 2002):

Sources: 1) atmospheric H^+ deposition, 2) net assimilation of cations excluding NH_4^+, 3) net anion mobilization, 4) deprotonation of carbonic acid or organic acids, and 5) H^+ generation by N transformations,

Sinks: 1) H^+ leaching loss, 2) net assimilation of non-nitrogen anions, 3) net cation mobilization, and 4) protonation of weak acid anions.

Soil chemistry is influenced by tree species. In addition to canopy interception, trees can affect soil chemistry through a number of other processes: organic acid exudation, nutrient uptake and turnover, and litter decomposition (affected by litterfall quality and quantity) and so on (Augusto et al., 2002; Binkley and Giardina, 1998; Knops et al., 2002; Rhoades, 1996), typically resulting in more acidic soils in conifer stands than in deciduous stands. Hence, coniferous trees can accelerate soil acidification in forest ecosystems affected by acid deposition, and deciduous stands may have greater resistance to acidification. It implies that the H^+ budget of soils may be influenced by tree species. Therefore, comparing the H^+ budget between coniferous stands and deciduous stands may provide better understanding of changes in soil acidity in boreal forests in the AOSR.

2.1.5 Potential future effects of acid deposition on boreal forests

Compared with historical emission rates, the total emission of acid causing materials in North America has now become substantially lower (Morrison, 2005). However, NO_x emissions in industrialized regions remain elevated while SO_2 emissions have decreased globally (Galloway et al., 2004). In the AOSR, the rate of NO_x emission is expected to increase, and that of SO_2 is expected to remain stable with increasing oil production for the near future as described in section 1 (Humphries, 2008; Niemi, 2005).

The response time of ecosystems to chronic acid deposition, especially N deposition may vary, depending on a number of factors such as deposition rates and nutrient demand by the biota (Gundersen et al., 1998). In North America, N saturation has been often found in temperate forests in eastern U.S. that have been impacted by high N deposition rates (Jeffries, 1995). Although several monitoring sites in eastern Canada, e.g., the Turkey Lake watersheds, have been N-saturated (Foster et al., 1989), most forests (temperate and boreal) in Canada did not show any sign of N saturation due to relatively low rates of N deposition (Houle et al., 1999).

Sulfur deposition in the AOSR has been a primary concern for soil acidification rather than N deposition due to greater emission rates of S than N, a low capacity for sulfate adsorption of soils (Jung et al., 2011b), and N limitation of the regions ecosystems (NSMWG, 2004). In other acid-sensitive regions of Alberta where emissions of SO_2 have been elevated over extended periods, high S inputs induced top soil acidification and depletion of cationic soil nutrients (Prietzel et al., 2004) and forest growth has been impacted (Legge et al., 1996). However, the concern regarding N deposition has increased due to the expected increase in N deposition rates in the AOSR and western Canada (Aherne and Shaw, 2010). Based on our literature review, N saturation has not been reported in western Canada and boreal forests in the AOSR. Meanwhile, increasing NO_2 concentrations in the atmosphere and N deposition rates have influenced N cycles in forest ecosystems in the AOSR (Laxton et al., 2010), which suggests that there is latent progressing of the N cycle towards N saturation. Therefore, it is important to evaluate prospective impacts of elevated levels of N and S depositions on forest ecosystems in the AOSR to keep ecosystems from adverse effects of acid deposition.

Simulated studies with elevated deposition rates have been conducted in forests to study potential changes in ecosystem properties and processes (Moore and Houle, 2009). Simulated N deposition studies have mostly reported beneficial impacts on tree growth in boreal forests within a decade (e.g., Newton and

Amponsah, 2006) and fertilization effects were clearly shown in nutrient-poor sites (Olsson and Kellner, 2006) while repeated N addition could affect induce nutrient imbalance in soil and plant and, ultimately decline of tree growth (Kishchuk et al., 2002; Amponsah et al., 2005). Meanwhile, simulated studies presented that a significant portion of added SO_4^{2-} could lead to increasing base cation leaching and reducing soil exchangeable cations while most added N could be taken up by plants (Liu et al., 2007) and SO_4^{2-} leaching is mainly affected by sulfate adsorption capacity of each soil and deposition rate (Reuss and Johnson, 1986). Therefore, simulated experiments with elevated levels of N and S deposition can help us predict potential impacts of acid deposition on boreal forests in the AOSR.

2.2 Thesis structure

Based on current knowledge gaps and objectives of the larger project of NSMWG, I conducted this thesis study 1) to assess long-term impacts of acid deposition on forest ecosystems in the AOSR, 2) to determine risk of soil acidification based on CLs, EXs, and H^+ budget of soils considering effects of tree species, and 3) to study changes in boreal forest ecosystems caused by chronic acid deposition using simulated N and S deposition treatments. For the first objective, I investigated tree ring chemistry such as $\delta^{13}C$ and $\delta^{15}N$, spatial variation of soil chemistry surrounding trees, and Ca/Al ratios of soil solution and roots as acid stress indicators (Chapter 2 and 3). For the second objective, I assessed interception deposition of each strong acid anion and each base cation using the canopy budget model. The model was modified so that it could evaluate H^+ supply or removal in throughfall by canopy-deposition interaction including bulk deposition, interception deposition, canopy uptake, and canopy leaching (Chapter 4). I also assessed CLs, EXs, and H^+ budgets of soils and tested the hypothesis that CLs and EXs are underestimated by the conventional method that excludes interception deposition (Chapter 5). These studies were performed in *Pinus banksiana* (jack pine) and *Populus tremuloides* (trembling aspen, aspen) stands in two acid-sensitive watersheds having different acid deposition rates (NE7: relatively high deposition rate and SM8: relatively low deposition rate) (the intensive monitoring study). For the last objective, I conducted a simulated N and S deposition experiment to evaluate effects of increasing acid deposition on boreal forests in the AOSR (Chapter 6; the artificial acidification study). Three hypotheses were tested in this thesis research: 1) boreal forests surrounding the AOSR are N-limted but not S-limited, and thus the growth rates of dominant tree species will be increased by elevated levels of N deposition, but not by elevated levels of S deposition, 2) N leaching will not be increased in the short-term by elevated levels of N and S depositions in the N-limited boreal forest, and 3) cationic nutrient leaching will not be increased in the short-term by the elevated levels of N deposition, consistent with the lack of N leaching.

This thesis consists of seven chapters. Chapter 1 describes background information and study overview (this chapter). Each of the data chapters (2 to 6) constitutes a manuscript that has already been published, under review or will be submitted for publication:

Chapter 2, “Soil and tree ring chemistry of *Pinus banksiana* and *Populus tremuloides* stands as indicators of changes in atmospheric environments in the oil sands region of Alberta, Canada”. This chapter is to be submitted for publication.

Chapter 3, “Soil and tree chemistry reflected the cumulative impact of acid deposition in *Pinus banksiana* and *Populus tremuloides* stands in the Athabasca oil sands region in western Canada”. This chapter is to be submitted for publication.

Chapter 4, “Effects of canopy-deposition interaction on H^+ supply to soils in *Pinus banksiana* and *Populus tremuloides* ecosystems in the Athabasca oil sands region in Alberta, Canada”. This chapter has been published in Environmental Pollution.

Chapter 5, “Critical loads and H^+ budgets of forest soils affected by air pollution from oil sands mining in Alberta, Canada”. This chapter is to be submitted for publication.

Chapter 6, “Four years of simulated N and S depositions did not cause N saturation in a mixedwood boreal forest ecosystem in the oil sands region in northern Alberta, Canada”. This chapter is under review by the Journal of Environmental Management.

Chapter 7 provides a summary of key findings and general conclusions. In addition, suggested future research is described in this chapter.

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Chapter 2. Soil and tree ring chemistry of *Pinus banksiana* and *Populus tremuloides* stands as indicators of changes in Atmospheric environments in the oil sands region of Alberta, Canada

1. Introduction

Changes in the Atmospheric environment including atmospheric CO_2 concentration and nitrogen (N) and sulphur (S) depositions caused by industrial activities have been demonstrated to affect forest ecosystems (Martin and Sutherland, 1990; Sakata et al., 2001). Oil sands mining activities are one of the industrial activities that cause atmospheric pollution and threaten forest health (Aherne and Shaw, 2010). The Athabasca oil sands region (AOSR) is the largest area for open-pit oil sands mining in Alberta, Canada, and air pollution caused by oil mining activities has been of concern (Fung and Macyk, 2000). Commercial oil production in the AOSR was started by the Great Canadian Oil Sands (currently Suncor) that officially began in 1967, followed by the second and third mines that started in 1978 (Syncrude) and 2003 (Shell Canada), respectively (Figure 2-1) (Shell, 2006; Suncor, 2010; Syncrude, 2009). As a result, a large amount of air pollutants has been released in the past several decades in the oil

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sands region. Specifically, NO_x emission increased continuously from approximately 20 Mg day^{-1} in 1970 to 76 Mg day^{-1} in 2006; meanwhile SO_2 emission increased from approximately 200 Mg day^{-1} in 1970 to 400 Mg day^{-1} in the 1980s, followed by substantial decreases since the mid-1990s (Hazewinkel et al., 2008) due to SO_2 curtailment policies and technical improvement (Morrison, 2005).

The effects of air pollution on forest ecosystems are the result of long-term chronic exposure; as such, time-integrating indicators may be useful in understanding how air pollution has affected tree and soil chemistry (Legge et al., 1984). Tree ring chemistry such as isotope ratios of C and N ($\delta^{13}C$ and $\delta^{15}N$, respectively) and nutrient concentrations has been used as an archive of historical environmental changes caused by air pollution, as tree ring chemistries are susceptible to the growth condition in the year when the specific growth ring was formed (Martin and Sutherland, 1990; Kwak et al., 2009b; Watmough et al., 1999). For example, fossil fuel combustion generally releases ^{13}C-depleted CO_2, tree rings formed in ecosystems under more severe air pollution may show more negative $\delta^{13}C$ unless other factors such as water and nutrient availabilities are limited (Bert et al., 1997; Choi et al., 2005b; Farmer and Baxter, 1974). Meanwhile, air pollutants such as NO_x that are co-emitted with CO_2 have been shown to cause stomatal closure, leading to less negative $\delta^{13}C$ (Savard, 2010). Therefore, $\delta^{13}C$ of tree rings is determined by the balance between the effects of ^{13}C-depleted CO_2 and stomatal closure induced by pollutants.

The $\delta^{15}N$ of tree rings can serve as another indicator of Atmospheric environmental changes (Savard et al., 2009; Norby, 1998) as anthropogenic NO_x, which is emitted from fossil fuel combustion and one of the N sources for tree uptake in forests, has lower $\delta^{15}N$ than available soil N (Nadelhoffer and Fry, 1994). Several studies reported that tree ring $\delta^{15}N$ was correlated with the historical amount of NO_x emission and deposition (Kwak et al., 2009b; Poulson et al., 1995). Soil chemistry is also susceptible to acid deposition caused by NO_x emissions. Chronic acid deposition leads to leaching of soil exchangeable cations such as Ca^{2+} and, subsequently, to increasing soil acidity. Increased soil acidity would increase the release of toxic Al ion species (Clark and Baligar, 1995) and decreases soil Ca/Al ratios, which affects the Ca/Al ratio of plant tissues (Hirano et al., 2007; Innes, 1995; Shortle and Smith, 1988). Such patterns of $\delta^{13}C$, $\delta^{15}N$, and Ca/Al in tree rings with the progress of air pollution in an area have been demonstrated in industrial (Kwak et al., 2009b) and rural areas (Kwak et al., 2011); however, the responses of tree and soil chemistry to air pollution is likely affected by the distance from pollution sources as air pollutant concentrations in the area close to emission sources such as mining or upgrading facilities are likely higher than those in remote areas (WBEA, 2010). In addition, the susceptibility of tree and soil chemistry to air pollution can vary among tree species (e.g., coniferous vs. deciduous) due to contrasting N cycling rates (Garten Jr and Van Miegroet, 1994), leaf morphology (Cole and Rapp, 1981), and soil characteristics such as pH (Augusto et al., 2002; Staelens et al., 2008). In this study, we investigated differences in soil and tree ring chemistry ($\delta^{13}C$, $\delta^{15}N$, and Ca/Al) between *Pinus banksiana* (jack pine) and *Populus tremuloides* (trembling aspen,

aspen) stands in two watersheds located at different distances from the main emission sources in order to evaluate chemical bio-indicators for evaluating the impact of air pollution on forest health in the AOSR.

2. Materials and Methods

2.1 Site description

Two watersheds, NE7 and SM8 in the AOSR, were selected for this research. Those are acid-sensitive watersheds due to coarse textured soils with a low pH buffering capacity (Ok et al., 2007) and a low sulfate adsorption capacity (Jung et al., 2011b). Watershed NE7 (57.15° N, 110.86° W) is located northeast of Fort McMurray, while SM8 (56.21° N, 111.20° W) is located south of Fort McMurray (Figure 2-2). As mining areas are mostly located north of Fort McMurray and the prevailing wind direction in the area is east to east-southeast, NE7 has been exposed to greater acid deposition (Jung et al., 2011a; Wieder et al., 2010); annual depositions of SO_4^{2-} and NO_3^- were 4.1 kg S ha^{-1} and 2.2 kg N ha^{-1} yr^{-1}, respectively, in NE7, and 3.2 and 1.8 kg ha^{-1} yr^{-1}, respectively, in SM8, between 2006 and 2009 (Jung et al., 2011a).

Climate conditions were similar in both watersheds in terms of temperature and humidity. Based on global climatology data between 1960 and 1990, the mean annual temperature was 0.7 ˚C with a mean relative humidity of 66 to 67%, and the mean annual precipitation and evaporation were almost balanced (Ok et al., 2007). Based on climate data collected from 1967 to 2007 in weather stations close to the watersheds: Muskeg station (57.13° N, 110.9° W) for NE7 and Stony Mountain station (56.38° N, 111.23° W) for SM8 (Environment Canada, 2010), mean temperature and precipitation between May and August were 13.0 ˚C and 248 mm, respectively, in NE7 and 12.6 ˚C and 371 mm, respectively, in SM8 (Figure 2-3a); however, winter climate data were not collected at those stations.

Dominant tree species based on relative tree height and number of trees were 50 to 60-year-old jack pine and aspen trees in upland sites and black spruce (*Picea mariana*) in low-lying areas and wetlands. Common soil types in upland forests of both watersheds were Elluviated Dystric Brunisols and Orthic Gray Luvisols in the Canadian system of soil classification (Soil Classification Working Group, 1998) or Boralf in US Soil Taxonomy (Soil Survey Staff, 1994). Five 20 × 20 m plots were installed in each watershed in 2005. Three plots were jack pine dominated stands and the other two were aspen dominated stands in each watershed. The detail information of each plot was described in Appendix I and II. Atmospheric deposition, canopy uptake, and canopy leaching in each plot were studied from 2006 to 2010 (Jung et al., 2011a) and sulfate adsorption capacities and weathering rates in each plot were also studied (Jung et al., 2011b).

2.2 Sampling of soil and tree ring samples

Soil samples were collected from two layers in each plot in October 2009: forest floor (an organic layer with LFH horizons) and 0-5 cm surface mineral soil, the most sensitive soil layers to changes in atmospheric deposition. Soil samples were air-dried, crushed, and passed through a 2-mm sieve. For tree ring sampling, four trees with similar growth characteristics such as age and exposure to light but with a range of diameters were selected in each plot. Tree cores were collected at breast height (1.3 m) using a 5-mm diameter stainless steel increment borer. Samples were immediately sealed in dry plastic tubes for storage, transported to the laboratory, and kept in a freezer at -10 ˚C before the analyses. Tree rings were dated and each ring width was measured using a tree ring measuring system with 0.001 mm resolution (TA System, Velmex, USA). Wood samples for 3-year bands between 1964 and 2008 (growth ring in 2009 was included in the band between 2006 and 2008) were taken from each core. Three-year band samples in the same periods were composited for the four trees in each plot to obtain enough samples for chemical analysis. For chemical analysis, all tree ring samples were dried at 70 ˚C for 72 hours in a drying oven and ground to pass a 40-mesh sieve with a Wiley mill (GE motors, USA). Soil and tree samples were further ground to fine powder with a MM200 ball grinder (Retsch, USA) for C and N isotope and metal analysis as described below.

2.3 Analysis of soil and tree ring

Soil pH was measured in deionized water using 10 g of air-dried soil in 40 mL of water for forest floor and 20 mL of water for surface mineral soil with an AR20 pH meter (Fisher Scientific Ltd., US). Soil exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Al^{3+}, Fe^{3+}, and Mn^{2+}) were determined with an ICP-MS (Elan 6000 quadrupole, Perkin-Elmer, Inc., CT) after extraction with 1 mol L^{-1} NH_4Cl at a ratio of 5 g surface soil or 2 g forest floor to 100 mL extractant and after shaking for 1 hour. Effective cation exchange capacity (CECe) of each soil sample was calculated as the sum of the exchangeable cations (Ruan et al., 2004). Base saturation (%) was assessed as the sum of exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) divided by CECe. Total C and N concentrations and their corresponding $\delta^{13}C$ and $\delta^{15}N$ were analyzed with a continuous-flow stable isotope ratio mass spectrometer (Optima, VG Isogas, UK) linked to an elemental analyzer (Carlo Erba NA1500, CE Instruments, Italy). The isotope values were expressed in per mil (‰) as a relative deviation from the international standard: Pee Dee Belemnite (PDB) for $\delta^{13}C$ and atmospheric N_2 for $\delta^{15}N$. Total Ca and Al concentrations of tree ring samples were determined with the ICP-MS described above after digestion using concentrated HNO_3 and 30% H_2O_2 on a digestion block at 125 ℃ for 4 hours (Cambell and Plank, 1998).

2.4 Calculation and statistical analysis

All statistical analyses were performed using SAS 9.01 (SAS Institute Inc., Cary, NC). An autoregressive model or a simple regression model was used to analyze temporal trends of tree growth and tree ring chemistry. The autoregressive model was used for most variables which show Durbin Watson statistics less than 1.5 or greater than 2.5, while a simple regression model was used for variables including C, Al, and Ca/Al as Durbin Watson statistics for those parameters were between 1.5 and 2.5 (Ott and Longnecker, 2008). Three time-series datasets were applied to the model: the entire period between 1964 and 2009, the first stage of mine operation between 1964 and 1981, and the second stage of mine operation between 1982 and 2009, representing far increased mining activities (Figure 2-1). A multiple regression analysis was conducted to examine the relationships between climate variables (summer temperature and precipitation) and annual tree ring area. As tree chemistry was analyzed with 3-year bands, relationships with annual climate variables were not explored.

Analysis of variances (ANOVA) was performed to determine the effects of watersheds and tree species on tree and soil chemistry. For tree ring samples, all three time-series datasets were used for ANOVA. As evaluating the difference in tree ring chemistry between sites with different distance from the pollution source can be an approach to investigate atmospheric pollution impact (Savard, 2010), the difference of each variable for each species between watersheds (Diff_x, where x is a specific variable) was calculated by subtracting the value in SM8 from that in NE7. Therefore, a negative value of Diff_x indicates that the value of a variable was greater in SM8 than in NE7 and *vice versa*. Temporal trends of Diff_x were also explored using regression analysis.

3. Results

3.1 Soil chemistry

The effects of tree species and watersheds on soil chemistry were variable depending on the soil layer (Table 2-1 and 2-2). For example, pH in the forest floor was affected by tree species ($p<0.001$, Table 2-2), with values of 4.30 and

4.15 in NE7 and SM8, respectively, for jack pine stands and 5.58 and 4.79 in NE7 and SM8, respectively, for aspen stands (Table 2-1). However, pH in surface mineral soil was not influenced by tree species. Total C and N in the forest floor were not different between watersheds whereas total N in the forest floor was greater ($p<0.05$) in aspen than in jack pine stands, leading to a lower ($p<0.05$) C/N ratio in aspen stands (Table 2-1). Total C and N in the surface mineral soil were greater ($p<0.05$) while C/N ratio was lower ($p<0.05$) in aspen than in jack pine stands (Table 2-1 and 2-2).

The $\delta^{13}C$ in the forest floor and mineral soil was not different between watersheds or stand types (Table 2-1 and 2-2). However, $\delta^{15}N$ in the forest floor was affected ($p<0.05$) by tree species, watershed, and their interaction, decreasing in the order of aspen stands in SM8 (1.4‰) > jack pine stands in SM8 (-0.5‰) > aspen stands in NE7 (-0.9‰) > jack pine stands in NE7 (-1.4‰). For the surface mineral soil, $\delta^{13}C$ and $\delta^{15}N$ were not affected by watersheds or tree species, with their values greater ($p<0.001$) than in the forest floor. Exchangeable cations and Ca/Al were affected by both tree species and watershed. Exchangeable base cations and Ca/Al ratios were greater ($p<0.05$) in aspen than in jack pine stands in both soil layers. The Ca/Al ratios were greater in NE7 than in SM8 in both soil layers while exchangeable cation concentrations were lower in NE7 than in SM8.

3.2 Annual basal area increment

In both watersheds, annual growth ring width of both species decreased over time ($p<0.001$) between 1963 and 2009 (Figure 2-3b). Annual tree ring area of jack pine ranged from 2.3 to 4.2 cm^2 yr^{-1} in NE7 and from 0.8 to 4.7 cm^2 yr^{-1} in SM8 and did not show any temporal trend (Figure 2-3c). Meanwhile, growth ring area of aspen increased over time ($p<0.01$) in both watersheds and ranged from 0.7 to 4.8 cm^2 yr^{-1} in NE7 and from 0.3 to 9.4 cm^2 yr^{-1} in SM8. No significant relationship was found between climate variables and annual ring growth in NE7 while annual growth ring area was positively correlated with the summer temperature ($r^2=0.37$ and $P<0.001$ for jack pine and $r^2=0.96$ and $P<0.001$ for aspen) but was negatively correlated with summer precipitation ($r^2=0.24$ and $P<0.01$ for jack pine and $r^2=0.49$ and $P<0.001$ for aspen) in SM8, with temperature and precipitation in the summer seasons negatively correlated ($r=-0.69$ and $P<0.001$) (data not shown).

3.3 Tree ring chemistry

Carbon concentrations in tree rings were relatively stable while N concentration increased sharply towards the outermost tree rings formed between 2006 and 2009 (Figure 2-4a and 2-4b), without differences between watersheds (Table 2-3). Interestingly, however, Diff_N (N in NE7 – N in SM8) for aspen stands increased during the overall study period ($r^2=0.64$, $P<0.001$) and for jack pine, it started to increase in recent years ($r^2=0.51$, $P<0.05$)) (Figure 2-5b).

Gradual decrease of $\delta^{13}C$ over time was found for both stands in both watersheds that coincide with the commencement of oil sands mining activities (Figure 2-4c). Between 1982 and 2009, $\delta^{13}C$ in tree rings decreased linearly ($p<0.001$ for both tree species) at rates of -0.053‰ yr^{-1} for jack pine and -0.054‰

yr^{-1} for aspen. The $\delta^{13}C$ in tree rings was less negative ($p<0.001$) in jack pine than in aspen in the entire study period, except for the mid 1960s, regardless of the watershed. The $\delta^{15}N$ in tree rings did not show any difference between tree species nor did it change with time (Figure 2-4d); however, Diff_$\delta^{15}N$ ($\delta^{15}N$ in NE7 – $\delta^{15}N$ in SM8) in aspen stands decreased over time ($p<0.05$) (Figure 2-5d).

Calcium concentrations in tree rings decreased over time ($p<0.05$) in aspen (range: 0.16 to 0.85 g kg^{-1}) but did not change over time in jack pine trees (range: 0.06 to 0.25 g kg^{-1}) (data not shown). Aluminum concentration in tree rings (range: 0.007 to 0.041 g kg^{-1}) did not show any pattern of change with time in both tree species. The molar ratio of Ca/Al was significantly lower ($p<0.01$) in jack pine (range: 4.0 to 13.7) than in aspen (range: 4.5 to 40.3) (Table 2-3 and Figure 2-4e). The Ca/Al was greater ($p<0.01$) in NE7 than in SM8 for aspen whereas no difference between watersheds was found for jack pine.

4. Discussion

4.1 Soil chemistry

Soil chemistry was affected by both air pollution and site-specific conditions such as tree species composition and type of parent material. Therefore, we need to be cautions about making conclusions about causes inducing differences in soil chemistry between watersheds and between tree stands to investigate cumulative impacts of air pollution on soil chemistry. Total N concentration in the forest floor was higher in aspen than in jack pine stands by 3.8 and 7.9 g kg^{-1} in NE7 and

SM8, respectively (Table 2-1). The total N concentration in the forest floor was likely affected by litter amount and quality (e.g., decomposability), as litter from broadleaf trees are more decomposable than those from conifer trees (Johansson, 1995; Van Hees et al., 2002), leading to lower C/N of the resulting organic matter (Table 2-1). The effects of tree species on soil properties were thus profound in the oil sands region, consistent with the literature on the general understanding of tree species effects on soils (Binkley and Giardina, 1998; Kamei et al., 2009; Reich et al., 2005).

The δ^{15}N in the forest floor was greater in aspen than in jack pine stands by 0.55‰ in NE7 and by 0.89‰ in SM8 (Table 2-1). The faster decomposing deciduous litter would experience greater net N mineralization rates followed by N transformation processes such as ammonia volatilization, nitrification, leaching, and denitrification associated directly or indirectly with N loss (Garten Jr and Van Miegroet, 1994). Because N isotopic fractionation during N loss that results in ^{15}N enrichment of the remaining N is proportional to N availability (Högberg, 1997), the higher soil N availability in aspen stands would eventually lead to a higher δ^{15}N in the forest floor (Table 2-1), which was linked to the higher δ^{15}N in the mineral soil than that in the forest floor in both watersheds as the more decomposed organic matter translocated to the mineral soil layers (Kwak et al., 2009a). The lower ($p<0.001$) δ^{15}N in the forest floor in NE7 than in SM8 likely reflected the greater amount of ^{15}N-depleted N deposition in NE7 than in SM8, with the former closer to N emission sources and had greater rate of N deposition than the latter (Jung et al., 2011a).

The higher Ca/Al in the forest floor and mineral soils in aspen than in jack pine stands (Table 2-1) reflected the higher Ca concentration in deciduous than in coniferous litters resulting from their different Ca requirement (Augusto et al., 2002; van Breemen and Finzi, 1998). Effects of tree species on Ca/Al in the forest floor but not in the mineral soil were reflected by soil pH in the forest floor. The Ca/Al was higher ($p<0.01$) in NE7 than in SM8 (Table 2-1), contrary to our initial hypothesis, implying that Ca/Al ratio was strongly affected by intrinsic soil chemistry before oil sands development rather than acid deposition. It suggests that soil chemistry alone may not be reliable indicators of the magnitude of exposure of forest stands to atmospheric pollution.

4.2 Tree ring $\delta^{13}C$

The $\delta^{13}C$ in rings were lower in aspen than in jack pine trees by approximately 1‰ (Figure 2-4c) due to different C isotope fractionation processes in the photosynthetic and/or the post-photosynthetic processes such as translocation of photosynthates from the leaves to the trunk (Badeck et al., 2005; Damesin and Lelarge, 2003). Regardless of the tree species or watershed location, $\delta^{13}C$ in tree rings decreased over time, especially since the early 1980s (Figure 2-4c), coincident with the increase of CO_2 emission by increased oil production in the AOSR (Suncor, 2010; Syncrude, 2009); emission of ^{13}C-depleted CO_2 per volume of oil production ranged from 0.57 to 1.0 Mg m^{-3} (Furimsky, 2003). However, $\delta^{13}C$ in tree rings was not different between watersheds for each species and the decreasing rates (~0.05‰ yr^{-1}) of $\delta^{13}C$ were not different between tree species.

The rate of decrease of ^{13}C (~0.05‰ yr^{-1}) in the tree rings observed in this study is similar to those reported for moderately polluted areas (Sakata et al., 2001; Dongarrà and Varrica, 2002; Li et al., 2010), but much lower than those (~0.1‰ yr^{-1}) reported for highly polluted areas such as in the vicinity of industrial complexes (Kwak et al., 2009b; Guerrieri et al., 2011). As plant $\delta^{13}C$ is affected by the properties of the atmospheric CO_2 (the source effect) and other factors associated with water use efficiency, determined by the balance between CO_2 diffusion (CO_2 supply) through stomata and carboxylation in leaf tissue (CO_2 consumption), as such processes cause C isotope discrimination (Choi et al., 2005a), it may not be a simple relationship between increased CO_2 concentration and the $\delta^{13}C$ signal recorded in tree rings, particularly when other air pollutants co-existed (Kwak et al., 2009b; Choi et al., 2005b; Savard, 2010).

There are three possible mechanisms for the similar patterns of tree ring $\delta^{13}C$ between the two watersheds. First, NE7 and SM8 might not be distant enough to reflect different degrees of ^{13}C-depleted CO_2, partly because of the mixing of CO_2 in the atmosphere in the local area and that increases in atmospheric CO_2 concentration has been a global trend (February and Stock, 1999). Second, air pollutants such as SO_2 and NO_x co-emitted with CO_2 in the mining area would induce stomatal closure, leading to less negative $\delta^{13}C$ (Savard, 2010). Since NE7 is closer to and downwind from the mining and upgrading area, pollution-induced stomatal closure and the resulting reduction in ^{13}C discrimination in the photosynthesis process might somewhat mute the ^{13}C-depleted CO_2 effect on tree ring $\delta^{13}C$. As such, tree ring $\delta^{13}C$ alone may not be a reliable surrogate of atmospheric pollution impact on forest ecosystems in the study sites due to the counterbalancing effects of ^{13}C-depleted CO_2 and pollution-induced stomatal closure on tree ring δ^{13}C. The last possible scenario is that decreasing trends of δ^{13}C in tree rings were more related to water availability of sites than CO_2 emission. Stand volume may decline over time due to increasing mortality of dominant trees (Pothier et al., 2004) though basal area increment of individual trees increases. It can induce decreasing competition for soil water and reducing ^{13}C discrimination in photosynthetic processes.

4.3 Tree ring N concentration and δ^{15}N

The increasing N concentration towards the outermost tree rings (Figure 2-4b) is believed to be due to translocation of N from old to new tissues, making it difficult to use N concentrations in tree rings as an indicator of historical changes in N availability in ecosystems (Poulson et al., 1995; Bukata and Kyser, 2005; Sheppard and Thompson, 2000) unless there were precipitous changes in the ecosystem such as drainage of peatland (Choi et al., 2007). On the other hand, δ^{15}N is regarded as a stronger indicator of historical changes in local environments associated with N dynamics as inter-tree ring translocation does not provide any significant bias to a trend of tree ring δ^{15}N in spite of the potential N isotopic fractionation (Savard, 2010). In this regard, decreasing δ^{15}N in the younger tree rings have been regarded as records of long-term anthropogenic impacts of ^{15}N-depleted N deposition (Kwak et al., 2009b; Choi et al., 2005b;

Savard et al., 2009; Poulson et al., 1995; Bukata and Kyser, 2007) though the $\delta^{15}N$ signal stored in the ring formed in a specific year might be affected by inter-tree ring translocation of N. However, in this study, $\delta^{15}N$ of tree rings did not show any temporal pattern regardless of tree species and watershed (Figure 2-4d), and this could be attributed to increased rate of N deposition and thus availability of N for transformations (such as NH_3 volatilization, leaching of NO_3^- produced from incomplete nitrification, and denitrification) that cause ^{15}N enrichment of soil N due to isotopic fractionation (Garten Jr and Van Miegroet, 1994). The greater contribution of isotopic fractionation in recent years would mute the direct effect of the ^{15}N-depleted N deposition.

The $\delta^{15}N$ of total N in the forest floor was lower in NE7 (-1.4‰ in jack pine and -0.9‰ in aspen stands) than in SM8 (-0.5‰ in jack pine and 1.4‰ in aspen stands) (Table 2-1) likely reflected the greater deposition of ^{15}N-depleted N in NE7 which is closer to the mining and upgrading area. However, the $\delta^{15}N$ was lower in SM8 than in NE7 in the mineral soil, opposite to that in the forest floor, and was greater in the mineral soil (range: 2.5 to 4.6‰) than in the forest floor (range: -1.4 to 2.2). These results suggest that N isotopic fractionation altered the $\delta^{15}N$ signature of N deposited and the N translocated from the forest floor to the mineral soil had gone through greater degrees of isotopic fractionation. Our study indicates that the $\delta^{15}N$ of tree rings in the study sites has limited utility for indicating changes in atmospheric N deposition. The $\delta^{15}N$ in the mineral soil in this study was slightly higher than in other studies, e.g., from 2.2 to 2.8‰ in *Pinus* *taeda* stands (Choi et al., 2005a) and from 0.6 to 2.5‰ in *Picea mariana-Larix laricina* stands (Choi et al., 2007) and from 0.4 to 2.1‰ in *Picea jezoensi*, *Abies ephrolepis*, and *Betula ermanii* stands (Cheng et al., 2010), indicating the relatively high N isotopic fractionation potential in our study sites.

The Diff_δ^{15}N, however, showed decreasing trends in conjunction with increasing Diff_N over time, particularly in aspen stands (Figure 2-5b), indicating that NE7 has been exposed to ^{15}N-depleted N deposition to a greater degree as compared with SM8. This is consistent with the greater N deposition in NE7 than in SM8 (Jung et al., 2011a; Wieder et al., 2010). The greater changes in Diff_δ^{15}N and Diff_N over time in aspen than in jack pine stands could be due to faster N cycling in deciduous than evergreen stands (Augusto et al., 2002). We suggest that Diff_δ^{15}N and Diff_N rather than δ^{15}N and N concentrations are more useful indicators of the impacts of atmospheric N deposition between different locations because δ^{15}N and N concentrations are affected by a number of site-specific characteristics such as N availability and N transformation processes (Garten Jr and Van Miegroet, 1994).

4.4. Tree ring Ca/Al ratio

Although Ca/Al ratios in tree rings are known to be less sensitive to acidity stress than that in fine roots or leaves (Vanguelova et al., 2007), a decreasing pattern of tree ring Ca/Al ratios has been reported to be an indicator of acidification of soils in polluted areas (Kwak et al., 2009b; Bondietti et al., 1989). However, in this study, the Ca/Al ratio in tree rings showed no temporal trend, indicating that tree ring Ca/Al ratios have been affected not only by acid precipitation but also other factors such as precipitation pattern and parent materials that may concurrently influence Ca/Al ratios in the soil solution and thus tree uptake of Ca and Al ions (Kwak et al., 2009a). For example, while NE7 has been exposed to greater rates of acid deposition than SM8 (Jung et al., 2011a; Wieder et al., 2010), the Ca/Al ratio in aspen tree rings was greater in NE7 than in SM8 because of greater Al concentrations in soil profiles in SM8 than in NE7 (Ok et al., 2007; Jung et al., 2011b; see also Table 2-1). Therefore, the Ca/Al may not be a reliable indicator for the impact of acid deposition in some sites as the ratio is likely to be strongly affected by site-specific soil chemistry.

5. Conclusions

In spite of differences in the distance of the two watersheds from pollution sources (mining and upgrading activities), $\delta^{13}C$, $\delta^{15}N$, and Ca/Al ratios in soil and tree ring samples in the studied forest stands did not show a systematic pattern consistent with the expected impact of atmospheric depositions; instead, different mechanisms were in play in causing the trends we observed. The lower $\delta^{15}N$ in the forest floor in NE7 than in SM8 indicated greater impacts of ^{15}N-depleted N deposition in NE7 than in SM8. The Ca/Al ratio in the soil was affected by soil properties such as soil pH and cationic compositions. Tree ring $\delta^{13}C$ showed a decreasing pattern due to global increases in ^{13}C-depleted CO_2, but they were not different between NE7 and SM8 due to the counterbalancing effect of other air pollutants such as NO_2 and SO_2 that induce stomatal closure and reduce ^{13}C isotopic discrimination during photosynthesis; the rate of such pollution was greater in NE7. Temporal changes in Diff_N and Diff_$\delta^{15}N$ also reflected greater anthropogenic N deposition in NE7 than in SM8, consistent with results of $\delta^{15}N$ in the forest floor; Diff_N and Diff_$\delta^{15}N$ in aspen tree rings were believed to be more sensitive to air pollution than those in jack pine because deciduous stands have relatively quicker N cycling than evergreen conifers. We conclude that $\delta^{15}N$ in the forest floor and Diff_N and Diff_$\delta^{15}N$ of tree rings were useful indicators of the impact of N deposition on forest stands in the study area.

Table 2-1 Soil properties in jack pine and trembling aspen (aspen) stands in the Athabasca oil sands region in Alberta, Canada. Values are mean (SE).

Water-shed	Tree	pH	Total C	Total N	C/N	$\delta^{13}C$	$\delta^{15}N$	Exchangeable cations				CECe[1]	Base Saturation	Ca/Al[2]
								Ca^{2+}	Mg^{2+}	K^+	Al^{3+}			
			(g kg^{-1})			(‰)		($cmol_c^{-1}$ kg^{-1})					(%)	
Forest Floor														
NE7	Jack pine	4.3	367	12.9	29.1	-27.7	-1.4	22.9	3.8	2.0	1.1	25.9	93.3	51.2
		(0.1)	(31.9)	(2.6)	(4.0)	(0.05)	(0.1)	(8.4)	(1.3)	(0.2)	(0.8)	(2.7)	(1.4)	(51.9)
	Aspen	5.6	335	16.7	21.0	-28.7	-0.9	44.0	8.4	2.8	0.1	46.1	98.9	1090
		(0.2)	(20.9)	(5.5)	(5.7)	(0.13)	(0.2)	(6.5)	(1.4)	(0.9)	(0.03)	(1.6)	(0.2)	(426)
SM8	Jack pine	4.1	323	10.9	30.6	-29.2	-0.5	14.8	3.7	2.0	1.5	21.5	90.1	20.1
		(0.04)	(28.6)	(2.9)	(4.9)	(0.19)	(0.6)	(4.7)	(1.2)	(0.8)	(0.6)	(2.6)	(1.5)	(17.7)
	Aspen	4.8	361	18.8	19.6	-27.7	1.4	36.8	7.1	5.2	0.2	41.2	96.4	324
		(0.4)	(2.3)	(3.6)	(3.9)	(0.15)	(1.1)	(4.4)	(0.8)	(0.6)	(0.01)	(1.7)	(0.4)	(52.2)
Surface mineral soil														
NE7	Jack pine	4.0	7.8	0.32	25.3	-25.7	3.1	0.26	0.07	0.07	0.17	1.7	80.7	2.99
		(0.3)	(1.3)	(0.11)	(5.7)	(0.50)	(0.7)	(0.12)	(0.02)	(0.02)	(0.10)	(0.1)	(3.5)	(2.13)
	Aspen	4.0	7.9	0.37	22.0	-27.1	4.6	0.93	0.23	0.11	0.10	3.3	90.4	14.3
		(0.1)	(0.1)	(0.08)	(4.9)	(0.03)	(0.9)	(0.21)	(0.02)	(0.02)	(0.03)	(0.4)	(2.2)	(5.90)
SM8	Jack pine	4.4	11.9	0.41	29.4	-26.3	2.5	0.33	0.10	0.10	0.73	3.4	61.9	1.05
		(0.3)	(2.5)	(0.09)	(2.5)	(0.01)	(1.4)	(0.21)	(0.05)	(0.03)	(0.62)	(0.7)	(5.8)	(1.01)
	Aspen	4.3	25.3	1.93	13.3	-27.3	3.9	1.56	0.35	0.18	1.17	6.8	68.9	2.01
		(0.1)	(2.5)	(0.18)	(2.5)	(0.12)	(1.1)	(0.57)	(0.03)	(0.04)	(0.08)	(0.5)	(3.7)	(0.75)

[1] CECe is effective cation exchange capacity calculated as the sum of exchangeable Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, and Fe^{2+}.

[2] Ca/Al was calculated based on exchangeable Ca^{2+} and Al^{3+} on molar unit.

Table 2-2 ANOVA results (P values) for the effects of tree species (jack pine and trembling aspen) and watershed (NE7 and SM8) on soil chemistry.

Soil layer	Factor	pH	Total C	Total N	C/N	$\delta^{13}C$	$\delta^{15}N$	Exchangeable cations				CECe	Base saturation	Ca/Al[1]
								Ca^{2+}	Mg^{2+}	K^{+}	Al^{3+}			
Forest floor	Species (S)	<0.01	0.87	0.04	0.02	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Watershed (W)	0.20	0.60	0.99	1.00	0.03	0.03	0.09	0.14	0.02	0.45	0.07	<0.02	<0.01
	S x W[2]	0.12	0.08	0.41	0.65	<0.01	<0.01	0.90	0.88	0.02	0.66	0.92	0.77	<0.01
Surface mineral soil	Species (S)	0.44	<0.01	<0.01	0.02	0.01	0.46	<0.01	<0.01	0.02	0.33	<0.01	0.06	0.01
	Watershed (W)	0.58	<0.01	<0.01	0.38	0.16	0.52	0.10	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
	S x W	0.28	<0.01	<0.01	0.08	0.65	0.56	0.17	0.02	0.31	0.20	0.06	0.75	0.02

[1] Ca/Al was calculated based on exchangeable Ca^{2+} and Al^{3+} on molar unit.

[2] S x W indicates tree species × watershed interaction.

Table 2-3 ANOVA results (P values) for the effects of tree species (jack pine and trembling aspen) and watershed (NE7 and SM8) on tree ring chemistry in three different time periods.

Factor	1964 - 1981					1982 - 2009					1964 - 2009				
	C	N	δ^{13}C	δ^{15}N	Ca/Al[1]	C	N	δ^{13}C	δ^{15}N	Ca/Al	C	N	δ^{13}C	δ^{15}N	Ca/Al
Species (S)	<0.01	<0.01	<0.01	0.47	0.32	<0.01	<0.01	<0.01	0.07	0.41	<0.01	<0.01	0.05	0.50	<0.01
Watershed (W)	0.31	0.02	0.80	0.39	0.05	0.31	0.49	0.89	0.08	<0.01	0.22	0.48	0.96	0.91	0.68
S x W[2]	<0.01	0.52	0.07	0.42	0.01	0.11	0.06	0.57	0.07	0.41	<0.01	0.78	0.68	0.63	0.19

[1] Ca/Al was calculated based exchangeable Ca^{2+} and Al^{3+} on molar unit.

[2] S x W indicates tree species × watershed interaction.

Table 2-4 The R^2 values for time effects on tree ring chemistry using a simple regression model for C and a autoregressive model for other parameters.

Period	Tree species	Water -shed	C	N	Diff_C[1]	Diff_N[2]	$\delta^{13}C$	$\delta^{15}N$	Diff_$\delta^{13}C$ [3]	Diff_$\delta^{15}N$ [4]	Ca/Al	Diff_Ca/Al[5]
1964 -1981	Jack pine	NE7	0.64^{**}	0.56^{*}	0.69^{*}	0.16	0.10	0.02	0.23	0.09	0.003	0.33
		SM8	0.05	0.54^{*}			0.02	0.40			0.23	
	Aspen	NE7	0.05	0.01	0.19	0.21	0.22	0.06	0.01	0.001	0.49	0.54^{*}
		SM8	0.07	0.79^{***}			0.01	0.10			0.26	
1982 -2009	Jack pine	NE7	0.01	0.52^{**}	0.50^{*}	0.52^{*}	0.77^{***}	0.02	0.10	0.08	0.001	0.003
		SM8	0.43^{**}	0.61^{**}			0.88^{***}	0.01			0.27	
	Aspen	NE7	0.05	0.61^{**}	0.003	0.61^{**}	0.85^{***}	0.001	0.06	0.17	0.11	0.11
		SM8	0.04	0.25			0.78^{***}	0.003			0.09	
1964 -2009	Jack pine	NE7	0.29	0.48^{**}	0.03	0.28	0.35^{*}	0.01	0.18	0.05	0.01	0.09
		SM8	0.41^{**}	0.61^{***}			0.24	0.02			0.19	
	Aspen	NE7	0.13	0.38^{*}	0.01	0.64^{***}	0.76^{***}	0.02	0.11	0.44^{**}	0.03	0.30
		SM8	0.19	0.01			0.55^{***}	0.12			0.03	

[1,2,3,4] and [5] Diff_x means the difference of parameter x between watersheds as x in NE7 – x in SM8.

*, **, and *** indicate $p<0.05$, $p<0.01$, and $p<0.001$, respectively.

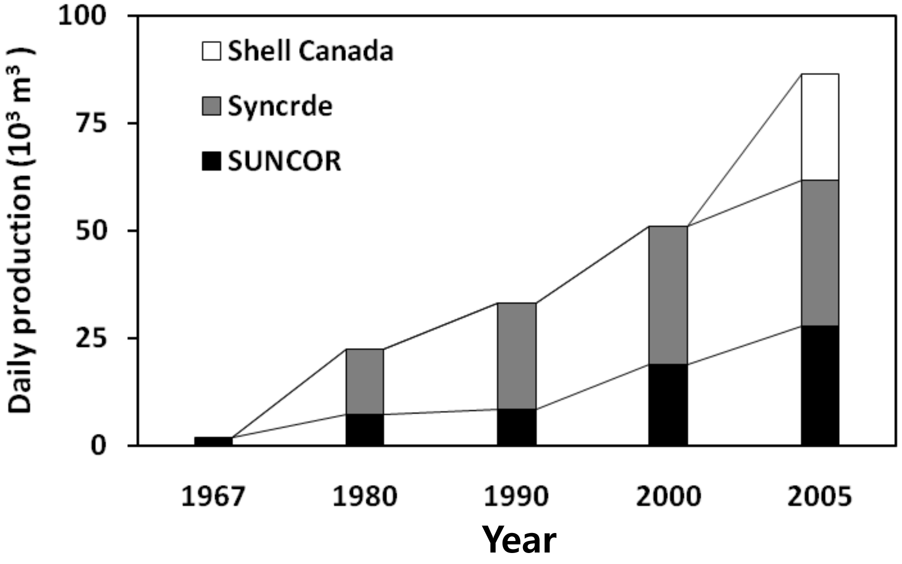

Figure 2-1 Daily oil production by the three major oil companies in the Athabasca oil sands region, Alberta, Canada. Suncor, Syncrude, and Shell Canada started their operations in 1967, 1978, and 2003, respectively.

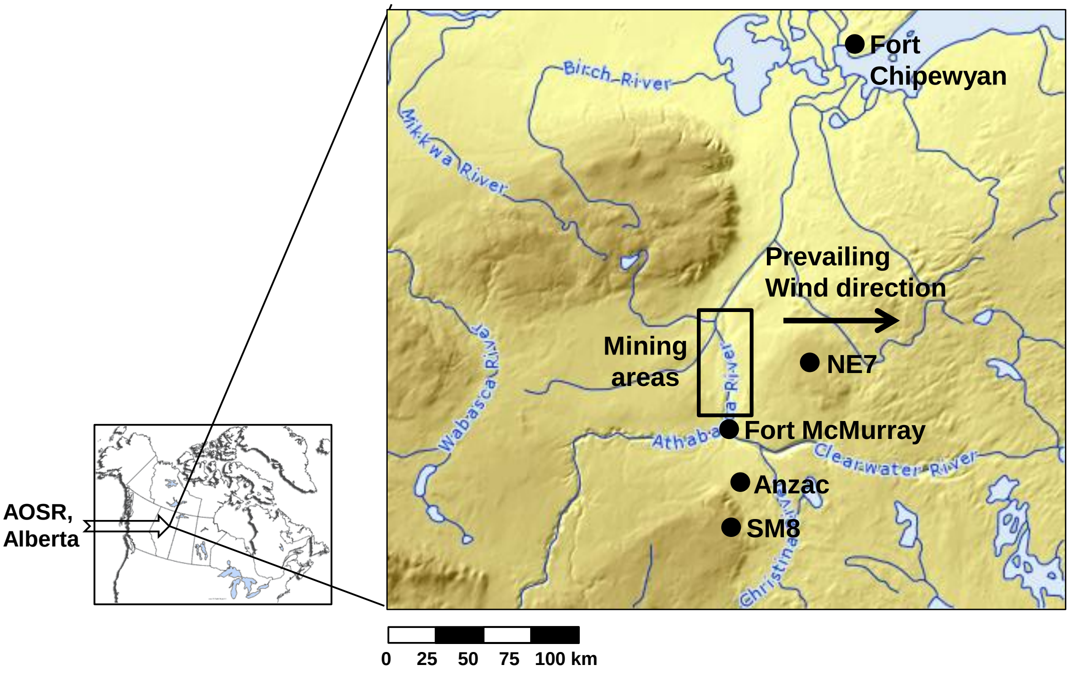

Figure 2-2 The location of the two studied watersheds, NE7 (57.15° N, 110.86° W) and SM8 (56.21° N, 111.20° W), in the Athabasca oil sands region, Alberta, Canada. Prevailing wind directions in the area were east to southeast.

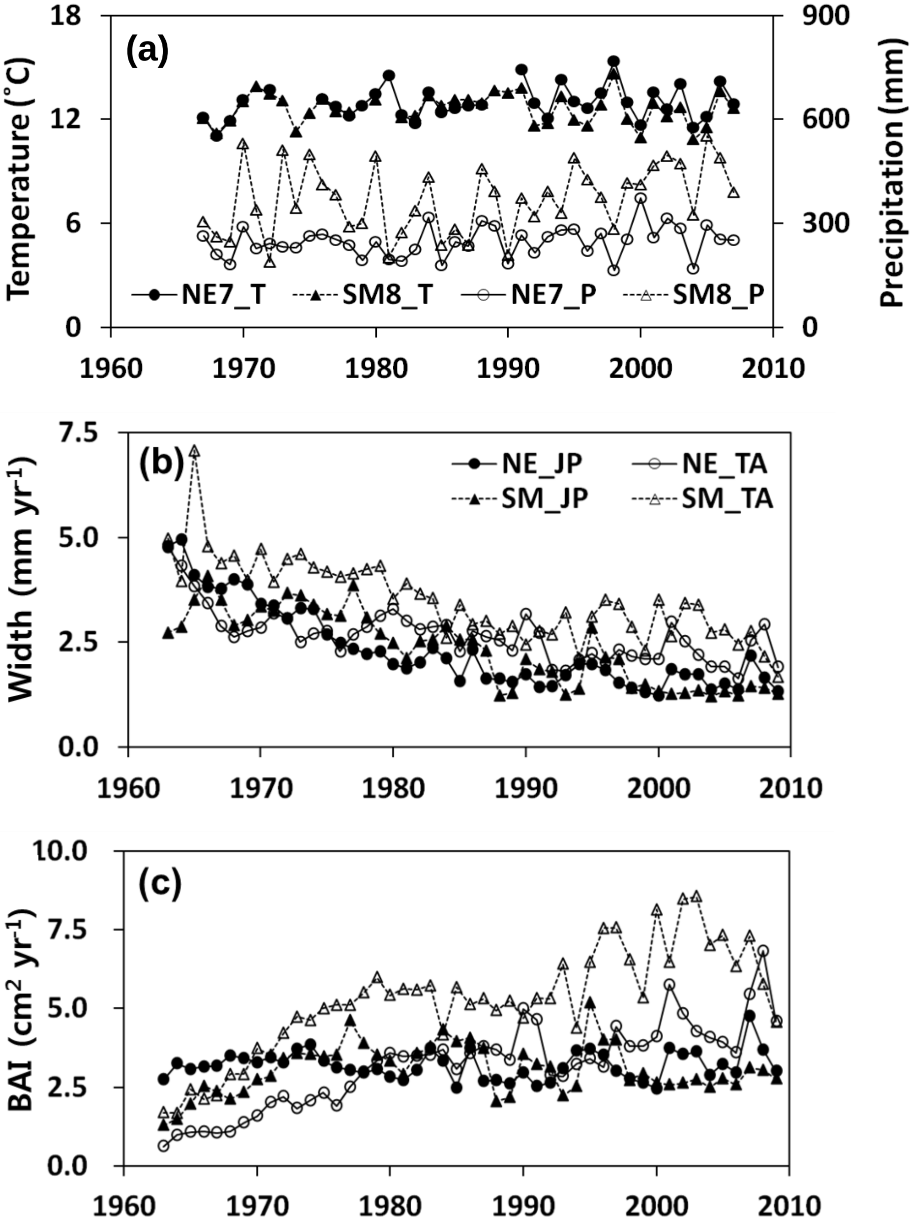

Figure 2-3 Data on (a) summer temperature (T) and precipitation (P) from May to August, (b) annual increment of tree ring width, and (c) BAI (basal area increment of jack pine (JP) and trembling aspen (TA) in NE7 and SM8. Watershed NE7 was closer to the mining and upgrading area.

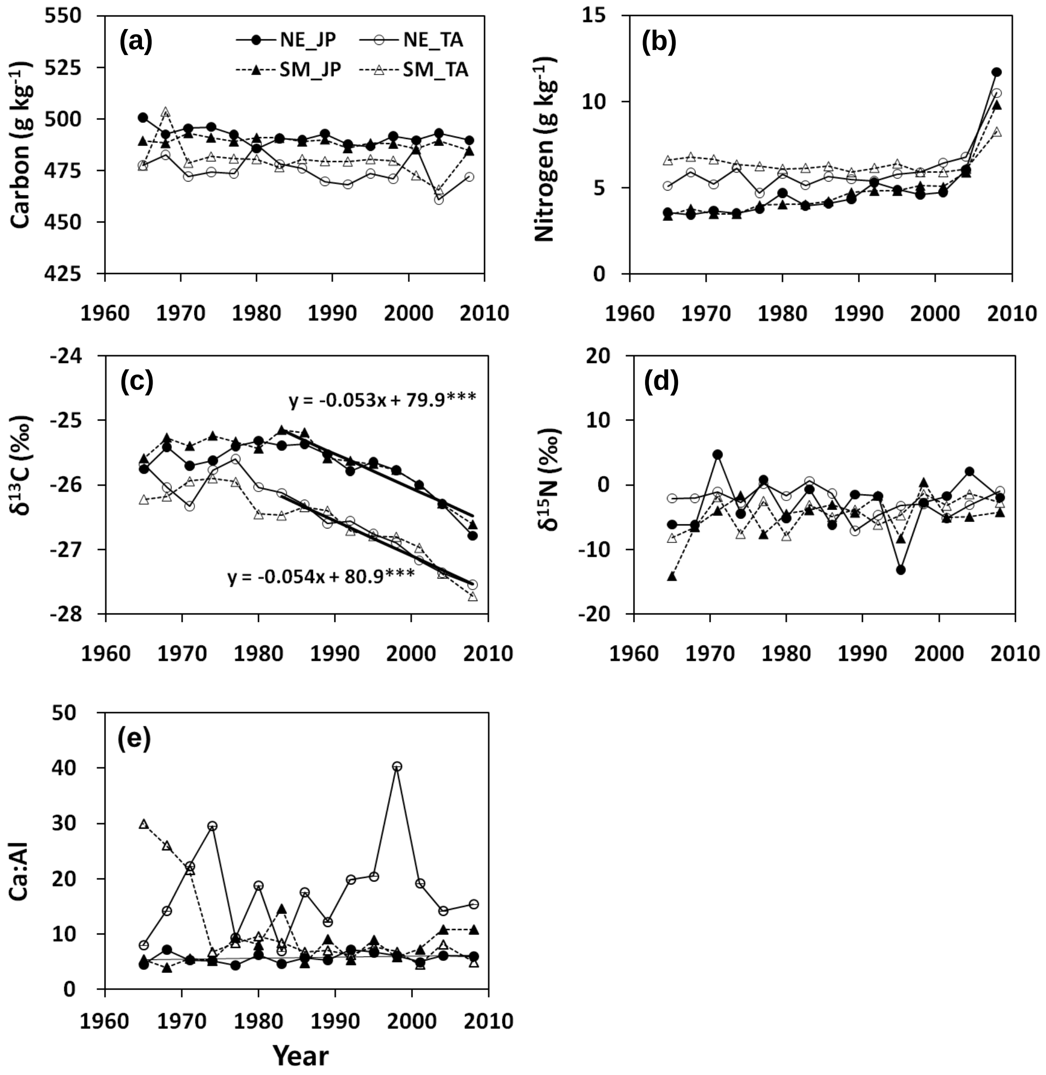

Figure 2-4 Temporal changes in (a) C, (b) N, (c) δ^{13}C, (d) δ^{15}N, and (e) Ca/Al of annual growth rings of jack pine (JP) and trembling aspen (TA) in NE7 and SM8. Watershed NE7 was closer to the mining and upgrading area. The bold solid line in the δ^{13}C graph is the regression line for each tree species from 1982 to 2009.

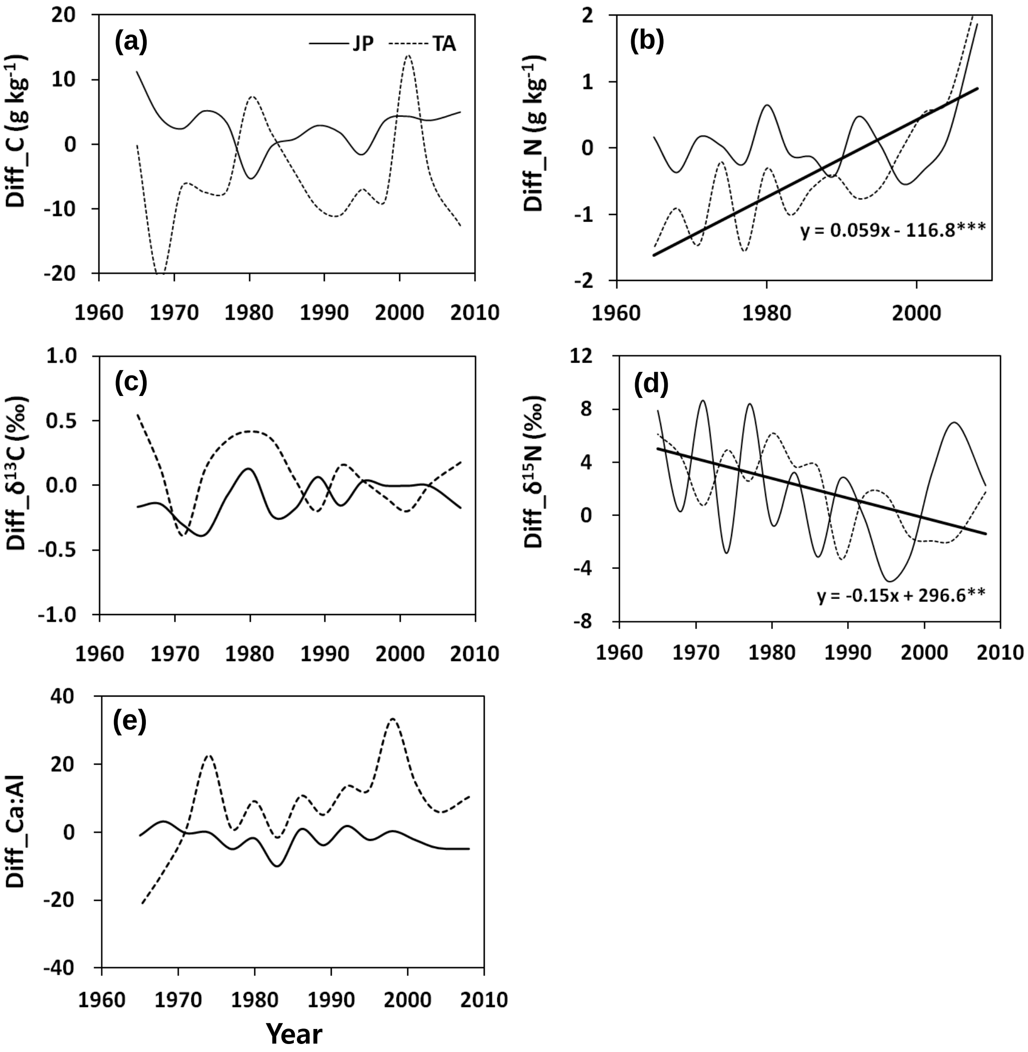

Figure 2-5 Changes over time in the difference of (a) C, (b) N, (c) δ^{13}C, (d) δ^{15}N and (e) Ca/Al between watershed NE7 and SM8 (Diff_x, x is each variable) for jack pine (JP) and trembling aspen (TA) in the Athabasca oil sands region. Watershed NE7 was closer to the mining and upgrading area. Diff_x was calculated as x in SM8 subtracted from x in NE7. The bold lines in Diff_N and Diff_δ^{15}N graphs are the regression lines for trembling aspen.

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Chapter 3. Soil and tree chemistry reflected the cumulative impact of acid deposition in *Pinus banksiana* and *Populus tremuloides* stands in the Athabasca oil sands region in western Canada

1. Introduction

The Athabasca oil sands region (AOSR) is the largest area for open-pit oil sands mining in Alberta, Canada (Humphries, 2008) and a large amount of acid forming compounds has been released to the atmosphere over the past several decades (Hazewinkel et al., 2008). Therefore soil acidification and its adverse effects on forest ecosystems are of concern in the AOSR, especially in acid-sensitive watersheds with soils with low capacities for pH buffering (AMEC, 2009) and SO_4^{2-} adsorption (Jung et al., 2011b) . As the impact of acid deposition on forest ecosystems is the result of long-term chronic exposure, a cumulative indicator can be more useful to show the long-term impact of acid deposition than indicators that respond quickly to recent changes in air quality (Vanguelova et al., 2007a).

Acid deposition and subsequent leaching of strong acid anions such as SO_4^{2-} increase soil acidity and reduce the availability of cationic nutrients such as Ca^{2+} in the ecosystem (Likens and Bormann, 1995). Increasing soil acidity raises

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Jung, K., Chang, S.X., Arshad, M.A., 2012. Soil and tree chemistry reflected the cumulative impact of acid deposition in *Pinus banksiana* and *Populus tremuloides* stands in the Athabasca oil sands region in western Canada. Ecological Indicators

Al solubility and Al concentrations (particularly in the forms of Al^{3+} and $AlOH^{2+}$) in the soil (Tejnecký et al., 2010). In acidic soils major forms of Al ions such as Al^{3+} and $AlOH^{2+}$ are toxic to plants (Delhaize and Ryan, 1995). Therefore, soil Al and Ca concentrations are affected by acid deposition, and Al toxicity and Ca deficiency can be common in acidic soils (Clark and Baligar, 1995). In addition to Al^{n+} and Ca^{2+} concentrations in the soil solution, Ca/Al ratios in soil solution and fine roots have been suggested as sensitive indicators for acidity stress in forest ecosystems under elevated levels of acid deposition (Hirano et al., 2007; Innes, 1995; Shortle and Smith, 1988) due to antagonism between Al and Ca uptake (Delhaize and Ryan, 1995). The Ca/Al ratio of soil solution results from changes in soil chemistry due to acid deposition, and the Ca/Al ratios of fine roots can reflect cumulative adsorption of toxic Al in fine roots to exclude Al transport to aboveground plants in acidic soils.

Spatial patterns of soil chemistry such as pH and SO_4^{2-} concentrations around trees can reflect the interaction between acid deposition and tree canopies. Atmospheric deposition occurs through two processes: precipitation deposition (= bulk deposition) and interception deposition (Ulrich, 1983). Bulk deposition occurs vertically by gravity while interception deposition involves aerosols or particulate matters being intercepted by obstacles, which normally happens through fogs, clouds, or dews. Interception deposition leads to increasing atmospheric deposition around trees by throughfall and stemflow; especially, acid materials such as SO_2 mainly travel as aerosols. For example, interception deposition was similar to bulk deposition for base cations but more than twice that of bulk deposition for SO_4^{2-} in Douglas-fir (*Pseudotsuga menziesiis*) stands in the Netherlands (Draaijers and Erisman, 1995). Similar trends were found in European beech (*Fagus sylvatica* L.) stands in Belgium (Staelens et al., 2008), and jack pine (*Pinus banksiana*) and trembling aspen (*Populus tremuloides*) stands in the AOSR (Jung et al., 2011a), indicating that soils around trees are exposed to greater amounts of acid deposition and experience greater changes in soil chemistry than those in open fields.

In addition to differences in depositional processes, tree species affects soil chemistry through a number of other processes: canopy uptake and leaching, organic acid exudation, nutrient uptake and turnover, and litterfall decomposition as affected by the quality and quantity of the litterfall (Augusto et al., 2002; Binkley and Giardina, 1998; Knops et al., 2002; Rhoades, 1996), typically resulting in more acidic soils in conifer stands than in deciduous stands. Decreasing patterns of soil pH and concentrations of base cations in the soil and/or soil solution towards the tree bole have been reported in conifer stands in industrial areas (Zinke, 1962; Riha et al., 1986a; Skeffington, 1983), accompanying decreasing pH and increasing SO_4^{2-} concentrations in stemflow (and throughfall) as compared with bulk deposition due to accumulated acid deposition and organic acid canopy leaching (Staelens et al., 2008; Jung et al., 2011a). On the other hand, reports on spatial patterns of soil chemistry in deciduous stands have not been consistent, with both lower (Sato and Wakamatsu, 2001) and greater acidity towards a tree bole (Skeffington, 1983; Chang and Matzner, 2000) being reported. The deciduous canopy can raise pH of throughfall and stemflow through canopy uptake of H^+ associated with canopy leaching with base cations. Soil acidity in deciduous stands can decrease towards tree boles in the non- or less-polluted areas due to canopy leaching of base cations, while increasing soil acidity can be found towards deciduous tree boles in highly polluted areas due to interception deposition of acid substances.

In this study, we assessed the acid stress of trees in acid-sensitive watersheds in the AOSR, based on Ca/Al ratios of soil solution and fine roots and investigated the spatial variation of soil chemistry such as pH and SO_4^{2-} concentrations that can indicate cumulative changes in soil chemistry caused by acid deposition. A better understanding of soil solution chemistry and the spatial variability in soil properties caused by tree species and canopy interaction will substantially help us better assess and understand the impact of atmospheric deposition on terrestrial ecosystems.

2. Materials and methods

2.1 Site description

Two watersheds, NE7 and SM8, in the AOSR were selected for this research. Watershed NE7 (57.15° N, 110.86° W) is located northeast of Fort McMurray, Alberta, Canada, while SM8 (56.21° N, 111.20° W) is located south of Fort McMurray. Climate conditions are similar in both watersheds. The mean annual temperature is 0.7 ˚C with a mean relative humidity of about 67%. The mean annual precipitation and evaporation are 456.4 and 486.3 mm, respectively (Ok et al., 2007). Both watersheds are dominated by approximately 60-year-old trembling aspen (aspen) and jack pine () trees in upland forests. Black spruce was dominant in low-lying areas and wetlands. Common soil types in upland forests of both watersheds are coarse textured Dystric Brunisolic soils and Gray Luvisolic soils (Bertsch and Bloom, 1996) in the Canadian system of soil classification (Soil Classification Working Group, 1998) and they belong to Boralf in US Soil Taxonomy (Soil Survey Staff, 1994).

Five 20 × 20 m plots were established in each watershed in 2005. Three plots were jack pine dominated stands and the other two plots were aspen dominated stands distributed across the landscape in each watershed. Detailed information is described in Appendix I and II.

2.2 Water sampling and analysis

Bulk precipitation, throughfall, and stemflow collectors were installed in November 2005 to collect the first sample in May, 2006. The collectors for bulk deposition and throughfall consisted of a 1 L bottle, a funnel (10 cm radius) with a screen (1 x 1 mm opening size), and a PVC tube covered by aluminum foil. The PVC tube was pushed about 5 cm into the soil and served as a stand for the funnel and the bottle for collecting the water sample was housed within the PVC tube. Three bulk deposition collectors were installed in open areas near experimental plots for collecting in each watershed. Three throughfall collectors were installed in each plot by placing the collectors below the canopy of dominant trees. Three stemflow sample collectors were also set up in each plot. Stemflow was gathered in collecting bottles of 4 L capacity through an opened-up tygon tube glued around a bole from breast height to collectors on the ground, placed alongside the tree bole. Collectors for bulk deposition, throughfall, and stemflow were replaced every month during the growing season from May to October from 2006 to 2009 and in May 2010.

To collect soil solutions, two stainless steel zero-tension lysimeters were installed at each of the 15 (within the main rooting zone) and 45 cm (beyond the main rooting zone) soil depths in May, 2008. The water collection area of each lysimeter was 500 cm^2. Soil solution was collected every month during the growing season from June to October in 2008, from May to October in 2009, and in May 2010. All collecting bottles were washed with 20% HCl solution and rinsed with deionized water in the laboratory. A few drops of 0.1 g L^{-1} phenyl mercury acetate were added to each container prior to deployment to the field to minimize microbial activities in water samples in between samplings.

All samples were stored in a refrigerator before analysis. A portion of each sample was filtered with 0.22 μm syringe filters before chemical analysis. The pH was measured with an AR20 pH meter (Fisher Scientific Ltd., US). Concentrations of Ca^{2+}, Mg^{2+}, K^+, and Al^{n+} were measured using an ICP-MS (Elan 6000 quadrupole, Perkin-Elmer, Inc., USA). Concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ ions were analyzed with ion chromatography (DX 600, Dionex Corp., USA). The Ca/Al ratio was calculated based on a molar unit (same below for soil and plant samples).

2.3 Soil sampling and analysis

To collect soil samples, three canopy trees were selected in each plot. Soil samples were collected at 5 cm and 90 cm away from each tree bole from two layers in July, 2009: forest floor, i.e., the organic LFH (litter, partially decomposed litter and humified organic matter) horizons over the mineral soil, and 0-5 cm surface mineral soil (defined as surface mineral soil) in July, 2009, to evaluate the response of soils to changes in atmospheric deposition. The samples from the same layer were mixed to form a composite sample for each plot. Soil samples were air-dried and crushed to pass through a 2-mm sieve. Soil pH was measured using 10 g of air-dried soil in 20 mL of deionized water (40 mL for forest floor) using an AR20 pH meter (Fisher Scientific Ltd., USA). Available SO_4^{2-} as the sum of water soluble and adsorbed forms was extracted from 5 g of soil with 50 mL 500 mg P L^{-1} solution made from $Ca(H_2PO_4)_2$ (Kalra and Maynard, 1991). After filtration through a 0.45 µm nylon membrane filter, available SO_4^{2-} was analyzed with a DX 600 ion chromatograph. Exchangeable and water soluble cations (including Ca^{2+}, Mg^{2+}, K^+, Na^+, and Al^{n+}) were determined after extraction with 1 mol L^{-1} NH_4Cl and deionized water, respectively, at a ratio of 5 g soil (2 g for forest floor) to 100 mL extractant and after being shaking for 1 hour (Kalra and Maynard, 1991). The Cu-extractable Al was determined to include soluble, exchangeable and organic forms of Al (Ritchie, 1995). Five grams of soil (2 g for forest floor) was extracted with 100 mL of 0.5 mol L^{-1} $CuCl_2$ and shaken for 1 hour (Bertsch and Bloom, 1996). After filtration through a 0.45 µm nylon membrane filter, cation concentrations in the filtrates were analyzed using a Perkin Elmer Elan ICP-MS described above.

2.4 Tree sampling and analysis

Four canopy trees of the dominant species with a range of diameter at breast height (DBH) were selected near each plot for destructive sampling so that the research plots were not disturbed. The following components of each tree were collected in July, 2008: foliage, branch, bark, wood, coarse roots (diameter > 50 mm), medium roots (2 to 50 mm), and fine roots (< 2 mm). Foliage and branch samples were collected from the middle part of the canopy with a pole pruner, bark samples were collected at breast height (130 cm) using a chisel, and wood samples were obtained at breast height with an increment borer with 5 mm diameter. To collect root samples, soils pits (approximately 30 × 30 × 30 cm) around the selected trees were dug out and roots were cut from the stump for collecting coarse and medium root samples. A part of the dug soil was transported to the lab and fine root samples were separated from the sampled soil in the lab. Six litterfall traps of 10 cm diameter and 10 cm deep were set up in each plot and litter samples were collected every month during the growing season from May to October from 2006 to 2009 and in May 2010. Samples were rinsed using running distilled water to remove surface contamination that maybe caused by deposition and soil particles. All samples were placed in the oven and dried for 72 hours at 70 ˚C. Samples were ground to pass through a 40-mesh sieve using a Wiley mill (GE motors, US). For analysis of total Ca, Mg, K and Al concentrations, ground plant samples were digested at 125 ℃ for 4 hours using concentrated HNO_3 in a digestion block and 30% H_2O_2 was added to remove residuals (Cambell and Plank, 1998). Cation concentrations were determined using a Perkin Elmer Elan ICP-MS described above.

2.5 Statistical analysis

Analysis of variances (ANOVA) was performed to determine the effects of watershed and tree species on water, soil, and plant chemistry. Paired t-tests were performed to analyze the effects of the distance from a tree bole on soil chemistry. Ion concentrations in precipitation water and Ca/Al ratios of soil solutions were logarithmic transformed before ANOVA to ensure normality of distribution and homogeneity of distribution. All statistical analyses were performed using version 9.01 of SAS (SAS Institute Inc., Cary, NC), using an α value of 0.05.

3. Results

3.1 Effects of canopy on precipitation chemistry

The chemistry of precipitation changed after passing through the canopy (Figure 3-1). The pH of bulk deposition, on average, was 5.2 in NE7 and 4.7 in SM8. The pH of jack pine stemflow decreased by 1.6 and 0.7 units in NE7 and SM8, respectively, from those of bulk deposition in each watershed while pH of aspen stemflow increased by 0.5 and 1.4 units in NE7 and SM8, respectively (Figure 3-1). Sulfate concentrations in bulk deposition, on average, were 2.0 and 1.3 mg L^{-1} in NE7 and SM8, respectively, and concentrations of base cations as the sum of

Ca^{2+}, Mg^{2+}, and K^+, on average, were 1.6 and 1.2 mg L^{-1} in NE7 and SM8, respectively. Compared to the bulk deposition, ion concentrations of SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, and Al^{n+} increased in stemflow and throughfall with both tree species in both watersheds while NO_3^- and NH_4^+ concentrations remained the same or even decreased after passing through the tree canopy due to canopy uptake of N (Figure 3-1). Sulfate concentrations in stemflow were greater ($p<0.05$) in jack pine than in aspen while the reverse ($p<0.01$) was true for Ca^{2+}, Mg^{2+}, and K^+.

3.2 The spatial variability of soil chemistry

Most of the studied soil chemical properties were affected by tree species and watershed. The pH was lower ($p<0.001$) in jack pine than in aspen in the forest floor but was not affected by tree species in the surface mineral soil. The pH of both forest floor and surface mineral soil decreased ($p<0.05$) towards jack pine boles (except for forest floor in SM8) while pH values were similar or greater at 5 cm than at 90 cm from aspen boles (Figure 3-2). Available SO_4^{2-} concentrations were similar between watersheds even though SO_4^{2-} deposition rates were different ($p<0.05$) between the watersheds. Available SO_4^{2-} in the forest floor accumulated ($p<0.05$) near tree boles compared to 90 cm from tree boles (Figure 3-2), with concentrations greater ($p<0.05$) in jack pine than in aspen stands. Exchangeable and water soluble base cation concentrations were affected by watersheds and tree species while effects of distance from tree boles were found in water soluble base cation concentrations but not in exchangeable base cation concentrations (Table 3-1 and Figure 3-2). Water soluble base cation concentrations were greater ($p<0.05$) in SM8 than in NE7 and greater ($p<0.01$) in aspen than in jack pine stands. Soluble base cation concentrations decreased ($p<0.05$) towards jack pine tree boles in both soil layers while they remained similar or increased ($p<0.05$ in forest floor in NE7) towards aspen tree boles (Figure 3-2). Soluble and exchangeable Al^{n+} concentrations were greater ($p<0.01$) in SM8 than in NE7, and were greater ($p<0.01$) in jack pine than in aspen stands in the forest floor while not different between the species in the mineral soil (Table 3-1). Differences between tree species on base cation and aluminum concentrations resulted in characteristic Ca/Al ratios in the soil. The Ca/Al ratios in soil solution in the forest floor in aspen stands ranged from 4.3 to 9.1 near a tree bole but decreased to a range between 0.4 and 5.3 at 90 cm from a tree bole. On the other hand, jack pine stands showed increasing ($p<0.01$) water soluble Ca/Al ratios in the forest floor with a distance from a bole: 0.3 to 1.5 at 5 cm and 1.5 to 4.8 at 90 cm. The Ca/Al ratios in soil solution of surface mineral soils had similar trends with those of forest floor but with much lower values ($p<0.01$) in surface mineral soil. The Ca/Al ratios in soil solution in surface mineral soils ranged from 0.1 to 3.1 in aspen stands and from 0.1 to 0.8 in jack pine stands.

3.3 Soil solution chemistry with soil depth

The pH of soil solution was lower ($p<0.01$) than that of throughfall in jack pine stands while the reverse ($p<0.01$) was found in aspen stands; no difference in pH was found between soil solutions at 15 cm and 45 cm depths (Figure 3-1 and 3-3). Sulfate concentrations decreased ($p<0.05$) with soil depth in both watersheds

(Figure 3-3). Sulfate concentrations were greater ($p<0.05$) in NE7 than in SM8 in jack pine stands while no difference between watersheds was found for aspen stands. Cation concentrations decreased ($p<0.05$) with soil depth in NE7 associated with decreasing SO_4^{2-} concentrations but similar between the 15 and 45 cm depths in SM8 (Figure 3-3). Aluminum concentrations in the soil solution were greater ($p<0.05$) in SM8 than in NE7. With seasonal and spatial variations, Al^{n+} concentrations in NE7 ranged from 0.6 to 4.1 mg L^{-1} in aspen stands and from 0.2 to 2.3 mg L^{-1} in jack pine stands and in SM8 the values ranged from 0.4 to 7.9 mg L^{-1} in aspen stands and from 0.1 to 8.5 mg L^{-1} in jack pine stands. As a result of greater ($p<0.05$) Al^{n+} concentrations in soil solutions in SM8 than in NE7 and similar Ca^{2+} concentrations in soil solutions between watersheds, Ca/Al ratios were lower ($p<0.01$) in SM8 than in NE7 (Figure 3-3). The Ca/Al ratios of soil solutions in NE7 ranged from 1.1 to 3.0 in jack pine stands and from 2.6 to 4.1 in aspen stands. The Ca/Al ratios of soil solutions in SM8 ranged from 2.4 to 3.5 in jack pine stands and from 1.0 to 1.8 in aspen stands.

3.4 Nutrient concentrations and Ca/Al ratios in tree compartments

Calcium, Mg, and K concentrations in each tree component were normally greater ($p<0.05$) in aspen than in jack pine trees whereas the reverse ($p<0.05$) was true for Al concentrations (Figure 3-4). Calcium in bark, wood, and roots, and K in wood in aspen trees were lower ($p<0.05$) in SM8 than in NE7. For jack pine trees, Ca concentrations in bark and fine roots were lower ($p<0.05$) and Al concentrations in roots were greater ($p<0.05$) in SM8 than in NE7. As a result, molar Ca/Al ratios of both tree species were lower ($p<0.01$) in SM8 than in NE7 in live tree components. Aluminum concentrations were greater ($p<0.05$) in roots than in aboveground biomass; they ranged from 0.6 to 0.8 g kg^{-1} for aspen and 0.8 to 1.4 g kg^{-1} for jack pine in fine roots, and from 0.02 to 0.06 g kg^{-1} for aspen and 0.05 to 0.5 g kg^{-1} in aboveground biomass. The Ca/Al ratio of fine roots were greatest ($p<0.05$) in aspen stands in NE7, lowest ($p<0.05$) in aspen stands in SM8. The Ca/Al ratio of fine roots in NE7 ranged from 6.5 to 7.9 for aspen and from 1.4 to 4.1 for jack pine and those in SM8 ranged from 2.0 to 4.1 for aspen and from 0.7 to 1.1 for jack pine.

4. Discussion

4.1 Soil chemistry reflected the cumulative impact of acid deposition

The greater ($p<0.05$) concentrations of SO_4^{2-} in bulk deposition, throughfall, and stemflow in NE7 than in SM8 were consistent with previous reports that watershed NE7 had been exposed to greater SO_2 concentrations in the air (WBEA, 2010) and greater SO_4^{2-} deposition rates (Wieder et al., 2010). However, available SO_4^{2-} concentrations in the soil were not different between watersheds, implying that cumulative SO_4^{2-} leaching was greater in NE7 than in SM8. This was also supported by greater ($p<0.05$) SO_4^{2-} concentrations of soil solutions in NE7 than in SM8 for jack pine stands; but not for aspen stands. Meanwhile, cation concentrations in soil solutions did not reflect SO_4^{2-} concentrations in soil solutions, likely due to natural variation between sites such as greater exchangeable cation concentrations in SM8 than in NE7 (Jung et al., 2011a).

The cumulative effect of SO_4^{2-} leaching can be exacerbated near tree boles because SO_4^{2-} deposition can increase by interception deposition of tree canopy (Draaijers and Erisman, 1995). In this study, pH and water soluble base cations in the forest floor decreased ($p<0.05$) towards jack pine boles. On the other hand, effects of deciduous trees on the spatial variability of soil chemistry were more complicated, as accumulated interception deposition provides stemflow with acid substances whereas canopy exchange processes can remove H^+ from stemflow and add base cations, and the balance of those opposing processes determines the net effect. Therefore, some studies did not report any significant change of soil pH (Riha et al., 1986a; Riha et al., 1986b) while others suggested increasing (Sato and Wakamatsu, 2001) or decreasing trends (Skeffington, 1983; de Faria et al., 2009) although exchangeable or water soluble cations normally had a tendency to increase towards a tree bole. In this study, soil pH and water soluble Ca^{2+} decreased ($p<0.05$) with increasing distance from aspen trees, which led to the increase ($p<0.05$) of soluble Ca/Al ratios in the vicinity of individual aspen trees, suggesting that base cation supply through canopy leaching from aspen trees was greater over base cation removal by SO_4^{2-} leaching in the AOSR.

Both jack pine and aspen trees influenced the spatial variability of Ca/Al ratios in soil solution. The opposite trend of spatial variability of soil chemistry caused by jack pine and aspen trees led to 5 to 20 times lower Ca/Al ratios in soil solution in the soil around jack pine than around aspen trees. This remarkable difference in the spatial pattern of soil chemistry between different tree species can affect other aspects of boreal forest ecosystems in AOSR such as their succession pathway; seedlings of different species have different sensitivities to Al toxicity (Vanguelova et al., 2007a).

4.2 Assessment of acidity and Al stress in AOSR

The ratio of Ca/Al in soil solution and fine roots has been used to assess acidity and Al stress in forest ecosystems (Vanguelova et al., 2007a; Cronan and Grigal, 1995). In general, threshold levels of Ca/Al ratios leading to a 50:50 risk of acidity stress were suggested to be 1.0 for soil solution and 0.2 for fine roots for the purpose of assessing forest health (Cronan and Grigal, 1995). Based on these critical limits, Ca/Al ratios of soil solution and fine roots did not reach threshold levels of acidity stress in both NE7 and SM8; Ca/Al ratios in soil solution varied from 1.0 to 4.1 and Ca/Al ratios in fine roots varied from 0.7 to 7.9.

Although these threshold levels proposed above have been shown to be practicable for many tree species, threshold levels and sensitivity to Al stress may change for different tree species (Á lvarez et al., 2005; Brunner et al., 2002) and seedlings can be more sensitive to stress than mature trees (Vanguelova et al., 2007b). For example, *Populus* species have been known to be relatively sensitive to acid stress and Al toxicity while *Pinus* species have been reported to be tolerant species (Schaedle et al., 1989). Seedlings of trembling aspen were reported to show visible symptoms of Al toxicity and/or Al-induced Ca deficiencies when soil solution Al concentration was over 0.01 mmol L^{-1} (Lu and Sucoff, 2003) and significant reduction of seedling growth was found for hybrid poplar seedlings at 0.1 mmol Al L^{-1} (Steiner et al., 1984). Since Al concentrations in the soil solution in aspen stands, on average, were 0.07 mmol L^{-1} at 15 cm and 0.03 mmol L^{-1} at 45 cm in NE7 and 0.10 mmol L^{-1} at 15 cm 0.09 mmol L^{-1} at 45 cm in SM8, aspen seedlings in NE7 and SM8 may had already been exposed to Al toxicity even though dominant canopy aspens might not had been suppressed by acid stress.

In boreal forests in northern Alberta, aspen stands are commonly succeeded by *Picea* species: white spruce in upland sites and black spruce in wetlands (Beckingham and Archibald, 1996). Black spruce seedlings are relatively tolerant to Al toxicity (Hutchinson et al., 1986) while white spruce seedlings have been known to be sensitive to Al toxicity and their growth can be inhibited by 0.05 to 0.25 mmol L^{-1} of Al^{n+} in the soil solution (Hutchinson et al., 1986; Nosko et al., 1988). Based on our data, the acidity and Al concentrations in the studied soils may alter the succession of the current forest to white spruce dominated stands. Future research on the effects of Al toxicity on forest succession would help us understand the impact of acid deposition on forest ecosystem dynamics in acid-sensitive watersheds.

5. Conclusions

Available SO_4^{2-} accumulated in forest floor near trees reflected increased SO_4^{2-} deposition by interception deposition in the AOSR, regardless of tree species or watershed studied. In jack pine stands, because of increased SO_4^{2-} leaching pH and soluble base cation concentration decreased towards tree boles while the reverse was found in aspen stands due to canopy leaching of base cations. Such contrasting effects resulted in remarkable difference in the spatial distribution of soil chemistry near trees between jack pine and aspen stands. The Ca/Al ratios of soil solution and fine roots did not reach the threshold level of acidity stress even though chronic S deposition had occurred for the past several decades in the acid-sensitive watersheds we studied. Because of temporal and spatial variations, however, acid stress resulting from localized soil acidification can still be a concern in the studied watersheds. Aluminum concentrations in soil solution reached the level that could inhibit the growth of aspen and white spruce seedlings; the effects of acid deposition on forest succession should be an area for future research.

Table 3-1 Soil pH, Ca^{2+} and Al^{n+} concentrations of various forms, and molar Ca/Al ratios at 5 and 90 cm from jack pine (JP) and trembling aspen (TA) tree boles in the forest floor and surface mineral soil (0-5 cm) in watersheds NE7 and SM8 in the Athabasca oil sands region, Alberta, Canada

Soil layer	Water-shed	Tree species	pH		Ca_w[1]		Ca_{ex}[2]		Al_w		Al_{ex}		Al_{Cu}[3]		Ca_w:Al_w		Ca_{ex}:Al_{ex}	
					(mmol kg^{-1})													
			5 cm	90 cm	5 cm	90 cm	5 cm	90 cm	5 cm	90 cm	5 cm	90 cm	5 cm	90 cm	5 cm	90 cm	5 cm	90 cm
Forest floor	NE7	JP	3.8b	4.3a	0.6	0.6	35	37	0.24a	0.12b	0.4b	0.7a	11	6.4	1.5b	4.4a	68	34
		TA	6.1a	5.6b	1.3a	0.4b	70	70	0.04	0.13	0.1	0.1	3.5	5.0	9.1a	1.6b	247	264
	SM8	JP	3.9	4.1	0.7b	1.3a	30	24	0.30	0.38	0.7b	1.6a	9.5	12.1	0.3b	1.9a	36	13
		TA	4.8	4.8	1.2	1.3	56	59	0.13	0.24	0.4	0.2	8.2	6.0	6.1a	2.9b	119	216
Surface mineral soil (0-5 cm)	NE7	JP	3.8b	4.0a	0.02	0.02	2.3	2.6	0.03	0.02	0.4	0.6	5.8	3.9	0.2	0.3	2.1	2.0
		TA	4.4	4.0	0.4a	0.2b	8.6	9.3	0.05	0.04	0.4	0.4	5.2	6.9	2.2a	1.0b	11	13
	SM8	JP	4.1b	4.4a	0.07	0.15	5.7	3.3	0.06	0.06	1.9	2.4	11	13	0.2	0.8	1.1	0.7
		TA	4.3a	3.8a	0.6	0.5	21	16	0.14	0.15	2.3b	3.9a	18b	27a	1.1	0.8	4.6	2.0

[1,2, and 3] The subscripts of w, ex, and Cu mean water soluble, exchangeable, and Cu-extractable (including water soluble, exchangeable, and organic) forms of cations, respectively.

Lowercase a and b indicate significant difference between 5 cm and 90 cm at $p<0.05$ for each species and within each watershed.

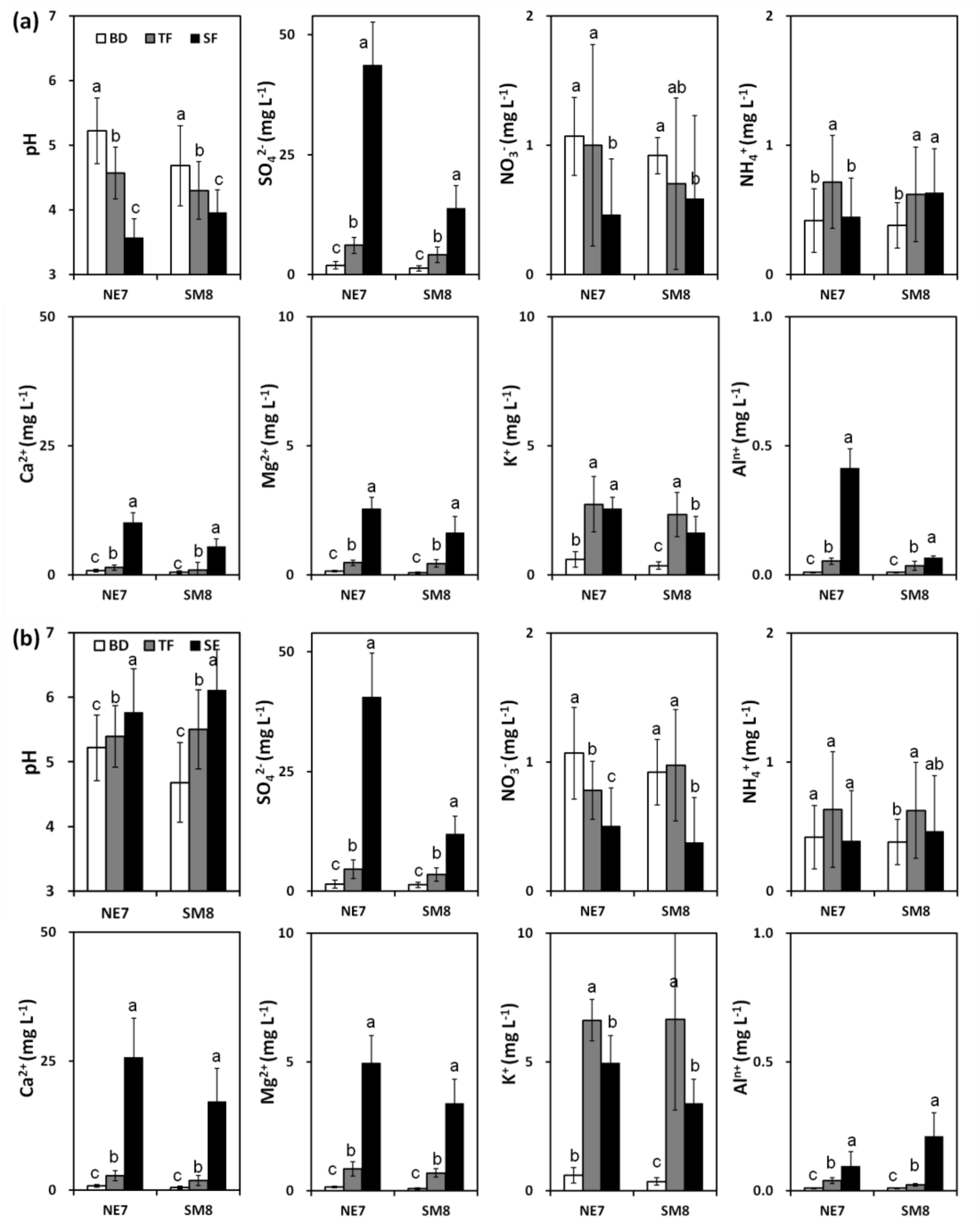

Figure 3-1 Changes in water chemistry through bulk deposition (BD), throughfall (TF), and stemflow (SF) in jack pine (a) and trembling aspen (b) in watersheds NE7 and SM8 in Alberta, Canada. Error bars are standard errors of the mean. Lowercase letters indicate significant differences between deposition type in each watershed at $p<0.05$.

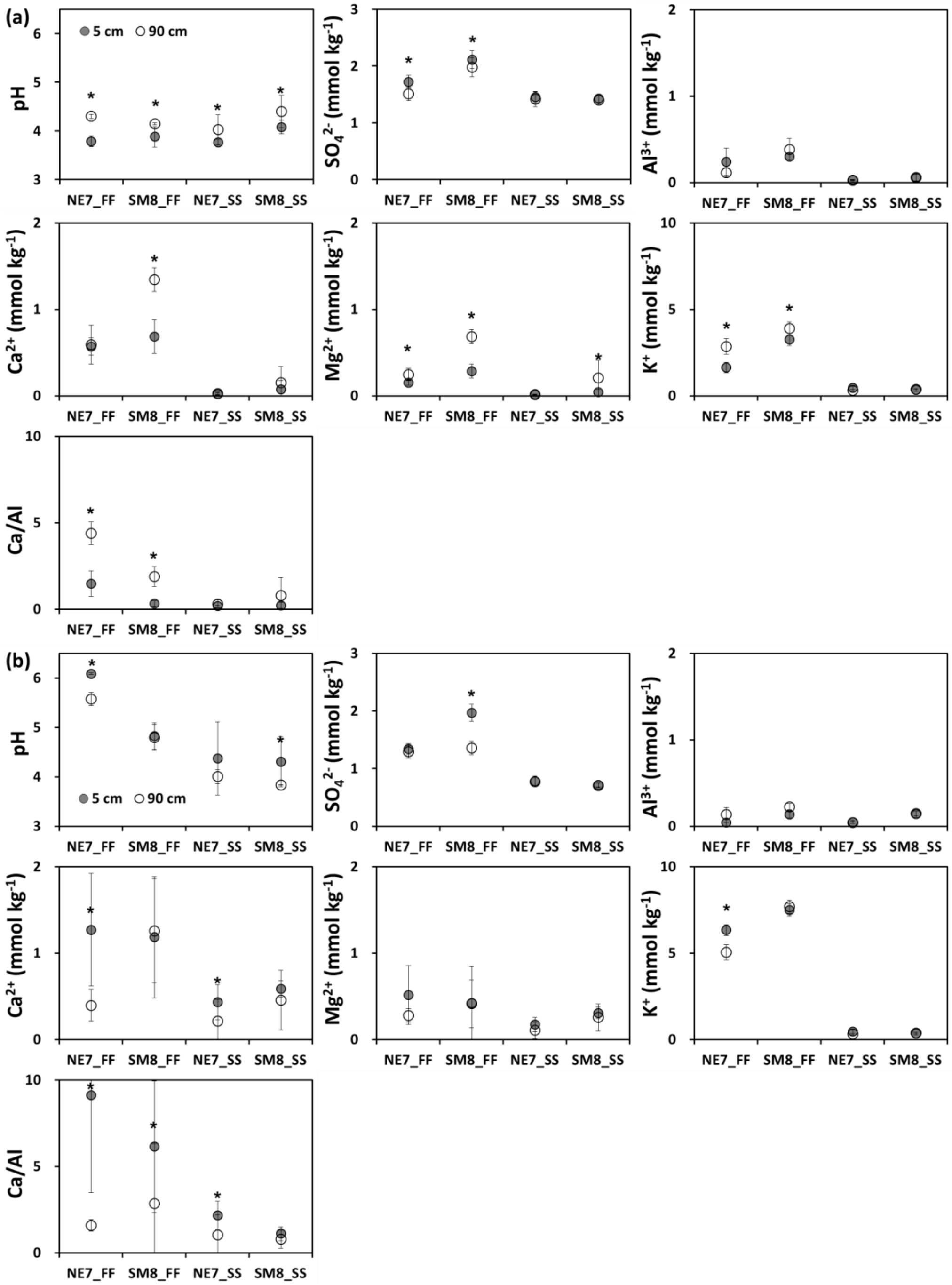

Figure 3-2 Soil chemistry of forest floor (FF) and 0-15 cm surface mineral soil (SS) at 5 cm and 90 cm distance from tree boles of jack pine (a) and trembling aspen (b) in watershed NE7 and SM8 in Alberta, Canada. Sulfate is a sum of soluble and adsorbed forms and cations are soluble forms. * indicates a significant difference between 5 cm and 90 cm in each variable at $p<0.05$. Error bars are standard errors of the mean.

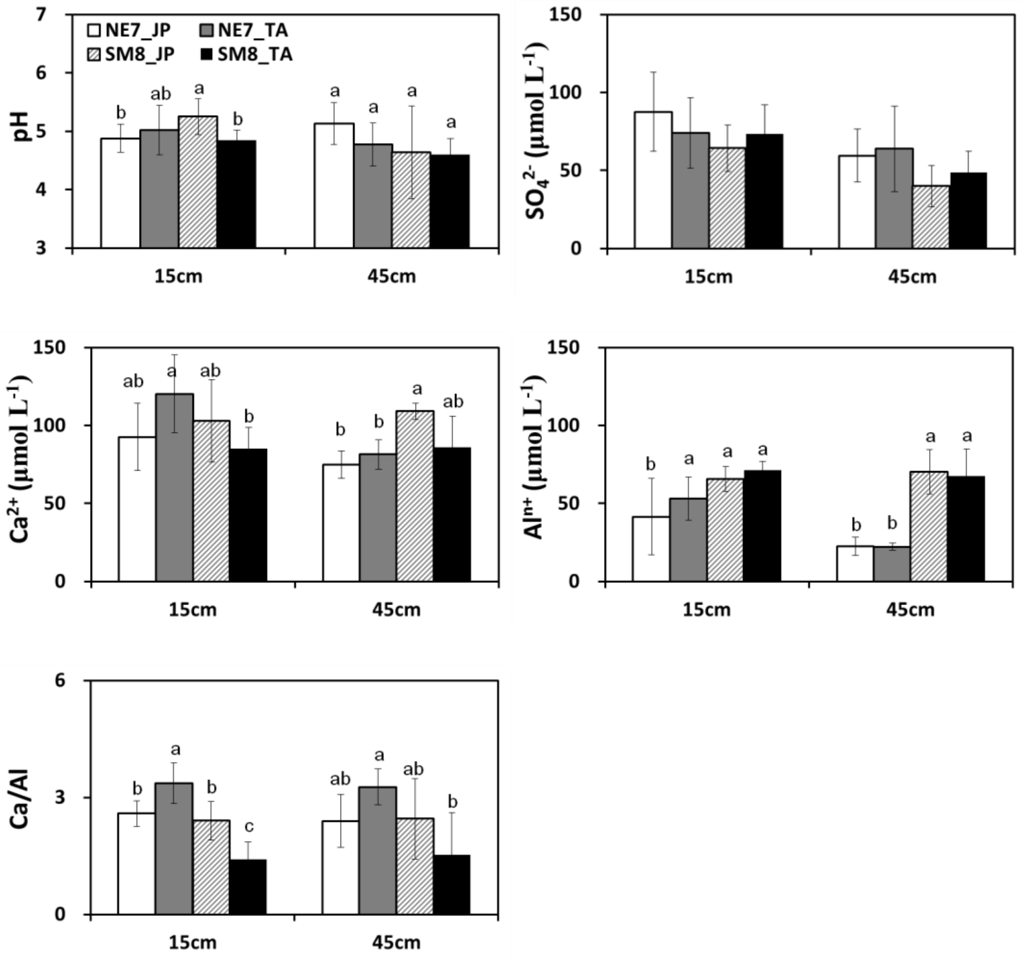

Figure 3-3 Chemistry of soil solution based on leachates collected at 15 and 45 cm depth below the soil surface in jack pine (JP) and trembling aspen stands (TA) in watersheds NE7 and SM8 in Alberta, Canada. Error bars are standard errors of the mean. Lowercase letters indicate significant differences at each depth at $p<0.05$.

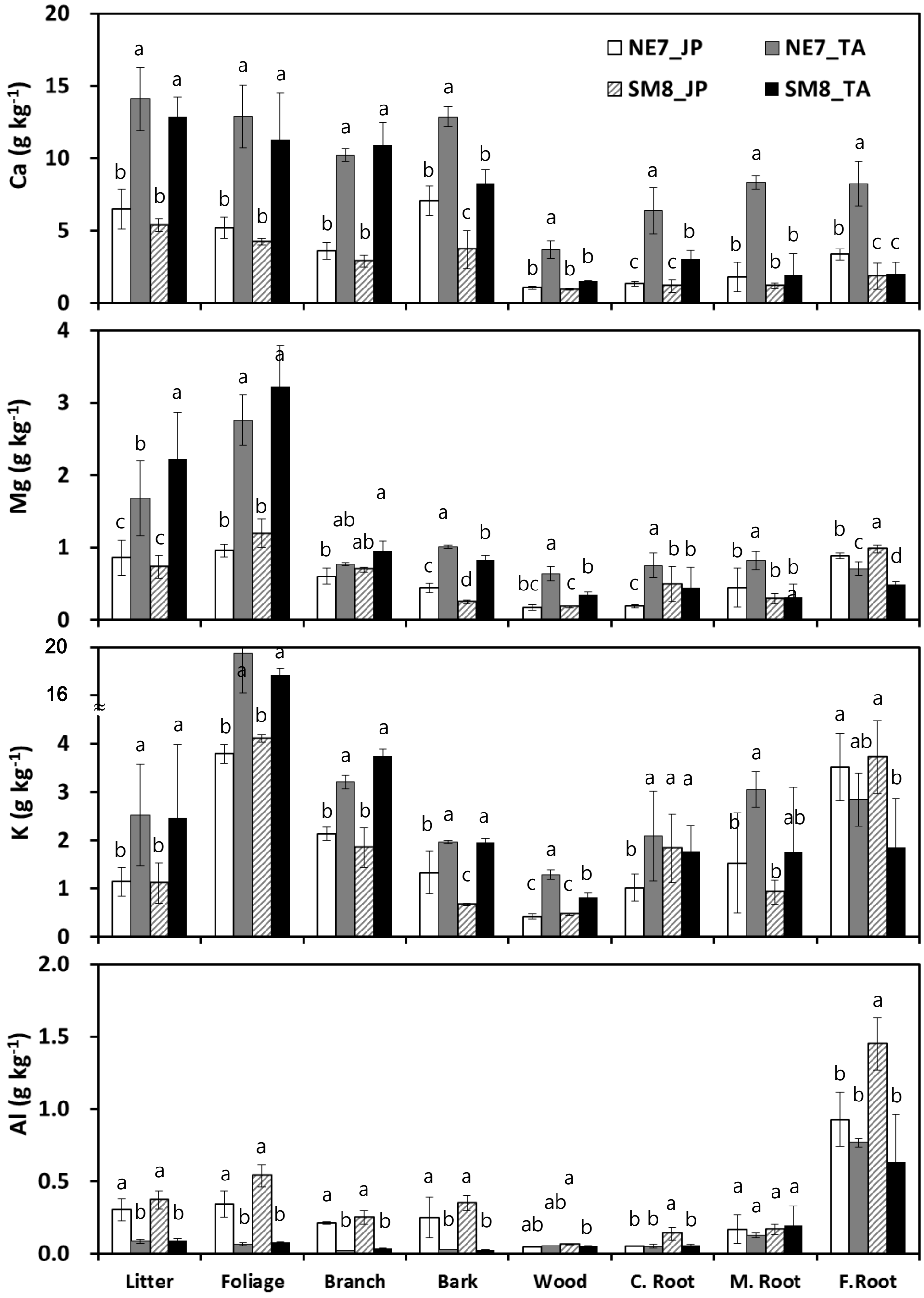

Figure 3-4 Cationic nutrient concentrations in compartments of jack pine (JP) and trembling aspen (TA) trees in watersheds NE7 and SM8, Alberta, Canada. Abbreviations C.root, M.root, and F. root refer to coarse root (>50 mm), medium root (2 to 50 mm), and fine root (<2 mm), respectively. Error bars are standard errors of the mean. Lowercase letters indicate significant differences at each compartment at $p<0.05$.

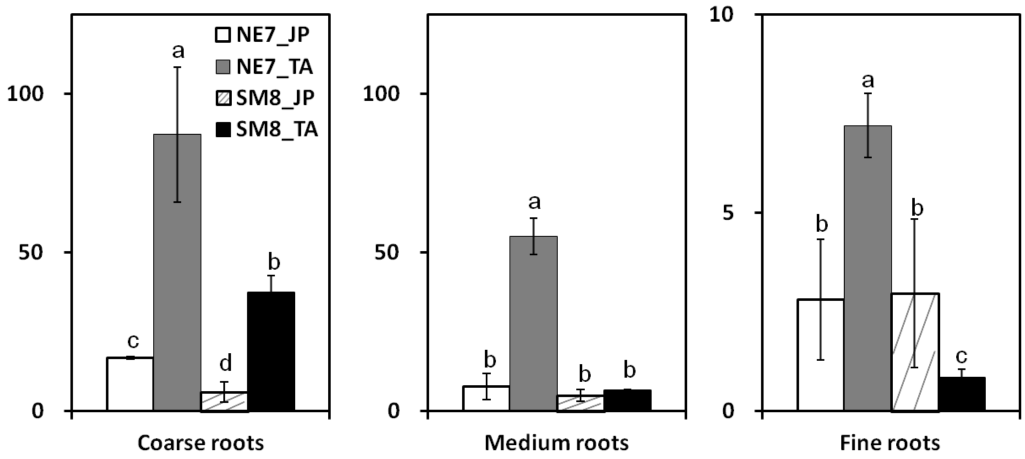

Figure 3-5 The Ca/Al ratios of roots of jack pine (JP) and trembling aspen (TA) in watersheds NE7 and SM8, Alberta, Canada. Diameters of coarse roots, medium roots, and fine roots were >50, between 2 and 50 and <2 mm, respectively. Error bars are standard errors of the mean. Lowercase letters indicate significant differences at $p<0.05$.

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Chapter 4. Effects of canopy-deposition interaction on H^+ supply to soils in *Pinus banksiana* and *Populus tremuloides* ecosystems in the Athabasca oil sands region in Alberta, Canada*

1. Introduction

The Athabasca oil sands region (AOSR) is the largest area for open-pit oil sands mining in Alberta, Canada (Fung and Macyk, 2000). As a result, a large amount of acid forming compounds is released to the atmosphere on a daily basis; this includes 289-359 Mg day^{-1} of SO_2 and 182-334 Mg day^{-1} of NO_x (NSMWG, 2004). With the increased oil sands mining activities that are already occurring and those that have been planned for the near future, the rate of NO_x emission is expected to increase while that of SO_2 is expected to remain stable through increased recovery of S in the upgrading process (Niemi, 2004). The return of acid substances such as nitric acid and sulfuric acid back to ecosystems surrounding the AOSR through dry and wet deposition becomes a significant source of acidity. Therefore, soil and water acidification is of concern in the AOSR to all levels of governments, the industry and the general public.

Acid materials are deposited to forest ecosystems mainly through the canopy. The chemistry of throughfall can be very different from that of bulk

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precipitation as tree canopies can alter precipitation chemistry such as cation and anion concentrations. Interception deposition and canopy exchange are two major processes involved in canopy-deposition interaction that alter throughfall chemistry. Interception deposition involves aerosols or particulate matters being intercepted by the tree canopy, especially through fogs, clouds, or dews, and the dissolution of them on wet surfaces of the canopy (Ulrich, 1983). In areas where atmospheric deposition is affected by emissions of acidic compounds such as SO_2 and NO_x, interception deposition may increase H^+ input into forest soils.

Interception deposition is influenced by tree characteristics. For example, canopies of conifer trees acquire acid deposition more efficiently than that of deciduous trees under the same condition due to the shape of needles and higher crown density (Augusto et al., 2002; Schrijver et al., 2004). Canopy exchange, the other process involved in canopy-deposition interaction, includes canopy uptake and canopy leaching. Canopy uptake of solutes such as NH_4^+, H^+, and NO_3^- takes place through stomatal uptake and ion exchange at the cuticle layer on a leaf surface (Draaijers et al., 1997; Zeng et al., 2005). Canopy leaching occurs through diffusion of cations and the paired anions, mainly organic anions, between the water layer covering the leaf surface and the underlying apoplast as well as a counter process of canopy uptake (Ulrich, 1983; Schrijver et al., 2007; Staelens et al., 2008). Canopy exchange is typically greater in deciduous than in coniferous trees under the same conditions (Schrijver et al., 2007).

The canopy budget model was developed to estimate canopy-deposition interaction (Ulich, 1983). The original model assumed that the ion exchange between H^+ and NH_4^+ and base cations is the only process that induces canopy leaching of base cations. Later, the model was revised to consider canopy leaching of base cations paired with canopy leaching of weak acid anions such as organic anions and bicarbonate (Draaijers et al., 1995; Staelens et al., 2008). However, canopy leaching of H^+ with organic anions is still not clearly accounted for in the model though organic acids have been regarded as a possible source of H^+ in throughfall (Inagaki et al., 1995; Chiwa et al., 2008). Inclusion of H^+ canopy leaching with organic anion leaching in the model would improve our understanding of the role of canopy characteristics in canopy-deposition interaction.

Trembling aspen (aspen, *Populus tremuloides*) and jack pine (*Pinus banksiana*) are widely distributed in AOSR. Aspen as a deciduous tree species has relatively active canopy exchange while jack pine as an evergreen coniferous species is able to intercept aerosols more effectively in the whole year. Such differences between species may cause different canopy-deposition interactions, resulting in different throughfall chemistry and, consequently, different impacts on soil chemistry. This research was conducted to evaluate the rate of H^+ deposition through aspen and jack pine canopies in AOSR and to determine the effects of interception deposition and canopy exchange on H^+ supply between watersheds with different distance from the centre of oil sands mining activities and between stands of different tree species. We incorporated a new term in the canopy budget model to evaluate H^+ canopy leaching paired with organic anions.

2. Materials and methods

2.1 Site description

Two watersheds, NE7 and SM8, selected for this research, are located at different distances from the main acid emission sources of oil sands open-pit mining and upgrading facilities and thus may have different rates of acid deposition (Ok et al., 2007). Watershed NE7 (57.15° N, 110.86° W) is located northeast of Fort McMurray, Alberta, Canada, while SM8 (56.21° N, 111.20° W) is located south of Fort McMurray. Mining areas are mostly located north of Fort McMurray and NE7 was expected to be affected more by anthropogenic emission due to its closeness to the mining area. Climate conditions are similar in both watersheds. The mean annual temperature is 0.7 ˚C with a mean relative humidity of about 67%. The mean annual precipitation and evaporation are 456.4 and 486.3 mm, respectively (Ok et al., 2007).

Both watersheds are dominated by jack pine and aspen in upland forests and black spruce (*Picea mariana*) in low-lying areas and wetlands. The common soil types in upland forests of both watersheds are Elluviated Brunisolic soils and Luvisolic soils in the Canadian system of soil classification (Soil Classification Working Group, 1998) and they belong to Boralf in US Soil Taxanomy (Soil Survey Staff, 1994). Five 20 × 20 m plots were established in each watershed in 2005. Three plots were jack pine dominated stands and the other two plots were aspen dominated stands in each watershed.

2.2 Water sample collection and analysis

2.2.1 Water sample collection

Collectors for bulk precipitation and throughfall were replaced every month during the growing season from May to October from 2006 to 2009. The collectors consisted of a 1 L bottle, a funnel (10 cm radius) with a screen (1 x 1 mm opening size), and a PVC tube covered by aluminum foil. The PVC tube was pushed into the soil about 5 cm and served as a stand for the funnel and the bottle for collecting water was housed within the PVC tube. The collectors were installed in November 2005 and the first sample collection occurred in May, 2006. The bottles were all acid (20% HCl solution) washed and rinsed with deionized water in the laboratory. A few drops of 0.1 g L^{-1} phenyl mercury acetate were added to each container prior to deployment to the field to minimize microbial activities in the water samples in between samplings. Three collectors were installed in open areas near experimental plots for collecting bulk precipitation samples in each watershed. Bulk precipitation includes wet and dry deposition falling vertically into the collector. Three collectors for throughfall samples were installed in each plot by placing the collectors below the dominant tree canopy.

2.2.2 Laboratory analysis

All samples were measured for their volume and kept in a refrigerator. A portion of each sample was filtered with 0.22 μm syringe filters before analysis. The pH, major cation and major anion concentrations of water samples were determined. The pH was measured with an AR20 pH meter (Fisher Scientific Ltd., US). Concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, and Al^{3+} were measured using an ICP-MS (Elan 6000 quadrupole, Perkin-Elmer, Inc., Shelton, CT). Concentrations of SO_4^{2-}, Cl^-, NO_3^-, and NH_4^+ ions were analyzed with ion chromatography (DX-600, Dionex Corp., Sunnyvale, CA). The sum of weak acid anions was calculated as the difference in charge equivalent concentration of cations (Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, and NH_4^+) minus strong acid anions (SO_4^{2-}, NO_3^-, and Cl^-). Charge valence of Al ion was calculated based on $Al(OH)_3$ equilibrium in water (Marion et al., 1976; Bohn et al., 2001). Concentrations of each carbonate ion species were calculated using equilibrium constants of H_2CO_3 in water, pH of water, and atmospheric CO_2 concentration of 387 ppm in 2009 (Bohn et al., 2001; NOAA, 2010).

2.3 Canopy-deposition interaction

The canopy budget method was used to separate throughfall into bulk precipitation, interception deposition and canopy exchange (Staelens et al., 2008):

$$TF_x = BD_x + ID_x + CE_x \qquad (1)$$

where TF is throughfall deposition, BD is bulk deposition, ID is interception deposition, CE is canopy exchange, and x denotes a solute.

Canopy exchange includes both canopy leaching and canopy uptake. Canopy leaching has a positive sign and canopy uptake has a negative sign. Canopy exchange of Na^+, Al^{3+}, SO_4^{2-} and Cl^- was assumed to be negligible (Ulich, 1983; Draaijers et al., 1996) and interception deposition of them was calculated as $TF_x - BD_x$. To estimate interception deposition and canopy leaching of Ca^{2+}, Mg^{2+}, and K^+, it was assumed that particles containing them have the same deposition velocity as particles containing Na^+ (Ulich, 1983; Schrijver et al., 2007). Interception deposition and canopy leaching of these ions were calculated using the following equations:

$$IDF_{Na} = (TF - BD)_{Na} / BP_{Na} \qquad (2)$$

$$ID_x = BD_x \times IDF_{Na} \qquad (3)$$

$$CL_x = TF_x - BD_x - ID_x \qquad (4)$$

where IDF is the interception deposition fraction, CL is canopy leaching, and x denotes Ca^{2+}, Mg^{2+} or K^+.

Canopy uptake and interception deposition of NH_4^+ were estimated using four different methods with a contribution of ion exchange processes to canopy leaching of base cations; canopy uptake of NH_4^+ and H^+ equal to 100, 75, 50, and 25% of canopy leaching of base cations (CU100, CU75, CU50, CU25, respectively) (van der Mass and Pape, 1991; Thimonier et al., 2005).

$$\sum LE_{BC} = [CU_H + CU_{NH4}] + LE_{WA\_BC} \qquad (5)$$

$$a = [CU_H + CU_{NH4}] / \sum LE_{BC} \qquad (6)$$

$$CU_H = a \times \sum LE_{BC} / \{1 + 1 / [6 \times (TF_H / TF_{NH4} + BD_H/BD_{NH4}) /2]\} \qquad (7)$$

$$CU_{NH4} = a \times \sum LE_{BC} - CU_H \qquad (8)$$

where LE and CU are canopy leaching and canopy uptake, respectively, BC is base cations as the sum of Ca^{2+}, Mg^{2+}, and K^{+}, WA_BC is weak acid anion associated with base cation leaching, and a is the contribution factor of ion exchange to base cation leaching as 1, 0.75, 0.5, or 0.25.

Canopy uptake and interception deposition of NO_3^- were calculated using IDF_{SO4} (Ignatova and Dambrine, 2000; Zimmermann et al., 2006). Interception deposition of H^+ was calculated using the following equation modified from Mulder et al. (1987):

$$ID_H = ID_{SO4} + ID_{NO3} - ID_{NH4} \qquad (9)$$

Canopy leaching of H^+ with weak acid anions and with organic anions, respectively, was evaluated using the following equations:

$$\sum LE_{WA} = LE_{WA\_H} + LE_{WA\_BC} \qquad (10)$$

$$\sum LE_{WA\_H\_OA} = LE_{WA\_H} - LE_{WA\_H\_CO3} \qquad (11)$$

where WA, WA_H, WA_H_OA, and WA_H_CO3 are weak acid anions, weak acid anions associated with H^+ leaching, organic anions associated with H^+ leaching, and carbonate ions associated with H^+ leaching.

To determine the $LE_{WA\_H\_OA}$ and the contribution factor of ion exchange (a in equation 6), regression equations were developed using estimated $LE_{WA\_H\_OA}$

at CU100, CU75, CU50, and CU25 for jack pine and aspen stands, respectively. The $LE_{WA\_H\_OA}$ and the contribution factor were estimated using the regression curves and two boundary conditions: 1) ID:BD of NH_4^+ was not greater than ID:BD of SO_4^{2-} (Ignatova and Dambrine, 2000; Zimmermann et al., 2006) and 2) release of organic acids should be equal to or greater than zero.

2.4 Soil sampling and analysis

Soil samples were collected from 3 layers: forest floor (the organic LFH horizons over the mineral soil), 0-15 cm mineral soil (defined as surface mineral soil), and 15-45 cm (subsurface) mineral soil from each plot in July 2005. Soil samples were air-dried and crushed to pass through a 2-mm sieve. Soil texture was determined using the hydrometer method (Gee, 2002). Soil pH was measured in 0.01 mol L^{-1} $CaCl_2$ (pH_{CaCl2}) using 10 g of air-dried soil in 20 mL of solution (40 mL for forest floor). Each sample was further ground with a ball mill and used for total C and N analysis with a Carlo Erba NA 1500 elemental analyzer (Carlo Erba Instruments, Milano, Italy). Available ammonium and nitrate concentrations were determined using a Dionex DX-600 ion chromatography after extracting the soil samples using 2 mol L^{-1} KCl at the 1:10 (w:v) ratio (Kalra and Maynard, 1991). Exchangeable cations including Ca^{2+}, Mg^{2+}, K^+, Na^+, and Al^{3+} were determined after extraction with 1 mol L^{-1} NH_4Cl at a ratio of 5 g soil to 100 mL extractant and after being shaking for 1 hour. After filtration through a 0.45 μm nylon membrane filter, cation concentrations in the filtrates were analyzed using a Perkin Elmer Elan ICP-MS.

2.5 Statistical analysis

Paired t-test was conducted to compare differences between watersheds of properties related to bulk deposition, while analysis of variances (ANOVA) was performed to determine effects of watershed and tree species on soil properties, interception deposition, and canopy exchange. Regression equations were developed to estimate canopy leaching of organic acids. All statistical analyses were performed using version 9.01 of SAS (SAS Institute Inc, Cary, NC).

3. Results

3.1 Soil properties

The pH was lower in jack pine than in aspen stands in both watersheds in the forest floor ($p<0.01$) but was not different in the mineral soil (Table 4-1). In mineral soils, total C and N were similar between watersheds (Table 4-1). Exchangeable base cation (BC) concentrations in the whole soil profile were generally greater ($p<0.05$) in aspen than in jack pine stands in both watersheds (Table 4-1). Exchangeable Al concentrations in the forest floor were greater in jack pine than in aspen ($p<0.05$), but the highest exchangeable Al concentration was found in mineral soils in aspen stands in SM8 (Table 4-1). The BC:Al ratios were significantly greater in aspen than in jack pine stands in both watersheds ($p<0.01$ in the forest floor, $p<0.001$ in the surface mineral soil, and $p<0.01$ in the subsurface mineral soil). Subsurface mineral soils had greater BC:Al than surface mineral soils ($p<0.001$). Surface mineral soils generally had a higher sand content and had lower nutrient availabilities than subsurface soils.

3.2 Bulk precipitation and throughfall

The annual SO_4^{2-} deposition in bulk precipitation was greater ($p<0.05$) in NE7 than in SM8 while no difference in NO_3^- deposition was found between the watersheds (Figure 4-1a). Bulk depositions of SO_4^{2-} and NO_3^- were as much as 2.3 kg S ha^{-1} yr^{-1} and 0.9 kg N ha^{-1} yr^{-1}, respectively, in NE7, and 1.6 kg S ha^{-1} yr^{-1} and 0.9 kg N ha^{-1} yr^{-1}, respectively, in SM8. Bulk depositions of Ca^{2+} and Mg^{2+} were greater ($p<0.05$) in NE7 than in SM8 (Figure 4-1a). No difference between the watersheds was found for depositions of Cl^-, K^+, NH_4^+, and Al^{3+}. Bulk deposition of H^+ was greater ($p<0.001$) in SM8 than in NE7 even though SO_4^{2-} deposition was greater in NE7 (Figure 4-1a).

Annual deposition of H^+ in throughfall was lower in jack pine stands than that in bulk precipitation while the reverse was true in aspen stands (Figure 4-1). Annual throughfall depositions of most ions (except Na^+ and Cl^-) were significantly different between tree species, especially in SM8 that was less affected by atmospheric deposition (Figure 4-1b). Sulfate deposition in throughfall was greater ($p<0.05$) in NE7 than in SM8 and greater ($p<0.05$) in jack pine than in aspen stands (Figure 4-1b). For other ions, annual throughfall depositions in jack pine stands was greater ($p<0.05$) in NE7 than in SM8 but no significant difference was found between watersheds in aspen stands (Figure 4-1b).

3.3 Canopy-deposition interaction

Of the canopy-deposition interaction that includes interception deposition, canopy uptake, and canopy leaching, SO_4^{2-} and Ca^{2+} were the dominant anion and cation, respectively. Interception depositions of SO_4^{2-}, NO_3^-, and Mg^{2+} were greater ($p<0.05$, respectively) in jack pine than in aspen stands in NE7 but no species effect was observed in SM8 (Figure 4-2). Interception depositions of SO_4^{2-}, Ca^{2+}, and Mg^{2+} were greater ($p<0.05$, respectively) in NE7 than in SM8 in jack pine stands only (Figure 4-2). The ratios of interception deposition to bulk deposition (ID:BD) for SO_4^{2-} in throughfall were 1.62 in jack pine and 1.39 in aspen while those for Ca^{2+}, Mg^{2+} and K^+ were between 0.41 and 0.52 for both tree species (Figure 4-2). Interception deposition of NH_4^+ was greater ($p<0.01$) in aspen stands using CU100, CU75, and CU50 while no difference was found between tree species and watersheds using CU25 (Figure 4-2c).

Canopy leaching of Ca^{2+} ($p=0.024$), Mg^{2+} ($p<0.001$), and K^+ ($p<0.001$) was greater in aspen than in jack pine with no difference between the watersheds, with canopy uptake of NH_4^+ greater ($p<0.001$) in aspen than in jack pine stands in both watersheds (Figure 4-3).

3.4 Sources and sinks of H^+ in throughfall

Sources of H^+ in throughfall were bulk deposition, interception deposition, and canopy leaching while canopy uptake was a sink for the H^+ (Table 4-2). Bulk deposition of H^+ was greater ($p<0.001$) in SM8 than in NE7. Jack pine canopies intercepted more H^+ in NE7 than in SM8 ($p<0.05$) while no significant difference of canopy uptake and canopy leaching was found between watersheds. Interception deposition was greater ($p<0.001$) in jack pine than in aspen while canopy uptake was the opposite ($p<0.01$). The amount of interception deposition, canopy uptake, and canopy leaching of H^+ varied with the method of calculation used. For example, values of canopy leaching using CU100 ranged from 267.0 to 279.0 mol_c ha^{-1} yr^{-1} in aspen and from 152.1 to 150.9 mol_c ha^{-1} yr^{-1} in jack pine, while they had even negative values with CU25.

Canopy leaching from equilibrium of carbonic acids was similar between watersheds with each tree species. Equilibrium of carbonic acids removed 2.31 mol_c ha^{-1} yr^{-1} of H^+ through canopy-deposition interaction in jack pine stands and added 4.95 mol_c ha^{-1} yr^{-1} of H^+ in throughfall in aspen stands. Estimates of H^+ leaching by organic acids were similar between watersheds for each tree species and ranged from 0 to 6.0 mol_c ha^{-1} yr^{-1} in aspen and from 127.1 to 128.7 mol_c ha^{-1} yr^{-1} in jack pine (Figure 4-4). This means that canopy uptake of H^+ and NH_4^+ could account for 40.1 to 41.4% of base cation canopy leaching in jack pine and 87.9 to 88.6% in aspen. When ID and CU of H^+ were recalculated with these values, on average, ID and CU of H^+ were 169.1 and 189.0 mol_c ha^{-1} yr^{-1}, respectively, in jack pine, and 130.5 and 124.1 mol_c ha^{-1} yr^{-1}, respectively, in aspen stands in NE7 and 139.7 and 165.9 mol_c ha^{-1} yr^{-1}, respectively, in jack pine and 95.4 and 158.6 mol_c ha^{-1} yr^{-1}, respectively, in aspen stands in SM8.

4. Discussion

4.1 Atmospheric deposition in AOSR

Atmospheric deposition of SO_4^{2-} and NO_3^- in NE7 and SM8 were moderately low compared with values of greater than 10 kg ha^{-1} yr^{-1} each for SO_4^{2-} and NO_3^- in areas affected by air pollution in eastern North America (Vet et al., 2004; WMO, 2005), Europe (e.g., Vanguelova et al., 2007), and eastern Asia (e.g., Fujii et al., 2008). However, rates of SO_4^{2-} deposition in NE7 and SM8 that are located in northern Alberta were greater than that in Esther, located in southern Alberta, based on a survey conducted between 1986 and 2002 (Vet et al., 2004).

The rates of SO_2 and NO_x emissions would be different from location to location. In this study, NE7 was expected to have greater acid deposition than SM8 as the former was located closer to and downwind of those emission sources. However, H^+ input through bulk deposition was smaller in NE7 than in SM8 even though the bulk deposition of SO_4^{2-} and NO_3^- was greater in NE7 (Figure 4-1). Base causing materials were also emitted from industrial areas in AOSR, causing greater base cation deposition in NE7 than in SM8 (Figure 4-1). As H^+ input is related to the difference between acid and base depositions (van Breemen et al., 1983), the deposition of acid anions is likely not the best indicator of H^+ input in the AOSR. The emitted SO_2 may travel as aerosols while the major forms of base materials may exist and travel as particulate matters (Niemi, 2004). As particulate matters with base cations travel shorter distances than aerosols carrying SO_2 and NO_x, deposition of base cations from industrial sources was less in SM8 than in NE7 and that would have resulted in greater H^+ deposition in SM8, suggesting that the risk for soil acidification can be greater in forest ecosystems with a greater distance from than those adjacent to emission sources, due to differences in deposition rates of base cations from industrial sources.

Even though the rate of acid deposition in the AOSR was relatively low, the long-term impact of chronic acid deposition still remains a major concern due to increased anthropogenic acid emission over time (Aherne and Shaw, 2010). As the soils in AOSR has been reported to have low pH buffering capacities (Ok et al., 2007; AMEC, 2009), low sulfate adsorption capacities (Whitfield et al., 2010a), and low base cation weathering rates (Whitfield et al., 2010c), the risk for soil and ecosystem acidification is comparatively high and efforts to reduce acid emission should be continued.

4.2 Effects of canopy-deposition interaction on throughfall and soil chemistry

The change in throughfall chemistry has been known to be caused by interception deposition of aerosols in fog, cloud or dew droplets and canopy exchanges including both canopy leaching and canopy uptake (Ulrich, 1983; Draaijers et al., 1997). Interception deposition was normally greater in jack pine than in aspen stands. Leaves that are long and narrow such as needles leaves of conifers can be more efficient to intercept aerosols and particulate matter than circular leaves (Augusto et al., 2002) and coniferous stands are normally taller and have greater leaf area index than deciduous stands on the same site (Cole and Rapp, 1981). The greater difference in acid material interception between tree species in NE7 implied that intercepted materials mainly originated from emissions in surrounding industrial areas. Sulfate was deposited mainly by interception deposition rather than by bulk precipitation while most other solutes were supplied through bulk precipitation, indicating that major deposition pathways of SO_2 may be fogs, clouds, and dews in forest ecosystems in AOSR. It may be caused by the humid continental climates with large diurnal temperature variations, and high relative humidity in the morning in the summer, and low precipitation (Lutgens and Tarbuck, 2007).

In this study, the canopy leaching of base cations was greater in aspen than in jack pine stands (Figure 4-3) and aspen stands had greater concentrations of base cations and BC:Al ratios in the soils than jack pine stands (Table 4-1). Calcium, Mg and K ions can be exchanged or diffused between the water layer covering foliage and bark and the underlying apoplast (Draaijers et al., 1997), indicating that greater leaching in aspen may be influenced by higher concentrations of Ca, Mg, and K in foliage and bark in aspen than in jack pine (Gower et al., 2000). Deciduous trees have been reported to have higher canopy leaching of base cations than coniferous trees, especially pine trees, in various regions (e.g., Augusto et al., 2002; Schrijver et al., 2007). In eastern Canada, canopy leaching from deciduous trees such as sugar maple (*Acer saccharum*) and large-tooth aspen (*Populus grandidentata*) was reported to supply more base cations through throughfall compared with conifer trees such as balsam fir (*Abies Balsamea*) and eastern white pine (*Pinus strobus*) (Neary and Gizyn, 1994; Houle et al., 1999). The greater canopy leaching of cationic nutrients can increase their concentration in infiltration and percolation water. However, loss of base cations through deep seepage has been known to be lower in deciduous stands than in coniferous stands as seepage of base cation is closely related to SO_4^{2-} and NO_3^- leaching and soils in deciduous stands are thus less exposed to acid deposition (Schrijver et al., 2007). It is quite likely that greater amounts of base cations are stored in soils in deciduous stands than in coniferous stands in soluble or exchangeable forms, thereby neutralizing acidity and restricting Al toxicity in acidic soils (Augusto et al., 2002). In addition to canopy-deposition interaction, H^+ leaching from litterfall may also affect soil chemistry. Coniferous litter releases more organic acids and less cationic nutrients than deciduous litter (Augusto et al., 2002; Johansson, 1995). The production of H^+ by litter decomposition should be considered in future studies in estimating the effect of tree species on soil acidification as well as H^+ input by canopy-deposition interaction.

4.3 Canopy leaching of weak acid anion and cation

After the precipitation passed through the tree canopy, weak acid anion concentrations significantly increased in throughfall with both tree species but the weak acid anion composition was affected by tree species (Figure 4-1). The main weak acid anions were organic anions rather than carbonate ion species. Organic anions released in aspen stands were almost balanced with base cations while most organic anions contributed to H^+ supply in jack pine stands (Figure 4-4). To determine the effects of canopy leaching of weak acids or organic acids on throughfall chemistry, some studies directly calculated H^+ supply by organic acids using increment of H^+ and organic C (e.g., Mosello et al., 2008) and others applied the canopy budget model (e.g., Staelens et al., 2008). The former could overestimate the contribution of organic anions in H^+ canopy leaching as excluding canopy leaching of organic anions that are paired with base cations while the latter has focused on contribution of weak acid anion leaching to canopy leaching of base cations. Using the model, canopy leaching of base cations with weak acid anions has been found to be responsible for 23% of canopy leaching of total base cations in mixed evergreen subtropical forests (Zhang et al., 2006), 38-70% in beech (*Fagus sylvatica* L.) forests and 17-53% in sugar maple forests (Staelens et al., 2008), and 50-70% in a northern hardwood forest (Cronan and Reiners, 1983).

In this study, canopy leaching of base cations with weak acid anions was responsible for 58.6-59.9% and 11.4-12.1% of total base cation canopy leaching in aspen and jack pine stands, respectively (Figure 4-4). Canopy leaching of H^+ with organic anions was negligible in aspen stands while it supplied 127.1-128.7 mol_c ha^{-1} yr^{-1} of H^+ in jack pine stands (Figure 4-4). Canopy leaching of H^+ with organic anions from jack pine canopy was about 2/3 that of atmospheric H^+ deposition. Organic acids released from the canopy can include relatively strong organic acids such as oxalic acid ($pK_{a1} = 1.23$, $pK_{a2} = 4.19$) and malic acid ($pK_{a1} = 3.40$, $pK_{a2} = 5.11$) (Chiwa et al., 2008). Organic acids from coniferous trees have been reported to supply significant amounts of H^+ when pH of precipitation water was between 4.0 and 4.5 (Köhler et al., 2000; Mosello et al., 2008). This suggests that H^+ load by organic acid release can be substantial, even greater than atmospheric deposition in unpolluted or slightly polluted forest ecosystems, especially in coniferous stands.

By incorporating a new term in the canopy budget model to account for canopy leaching of organic anions, we were able to determine H^+ supply by canopy leaching of organic acids in this study and we illustrated that such an H^+ source can be significant for coniferous stands. Loading of H^+ by canopy leaching of organic acids has not been considered when critical loads of S and N deposition were assessed (Sverdrup and de Vries, 1994; UBA, 2004; Whitfield et al., 2010b). This study illustrates that if the contribution of H^+ by canopy leaching of organic acids is not considered in establishing critical loads of acid deposition, overestimation of critical loads can occur, especially in conifer stands. We recommend that H^+ loading from organic acid release from canopy should be included in calculating critical loads in coniferous stands in AOSR.

5. Conclusions

Sulfur deposition was relatively high while N deposition was in a relatively low level in forest ecosystems in AOSR based on a three-year study. The dominant anion and cation in atmospheric deposition were SO_4^{2-} and Ca^{2+}, respectively. Sulfate was deposited mainly by canopy interception while base cations through bulk precipitation. In jack pine stands, H^+ deposition in throughfall was greater than that in bulk precipitation while the opposite was true in aspen stands; such differences resulted from the interception deposition and canopy exchange.

Greater deposition of H^+ in throughfall in jack pine than in aspen stands was caused by greater SO_4^{2-} interception deposition, greater organic acid release, and less canopy uptake of H^+ in the former. A modified canopy budget model allowed the evaluation of canopy uptake and canopy leaching of H^+ in both aspen and jack pine stands. Forest soils in jack pine stands were exposed to greater H^+ deposition and had lower BC:Al ratio in both the forest floor and mineral soils than those in aspen stands, due to greater H^+ input by canopy leaching in addition to atmospheric H^+ deposition in the former than in the latter. Therefore, determination of critical loads needs to consider internal processes of forest ecosystems to avoid overestimation, especially in coniferous stands.

Table 4-1 Soil chemistry with soil layers in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in 2005.

Soil layer	Water-shed	Tree species	pH	Total C	Total N	Ex. BC[a]	Ex. Al[b]	BC:Al	Sand	Silt	Clay
				(g kg^{-1})		(cmol$_c$ kg^{-1})			(kg kg^{-1})		
Forest Floor	NE7	JP	3.14	312.8	9.74	18.34	1.01	18.2	/	/	/
		TA	4.26	319.9	15.51	56.36	0.20	279.5	/	/	/
	SM8	JP	3.04	323.0	10.87	21.60	1.71	12.7	/	/	/
		TA	3.60	360.8	18.76	37.65	0.35	106.2	/	/	/
Mineral soil 0-15 cm	NE7	JP	3.55	2.88	0.31	0.66	0.72	0.91	0.78	0.18	0.04
		TA	3.58	3.35	0.34	0.74	0.18	4.03	0.86	0.12	0.02
	SM8	JP	3.80	3.97	0.38	0.34	1.20	0.28	0.81	0.15	0.04
		TA	3.45	6.15	0.59	2.09	3.08	0.68	0.64	0.27	0.10
Mineral Soil 15-40 cm	NE7	JP	3.87	3.47	0.35	2.20	2.28	0.96	0.67	0.19	0.14
		TA	4.06	2.32	0.30	1.04	0.26	4.05	0.84	0.13	0.04
	SM8	JP	4.27	3.43	0.36	0.45	0.89	0.51	0.84	0.12	0.05
		TA	3.68	7.25	0.73	7.93	8.12	0.98	0.34	0.31	0.35

[a] Ex. BC was exchangeable base cation concentration as the sum of Ca^{2+}, Mg^{2+}, K^+, and Na^+.

[b] Ex. Al was exchangeable Al concentration.

Table 4-2 H^+ sources and sinks in throughfall in aspen stands and jack pine stands in NE7 and SM8 calculated by the canopy budget model. Unit used in the table is mol$_c$ ha^{-1} yr^{-1} and the numbers in parentheses are standard errors of the means.

Model	NE7								SM8							
	Jack pine				Aspen				Jack pine				Aspen			
	BD[a]	ID	LE	CU	BD	ID	LE	CU	BD	ID	LE	CU	BD	ID	LE	CU
CU100[b]	39.5	163.5	152.1	203.6	34.3	64.2	267.0	316.9	100.6	137.7	150.9	186.3	106.2	46.5	279.0	396.4
	(5.35)	(36.5)	(40.6)	(32.6)	(6.65)	(43.1)	(43.0)	(53.2)	(30.1)	(12.2)	(25.0)	(51.8)	(35.8)	(24.0)	(59.7)	(69.7)
CU75	/	176.5	108.7	173.1	/	93.1	161.8	237.7	/	142.5	98.5	138.7	/	68.3	158.1	297.3
		(32.5)	(32.3)	(31.7)		(37.9)	(32.3)	(39.9)		(12.8)	(21.6)	(17.5)		(22.5)	(45.8)	(52.2)
CU50	/	189.2	24.9	102.2	/	117.0	53.6	153.5	/	146.8	48.2	92.7	/	85.4	37.2	193.6
		(30.8)	(34.8)	(16.1)		(36.3)	(24.8)	(28.3)		(13.2)	(20.2)	(12.1)		(19.5)	(34.9)	(35.8)
CU25	/	201.7	-38.6	51.1	/	148.5	-54.6	76.7	/	151.8	-3.2	46.4	/	109.5	-83.7	96.8
		(28.6)	(35.5)	(8.1)		(30.8)	(23.7)	(14.1)		(14.1)	(20.8)	(6.0)		(20.4)	(30.5)	(17.9)

[a] BD, ID, LE, and CU denote bulk deposition, interception deposition, canopy leaching, and canopy uptake.

[b] CU100, CU75, CU50, and CU25 mean the canopy budget model using the assumption that canopy uptake of NH_4^+ and H^+ was 100, 75, 50, and 25%, respectively, of base cation leaching.

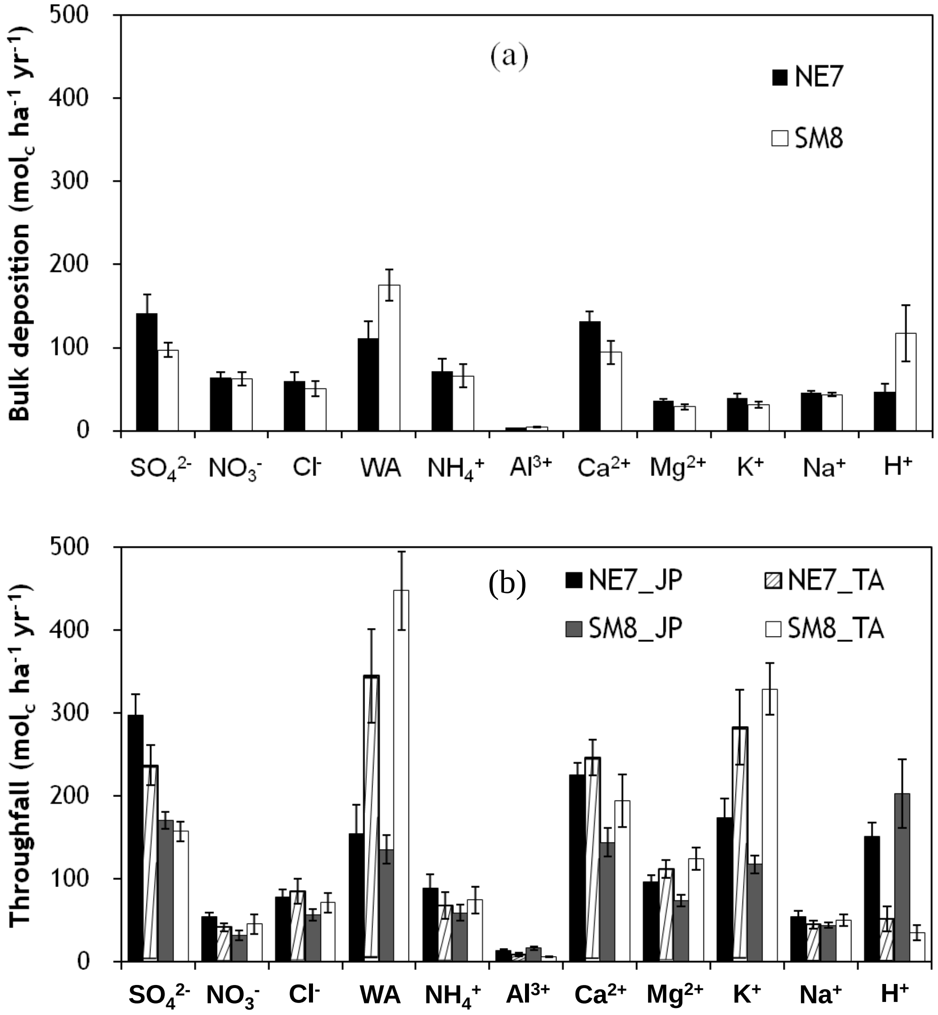

Figure 4-1 Annual deposition by (a) bulk precipitation and (b) throughfall in jack pine (JP) and trembling aspen (TA) stands in NE7 and SM8. WA means weak acid anion calculated based on ion charge balance. Error bars indicate standard errors of the means.

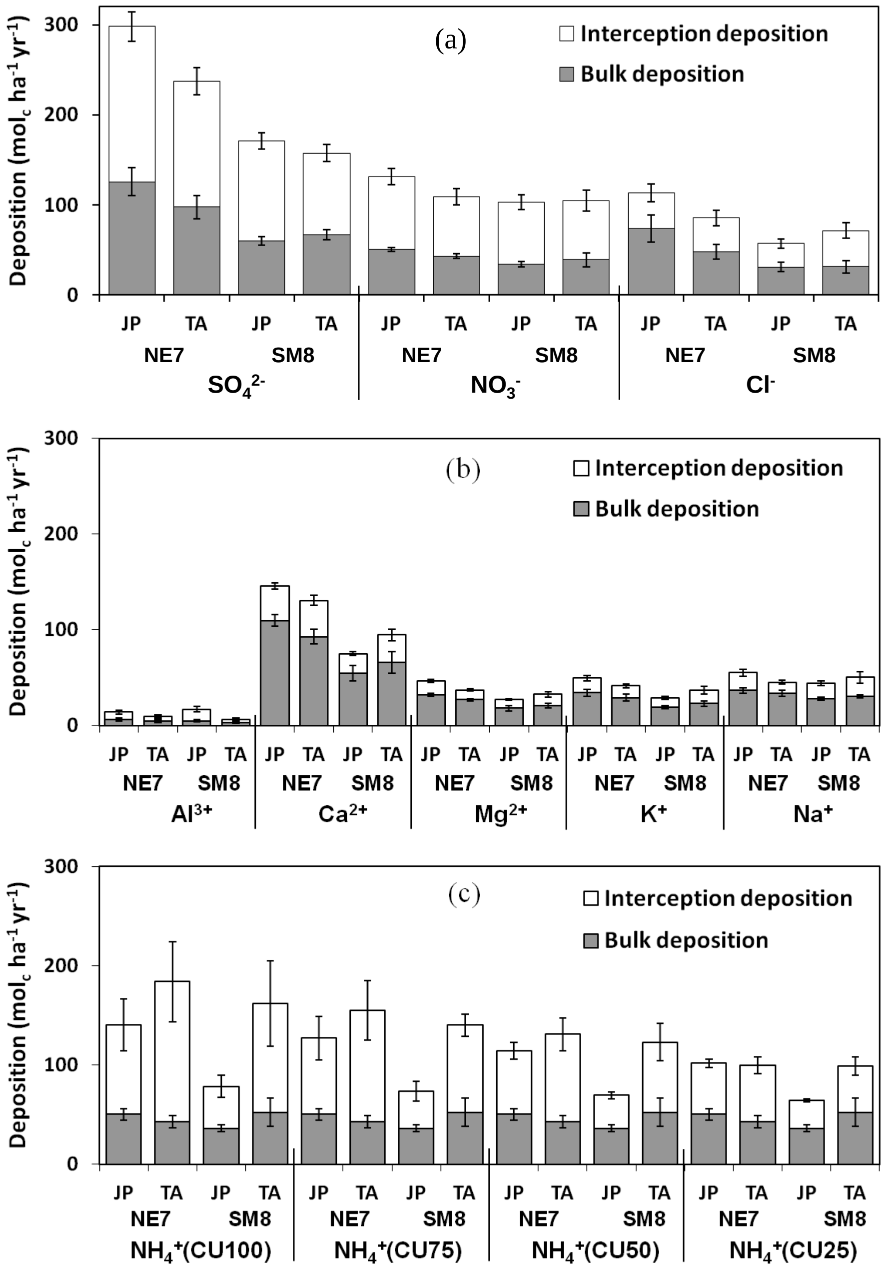

Figure 4-2 Bulk deposition and interception deposition in throughfall in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8: (a) strong acid anions, (b) metallic cations, and (c) NH_4^+. Interception deposition of NH_4^+ was calculated assuming that 100% (CU100), 75% (CU75), 50% (CU50), and 25% (CU25), respectively, of base cation leaching were caused by ion exchange with NH_4^+ and H^+. Error bars indicate standard errors of the means.

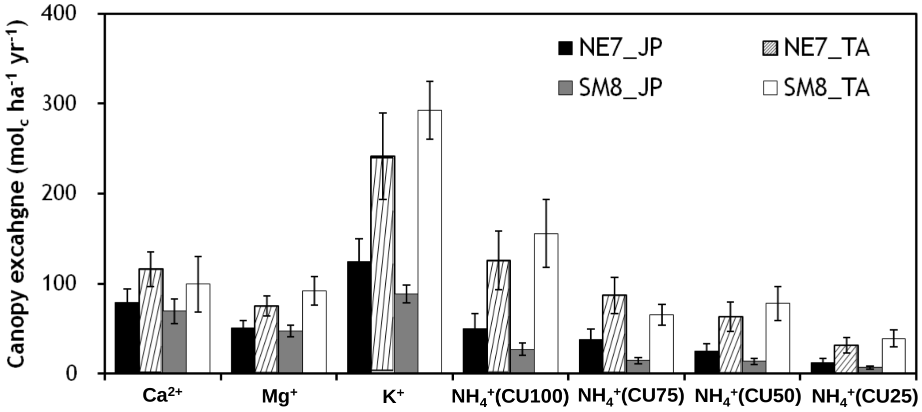

Figure 4-3 Canopy leaching of Ca^{2+}, Mg^{2+}, and K^+ and canopy uptake of NH_4^+ in jack pine (JP) and aspen (TA) stands in watersheds NE7 and SM8. Canopy uptake of NH_4^+ was calculated assuming that 100% (CU100), 75% (CU75), 50% (CU50), and 25% (CU25), respectively, of base cation leaching were caused by ion exchange with NH_4^+ and H^+. Error bars indicate standard errors of the means.

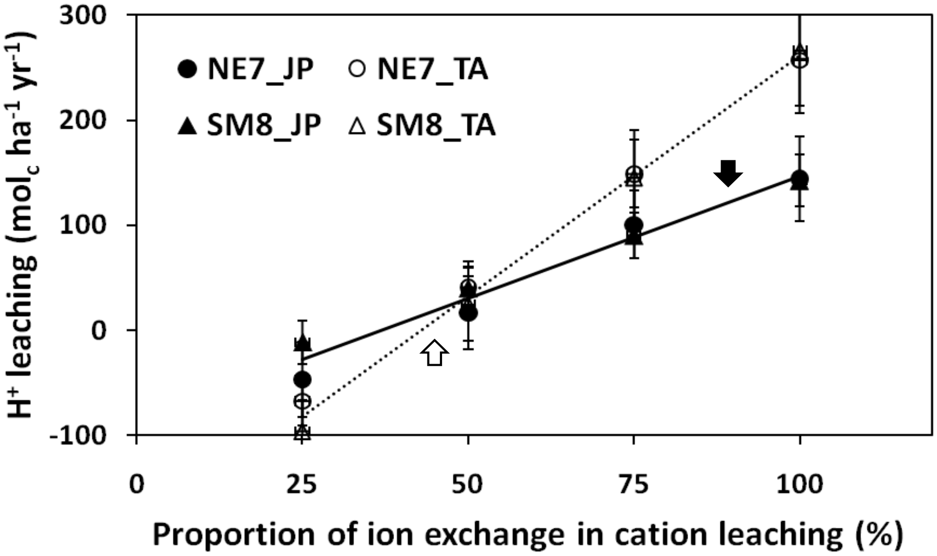

Figure 4-4 The H^+ canopy leaching by organic acids in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 estimated with the canopy budget model. The H^+ leaching was calculated assuming that 100%, 75%, 50%, and 25% of base cation leaching were caused by ion exchange with NH_4^+ and H^+. Close and open arrows indicate points of H^+ leaching and the proportion of canopy uptake in JP and TA, respectively, using interception deposition fraction of SO_4^{2-} for NH_4^+ interception deposition. Solid and dashed lines are regression lines for JP and TA, respectively. Error bars indicate standard errors of the means.

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Chapter 5. Critical loads and H^+ budgets of forest soils affected by air pollution from oil sands mining in Alberta, Canada

1. Introduction

Atmospheric emission of SO_2 and NO_x and their subsequent deposition have been shown to cause changes in elemental biogeochemical cycles and soil acidification in forest ecosystems (Aber et al., 1989; Johnson and Siccama, 1983). The concept of critical load (CL) has been used to estimate acceptable levels of acid deposition and to identify acid sensitive regions (Nilsson and Grennfelt, 1988; Sverdrup and De Vries, 1994), and exceedance (EX) of acid deposition to CL allows us to determine whether the area is under acidification. However, the concept of CL has been developed for practical purposes and CLs have been evaluated by a simple mass balance model (SMB) (Sverdrup and De Vries, 1994; UBA, 2004) including a finite number of parameters. It implies that EX may have limited utility to indicate actual changes in soil acidity. Soil acidification involves a large number of processes where H^+ is either produced or consumed in the soil. The H^+ budget model has been used to quantify soil acidification or alkalinization rate (Fujii et al., 2008; van Breemen et al., 1983) calculating sources (atmospheric H^+ deposition, net assimilation of cations excluding NH_4^+, net anion mobilization, deprotonation of CO_2 or organic acids, and H^+ generation by N transformations) and sinks (H^+ leaching loss, net assimilation of non-nitrogen anions, net cation mobilization, and protonation of weak acid anions) of H^+.

The Athabasca oil sands region (AOSR) is the largest area for open-pit oil sands mining in Alberta, Canada and daily oil production is approximately 90 thousands m^3 (Shell, 2006; Suncor, 2010; Syncrude, 2009). As a result, a large amount of air pollutants is released to surrounding ecosystems on a daily basis and soil acidification is of concern due to chronic acid deposition. The emission of SO_2 peaked at more than 400 Mg day^{-1} between the 1980s and the early 1990s, then decreased to approximately 300 Mg day^{-1} in the mid-2000s while NO_x emission increased gradually from 20 Mg day^{-1} in 1970 to 300 Mg day^{-1} in the mid 2000s (Hazewinkel et al., 2008). However, N deposition is not expected to contribute to soil acidification in the AOSR as boreal forests are N-limited (Hari and Kulmala, 2008); N saturation was not found even in a case of 3-year simulated N application study with 85 kg N ha^{-1} yr^{-1} in eastern Canada (Moore and Houle, 2009) and a 4-year simulated N application study with 30 kg N ha^{-1} yr^{-1} (Jung, 2012). Therefore S deposition has been regarded as the main cause of soil acidification while soil acidification by N deposition is of little concern.

Air pollutants return to the soil through two different pathways: precipitation deposition (= bulk deposition) and interception deposition (Ulrich, 1983). Precipitation deposition occurs through gravity while interception deposition involves aerosols or particulate matters being intercepted by obstacles such as the tree canopy, especially through fogs, clouds, or dews, and the dissolution of them on wet surfaces. The type of tree species can influence interception deposition, with conifer trees intercept acid deposition more efficiently than deciduous trees under the same condition due to the shape of needles and higher crown density (Augusto et al., 2002; De Schrijver et al., 2004). Bulk deposition has been usually used at estimating and mapping CLs in large areas (UBA, 2004), as determining interception deposition is much more complicated than determining bulk deposition (Draaijers and Erisman, 1995), even though interception deposition can constitute a significant portion of the total atmospheric deposition. The chemistry of interception deposition and bulk deposition can be very different, with the proportion of SO_4^{2-} normally greater in interception deposition than in bulk deposition (Draaijers and Erisman, 1995; Jung et al., 2011b; Staelens et al., 2008). Therefore, using bulk deposition only can mislead CLs and EXs in forest ecosystems.

In addition to interception deposition, tree species affects soil chemistry through a number of other processes: organic acid exudation, nutrient uptake and turnover, litterfall (quality and quantity), and so on (Augusto et al., 2002; Binkley and Giardina, 1998; Knops et al., 2002; Rhoades, 1996). Such differences can cause CLs, EXs, and H^+ budgets of soils to be different between tree stands under the same air quality. In this study, we assessed the risk of soil acidification by acid deposition in AOSR based on CLs, EX, and H^+ budgets and tested hypotheses that 1) EXs are underestimated using bulk deposition alone as compared to using both bulk deposition and interception deposition, 2) CLs are lower in coniferous stands than in deciduous stands, and 3) forest soils are being acidified by acid deposition, which is indicated by positive values of EXs and H^+ budgets of soils.

2. Materials and methods

2.1 Site description

Two watersheds, NE7 and SM8, were selected for this research. They were located at different distances from the main acid emission sources of oil sands open-pit mining and upgrading facilities and thus have different rates of acid deposition (Jung et al., 2011b). Watershed NE7 (57.15°N, 110.86°W) is located northeast of Fort McMurray, Alberta, Canada, while SM8 (56.21°N, 111.20°W) is located south of Fort McMurray. Mining areas are mostly located north of Fort McMurray and NE7 was expected to be affected by greater anthropogenic emission rates due to its proximity to the mining area. Climate conditions are similar in both watersheds. The mean annual temperature was 0.7 ˚C with a mean relative humidity of about 67% between 1960 and 1990. The mean annual precipitation and evaporation were 456.4 and 486.3 mm between 1960 and 1990, respectively (OK et al., 2007).

Both watersheds were dominated by *Pinus banksiana* (jack pine) and *Populus tremuloides* (trembling aspen, aspen) in upland forests and black spruce (*Picea mariana*) in low-lying areas and wetlands. The common soil types in upland forests of both watersheds were Dystric Brunisolic soils and Gray Luvisolic soils in the Canadian system of soil classification (Soil Classification Working Group, 1998) and they belonged to Boralf in US Soil Taxonomy (Soil Survey Staff, 1994). Five 20 × 20 m plots were established in each watershed in 2005. In each watershed, three plots were jack pine dominated stands and the other two plots were aspen dominated stands. Detailed information of each plot is provided in Appendix I and II.

2.2 Sampling and analysis

2.2.1 Field sampling and measurement

Soil samples were collected from 3 layers: forest floor (the organic LFH horizons over the mineral soil), 0-15 cm mineral soil (defined as surface mineral soil), and 15-45 cm (subsurface) mineral soil from each plot in July 2005 and in May 2010. Soil samples were air-dried and crushed to pass through a 2-mm sieve. In water sampling, collectors for bulk precipitation and throughfall were replaced every month during the growing season from May to October between 2006 and 2009 and in May, 2010. The collectors were installed in November 2005 to collect the first sample in May, 2006; the design of collectors is described in Chapter 3. Three collectors were installed in open areas near experimental plots to collect bulk deposition in each watershed. Three collectors for throughfall were installed in each plot by placing the collectors below the dominant tree canopy. To determine leaching loss, zero-tension lysimeters were installed at 45 cm soil depths in each plot in May, 2008; the design of the lysimeter was described in Chapter 3. Soil solutions in zero-tension lysimeters were collected every month during the growing season from June to October in 2008, from May to October in 2009, and in May 2010.

For destructive plant sampling, four canopy trees of dominant species in a range of diameter were selected near each plot. Foliage, branch, bark, wood, and course roots were sampled from each selected tree; detailed sampling methods are described in Chapter 3. Plant samples were rinsed quickly with distilled water to remove surface contamination. All plant samples were put in the oven and dried for 72 hours at 70 ˚C. To obtain homogenous samples, samples were ground to pass through a 40-mesh sieve. Diameter at breast height (DBH, measured at 130 cm from the ground) of each tree in each plot was measured in every summer from 2005 to 2009.

2.2.2 Analytical methods

Soil texture was determined using the hydrometer method (Gee and Or, 2002). Soil pH was measured using 10 g of air-dried soil in 40 mL of water for forest floor samples and 20 mL of water for mineral soil samples. Available ammonium and nitrate concentrations were determined using ion chromatography (IC) (DX 600, Dionex Corp., Sunnyvale, CA) after extracting the soil samples using 2 mol L^{-1} KCl at the 1:10 (w:v) ratio (Kalra and Maynard, 1991). Exchangeable cations including Ca^{2+}, Mg^{2+}, K^+, and Al^{3+} were extracted with 1 mol L^{-1} NH_4Cl at a ratio of 5 g soil to 100 mL extractant and after being shaken for 1 hour. After filtration through a 0.45 μm nylon membrane filter, cation concentrations in the filtrates were analyzed using ICP-MS (Elan 6000 quadrupole, Perkin-Elmer, Inc., CT). Available SO_4^{2-} and Cl^-, respectively, as the sum of water soluble and adsorbed forms, were extracted from 5 g of soil with 50 mL 500 mg P L^{-1} solution made from $Ca(H_2PO_4)_2$ (Kalra and Maynard, 1991). For water samples, volume, pH, and concentrations of major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, Al^{n+}, Fe^{n+}, and Mn^{n+}) and major anions (SO_4^{2-}, Cl^-, and NO_3^-) were determined. Each cation concentration and each anion concentration were determined using ICP-MS and IC, respectively. For plant samples, each ground sample was digested using concentrated HNO_3 on a digestion block at 125 ℃ for 4 hours and 30% H_2O_2 was added to remove residuals for the analysis of Ca, Mg, K, Na, Al, Fe, Mn, Cl, and P (Cambell and Plank, 1998) on an ICP-MS. Concentrations of Cl and P in digested-plant solutions were determined with $AgNO_3$ precipitation method and vanado-molybdo-phosphoric yellow color method, respectively (Kalra and Maynard, 1991). Sulfur concentration in each ground plant sample was analyzed with an element analyzer (4010 CHNSO analyzer, Costech analytical technologies, Inc., Switzerland).

2.3 Calculation of H^+ budget, CLs, and EXs

The H^+ budget was calculated considering all sources and sinks of H^+ (van Breemen et al., 1983; Marcos and Lancho, 2002):

$$\begin{aligned} H^+ \text{ budget} &= \sum(\text{Sources}) - \sum(\text{Sinks}) \\ &= H^+_{in} + H^+_{NT} + H^+_{Cat\_up} + H^+_{An\_w} - (H^+_{loss} + H^+_{An\_up} + H^+_{Cat\_w} + H^+_{WA}) \end{aligned}$$

where H^+_{in} is H^+ input in throughfall deposition, H^+_{NT} is net H^+ production by N transformation, $H^+_{Cat\_up}$ and $H^+_{An\_up}$ are net H^+ production and consumption by uptake of cations and anions, respectively, $H^+_{Cat\_w}$, and $H^+_{An\_w}$ are net H^+ consumption and production by weathering and adsorption-desorption of cations and anions, respectively, H^+_{loss} is H^+ loss through drainage, and H^+_{WA} is net H^+

consumption through protonation by weak acid anions. Annual nutrient uptake was calculated using the annual increment of tree biomass and nutrient concentration. Tree biomass was calculated with a set of DBH-based equations (Lambert et al., 2005; Lambert et al., 2005; Kurz et al., 1996; Kurz et al., 1996). H^+_{NT}, $H^+_{An\_w}$, $H^+_{Ca\_w}$, and H^+_{WA} were calculated with the following equations:

$$H^+_{NT} = [((NH_4^+)_{loss} – (NH_4^+)_{in}) – ((NO_3^-)_{loss} – (NO_3^-)_{in})]$$

$$H^+_{An\_w} = \sum(\mathrm{Anion})_{loss} + \sum(\mathrm{Anion})_{up} - \sum(\mathrm{Anion})_{dep}$$

$$H^+_{Ca\_w} = \sum(\mathrm{Cation})_{loss} + \sum(\mathrm{Cation})_{up} - \sum(\mathrm{Cation})_{dep}$$

$$H^+_{WA} = [\sum(\mathrm{cation}_{\ in} - \sum(\mathrm{Anion})_{\ in}] - [\sum(\mathrm{cation})_{loss} - \sum(\mathrm{Anion})_{loss}]$$

where $(X)_{loss}$, $(X)_{in}$, $(X)_{up}$, and $(X)_{dep}$ are drainage loss, input as throughfall deposition, net assimilation, and atmospheric deposition of element (X). ∑(cation) and ∑(anion) were calculated as the sum of H^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, Al^{n+}, Fe^{n+} and Mn^{2+}, and as the sum of $Cl^–$, $PO_4^{3–}$, $SO_4^{2–}$ and $NO_3^–$, respectively; NH_4^+ and NO_3^- were excluded for uptake and PO_4^{3-} was regarded minimal in throughfall and leaching loss. Charges of Al, Fe, Mn, S, and P were 3, 2, 2, -2, and -3, respectively, for nutrient uptake and those of Al^{n+}, Fe^{n+} in throughfall and leaching water were calculated with pH. Units are mol_c $ha^{–1}$ $yr^{–1}$.

The CL of S deposition was calculated with a simple mass balance model (SMB) (Sverdrup and De Vries, 1994; UBA, 2004):

$$CL = BC_{dep} – Cl_{dep} + BC_w – BC_{up} – Alk_{le,crit}$$

$$Alk_{le,crit} = -(H_{crit}Q + Al_{crit}Q)$$

$$H_{crit} = (Al_{crit}/ Q\ K_{Gibb})^{1/3}\ Q$$

$$Al_{crit} = 1.5\ (BC_w + BC_{dep} - BC_{up}) / (BC:Al)_{crit}$$

where BC is base cations as the sum of Ca^{2+}, Mg^{2+}, K^+, and Na^+, BC_{dep} is the atmospheric deposition of BC, Cl_{dep} is the atmospheric Cl^- deposition, BC_w is the weathering rate of BC, BC_{up} is net base cation uptake, Q is precipitation surplus ($m^3\ ha^{-1}\ yr^{-1}$), K_{Gibb} is a dissociation coefficient of gibbsite, and $Alk_{le,crit}$, H_{crit}, Al_{crit}, and $(BC:Al)_{crit}$ are critical leaching rate of alkalinity, H^+, Al^{n+}, and the ratio of BC to Al, respectively.

The CL was calculated with four different methods: two time-scales (long term and short term, $CL_{\_L}$ and $CL_{\_S}$, respectively) × two methods of atmospheric deposition (bulk deposition only and a sum of bulk deposition and interception deposition, $CL_{\_BD}$ and $CL_{\_BD+ID}$, respectively). As base cation taken up by plant can return to soil due to no harvest removal of base cations in AOSR in a long-term scale while base cation uptake can contribute to removal of base cation from soil in a shor-term, $CL_{\_S}$ was calculated including BC_{up} while BC_{up} was excluded for estimated $CL_{\_L}$. Interception deposition was calculated using the canopy budget model with bulk deposition and throughfall deposition (Jung et al., 2011b). The Q was leaching water below 45 cm. The $(BC:Al)_{crit}$ used was 10 and BC_w was based on 45 cm soil depth and determined using the following equation (Ouimet and Duchesne, 2005):

$$BC_w = (0.56\ \text{clay} - 3.72\ \text{clay}^2) \times 365 \times \text{Exp}(3600/281 - 3600/T)$$

where T is the soil temperature.

Exceedance of CL (EX) was calculated as atmospheric S deposition minus CLs.

2.4 Statistical analysis

Analysis of variances (ANOVA) was performed to determine effects of watershed and tree species on measured variables. Correlation analysis was performed among parameters for CLs and H^+ budgets. An α value of 0.1 was chosen to indicate statistical significance due to high variability of the measured variables under field conditions. All statistical analyses were performed using version 9.01 of SAS (SAS Institute Inc, Cary, NC).

3. Results

3.1 Changes in soil properties between 2005 and 2010

Most soil chemical properties were affected by tree species and/or watershed (Table 5-1) rather than sampling period, while changes in pH and available SO_4^{2-} over time were found (Figure 5-1). The pH increased with time in the forest floor ($p<0.01$) but not in the surface or subsurface mineral soils. The pH of the forest floor ranged from 3.31 to 3.87 in jack pine stands and from 3.91 to 4.89 in aspen stands in 2005 while it ranged from 3.79 to 4.04 in jack pine stands and 4.58 to

5.18 in aspen stands in 2010. The pH in jack pine stands was lower ($p<0.001$) than that in aspen stands in the forest floor but was not different in the surface and subsurface mineral soils. Available SO_4^{2-} in the forest floor ($p<0.10$) and surface soil ($p<0.05$) increased, 38.5 and 19.5 mg kg^{-1}, respectively, with time in both watersheds. However, available SO_4^{2-} in the subsurface soil significantly increased in NE7 ($p<0.05$) but not in SM8. Exchangeable cations did not change over time except for Al which showed an increasing trend in the surface and subsurface soil ($p<0.05$).

3.2 Sources and sinks of H^+

3.2.1 Atmospheric deposition, throughfall, and leaching loss

The annual bulk deposition of SO_4^{2-} and base cations were greater ($p<0.05$ for both) in NE7 than in SM8 (Figure 5-2b). The annual interception deposition for $SO_4^{2-}$and base cations was greater ($p<0.05$) in NE7 than in SM8 in jack pine stands whereas no difference was found between watersheds in aspen stands (Figure 5-2b). In addition, interception deposition of SO_4^{2-} and base cations were greater ($p<0.05$ and $p<0.1$, respectively) in jack pine stands than in aspen stands in NE7 but not in SM8. The H^+ input by throughfall in jack pine and aspen stands were 152 and 51 mol_c ha^{-1} yr^{-1} respectively, in NE7, and 203 and 35 mol_c ha^{-1} yr^{-1}, respectively, in SM8 (Table 5-2). The leaching loss of H^+ was not different between watersheds or dominant tree species and ranged from 2.6 to 7.5 mol_c ha^{-1} yr^{-1} (Table 5-2).

3.2.2 Nutrient uptake

Tree biomass increment was greater ($p<0.01$) in SM8 (ranged from 760 to 2035 kg $ha^{-1}yr^{-1}$) than in NE7 (ranged from 370 to 650 kg $ha^{-1}yr^{-1}$) (Table 5-3). Calcium, Mg, K, and S uptake were influenced ($P<0.05$) by tree species as well as watersheds. Net H^+ production caused by nutrient uptake was positive in all plots and greater ($p<0.05$) in SM8 than in NE7 and greater ($p<0.01$) in aspen than in jack pine stands (Figure 5-3).Net H^+ production by assimilation had a positive correlation with annual biomass increment and correlation coefficients were 0.89 ($p<0.1$) in aspen stands and 0.94 ($p<0.01$) in jack pine stands.

3.2.3 Weathering and adsorption

The base cation weathering rate was smaller ($p<0.05$) in NE7 (ranged from 40 to 258 mol_c ha^{-1} yr^{-1}) than in SM8 (56 to 514 mol_c ha^{-1} yr^{-1}) but was not different between dominant tree species (Figure 5-2b). The greater supply of base cations through weathering in SM8 implied greater H^+ consumption by cation weathering and adsorption in SM8 ($p<0.01$) than in NE7 (Figure 5-3). Net H^+ consumption by cation weathering and adsorption was also affected by tree species ($p<0.01$). Net H^+ production by cation weathering and adsorption was the greatest in aspen stands in NE7 at 226 mol_c ha^{-1} yr^{-1} and the lowest in jack pin stands in SM8 at -301 mol_c ha^{-1} yr^{-1}. Net H^+ production by anion weathering and adsorption was also differed between watersheds and dominant tree species (Figure 5-3). It was more negative in jack pine ($p<0.01$) than in aspen stands and more negative in NE7 ($p<0.01$) and in SM8 (Figure 5-3).

3.2.4 Nitrogen transformation

Throughfall depositions of NO_3^- and NH_4^+ did not differ between watersheds and dominant tree species (Table 5-2). The leaching loss of NO_3^- and NH_4^+, respectively, was minimal and not influenced by watershed or stand type.Net H^+ production by N transformation was positive in both watersheds and dominant tree species and ranged from 27.3 to 34.8 mol_c ha^{-1} yr^{-1}.

3.2.5 Protonation of weak acid anions

Throughfall deposition of weak acid anions was greater ($p<0.001$) in aspen than in jack pine stands, and greater ($p<0.001$) in SM8 than in NE7 (Table 5-2). However, leaching loss of weak acid anions was not influenced by watersheds nor dominant tree species. As a result, reduction of H^+ by protonation of weak acid anions was greater ($p<0.001$) in aspen than in jack pine stands, and greater ($p<0.001$) in SM8 than in NE7 (Figure 5-3). Protonation of weak acid anions in jack pine and aspen stands accounted for 376 and 440 mol_c ha^{-1} yr^{-1}, respectively, in NE7, and 405 and 543 mol_c ha^{-1} yr^{-1}, respectively, in SM8.

3.2.6 H^+ budget

In all plots, the estimated H^+ budgets were negative, indicating that soils in the two studied watersheds were being alkalinized rather than acidified (Figure 5-3). The H^+ budget was more negative ($p<0.001$) in aspen than in jack pine stands while no difference was found between watersheds. The H^+ budget was positively related to H^+ input ($r=0.99$, $p<0.001$) and negatively related to protonation by weak acid anion ($r=-0.80$, $p<0.01$). However, net H^+ production showed a negative relationship with H^+ budget ($r=-0.67$, $p<0.05$).

3.3. Critical loads and exceedances

In the long-term, CLs were not affected by any of watersheds and tree species for both models (Figure 5-2a). $CL_{\_L\_BD}$ ranged from 223 to 711 $mol_c\ ha^{-1}\ yr^{-1}$ and $CL_{\_L\_BD+ID}$ showed similar values with $CL_{\_L\_BD}$. EXs in the long-term scale did not occur in most of plots indicating that S deposition was less than CLs during the study period (Figure 5-2a). However, $EX_{\_L\_BD+ID}$ was less negative (<0.001) than $EX_{\_L\_BD}$ due to relatively high proportion of SO_4^{2-} in interception deposition. $EX_{\_L\_BD+ID}$ was less negative ($p<0.05$) in NE7 than in SM8 while no effect of watersheds was found on $EX_{\_L\_BD}$. Tree species did not affect $EX_{\_L}$. On average, $EX_{\_L\_BD}$ was -222 $mol_c\ ha^{-1}\ yr^{-1}$ in NE7 and -334 $mol_c\ ha^{-1}\ yr^{-1}$ in SM8 and $EX_{\_BD+ID}$ was -81 $mol_c\ ha^{-1}\ yr^{-1}$ in NE7 and -264 $mol_c\ ha^{-1}\ yr^{-1}$ in SM8.

In the short-term scale, the CLs were lower than those in the long-term scale approximately as much as BC_{up} (Figure 5-2a). The CLs in the short-term were likely influenced by tree species ($p=0.11$ for $CL_{\_S\_BP}$ and $p<0.1$ for $CL_{\_S\_BD+ID}$) and were lower in aspen than in jack pine stands due to greater BC_{up} in aspen stands. However, no watershed effect was found on $CL_{\_S}$. The $CL_{\_S\_BD}$ were, on average, 260 $mol_c\ ha^{-1}\ yr^{-1}$ in jack pine stands and 59 $mol_c\ ha^{-1}\ yr^{-1}$ in aspen stands. The $CL_{\_S\_BD+ID}$ were 256 $mol_c\ ha^{-1}\ yr^{-1}$ in jack pine stands and 45 $mol_c\ ha^{-1}\ yr^{-1}$ in aspen stands. In both watersheds, $EX_{\_S\_BD}$ was, on average, negative in jack pine stands but positive in aspen stands (Figure 5-2a). $EX_{\_S\_BD+ID}$ was more positive or less negative than $EX_{\_S\_BD}$. $EX_{\_S\_BD+ID}$ in jack pine and aspen stands were -65 and 205 $mol_c\ ha^{-1}\ yr^{-1}$, respectively, in NE7 and 22 and 99 $mol_c\ ha^{-1}\ yr^{-1}$, respectively, in SM8.

4. Discussion

4.1 Interception deposition and critical loads

Differences between $CL_{\_BD}$ and $CL_{\_BD+ID}$ ranged from 2 to 25 $mol_c\ ha^{-1}\ yr^{-1}$ in this study as proportions of base cations and Cl^- were similar between bulk deposition and interception deposition (Figure 5-2). However, $EX_{\_BD+ID}$ were much lower than $EX_{\_BD}$ (Figure 5-2) due to increasing proportion of SO_4^{2-} in interception deposition, indicating that the risk of acidification by S deposition would be underestimated in forest ecosystems using the conventional method. Interception deposition of tree canopies has not been included to estimate CL (Sullivan et al., 2011; Whitfield et al., 2010b) even though interception deposition occupies a significant portion of atmospheric deposition in forest ecosystems. Interception deposition was similar to bulk deposition for base cations and more than twice of bulk deposition for SO_4^{2-} in *Pseudotsuga menziesiis* stands in the Netherlands (Draaijers and Erisman, 1995) and similar trends were found in *Fagus sylvatica* L. stands in Belgium (Staelens et al., 2008); interception deposition of SO_4^{2-} were 913 $mol_c\ ha^{-1}\ yr^{-1}$ in *Pseudotsuga menziesiis* stands in the Netherlands and 780 $mol_c\ ha^{-1}\ yr^{-1}$ in *Fagus sylvatica* L. stands in Belgium. Interception depositions of

SO_4^{2-} in studied sites were smaller than in those regions but showed similar trends. Intercepted SO_4^{2-} occupied 62 and 58% of total deposition in jack pine and aspen stands, respectively, while that of base cations was responsible for approximately 32% of total deposition in both tree stands. Therefore, it is suggested that interception deposition should be included in atmospheric deposition when we evaluate critical loads. It allows us to avoid underestimation of exceedance of S deposition on forest ecosystems by the conventional evaluation method of critical loads.

4.2 Assessment of tree species effects on soil acidification

In this study, BC_{up} was greater in aspen than in jack pine stands, which led to lower $CL_{\_S}$ and greater $EX_{\_S}$ in aspen stands (Figure 5-2). This indicated that aspen stands were more susceptible to soil acidification than jack pine stands in the short-term. Due to greater concentration of base cations in deciduous trees than in conifers (Frelich et al., 1989; Riitters et al., 1991), CL with harvest removal of base cations has been estimated lower in deciduous trees than in conifers with similar aboveground biomass (Freer-Smith and Kennedy, 2003). On the other hand, the H^+ budget of the soil was less negative in jack pine than in aspen stands even though assimilation provided greater net H^+ production in aspen than in jack pine stands (Figure 5-3). This result was caused by greater H^+ throughfall input, lower H^+ consumption by cation weathering and adsorption, and lower protonation by weak acid anions (Figure 5-3).

Excess uptake of cationic nutrients to anionic nutrients has been suggested to speed up soil acidification (van Breemen et al., 1983) and can be a major source of H^+ in unpolluted or less polluted areas (Fujii et al., 2008; Marcos and Lancho, 2002). However, trees, especially conifer trees, contribute to soil acidification through a number of other processes such as organic acid exudation from roots (Augusto et al., 2002; Tuason and Arocena, 2009) and canopy (Chiwa et al., 2008; Mosello et al., 2008), organic acid release by litter decomposition (Augusto et al., 2002), and so on. Based on our results, increased H^+ budget of jack pine stands was about 200 mol_c ha^{-1} yr^{-1} by that of aspen stands, which was as much as 3.2 kg S ha^{-1} yr^{-1} of S deposition; S deposition ranged from 3.2 to 4.1 kg S ha^{-1} yr^{-1} in the two watersheds NE7 and SM8 (Jung et al., 2011b). It implies that a significant H^+ source has been excluded from assessing CL and EX, especially in conifer forests. Therefore, we need to modify the simple mass balance approach to incorporate H^+ production by trees.

4.3 Risk of soil acidification in AOSR

Atmospheric deposition of SO_4^{2-} and NO_3^- in NE7 and SM8 were moderately low compared with values of greater than 10 kg ha^{-1} yr^{-1} each for SO_4^{2-} and NO_3^- in areas affected by air pollution in eastern North America (Vet et al., 2004; World Meteorological Organization (WMO), 2005), Europe (Vanguelova et al., 2007), and eastern Asia (Fujii et al., 2008). The CLs and EXs of forests have been mapped using long-term data using bulk deposition only in Alberta, in which most forest ecosystems have been exposed to S and N deposition lower than CLs (Aherne, 2008). It implies that forests soils may not be susceptible to acidification in AOSR under current level of acid deposition. In addition, none of our data including changes in soil pH, EXs, and H^+ budgets supported that forest soils in AOSR were being acidified in the studied period (Figure 5-1, 5-2, and 5-3). However, we should be careful to conclude that forest soils in AOSR have never been acidified by acid deposition. Two scenarios can be suggested. One is that forest ecosystem in AOSR have not experienced soil acidification due to lower acid deposition than CLs and the other one is that forest ecosystem has been recovering from previous acidification. The emission of SO_2, the major air pollutant in AOSR, reached its zenith between the early 1980s and mid 1990s, and then decreased due to efforts to reduce acid deposition (Hazewinkel et al., 2008; Aherne and Shaw, 2010). The negative H^+ budget in this study may have resulted from decreasing S deposition. Based on expectation that synthetic oil production and subsequently acid emission will increase in AOSR (Humphries, 2008), soil acidification in AOSR is still of concern although no sign of soil acidification was found in this study.

4.4 Limitations of the H^+ budget model

The H^+ budget model has been used to assess soil acidification or alkalinization as the H^+ budget responds sensitively to environmental changes compared to other indicators such as exchangeable acidity presented by soil pH affected by pH buffering capacity (van Breemen et al., 1983) and can reflect current conditions of an ecosystem by evaluating H^+ sinks and sources. However, several assumptions of the model may cause potential errors. In order to net H^+ production or depletion by weathering and adsorption-desorption, the model has an assumption that changes in nutrient concentrations in soil water is minimal. While cation concentration in soil water is relatively stable due to a large pool of exchangeable cations, anion concentration in soil water can be significantly changed in soils with low anion exchangeable capacity. In this study, available S concentration increased over time, which was likely affected by artificial S deposition (Figure 5-1). Considering low SO_4^{2-} adsorption capacity of the studied soils (Jung et al., 2011a; Whitfield et al., 2010), stored SO_4^{2-} in the soil may not be adsorbed completely, resulting in the overestimation of H^+ consumption by net weathering and plant uptake of anions.

In addition, protonation by organic anions could be overestimated, especially in jack pine stands. The major organic anions in atmospheric deposition are normally formate and acetate (Zhang et al., 2011) while oxalate occupies most of organic anions released by canopy leaching from pine trees (Chiwa et al., 2008). The pK_a of formate and acetate are 3.75 and 4.75, respectively, between throughfall pH and the soil pH in studied sites, suggesting that these organic anions could protonate in the soil whereas pK_{a2} of oxalate is 1.38 lower than soil pH; pK_{a1} is 4.28. It means that a significant portion of oxalate released from pine trees may remain without protonation. Assuming that one half of oxalates protonate, H^+ depletion by the protonation can be overestimated by approximately 65 mol_c ha^{-1} yr^{-1} in jack pine stands (Jung et al., 2011b).

The limitations mentioned above suggest that real H^+ budgets in the studied area are less negative than estimated H^+ budget. Nevertheless, it was still concluded that acidic forest soils in AOSR were recovering from acidification as the estimated H^+ budget was low enough though considering potential overestimation.

5. Conclusions

The estimated EXs increased with the modified equation including interception deposition compared with EXs by the conventional method because of relatively great proportion of SO_4^{2-} in interception deposition. It indicated that the conventional method might lead to underestimating the risk of soil acidification by S deposition. The CLs were not affected by tree species in the long-term while $CL_{\_S}$ in aspen stands was lower than in jack pine stands due to greater net assimilation of base cations. The $EX_{\_S}$ in aspen stands was greater than in jack pine stands although the H^+ budget was less negative in jack pine than in aspen stands. It suggested that $EX_{\_S}$ based on limited parameters may not be available to compare the risk of soil acidification between tree species and indicate current changes in soil acidity. Due to greater H^+ input through processes such as atmospheric deposition and canopy exchange and greater net H^+ production by weathering and adsorption, jack pine stands had less negative H^+ budget than in aspen stands though net H^+ production by assimilation was greater in aspen stands. Based on our data including increased soil pH, negative EX, and negative H^+ budget, soil acidity has been decreasing in the AOSR by the decreasing trends of S emission. However, it is suggested that further study should be conducted to evaluate effects of acid deposition on forest soils based on the expected increase in synthetic oil production.

Table 5-1 Soil chemistry in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in Alberta, Canada in 2010. Numbers in parentheses are standard error of the mean.

Soil layer	Water-shed	Tree species	pH	Exchangeable				Available		Available[2]		Texture
				Ca^{2+}	Mg^{2+}	K^{+}	Al^{3+}	NH_4-N	NO_3-N	SO_4^{2-}	Cl^{-}	
				($cmol_c$ kg^{-1})				(mg kg^{-1})		(mg kg^{-1})		
Forest floor	NE7	JP	3.79 (0.08)	13.2 (4.7)	2.28 (0.69)	1.52 (0.19)	0.99 (0.10)	89.2 (10.8)	0.41 (0.002)	155 (10.1)	80.1 (4.3)	
		TA	5.18 (0.19)	44.2 (9.1)	7.78 (1.22)	2.64 (0.55)	0.09 (0.04)	57.5 (38.7)	[1]ND	253 (4.5)	76.9 (4.4)	
	SM8	JP	4.04 (0.04)	13.4 (4.5)	2.43 (0.48)	2.08 (0.72)	0.83 (0.10)	98.1 (42.9)	ND	196 (6.3)	69.7 (5.2)	
		TA	4.58 (0.45)	28.7 (4.2)	5.33 (0.69)	3.96 (0.60)	0.22 (0.07)	57.6 (20.6)	ND	319 (59.0)	94.0 (1.6)	
Surface mineral soil (0-15 cm)	NE7	JP	3.65 (0.20)	0.76 (0.24)	0.31 (0.12)	0.15 (0.05)	1.05 (0.45)	5.13 (0.93)	1.27 (0.69)	122 (2.7)	38.9 (0.1)	Loamy sand
		TA	3.97 (0.15)	0.52 (0.06)	0.17 (0.01)	0.06 (0.01)	0.29 (0.22)	4.20 (0.00)	0.42 (0.35)	122 (2.1)	38.8 (0.1)	Loamy sand
	SM8	JP	3.58 (0.02)	0.31 (0.13)	0.14 (0.06)	0.18 (0.03)	3.33 (1.47)	6.07 (2.47)	0.82 (0.42)	152 (25.9)	40.4 (0.1)	Loamy sand
		TA	3.52 (0.11)	1.96 (0.03)	0.75 (0.01)	0.33 (0.11)	7.06 (2.34)	6.30 (0.70)	0.05 (0.02)	126 (1.0)	44.3 (3.7)	Sandy loam
Subsurface mineral soil (15-45 cm)	NE7	JP	3.81 (0.17)	1.87 (0.60)	0.71 (0.25)	0.17 (0.01)	2.34 (0.44)	6.53 (1.68)	2.54 (2.27)	122 (2.6)	39.1 (1.4)	Sandy loam
		TA	4.29 (0.11)	0.96 (0.02)	0.30 (0.04)	0.11 (0.01)	0.47 (0.28)	3.50 (0.70)	0.31 (0.24)	122 (2.5)	39.5 (0.9)	Loamy sand
	SM8	JP	3.86 (0.18)	0.31 (0.13)	0.14 (0.07)	0.17 (0.04)	2.88 (1.52)	5.13 (2.03)	1.33 (0.91)	128 (2.9)	41.8 (0.6)	Loamy sand
		TA	3.87 (0.14)	3.45 (1.21)	1.81 (0.84)	0.33 (0.16)	10.37 (6.46)	4.90 (0.70)	0.05 (0.00)	128 (3.9)	39.8 (3.0)	Clay loam

[1] ND means not determined because the value was under detection limit, which was 0.05 mg kg^{-1}.

[2] Available SO_4^{2-} and Cl^- include soluble and adsorbed ions.

Table 5-2 Throughfall deposition (TF) and leaching loss (LL) of elements in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in Alberta, Canada. Numbers in parentheses are standard error of the mean.

Water type	Water-shed	Tree species	H^+	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{n+}	Fe^{n+}	Mn^{4+}	SO_4^{2-}	NO_3^-	Cl^-	WA[1]
									($mol_c\ ha^{-1}\ yr^{-1}$)						
TF	NE7	JP	151.5	89.3	225.2	96.9	173.7	55.0	13.8	4.6	4.6	298.0	54.4	78.3	383.8
			(21.2)	(10.8)	(21.2)	(10.8)	(45.2)	(4.5)	(1.9)	(1.0)	(0.7)	(24.5)	(4.8)	(15.1)	(52.9)
		TA	51.5	68.1	246.5	112.0	283.1	45.0	9.2	3.2	3.8	237.1	42.1	85.5	457.7
			(14.7)	(7.5)	(14.7)	(7.5)	(23.8)	(6.1)	(1.1)	(0.6)	(0.9)	(24.7)	(5.3)	(9.5)	(41.5)
	SM8	JP	202.9	59.4	144.1	74.2	117.6	44.3	16.7	3.5	10.9	170.8	32.0	57.1	413.6
			(9.2)	(16.0)	(31.7)	(13.8)	(31.4)	(6.7)	(0.9)	(0.9)	(1.4)	(10.3)	(6.3)	(6.9)	(48.5)
		TA	35.3	74.8	193.9	124.4	329.2	50.3	6.3	2.5	13.6	157.5	45.5	71.5	555.9
			(41.0)	(9.8)	(17.0)	(6.8)	(10.7)	(3.4)	(2.3)	(0.4)	(0.7)	(11.7)	(12.1)	(11.8)	(38.2)
LL	NE7	JP	5.3	0.11	0.49	0.24	0.68	1.18	0.27	0.07	0.00	0.43	0.26	0.04	2.2
			(7.8)	(0.14)	(0.59)	(0.24)	(0.54)	(1.38)	(0.26)	(0.07)	(0.00)	(0.64)	(0.25)	(0.06)	(1.93)
		TA	15.0	0.11	0.55	0.27	0.46	1.33	0.41	0.10	0.00	0.47	0.25	0.04	2.4
			(3.7)	(0.10)	(0.13)	(0.09)	(0.19)	(1.40)	(0.08)	(0.02)	(0.00)	(0.02)	(0.06)	(0.05)	(1.94)
	SM8	JP	11.4	0.04	0.43	0.20	0.36	0.51	0.28	0.07	0.00	0.13	0.65	0.01	0.7
			(15.2)	(0.02)	(0.01)	(0.01)	(0.02)	(0.55)	(0.06)	(0.01)	(0.00)	(0.06)	(0.33)	(0.00)	(0.65)
		TA	12.4	0.12	0.69	0.37	0.58	0.73	0.43	0.11	0.01	0.43	2.00	0.05	0.4
			(16.7)	(0.06)	(0.17)	(0.07)	(0.22)	(0.41)	(0.20)	(0.05)	(0.00)	(0.20)	(2.22)	(0.04)	(1.84)

[1] WA means weak acid anions

Table 5-3 Annual biomass increment and nutrient uptake of jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in Alberta, Canada. Numbers in parentheses are standard error of the mean.

Water-shed	Tree species	Biomass increment			Nutrient uptake[1]										Net H^+ production
		Above-ground	Root	Total	Ca	Mg	K	Na	Al	Fe	Mn	S	Cl	P	
		kg ha^{-1}			(mol_c ha^{-1} yr^{-1})										(mol_c ha^{-1})
NE7	JP	466	124	590	49.1	13.8	12.9	3.5	5.7	2.9	2.1	7.5	4.8	6.2	71.5
		(27.1)	(6.4)	(30.3)	(7.2)	(2.0)	(0.4)	(0.9)	(2.3)	(0.5)	(0.5)	(0.8)	(0.6)	(0.8)	(8.7)
	TA	383	108	491	162.8	32.0	24.5	2.6	2.5	3.3	0.6	18.2	7.7	9.7	193
		(116)	(5)	(121)	(70.1)	(13.4)	(5.6)	(0.4)	(0.8)	(1.4)	(0.2)	(6.8)	(0.8)	(2.7)	(80.8)
SM8	JP	919	228	1147	73.4	28.0	26.4	10.7	14.7	10.6	5.8	13.4	13.5	15.2	128
		(288)	(52)	(339)	(12.7)	(6.4)	(7.7)	(5.8)	(3.7)	(2.1)	(1.5)	(2.7)	(7.8)	(6.4)	(20.7)
	TA	1622	259	1881	341.2	80.2	70.2	19.8	9.8	9.5	4.1	40.3	20.1	24.8	450
		(168)	(15)	(153)	(106.6)	(10.6)	(9.9)	(4.8)	(1.2)	(1.4)	(1.5)	(10.8)	(1.1)	(0.2)	(123)

[1] Nutrient uptake were presented as the charge equivalent unit in order to evaluate net H^+ production by assimilation: the charges used were 2 for Ca and Mg, 1 for K and Na, 3 for Al and Fe, 4 for Mn, 2 for S as SO_4^{2-}, 1 for Cl, 3 for P as PO_4^{3-}.

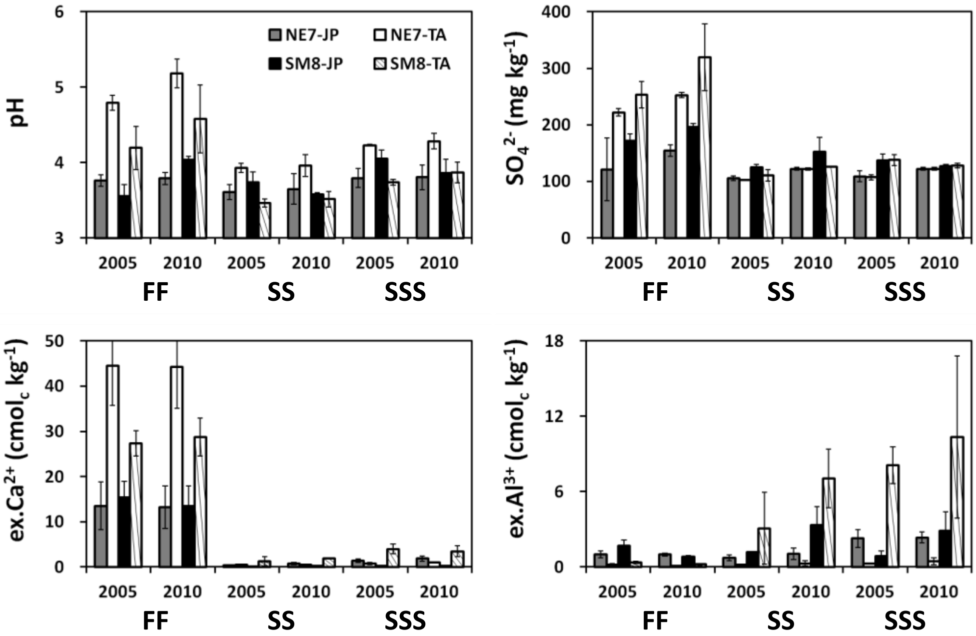

Figure 5-1 Changes in pH and available SO_4^{2-} of forest floor (FF), surface soil (SS, 0-15 cm) and subsurface soil (SSS, 15-45 cm) in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in Alberta, Canada between 2005 and 2010. Error bars are standard errors of the mean.

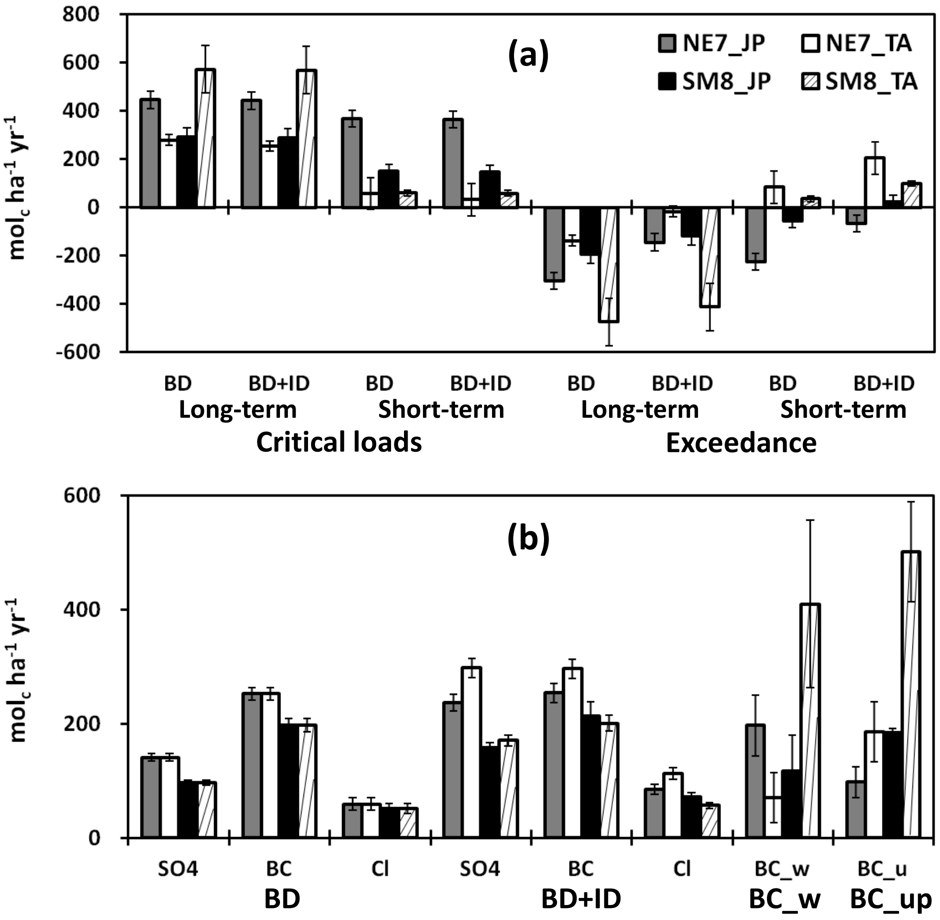

Figure 5-2 Critical loads and exceedances with various methods (a) and parameters of critical loads (b) in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in Alberta, Canada. BD, ID, BC_w, and BC_up mean bulk deposition, interception deposition, base cation weathering, and base cation uptake, respectively. Long-term CLs excluded BC_up and short-term CLs included BC_up at evaluating CLs. Error bars are standard errors of the mean.

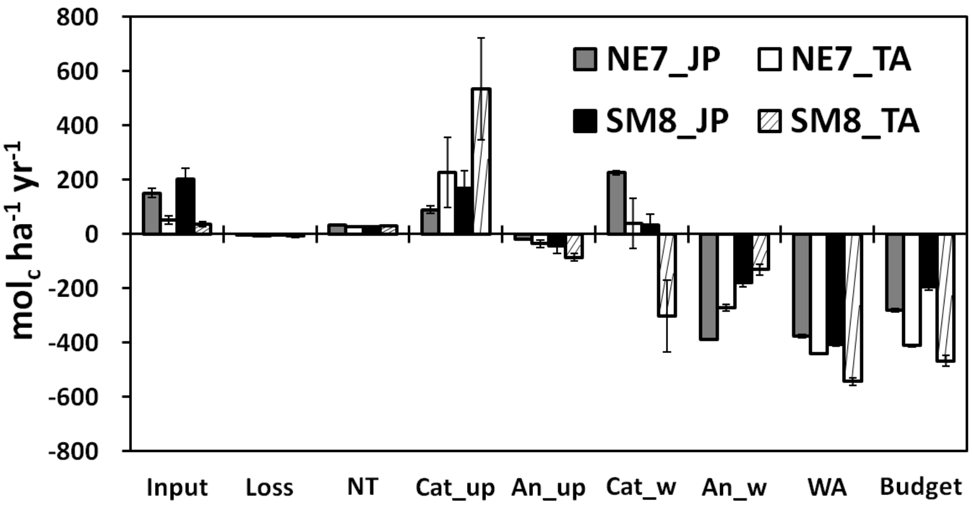

Figure 5-3 Hydrogen ion budgets, and sinks and sources of H^+ in the soil in jack pine (JP) and trembling aspen (TA) stands in watersheds NE7 and SM8 in Alberta, Canada. NT, $Cat_{\_up}$, $An_{\_up}$, $Cat_{\_w}$, $An_{\_w}$, and WA mean net H^+ production by N transformation, uptake of cations and anions, weathering and adsorption-desorption of cations and anions, and protonation of weak acid anions. Error bars are standard errors of the mean.

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Chapter 6. Four years of simulated N and S depositions did not cause N saturation in a mixedwood boreal forest ecosystem in the oil sands region in northern Alberta, Canada

1. Introduction

Long-term atmospheric nitrogen (N) and sulfur (S) depositions have been shown to cause changes in elemental biogeochemical cycles, soil acidification, and nutrient deficiency or imbalance in forest ecosystems (Aber et al. 1989; Johnson and Siccama 1983). Compared with historical emission rates, the total emission of acid-causing materials in North America is now substantially lower due to efforts such as the Eastern Acid Rain Program in Canada and the US Clean Air Act (Morrison 2006). However, while SO_2 emissions have decreased globally, NO_x emissions in industrialized regions remain elevated (Galloway et al. 2004). In the Athabasca oil sands region (AOSR), the largest area of open-pit oil sands mining in Alberta, Canada, SO_2 emission in the AOSR decreased in the 1990s from more than 400 Mg day^{-1} in the mid-1980s, similar to a general trend in North America while it remained at approximately 300 Mg day^{-1} in the 2000s (Hazewinkel et al. 2008). On the other hand, NO_x emission has increased since the beginning of commercial oil production and is expected to increase due to expansion of oil sands mining/extraction and upgrading activities and increase in the population

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(Aherne and Shaw 2010; Hazewinkel et al. 2008). Therefore, impacts of N and S depositions on boreal forests in the AOSR are of great concern and, furthermore, the influence of N deposition will increase in the future.

The N status of forest ecosystems can be divided into different stages in relation to responses of ecosystems to chronic N deposition: N limitation, alleviation of N limitation, and N saturation (Aber et al. 1998). In boreal forests, the initial stage has been normally known to be N-limited followed by a stage of alleviation of N limitation as N availability increases through chronic N deposition (Hari and Kulmala 2008). In the second stage, external N input may be taken up by plants and thus provide a beneficial effect on tree growth. Furthermore, the N may move into the soil as organic N through litterfall and fine root turnover (Aber et al. 1998; Nadelhoffer et al. 1999). Net N mineralization rates may increase in response to increased soil N content, which may increase inorganic N concentrations in the soil and, subsequently, N leaching and N emissions as the ecosystem becomes N saturated (Aber et al. 1998; Matson et al. 2002). Chronic N deposition affects the cycling of both N and other nutrients (Aberet al. 2003; Likens and Bormann 1995). While the N deposited plays the role of a fertilizer in N-limited forests, increased uptake in combination with leaching of cationic nutrients with nitrate may cause cationic nutrient deficiencies or nutrient imbalances for trees, which may ultimately cause forest decline (Erisman and De Vries 2000; Skeffington and Wilson 1988).

Even though chronic N and S depositions may induce detrimental effects on forest ecosystems, the response time of ecosystems to such effects may vary, depending on a number of factors such as deposition rates and nutrient demand by the biota, especially for the response to N deposition (Gundersenet al. 1998). In North America, N saturation has been often found in forests in eastern U.S. that have been impacted by high N deposition rates (Jeffries 1995). Although several monitoring sites in eastern Canada, e.g., the Turkey Lake watersheds, have been shown to be N-saturated (Foster et al. 1989), most forests in Canada did not show any evidence of N saturation due to relatively low rates of N deposition (Houleet al. 1999). Simulated studies with elevated deposition rates have been conducted in forests less impacted by acid deposition to evaluate potential changes in ecosystem properties and processes. Some simulated studies in N-limited forests showed short-term changes in the N cycle and conditions of other nutrients such as Ca and Mg uptake (Aberet al. 1998; Moore and Houle 2009).

Sulfur deposition in the AOSR has been a major concern for soil acidification due to greater emission rates of S than N (even after the curtailment of S emission rates as discussed earlier) and a low capacity for sulfate adsorption of soils (Jung et al. 2011). Meanwhile, the concern regarding N deposition has increased due to the expected increase in N emission rates in the AOSR and in western Canada (Aherne and Shaw 2010) though N saturation, based on our literature review, has not been reported in western Canada and boreal forests in the AOSR. Increasing atmospheric NO_2 concentrations and N deposition rates, however, have influenced N cycling in forest ecosystems in the AOSR (Laxton et al. 2010), suggesting that there was potential progress of the N cycle towards N saturation.

To evaluate the impact of elevated levels of N and S depositions on forest ecosystems in the AOSR, we conducted a simulated N and S deposition experiment examining changes in tree and understory growth rates, in N cycling (N leaching and N storage in microbial biomass), and in the leaching loss of cationic nutrients from soils. We hypothesized that 1) boreal forests in the AOSR are N but not S limited and thus the growth rates of dominant tree species will be increased by elevated levels of N deposition, but not by elevated levels of S deposition. One of the questions that needs to be answered is how do boreal forests in the AOSR respond to increased levels of N and S depositions, as such responses are site specific, 2) N leaching will not be increased in the short-term by elevated levels of N and S depositions in N-limited boreal forests, and 3) cationic nutrient leaching will not be increased in the short-term by the elevated levels of N deposition, consistent with the lack of N leaching.

2. Materials and Methods

2.1 Site description and experimental design

The research plots were established in a boreal forest stand (56.1° N 110.9° W) located about 100 km southeast of Fort McMurray in the AOSR in northern Alberta, Canada. Most of the mining sites and upgrading facilities in the AOSR were distributed within about a 100 km distance north of Fort McMurray. In the AOSR, the mean annual temperature is 0.7 ℃ with mean relative humidity of 68% and mean annual precipitation of 456 mm (Environment Canada 2010). The main canopy tree species were approximately 60-year-old trembling aspen (*Populus tremuloides*, referred to as aspen below) followed by white spruce (*Picea glauca*) aged between 25 and 55 years old, based on increment cores collected in 2011. Aspen and white spruce constituted 71 and 22% of the canopy trees by stem density, respectively, and most of the dominant trees (based on the tree's relative height) were aspens. White spruce trees were also found as seedlings growing in the understory as this species is very shade tolerant. Other canopy trees found in the plots were balsam fir (*Abies balsamea*), balsam poplar (*Populus balsamifera*), black spruce (*Picea mariana*), and paper birch (*Betula Papyrifera*). The dominant understory species were prickly rose (*Rosa acicularis*) and wild sarsaparilla (*Aralia nudicaulis*) based on coverage. The ecosite phase was d1 with medium nutrient regime and mesic moisture regime based on ecological site classification (Beckingham and Archibald 1996). Soils were mostly Gray Luvisols classified based on the Canadian system of soil classification (Soil Classification Working Group 1998) or Boralf in Soil Taxonomy (Soil Survey Staff 1994).

The experiment used a 2×2 factorial design with blocking. One of factors studied was N addition (with two levels) and the other was S addition also with two levels to simulate elevated levels of N and S deposition in the oil sands region. Thus, four treatments were set up: control (CK), N addition (+N, 30 kg N $ha^{-1}yr^{-1}$ asNH_4NO_3), S addition (+S, 30 kg S $ha^{-1}yr^{-1}$ as Na_2SO_4), and +NS additions (+NS), with addition of N and/or S started in 2006 and through 2009. For this experiment, four blocks were set up based on topographic position to ensure relatively uniform soil/site conditions within each block and four plots of 20 × 20 m were established in each block; detailed information of each block is described in Appendix III. Within each block, the treatments were randomly assigned to the plots. The proportion of canopy tree species was variable between blocks with between 56 and 91% aspen and between 5 and 29% white spruce. The blocking design allowed relatively similar composition of canopy trees between treatments within each block. Soil texture of surface mineral soil (0-15 cm) was sandy loam in two blocks and silt loam in the other two blocks. The deeper soil (15-45 cm) had greater clay content than surface mineral soil but texture was more variable between blocks.

Fertilizers were broadcast applied using a spreader in granule (NH_4NO_3) and powder (Na_2SO_4) forms. Between 2006 and 2008, the N and S were applied once in early summer because more than two thirds of deposition falls down in the AOSR in the growing season approximately between June to September (Wieder et al. 2010). Since 2009, the N and S were applied in three equal splits on July 2, July 22, and August 11; the split application method continued in 2010 and 2011. We changed the N and S addition method in 2009 because the split application better imitate deposition processes in the natural system that happen continuously with seasonal variation than one-shot application does even though a method to simulate the exact way N and S were deposited in the natural system was not possible.

2.2 Plant sampling and analysis

Diameter at breast height (DBH, measured at 1.3 m above ground) of all trees in each plot was measured in June 2006 (with the exception noted below) and in June 2009. Trees with DBH less than 0.5 cm in 2006 were excluded from the DBH measurement. Tree growth was assessed by evaluating the annual increment of aboveground biomass from 2006 to 2009, presented as kg ha^{-1} yr^{-1} to compare the effects of treatments on biomass of trees, understory and litterfall. Tree aboveground biomass was calculated with a DBH-based set of equations established for each of the tree species found in this study (Lambert et al. 2005). The aboveground portion of the understory vegetation was sampled from four quadrats of 30 × 30 cm in each plot in late July, 2009 to determine the aboveground biomass of the understory vegetation. Foliar samples were collected in late July, 2009 from healthy aspen trees that did not display any visual symptom of insect or disease damage. Three litterfall traps of 10 cm diameter and 10 cm depth were set up in each plot in late October, 2008, and litterfall samples were collected in late October, 2009. All plant samples were dried in an oven for 72 hours at 70 ℃ and weighed to determine dry biomass. The samples were ground to pass through a 0.42-mm sieve and homogenized. Nitrogen concentrations of plant samples were determined using a Carlo Erba NA 1500 elemental analyzer (Carlo Erba Instruments, Milano, Italy).

2.3 Soil sampling and analysis

Soil samples were collected from the forest floor and the surface mineral soil (0-15 cm) in each plot. The first sampling was on July 2, 2009 before the first addition of N and S in that growing season and samples were collected again 10, 20, 40, 80 and 320 days after July 2, 2009. After each sampling, the soil samples were placed in a cooler, transported back to the laboratory, and stored in a refrigerator. Fresh soil samples were crushed to pass through a 2-mm sieve, with coarse fragments, roots, and debris removed. Soil moisture content was determined in a forced air oven at 105 °C. Soil microbial biomass C (MBC) and N (MBN) were determined by the chloroform fumigation-extraction method (Voroneyet al. 2008) within a week after sampling. A 0.5 mol L^{-1} K_2SO_4 solution was used to extract C and N from fumigated and non-fumigated samples at a 1:10 (w:v) ratio. Then a 2 mol L^{-1} KCl was used to extract (at the 1:10 w:v ratio) available ammonium and nitrate (Kalra and Maynard 1991), with the ammonium and nitrate concentrations determined on a Dionex DX-600 ion chromatography (Dionex Corp., Sunnyvale, CA).

The following soil properties were analyzed using air-dried samples collected 320 days after the first addition of N and S in the 2009 growing season. Soil pH was measured using 10 g of air-dried soil in 40 mL of water for forest floor samples or 20 mL of water for surface mineral soil samples. Each soil sample was further ground with a ball mill and used for total C and N analysis on a Carlo Erba NA 1500 elemental analyzer (Carlo Erba Instruments, Milano, Italy). Exchangeable cations, including Ca^{2+}, Mg^{2+}, K^+, Na^+ and Al^{3+}, were determined after extraction with 1 mol L^{-1} NH_4Cl at a ratio of 5 g soil to 100 mL extractant. After filtration, the filtrates were analyzed using a Perkin-Elmer Elan 6000 quadrupole ICP-MS (Shelton, CT). The Ca/Al ratio was calculated with exchangeable Ca^{2+} and Al^{3+} based on a molar unit.

2.4 Soil solution sampling and analysis

Two stainless steel zero-tension lysimeters installed at each of the 15 (within the main rooting zone) and 45 cm soil depths (below the main rooting zone) in 2007 to collect soil solution samples. Soil solution samples were collected every month from May to October, 2009, in the growing season, and then in May, 2010, after spring thaw. The water collection area of each lysimeter was 500 cm^2. For samples collected in May, collecting bottles connected to lysimeters were put in place in October the year before. The bottles were washed with 20% HCl and rinsed with deionized water in the laboratory and 3-4 drops of 0.1 g L^{-1} phenyl mercury acetate were added to each container prior to deployment to the field to minimize microbial activities in the water samples between sampling intervals. All samples were measured for their volume and kept in a refrigerator. A portion of each sample was filtered with 0.22 μm syringe filters before chemical analysis. Concentrations of Ca^{2+}, Mg^{2+}, K^+ and Na^+ were measured using a Perkin-Elmer ICP-MS (Shelton, CT). Concentrations of SO_4^{2-}, NO_3^- and NH_4^+ ions were analyzed with a Dionex Corp DX 600 ion chromatography (Sunnyvale, CA). Leaching loss of each ion below each depth were determined using collected water volume and concentration of each ion.

2.5 Statistical analysis

All statistical analyses were performed using version 9.02 of the SAS software (SAS Institute Inc., Cary, NC). The datasets were checked for normality of distribution and they were all normally distributed. Analysis of variances (ANOVA) was performed to determine the effects of N and S additions and sampling time on the measured parameters. To analyze the effects of N and S additions on MBN, MBC and inorganic N, the compound symmetry covariance structure was selected to consider the effects of time-repeated measurement. All pair-wise comparisons among treatments were done with the Bonferroni correction. An α value of 0.1 was chosen to indicate statistical significance due to the high spatial variability of the measured parameters.

3. Results

3.1 Effects of N and S additions on plant growth and foliar N

Nitrogen addition increased tree biomass ($p<0.05$) and litterfall amount ($p<0.05$) (Figure 6-1a and 6-1b) but aboveground understory biomass was not affected by any of N and S additions (Figure 6-1c). The annual increase of tree biomass was the greatest in the +NS treatment which was greater than that in the +N treatment ($p<0.1$), indicating a synergistic interaction between N and S additions ($p<0.1$). However, no synergistic response between N and S additions was found for litterfall. None of the treatments affected N concentrations in foliar and litterfall of trees (Figure 6-1a and 6-1b). Nitrogen addition increased ($p<0.01$) whereas S addition decreased ($p<0.1$) N concentrations in the aboveground component of the understory vegetation (Figure 6-1c). Understory N concentration was greater in +N ($p<0.1$) and lower in +S ($p<0.1$) than that in CK while no difference was found between the CK and +NS treatments (Figure 6-1c).

3.2 Effects of N and S additions on soil properties

In the forest floor, N addition increased exchangeable Ca^{2+} and K^{+} ($p<0.1$ and $p<0.05$, respectively) while S addition increased exchangeable Na^{+} ($p<0.05$) (Table 6-1). In the surface mineral soil, both N and S additions decreased exchangeable Ca^{2+} ($p<0.1$). Exchangeable Ca^{2+} and Mg^{2+} was the lowest in the +NS and the greatest in the CK treatments. Exchangeable K^{+} in the surface mineral soil was not affected by any of the treatments and exchangeable Na^{+} increased in the +S and +NS treatments ($p<0.01$) compared to that in the CK. Both N and S additions decreased Ca/Al ($p<0.1$), with greater Ca/Al in the CK than in any other treatments in the surface mineral soil ($p<0.1$) but not in the forest floor.

3.3 Effects of N and S additions on MBC, MBN, and inorganic N

The treatments did not affect MBC and MBN in the forest floor or the surface mineral soil (Figure 6-2). The MBC and MBN in the surface mineral soil were about one tenth of that in the forest floor. After the summer season, MBC and MBN decreased in the forest floor but increased in the surface mineral soil ($p<0.01$). The NH_4-N concentration was much higher in the forest floor than in the mineral soil (Figure 6-2). In the forest floor, N addition increased NH_4-N concentration from the first addition ($p<0.05$), but the treatment effect disappeared 80 days after the first application. By the following spring, NH_4-N concentrations in the forest floor were lower ($p<0.05$) in the +S and +NS than in the CK and +N treatments, suggesting that there might be a negative effect of S addition on N mineralization in early spring. The NO_3-N concentrations in the surface mineral soil were several times those in the forest floor (Figure 6-2). The NO_3-N concentrations in the forest floor were not affected by the treatments and were relatively stable across the sampling dates. The NO_3-N concentrations in the surface mineral soil were much higher in the +N and +NS treatments 10 and 20 days after the first addition ($p<0.05$) than those in the CK while no difference was found between treatments in the other sampling periods.

3.4 Effects of N and S additions on leaching loss of cations and anions

Soil solution was collected 15 cm below the mineral soil surface in May, July, and August while minimal amounts of soil solution were collected 45 cm below the mineral soil surface except in May, when large quantities of water from melting snow presumably leached through the soil profile. The leaching of NO_3^- below 15 cm was increased by N addition ($p<0.05$) while that of NH_4^+ was not affected by any of the treatments (Table 6-2 and Figure 6-3). However, annual leaching loss of inorganic N below the 15 cm depth was low in all treatments, with losses of $NH_4^+<1.0$ $mmol_c$ m^{-2} yr^{-1} and those of NO_3^- ranging between 0.3 and 1.5 $mmol_c$ m^{-2} yr^{-1} (Table 6-2). For both NH_4^+ and NO_3^-, leaching loss below 45 cm was negligible (Table 6-2). Annual leaching loss of SO_4^{2-} was increased by S addition below both 15 cm and 45 cm ($p<0.001$ for both) depths (Table 6-3). Most SO_4^{2-} leaching took place in May (Figure 6-4). Leaching losses of Ca^{2+}, Mg^{2+} and Na^+

had a similar trend to that of SO_4^{2-} (Figure 6-3 and 6-4). However, leaching loss of K^+ in May (data not shown) was similar to that in August. Sodium ion was dominant in soil solutions in the two S addition (+S and +NS) treatments, but minor in non-S added treatments (Table 6-2).

4. Discussion

4.1 Plant growth responses to simulated N and S depositions

Nitrogen addition increased tree growth in this study, indicating that N was a limiting factor in the studied forest ecosystem (Figure 6-1). This result supports our first hypothesis and is also consistent with the N-limited ecosystems hypothesis of Aber et al. (1998) and results of short-term fertilization studies in Canadian boreal forests (e.g. Newton and Amponsah 2006). This implies that tree growth in the studied forest ecosystem would be improved by elevated atmospheric N deposition in the near future. Coupled with global warming, the net primary productivity of boreal forests is expected to increase by N deposition, facilitating CO_2 sequestration in boreal forests (Hari and Kulmala, 2008; Magnaniet al., 2007). On the other hand, warmer temperature can alter N cycle in forest ecosystems. Increased soil temperature may accelerate N mineralization and increase N availability (Butler et al., 2012), which could possibly advance N saturation.

Tree biomass increment in the +NS treatment was greater than that in the +N treatment, suggesting that N and S additions had a synergistic effect on tree growth in the studied forest. Repeated N fertilization studies have reported potential limitation of other nutrients as increasing tree growth demands more nutrients (Amponsah et al. 2005; Kishchuk et al. 2002). It simply implies that S might become a limiting factor when N limitation is alleviated. Another possibility is that base cations may be a second limiting factor in the studied sites and released base cations such as Ca^{2+} and Mg^{2+} from exchange sites by Na^{+} from the added Na_2SO_4 or Na^{+} itself could provide a benefit for tree growth. The litterfall data is not consistent with the tree biomass increment data and it is possible that due to the limited plot area represented by the small litter traps the litterfall data did not fully capture the spatial variation of litterfall.

Improved overstory tree growth following elevated levels of N deposition may decrease the growth of the understory vegetation (Thomas et al. 1999). On the other hand, N addition may not increase tree growth when the understory vegetation competes for the limited N supply in the soil (Matsushima and Chang 2006). In this study, N addition did not affect understory growth even though it increased N concentrations in the understory vegetation (Figure 6-1c), implying that the growth of the understory vegetation was likely limited by other factors, such as light availability. However, chronic N deposition can affect understory community structure. Increased N availability may facilitate growth of nitrophilic species and affect the competitive interaction between plants (Gilliam 2006), or affect plant community structure indirectly by influencing biotic conditions such as infestation of insects and pathogens (Nordinet al. 2009). In the studied forest ecosystem, N addition increased the percent cover of nitrophilic understory species such as wild sarsaparilla and Canada may flower (*Maianthemum canadense*), while S addition increased the percent cover of bunchberry dogwood (*Comus Canadensis*) but decreased that of prickly rose after three years of simulated N and S additions (Neufeld, unpublished data); though the total understory biomass was not affected by N and/or S additions (Figure 6-1c). Further research is needed to better understand the effects of N and S depositions on plant communities as well as nutrient cycling in the AOSR.

4.2 Soil N and nitrate leaching responses to simulated N and S depositions

The time required for significant responses to N deposition to occur varies with the specific N pool of concern. Soil inorganic N concentrations typically respond quickly to N deposition as compared with other N pools such as the soil organic N (Gundersenet al. 1998). Increased soil inorganic N concentration reflects the alleviation of N limitation and may subsequently be followed by N leaching (likely after many years of continued N deposition), a sign considered to indicate N saturation (Aber et al. 1998). In this study, N addition induced an immediate increase in soil NH_4^+ and NO_3^- concentrations that were not sustained (Figure 6-2), possibly related to several mechanisms. First, the added N may be transferred from inorganic to other N forms/pools in the ecosystem, such as being taken up by plants to support increased tree growth (see the previous section). Second, inorganic N may become immobilized by soil microbes that can increase with increased N deposition (Tietema 1998; Gouldinget al. 1998). Soil microbial biomass in this study was not affected by N and S treatments but by sampling time (Figure 6-2), likely due to seasonal changes of abiotic factors such as soil temperature and water availability (Tate 1995; Yang et al. 2010). Another potential is N leaching loss. However, our data indicate that leaching of NO_3^- below 45 cm of the soil profile was negligible in all treatments, due to the low annual precipitation, relatively low permeability of the illuviated B horizon in Luvisolic soils and the tight N cycling even after an artificial addition of 30 kg N ha^{-1} yr^{-1} for 4 years, implying that the studied ecosystem had not exceeded its N retention capacity.

Our result therefore supports the second hypothesis and is consistent with results in the accelerated N addition study in eastern Canada reporting no N saturation with deposition rates ranging from 9 to 85 kg N ha^{-1} yr^{-1} (Houle 2006; Moore and Houle 2009). On a long-term basis, however, 10 kg N ha^{-1} of deposition has been regarded as a threshold likely to lead to significant N leaching based on data from 126 forest sites in Europe and North America (Dise and Wright 1995; Stoddard et al. 2001). In Canada, the highest deposition rates were reported for south-central Ontario and south-western Quebec with about 13 kg N ha^{-1} yr^{-1} in the 1990s and currently normally less than 10 kg N ha^{-1} yr^{-1} based on the Canadian Air and Precipitation Monitoring Network (Vet et al. 2004). Those were moderate levels of deposition as compared to the much higher deposition rates in some areas in Europe and the United States (Jeffries 1995). So far only a few watersheds such as the Turkey Lake watershed have been reported to experience N saturation (Foster et al. 1989; Houle 2006). Current N deposition rates in the AOSR have been reported to be low, at about 2 kg N ha^{-1} yr^{-1} (Jung et al. 2011b; Wiederet al. 2010). Based on the reported N deposition rates in the AOSR and our results from this short-term simulated N and S deposition study, the risk of N saturation appears to be low in the studied forest ecosystem.

Care should be taken when applying the result from this study to the whole boreal forest ecosystem in the AOSR. Considering that N concentration in the atmosphere changes with distance from emission sources, N deposition would range widely depending on the location in relation to the emission sources; for example, in 2009, annual averages of N_2O concentration in the air around industry sites ranged from 4.8 to 29.7 ppb and were much higher than the 2.5 ppb near Anzac, a site located about35 km southeast of Fort McMurray (WBEA 2010). Furthermore, NO_x emissions have increased and are expected to further increase in the region. For example, emission rates of NO_x in the early 2000s were more than twice that of the rates in the early 1990s (Hazewinkelet al. 2008). Therefore, the effects of N deposition on ecosystems in the AOSR remain a major concern.

4.3 Soil exchangeable cations and cation leaching

In this study, simulated N and S depositions decreased exchangeable Ca^{2+} and/or Mg^{2+} in the surface mineral soil whereas N addition increased exchangeable Ca^{2+} in the forest floor (Table 6-1), likely due to calcium recycling from greater deposition of litterfall (Likens and Bormann 1995). Two possible processes may have caused the lower exchangeable cation concentrations in the surface mineral soil in the N and/or S added treatments: leaching and plant uptake. Base cation leaching and subsequent deficiency of cationic nutrients have been described as harmful effects of acid deposition (Aber et al. 1989; Binkley and Richter 1987). Numerous factors affect base cation leaching such as weather conditions and soil physical and chemical properties (Likens and Bormann 1995; De Schrijveret al. 2008). In the AOSR, a quarter of the annual precipitation (456 mm) (Environment Canada 2010) falls down to the soil as snow during the non-growing season and the majority of it may infiltrate into the soil or lost as surface runoff over a short snow-melting period with minimal transpiration. In contrast, water infiltration into the soil in the growing season is relatively low with the region having low annual precipitation and about half of the annual precipitation occurring between June and August (Environment Canada 2010). In this study, leaching loss in May following snowmelt was responsible for most of the annual loss for SO_4^{2-} and cations. Increased SO_4^{2-} leaching in early spring in the +S and +NS treatments accompanied the increased leaching of cations and the extent of SO_4^{2-} leaching loss was similar to the sum of cation leaching loss (Figure 6-3 and 6-4). Considering that H^+ deposition is normally paired with SO_4^{2-} deposition under natural conditions and more strongly adsorbed to cation exchange sites than Na^+ (Bohn et al. 2001) that was used in this study, the risk of Ca^{2+}, Mg^{2+} and K^+ leaching with SO_4^{2-} was probably greater than what was determined in this study at a given S addition level.

Nitrogen addition effects on exchangeable $Ca^{2+}$and Mg^{2+} concentrations in the surface mineral soil were significant and the combination with N and S additions intensified the decrease of exchangeable Ca^{2+} and Mg^{2+} (Table 6-1). Depletion of exchangeable Ca^{2+} and Mg^{2+} in the surface mineral soil could be caused by increased storage (through plant uptake) of Ca and Mg in plant biomass as well as increased leaching out of a particular soil layer or decreased deposition of those cations through litterfall (Likens et al. 1998). However, when the rooting zone was considered as a unit for evaluation, the third hypothesis is also supported by results from this study, that cationic nutrient leaching was not affected by the elevated level of simulated N deposition. Increased Ca and Mg uptake accompanying increased tree growth by N fertilization likely contributed to the reduction of exchangeable Ca^{2+} and Mg^{2+} in the mineral soil in the N addition treatments. Long-term studies have reported that repeated N fertilization or chronic N deposition with excessive amount of N may induce nutrient imbalance in the soil and plant (Aber et al., 1989; Skeffington and Wilson, 1988) as increased tree growth demands additional amounts of other nutrients. As S deposition is expected to have accelerated soil acidification in the AOSR, which has soils that are coarse textures and have low S adsorption capacity (Aherne and Shaw 2010; Jung et al. 2011a), reduction of the soil exchangeable cationic nutrient pool caused by increased N deposition can exacerbate nutrient imbalance or deficiency in combination with soil acidification (Erisman and De Vries 2000), even though significant nitrate leaching did not occur in the AOSR.

Based on our results, no sign of N saturation was found in the studied ecosystem after four years of N addition, which was consistent with previous research in other study sites with similar or greater application rates (Moore and Houle, 2009; Sogn and Abrahamsen, 1998). However, episodic surface runoff by snowmelt and torrential rain, not determined in this study, may temporarily contribute to increasing nitrate in downstream surface water channels though precipitation and evaporation are approximately balanced in the Athabasca oil sands region (Betts, 2004; Ok et al., 2007). In addition, expected increase in N mineralization by global warming may potentially increase the risk of N saturation. Therefore, the long-term effect of elevated levels of N deposition, especially coupled with significant S deposition, remains a concern, as nutrient imbalance or deficiency in the AOSR can rapidly occur due to reductions in soil cationic nutrient availabilities caused by increased tree growth/uptake and cation loss that accompanies SO_4^{2-} leaching.

5. Conclusions

There was no evidence of N saturation in the studied forest ecosystem in the AOSR after four years of elevated levels of simulated N and S depositions (with a total of 120 kg ha^{-1} of N or S added alone or in combination). There was no long-term increase of inorganic N concentrations in the soil, leaching of N beyond the main rooting zone in the soil profile was minimal, and tree growth was increased by simulated N deposition, all indications of N limitation in the studied forest stand. However, exchangeable Ca^{2+} and Mg^{2+} concentrations in the surface mineral soil layer were found to be reduced by N and S additions because of increased cation leaching associated with increased SO_4^{2-} leaching caused by S addition and increased nutrient uptake associated with increased tree growth resulting from N addition. This has implications for the potential risk of induced nutrient imbalance in boreal forests in the AOSR by long-term chronic N and S depositions. The long-term effects of N and S depositions on the cycling of N and other nutrients in ecosystems in the AOSR remain to be studied, even though the immediate risk of N saturation or causing negative environmental consequences in the boreal forest is low if the rates of N and S depositions can be controlled at the current level.

Table 6-1 Basic properties of soils sampled in 2010 from the studied site in a mixedwood forest in the Athabasca oil sands region. Lowercase letters indicate a significant difference at α=0.1. Values in parentheses are standard errors of the means.

Soil layer	Treat-ment	pH	Total C	Total N	Exchangeable cations					CECe[1]	Base saturation					Ca/Al[1]
					Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Al^{3+}		Total	Ca	Mg	K	Na	
			(g kg^{-1})		(cmol$_c$ kg^{-1})											
Forest floor	CK	5.5	296	13.7	41.2ab	5.5	7.5c	0.09c	0.06	54.7	99.1	74.9a	10.2	13.8	0.2c	1207
		(0.2)	(36)	(2.1)	(6.8)	(1.1)	(0.4)	(0.01)	(0.03)	(6.8)	(0.3)	(1.8)	(0.9)	(1.2)	(0.01)	(655)
	+N	5.5	308	14.4	47.5a	6.7	8.5b	0.11c	0.07	63.5	99.0	74.7a	10.7	13.4	0.2c	1140
		(0.1)	(37)	(1.2)	(6.1)	(1.0)	(0.8)	(0.01)	(0.04)	(7.1)	(0.2)	(1.0)	(1.3)	(0.5)	(0.01)	(397)
	+S	5.5	311	13.4	37.5b	5.5	8.2b	0.66b	0.06	52.5	98.8	71.4b	10.3	15.7	1.3b	953
		(0.2)	(52)	(2.2)	(5.6)	(1.2)	(0.8)	(0.2)	(0.03)	(7.7)	(0.2)	(0.3)	(0.7)	(0.4)	(0.3)	(298)
	+NS	5.5	311	13.9	45.8ab	6.6	8.9a	1.6a	0.05	63.5	99.0	72.1ab	10.1	14.3	2.6a	1630
		(0.2)	(24)	(1.8)	(9.1)	(3.1)	(1.1)	(1.0)	(0.02)	(11.9)	(0.2)	(0.8)	(0.9)	(1.5)	(0.8)	(891)
Surface mineral soil (0-15 cm)	CK	5.0a	5.7	0.35	3.5a	0.67a	0.56	0.06c	0.23	5.2a	93.1a	67.8a	13.1a	11.0c	1.3c	75.7a
		(0.1)	(0.8)	(0.07)	(0.7)	(0.11)	(0.05)	(0.01)	(0.28)	(0.3)	(3.1)	(3.5)	(1.2)a	(0.9)	(0.1)	(89.8)
	+N	4.5b	6.2	0.37	2.5ab	0.55ab	0.56	0.06c	0.38	4.2bc	87.8ab	59.9b	13.0a	13.4ab	1.5c	12.9b
		(0.2)	(0.6)	(0.06)	(0.2)	(0.11)	(0.04)	(0.00)	(0.21)	(0.1)	(2.5)	(2.0)	(1.0)	(0.9)	(0.1)	(7.7)
	+S	4.7ab	5.8	0.36	2.8ab	0.51ab	0.56	0.31a	0.35	3.70c	84.6b	53.5c	10.7b	15.1a	5.4b	14.3b
		(0.3)	(0.7)	(0.04)	(0.3)	(0.15)	(0.04)	(0.07)	(0.10)	(0.2)	(4.5)	(4.5)	(0.9)	(0.9)	(0.2)	(16.3)
	+NS	4.8ab	6.3	0.37	2.0b	0.39b	0.55	0.20b	0.40	4.7ab	89.5ab	59.9b	10.8b	12.1bc	6.7a	13.0b
		(0.1)	(0.3)	(0.03)	(0.6)	(0.08)	(0.05)	(0.02)	(0.26)	(0.2)	(1.6)	(2.0)	(1.1)	(0.5)	(0.8)	(4.6)

[1] CECe indicates the effective cation exchange capacity.

[2] Ca/Al is the ratio of exchangeable Ca^{2+} to exchangeable Al^{3+} based on a molar unit.

Table 6-2 Annual leaching loss of NO_3^-, SO_4^{2-}, $NH_4^+$and base cations in 2009 in a mixedwood forest in the Athabasca oil sands region, Alberta, Canada. Lowercase letters indicate a significant difference at α=0.1. Values in parentheses are standard errors of the means.

Depth	Treat-ment	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+
		---------- $mmol_c\ m^{-2}\ yr^{-1}$ ----------						
Below 15 cm soil depth	CK	6.9b	0.3b	0.7	7.9b	3.9ab	2.8bc	1.2c
		(2.4)	(0.1)	(0.1)	(1.4)	(1.1)	(0.8)	(0.3)
	+N	3.9b	1.5a	0.9	9.0ab	3.6b	6.1a	2.9b
		(2.4)	(0.7)	(0.3)	(1.3)	(0.4)	(2.1)	(0.6)
	+S	59.1a	0.1b	0.8	11.2a	4.9a	3.1b	46.5a
		(22.1)	(0.0)	(0.2)	(2.1)	(1.1)	(0.7)	(10.7)
	+NS	55.0a	1.3a	0.8	8.2ab	3.8ab	2.2c	41.3a
		(23.4)	(0.5)	(0.2)	(1.4)	(0.5)	(0.2)	(11.3)
Below 45 cm soil depth	CK	2.3c	0.03	0.2b	0.8c	0.2c	0.03	0.1b
		(1.2)	(0.01)	(0.1)	(0.1)	(0.1)	(0.01)	(0.1)
	+N	0.3d	0.02	0.1b	0.4d	0.1c	0.1	0.1b
		(0.2)	(0.01)	(0.05)	(0.1)	(0.1)	(0.01)	(0.2)
	+S	12.4a	0.02	0.1b	4.1a	0.9a	0.1	1.9a
		(3.5)	(0.02)	(0.04)	(0.6)	(0.6)	(0.1)	(1.2)
	+NS	6.1b	0.04	0.5a	1.6b	0.6b	0.1	1.3a
		(1.0)	(0.02)	(0.2)	(0.6)	(0.2)	(0.1)	(0.4)

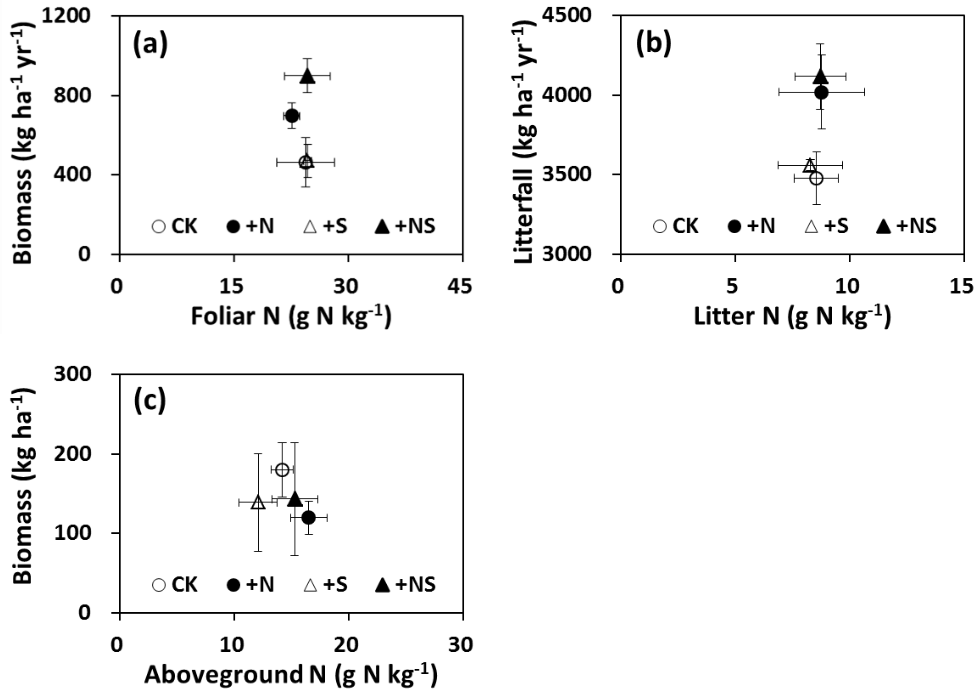

Figure 6-1 Effects of N and S additions on the forest vegetation: a) canopy trees (*Populus tremuloides*), b) litterfall, and c) understory in 2009 in a mixedwood forest in the Athabasca oil sands region, Alberta, Canada. Nitrogen and S were applied at the rate of 30 kg ha yr^{-1} as N and/or S from 2006. The CK, +N, +S and +NS refer to control, N addition, S addition and N+S addition, respectively. Error bars are standard errors of means.

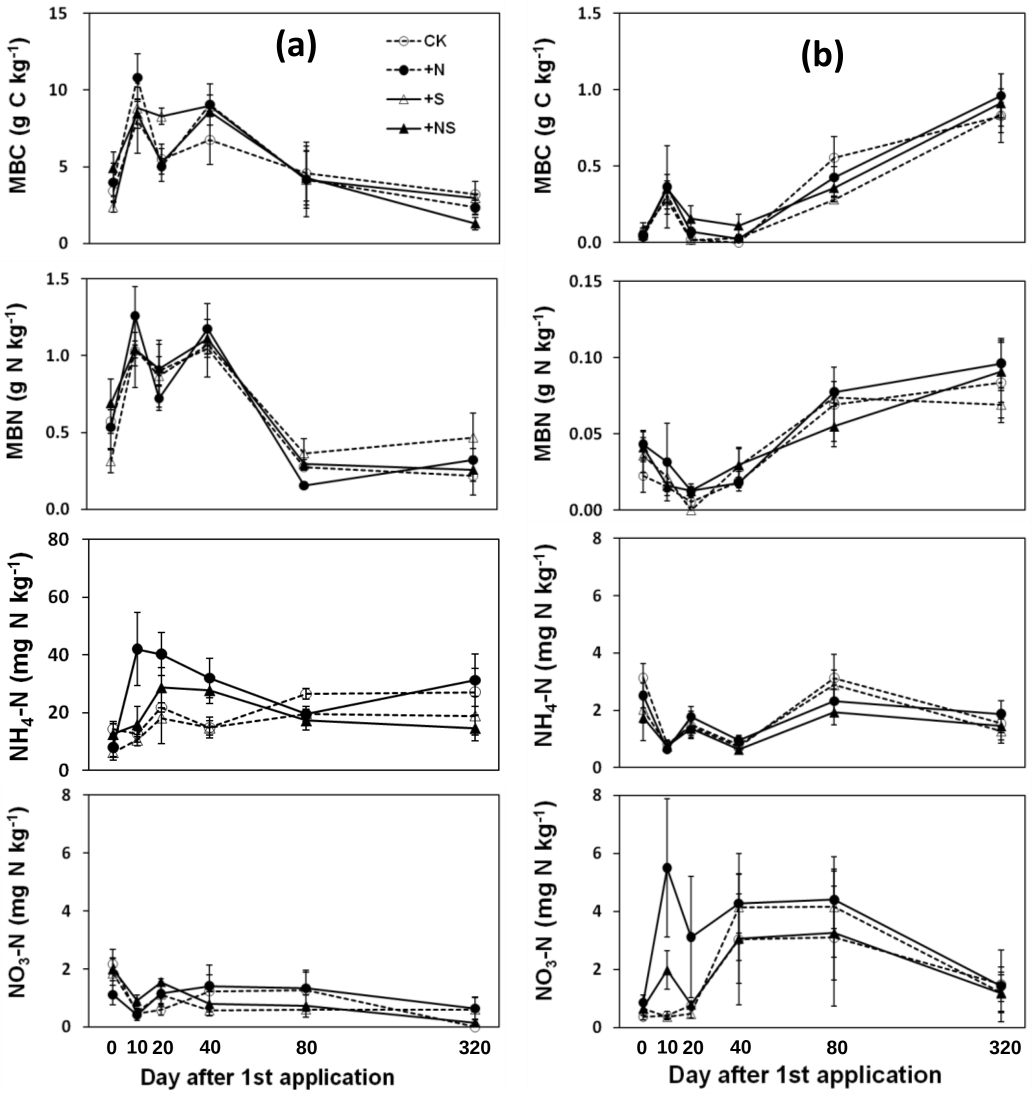

Figure 6-2 Effects of N and S additions on soil microbial biomass C (MBC), N (MBN), and inorganic N in a) the forest floor and b) the surface mineral soil in 2009 in a mixedwood forest in the Athabasca oil sands region, Alberta, Canada. The CK, +N, +S and +NS refer to control, N addition, S addition and N+S addition, respectively. First addition in 2009 was on July 2, with a rate of 10 kg N and/or S, and the 2nd and 3rd additions occurred 20 and 40 days after the 1st addition, respectively, with the same rate. Error bars are standard errors of means.

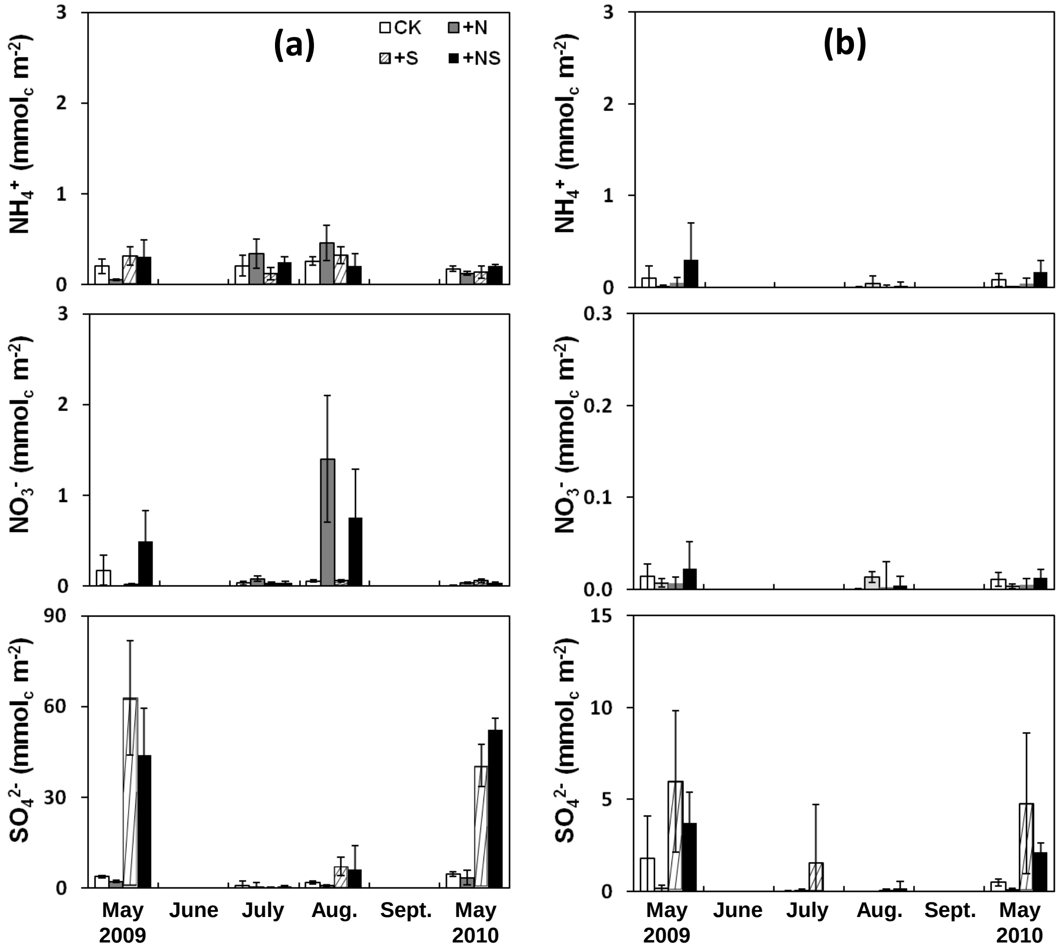

Figure 6-3 Effects of N and S additions on leaching loss a) below 15 cm and b) below 45 cm of NH_4^+, NO_3^- and SO_4^{2-} in 2009 in a mixedwood forest in the Athabasca oil sands region, Alberta, Canada. The CK, + N, +S and +NS refer to control, N addition, S addition and N+S addition, respectively. Error bars are standard errors of means.

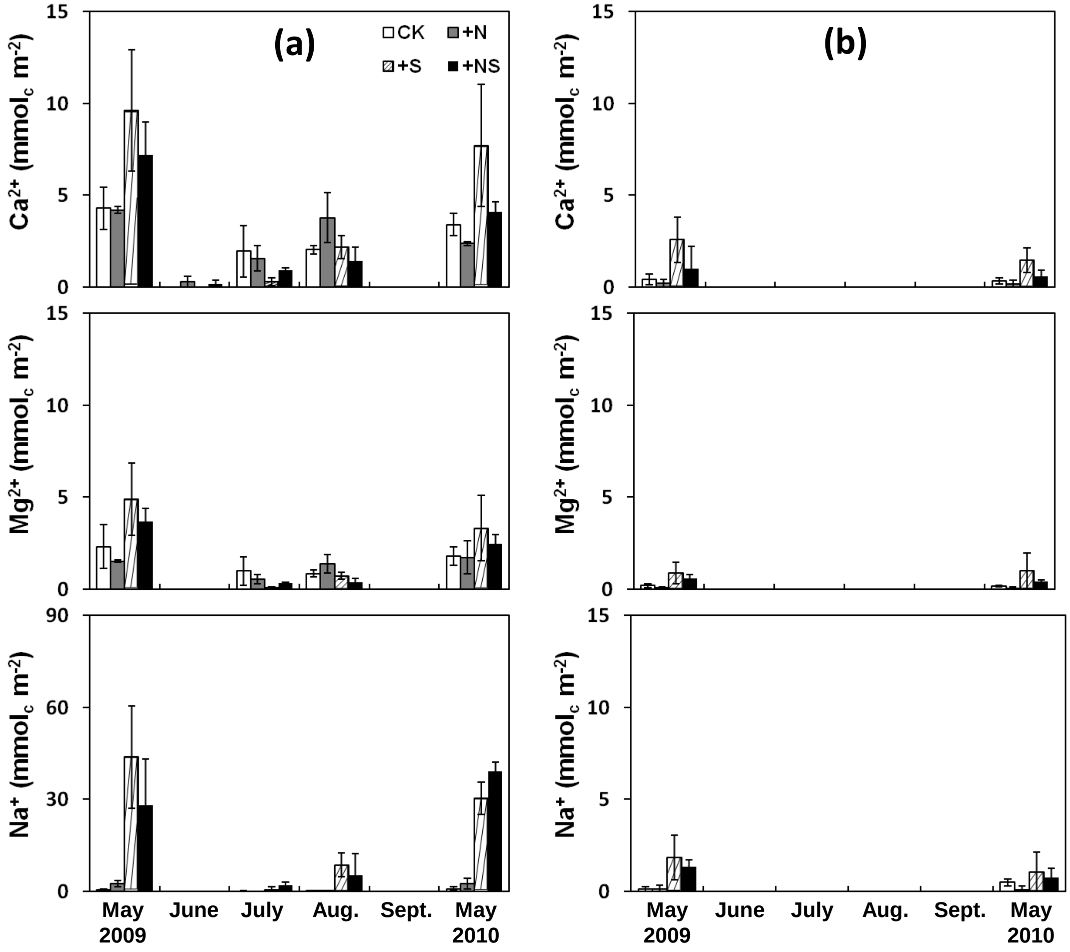

Figure 6-4 Effects of N and S additions on leaching loss a) below 15 cm, and b) below 45 cm of base cations in 2009 in a mixedwood forest in the Athabasca oil sands region, Alberta, Canada. The CK, + N, +S and +NS refer to control, N addition, S addition and N+S addition, respectively. Error bars are standard errors of means.

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Chapter 7. Synthesis, conclusions, and future research

1. Overview of study objectives

The objectives of the study were 1) to assess long-term impacts of acid deposition on forest ecosystems in the AOSR, 2) to determine current risk of acid deposition based on critical loads (CLs), exceedances of CLs (EXs), and H^+ budget of soils with models that are able to consider the effects of trees, and 3) to evaluate potential changes in boreal forest ecosystems caused by chronic acid deposition. Studies in chapters 2 and 3 were conducted to achieve the first objectives. I examined soil and tree chemistry that indicates long-term effects of air pollution. Indicators that are able to assess impacts of acid deposition among watersheds were selected. Studies in chapters 4 and 5 were carried out to accomplish the second objective. I selected the canopy budget model to calculate bulk deposition and interception deposition of each anion and each cation. The model was modified so that it could calculate H^+ input or removal in different components of throughfall: bulk deposition, interception deposition, canopy leaching, and canopy uptake. Based on the results, I calculated CLs and EXs with and without interception deposition and tested the hypothesis that CLs and EXs are underestimated by the conventional method that excludes interception deposition. Also, I determined H^+ budget of soils under current soil acidification or recovery rate. For the last objective, I conducted a simulated N and S deposition experiment to evaluate effects of increasing acid deposition on boreal forests in the AOSR (Chapter 6).

2. Summary and synthesis of the research results

2.1 Impacts of N deposition on N status of boreal forests

Rates of NO_x emission have increased in the AOSR since the commercial oil production started in 1967 (Hazewinkel et al., 2008). Chronic N emission and subsequent N deposition are expected to increase N availability in the N-limited boreal forests in the AOSR. The lower $\delta^{15}N$ in watershed NE7 than in watershed SM8 while the $\delta^{15}N$ of mineral soil did not show any difference between watersheds was likely due to disturbance of ^{15}N signals by N transformation and transportation processes in soils (Garten Jr and Van Miegroet, 1994); NE7 (57.15° N, 110.86° W) has been exposed greater atmospheric deposition than SM8 (56.21° N, 111.20° W) due to closeness to emission sources and wind direction (Wieder et al., 2010). Although there was a pattern of increasing NO_x emission, N concentration and $\delta^{15}N$ of tree rings of each species did not present any trend over time in both watersheds. Meanwhile, Diff_N and Diff_$\delta^{15}N$ indicated relative increase of N availability in NE7 caused by ^{15}N-depleted atmospheric N deposition, which was consistent with the $\delta^{15}N$ of forest floor; Diff_x was calculated as x of each tree ring in NE7 minus x of each tree ring in SM8. Diff_N and Diff_$\delta^{15}N$ of *Populus tremuloides* (trembling aspen, aspen) tree rings could explain the changes clearly compared to *Pinus banksiana* (jack pine) tree rings because deciduous stands have relatively quicker N cycling than evergreen conifers (Augusto et al., 2002). Based on our results, $\delta^{15}N$ of the forest floor and Diff_N and Diff_$\delta^{15}N$ of tree rings can be useful indicators to investigate impacts of atmospheric N deposition and relative changes in soil N availability.

Increasing N availability was identified clearly in simulated N and S deposition experiments with four years of elevated levels of simulated N and S depositions (a total 120 kg ha^{-1} of N or S added alone or in combination). Elevated N input improved tree growth due to greater N availability but not for understory growth. However, no signs of N saturation were found in the studied forest ecosystem: no increase of inorganic N concentrations in the soil and negligible leaching of N beyond the main rooting zone in the soil profile. Exchangeable Ca^{2+} and Mg^{2+} concentrations in the surface mineral soil layer were found to be reduced by increased cation uptake associated with increased tree growth caused by N addition. Increased uptake of cationic nutrient in combination with base cations leaching with SO_4^{2-} leaching has implications for potential risk of inducing nutrient imbalance in boreal forests in the AOSR. Therefore, further research is needed to establish critical loads of N deposition to prevent adverse effects of N deposition on forest ecosystems in the AOSR.

2.2 Impacts of S deposition on soil chemistry in boreal forests

With chronic S deposition for the past several decades, available SO_4^{2-} (as a sum of soluble and adsorbed SO_4^{2-}) of forest floor and surface soil (0-5 cm) increased toward tree boles in both tree stands and in both watersheds, which was consistent with increasing SO_4^{2-} concentrations in stemflow and throughfall as compared to bulk precipitation. With base cation leaching mainly associated with SO_4^{2-} leaching (NO_3^- leaching was negligible), pH and soluble base cations decreased toward jack pine tree boles. Meanwhile, pH and soluble base cations increased toward aspen tree boles due to canopy leaching of base cations. This remarkable difference of soil chemistry between different tree species can affect other aspects of boreal forest ecosystems in the AOSR such as succession pathway; seedlings of different species have different sensitivities to toxic Al ions (Vanguelova et al., 2007a).

From 2005 to 2010, increases of available SO_4^{2-} in the forest floor and surface mineral soil (0-15 cm) were found, which indicated that soils could have a capacity to adsorb some deposited SO_4^{2-} ions though chronic S deposition for the past decades. Meanwhile, excessive SO_4^{2-} moved down with drainage water inducing base cation leaching, at least below 15 cm, which could reduce exchangeable base cations from surface mineral soil; SO_4^{2-} leaching below 45 cm was much lower than that below 15 cm due to low precipitation in the AOSR. Simulated N and S deposition experiments clearly resulted in decrease of exchangeable Ca^{2+} and Mg^{2+} concentrations in the surface mineral soil layer due to SO_4^{2-} leaching. Therefore, acidification can occur in the surface mineral soil in the AOSR though H^+ budgets of soils or EXs were estimated lower than zero within effective rooting depth (45 cm).

2.3 Risk of soil acidification in boreal forests in the AOSR

Atmospheric deposition of SO_4^{2-} and NO_3^- were 4.1 kg S ha^{-1} and 2.2 kg N ha^{-1} yr^{-1}, respectively, in NE7, and 3.2 and 1.8 kg ha^{-1} yr^{-1} in SM8, respectively, based on data collected from 2006 to 2009. These deposition rates are moderately low compared with other areas showing adverse effects of acid deposition such as eastern North America (WMO, 2005; Vet et al., 2005), Europe (e.g., Vanguelova et al., 2007b), and eastern Asia (e.g., Fujii et al., 2008). However, these low deposition rates does not directly mean low risk of soil acidification as soil chemistry is affected by site-specific characteristics like weathering rates of base cations as well as deposition rates.

Sulfate and nitrate were deposited mainly by canopy interception while base cations were deposited through bulk precipitation. It implies that CLs and EXs calculated without considering bulk deposition are potentially underestimated. The CLs and the EXs were calculated with two methods: the conventional method with bulk deposition only and the modified method with bulk and interception deposition; CLs and EXs were evaluated for S deposition only because N deposition does not contribute to soil acidification before N saturation.

The CLs calculated by the conventional method were similar to those by the method considering both interception deposition and bulk deposition because a main depositional process of base cation was bulk deposition. Meanwhile, the EXs were significantly underestimated by excluding interception deposition as SO_4^{2-} was deposited into forest ecosystems mainly by canopy interception.

The CLs were 349 $mol_c\ ha^{-1}\ yr^{-1}$ in NE7 and 429 $mol_c\ ha^{-1}\ yr^{-1}$ in SM8 that are in the range of CLs of acid-sensitive watersheds in the AOSR assessed by simulated data ranging from 210 to 1440 $mol_c\ ha^{-1}\ yr^{-1}$ (Whitfield et al., 2010). The S deposition (the sum of bulk deposition and interception deposition) between studied period was similar to or somewhat lower than CLs in NE7 and SM8. This indicates that the risk of soil acidification is low at controlling SO_2 emission in the level of studied period with the assumption that boreal forests remains N-limited.

From 2005 to 2010, soil pH in the forest floor increased (no changes in mineral soils between 0 to 45 cm) and H^+ budgets of soils within 45cm (as an effective rooting depth) were evaluated negative values in NE7 and SM8. These imply recovery of soil acidification, which was consistent with negative values of EXs. Possible scenario is that the soil acidification rate started decreasing when SO_2 emission reached the acme in 1980s, and soil was being recovered from previous acidification in the studied period. Dominant H^+ sinks were storing SO_4^{2-} in soil and protonation of weak acid anions. Therefore, recovery of soil acidification may be limited when SO_4^{2-} adsorption capacity get close to saturation or soil pH reaches to dissociation coefficients of weak acid anions.

The Ca/Al ratios of soil solution and fine roots have been used as sensitive indicators of acid stress under soil acidification caused by acid deposition. The Ca/Al ratios of soil solution and fine roots, on average, did not achieve the threshold level of acid stress. Aluminum concentrations in soil solution, however, reached the level inhibiting growth of aspen and *picea glauca* (white spruce) seedlings, possibly affecting forest succession in the AOSR.

Based on EXs and H^+ budget of soils, the risk of soil acidification was low in NE7 and SM8 under studied S deposition level though these watersheds were expected sensitive to acidification due to low pH buffering capacity and low SO_4^{2-} adsorption capacity. Dominant trees were not exposed to acid and Al stress indicated by Ca/Al ratios of soil solution and fine roots. However, understory growth such as seedlings of Al-sensitive species could be inhibited by Al toxicity.

2.4 Assessing the H^+ budget in throughfall deposition

The canopy budget model was modified by incorporating a new term about canopy leaching of weak acid anion, dominantly organic anion. It allowed that the model could evaluate each source and sink of H^+ in throughfall deposition: sources included bulk deposition, interception deposition and canopy leaching and canopy uptake was the only sink. The deposition of H^+ through bulk precipitation, the principal depositional process of base materials, was lower in NE7 than in SM8 because of greater base cation deposition in NE7. Meanwhile, interception deposition of H^+ was greater in NE7, which was affected by greater acid deposition. The canopy leaching of H^+ of each tree species was similar between watersheds. Approximately 130 mol_c ha^{-1} yr^{-1} of H^+ was supplied as organic acids by jack pine canopy whereas organic acid leaching from aspen canopy was negligible.

3. Conclusions

The boreal forests in the AOSR have been affected by N and S deposition, as indicated by soil and tree chemistry. The atmospheric N deposition increased N availability in the AOSR. The impacts were greater in NE7 than in SM8 due to greater N deposition. It was indicated by lower $\delta^{15}N$ in the forest floor in NE7, increasing Diff_N and decreasing Diff_$\delta^{15}N$ of tree ring chemistry over time; N and $\delta^{15}N$ of tree ring in each watershed did not show a relationship with N deposition. This suggests that comparing chronological changes in N and $\delta^{15}N$ between watersheds with different deposition rates can be a more detectable approach under relatively low N deposition than just evaluating N and $\delta^{15}N$ alone in examining the long-term impacts. The chronic S deposition was reflected in the spatial variation of available SO_4^{2-} of soils. Due to increasing SO_4^{2-} input by throughfall and stemflow, Available SO_4^{2-} increased toward tree boles in both jack pine and aspen stands. With interception deposition of SO_4^{2-} in combination with canopy leaching of organic anions, soluble base cation and pH decreased toward jack pine tree boles while the reverse trends were found for aspen trees. It induced 5 to 20 times lower soluble Ca/Al near jack pine trees than aspen trees.

The dominant depositional process of acid material was interception deposition while base cations was deposited by precipitation deposition in the AOSR. With the difference of depositional processes, EXs were significantly underestimated with the conventional simple mass balance model that excludes interception deposition; however, CLs were not affected by excluding interception deposition. It suggests that EXs should be calculated including both interception deposition and bulk deposition in order to assess the risk of soil acidification caused by acid deposition in forest ecosystems.

The risk of soil acidification was low in NE7 and SM8 under studied S deposition level based on EXs and H^+ budget of soils and acid stress of dominant canopy trees were not found based on Ca/Al ratios of soil solutions and fine roots, understory growth was of concern due to Al toxicity.

The artificial N and S deposition with elevated deposition levels resulted in significant changes in soil and tree chemistry, and tree growth. The N deposition provides beneficial effects on tree growth, which decreased soil cationic nutrient concentrations in the surface mineral soil due to increased tree uptake. The S deposition caused significant base cation leaching without causing any effect on tree growth. Although the immediate risk of N saturation or base cation depletion is low under current deposition rates, changes in soil nutrients in the study suggested that the long-term impacts of N and S depositions on the health of boreal forests in the AOSR should be studied.

4. Suggestions for future research

4.1 Developing a model to estimate total deposition with bulk deposition

Interception deposition generally contributes a significant portion of atmospheric deposition in forest ecosystems. It is the dominant depositional process of acid materials in the AOSR. Nevertheless, CLs and EXs have been calculated with bulk deposition to map CLs and EXs and to select acid-sensitive regions in the AOSR and other areas in Alberta (Aherne, 2008; Whitfield et al., 2010) because bulk deposition has been monitored in many sites in the AOSR to assess atmospheric deposition (WBEA, 2011) and can be extrapolated with collected data and the geological information system (GIS) (Aherne, 2008; UBA, 2004). Due to technical complexity determining interception deposition and variation of interception deposition with canopy conditions such as tree species and leaf area index, constructing a monitoring system of atmospheric deposition including interception deposition is not realistic. The alternative approach is to develop a model to estimate total atmospheric deposition based on bulk deposition. As aerosols can travel longer than particulate matters, the portion of interception deposition can increase with the distance from emission sources. Therefore, the model can be developed based on changes in ratios of atmospheric deposition to bulk deposition with a distance from mining areas.

4.2 Quantifying canopy leaching of organic acids

Coniferous trees are known to acidify soils and canopy leaching of organic acids is one of important processes that conifers increase soil acidity (Inagaki et al., 1995; Chiwa et al., 2008). However, quantification of organic acid leaching from canopy is complicated because ions are deposited to soil by mixture of bulk deposition, interception deposition, and canopy leaching. In this study, the modified canopy budget model could allow calculating canopy leaching of organic acids from jack pine and produced reliable results. It means that the modified canopy budget model is applicable to various future researches. organic acid leaching may be affected by a number of factors such as tree species, tree age, and environmental conditions. Using the modified model can support to investigate response of organic acid leaching to changes in a variety of internal and external conditions of trees.

4.3 Changes in N status in the AOSR

The NO_x emission has increased gradually, but adverse effects of N deposition on forest ecosystems have never been reported in the AOSR due to N limitation of the ecosystems. However, impacts of chronic N deposition such as N saturation are of concern with the expected increase in NO_x emission, which implies an increasing demand in assessing and predicting changes in N status in the AOSR. The N status of forest ecosystems can be divided into different stages with relation to responses of ecosystems to chronic N deposition: N limitation, alleviation of N limitation, and N saturation (Aber et al., 1998). The progress to N saturation may not be affected by only N deposition but also the edaphic condition of each site. I found that Diff_N and Diff_δ^{15}N of tree ring chemistry could reflect changes in N availability over time; those indicators were less affected by inter-translocation of N in trees and site-specific characteristics such as N availability and N transformation processes. These indicators can be used for further researchers to assess and predict N status of forest ecosystems. Another finding in this thesis was increasing trend of annual basal area increment of aspen trees in NE7 and SM8 over time likely affected by ameliorated N-limitation. Therefore, evaluating changes in stand volume with a dendrochronological approach can be worth investigating trends of forest growth caused by chronic N deposition.

4.4 Impacts of acid deposition on understory plants

In this thesis, some findings implied potential impacts of N and S deposition on understory plants. Aluminum concentrations in soil solution at 15 cm and 45 cm reached the level to inhibit growth of Al-sensitive seedlings in NE7 and SM8. The simulated N and S deposition experiment showed decreasing exchangeable soil cations in the surface mineral soil, at least, by 15 cm. In addition, the beneficial effect of N deposition on growth of dominant canopy trees can increase intercepted light sources by tree canopy and decrease light for understory species. These findings suggested that changes in environment caused by N and S deposition may give adverse effects on understory plants sensitive to Al toxicity, cationic nutrient deficiency, and light-limitation. On the other hand, these environmental changes can provide better conditions for tolerant understory species to acid strains and/or light-limitation. Therefore, further researches on the effects of N and S deposition on understory vegetation and forest succession in the AOSR would be valuable for understanding the impact of acid deposition on ecosystem processes.

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Appendix I. Basic information of research plots in NE7 and SM8

Water-shed	Ecological unit	Plot	Location		Soil type	Dominant tree	Stand age[1]	DBH (cm)[2]		Understory
			Latitude (N)	Longitude (W)				Mean	Range	
NE7	BM-b1	1	57.1412	110.8909	Gray Luvisol	*Populus tremuloides*	53	11.6	2.6-22.6	*Rosa acicularis, Alnus crispa, Linnaea borealis, Viburnum edule*
		2	57.1412	110.8914	Dystric Brunisol	*Pinus banksiana*	53	9.2	3.1-18.9	*Vaccinium vitis-idaea, Rosa acicularis, Cornus canadensis, Ledum groenlandicum*
		3	57.1395	110.8922	Dystric Brunisol	*Populus tremuloides*	49	5.0	1.8-9.2	*Vaccinium myrtilloides, Rosa acicularis, Cornus canadensis, Epilobium angustifolium, Linnaea borealis, Vaccinium vitis-idaea*
		4	57.1384	110.8920	Gray Luvisol	*Pinus banksiana*	53	8.7	2.7-15.7	*Vaccinium myrtilloides, Ledum groenlandicum, Cladina spp.,*
		5	57.1370	110.8918	Gray Luvisol	*Pinus banksiana*	49	9.4	3.0-20.7	*Cladina spp., Picea glauca, Ledum groenlandicum, Alnus crispa, Cornus canadensis, Vaccinium myrtilloides*
SM8	BM-b1	6	56.2131	111.1753	Gray Luvisol	*Pinus banksiana*	57	7.6	2.7-16.8	*Picea glauca, Ledum groenlandicum, Vaccinium myrtilloides, Vaccinium vitis-idaea*
		7	56.2163	111.1766	Gray Luvisol	*Pinus banksiana*	57	11.9	2.7-20.3	*Cladina, spp., Cornus canadensis, Vaccinium myrtilloides, Vaccinium vitis-idaea*
		8	56.2165	111.1759	Gray Luvisol	*Populus tremuloides*	49	13.1	2.9-26.7	*Vaccinium vitis-idaea, Vaccinium vitis-idaea,*
		9	56.2174	111.1766	Gray Luvisol	*Populus tremuloides*	49	17.4	8.2-36.3	*Cornus canadensis, Ledum groenlandicum, Vaccinium myrtilloides, Vaccinium vitis-idaea, Rubus idaeus*
		10	56.2154	111.1775	Gray Luvisol	*Pinus banksiana*	57	10.6	2.5-18.3	*Cladina spp., Picea glauca, Vaccinium vitis-idaea, Vaccinium myrtilloides*

[1 & 2] Stand age and DBH (diameter at breast height) were determined in 2009

[3] Understory species are arranged in the order of coverage.

Appendix II. Soil profile information of research plots in NE7 and SM8

Water-shed	Plot	Horizon	Depth (cm)	pH	Total C	Total N	Exchangeable cation					CEC	Base saturation (%)	Particle size distribution			Texture
							Ca	Mg	K	Na	Al			Sand	Silt	Clay	
					(g kg^{-1})		(cmolc kg^{-1})							(g kg^{-1})			
NE7	1	LFH	+5-0	4.89	338.7	20.6	53.3	9.0	3.2	0.1	0.1	67.2	97.7				
		Ae1	0-20	4.60	2.7	0.3	0.6	0.1	0.1	0.0	0.2	1.1	75.7	0.81	0.17	0.02	LS
		Ae2	20-37	5.05	2.0	0.3	0.9	0.2	0.1	0.0	0.3	1.6	78.6	0.73	0.22	0.05	SL
		Bt1	37-63	5.04	2.9	0.3	1.9	0.9	0.1	0.0	0.5	3.6	83.5	0.65	0.24	0.11	SL
		Bt2	63+	5.30	2.2	0.3	4.2	3.5	0.2	0.1	0.6	8.7	93.2	0.58	0.19	0.23	SCL
	2	LFH	+1-0	3.81	330.5	9.8	14.9	2.1	2.6	0.1	1.4	21.7	90.9				
		Ae	0-18	4.68	1.6	0.3	0.1	0.0	0.1	0.0	0.3	0.6	45.5	0.89	0.10	0.01	S
		AB	18-31	4.55	5.1	0.4	1.1	0.5	0.2	0.0	3.8	5.7	30.3	0.64	0.20	0.17	SL
		Bm1	31-50	5.06	1.8	0.3	1.3	0.6	0.1	0.0	1.7	3.8	54.7	0.73	0.15	0.12	SL
		Bm2	50-70	5.59	0.4	0.2	0.5	0.2	0.1	0.0	0.2	1.0	77.9	0.93	0.03	0.04	S
		BC	70-95	5.86	0.3	0.2	0.4	0.1	0.1	0.0	0.1	0.8	84.1	0.96	0.02	0.02	S
		C	95+	6.02	0.9	0.2	0.6	0.2	0.1	0.0	0.1	1.0	89.6	0.93	0.04	0.03	S
	3	LFH	+3-0	4.69	301.0	10.4	35.7	7.4	3.9	0.1	0.3	48.6	97.0				
		Ae	0-25	4.19	4.0	0.3	0.4	0.1	0.1	0.0	0.1	0.8	78.1	0.91	0.08	0.01	S
		Bm1	25-50	5.34	1.4	0.3	0.5	0.1	0.1	0.0	0.3	1.0	71.8	0.95	0.02	0.03	S
		Bm2	50-82	5.59	1.5	0.3	0.6	0.2	0.1	0.0	0.1	1.1	83.0	0.92	0.05	0.03	S
		BC	82+	5.60	0.8	0.2	0.4	0.1	0.1	0.0	0.1	0.7	81.1	0.97	0.01	0.02	
	4	LFH	+4-0	3.61	212.9	5.3	3.8	0.9	1.1	0.1	1.2	7.5	79.4				
		Ae	0-11	4.44	2.4	0.3	0.1	0.0	0.1	0.0	1.0	1.3	18.4	0.76	0.21	0.03	LS
		Bt	11-34	5.10	2.6	0.3	1.0	0.2	0.1	0.0	1.1	2.5	55.3	0.72	0.17	0.11	SL
		BC	34-75	5.47	1.3	0.3	1.0	0.3	0.1	0.0	0.5	1.9	74.5	0.80	0.14	0.06	LS
		C	75+	5.51	1.8	0.3	2.8	1.4	0.1	0.1	0.5	4.8	89.8	0.49	0.38	0.12	LS
	5	LFH	+10-0	3.87	395.1	14.2	21.9	3.2	4.1	0.1	0.5	31.6	92.7				
		Ae	0-13	4.31	4.6	0.4	0.5	0.1	0.1	0.0	0.4	1.3	63.1	0.72	0.25	0.03	LS
		Bt1	13-35	4.51	4.9	0.4	1.9	1.0	0.3	0.0	3.6	7.0	46.3	0.58	0.23	0.19	SL
		Bt2	35-55	4.69	3.8	0.4	2.7	1.4	0.2	0.1	2.3	6.8	64.8	0.60	0.21	0.18	SL
		BC	55-80	4.90	1.9	0.3	2.8	1.4	0.1	0.1	1.0	5.5	81.2	0.56	0.30	0.14	SL
		Cgj	80+	5.53	1.1	0.3	1.3	0.6	0.1	0.0	0.1	2.3	92.5	0.82	0.13	0.05	LS

Water-shed	Plot	Horizon	Detph (cm)	pH	Total C	Total N	Exchangeable cation					CEC	Base saturation (%)	Particle size distribution			Texture
							Ca	Mg	K	Na	Al			Sand	Silt	Clay	
					(g kg^{-1})		(cmolc kg^{-1})							(g kg^{-1})			
SM8	6	LFH	+2-0	3.83	353.5	14.2	22.6	5.8	3.1	0.1	0.9	33.7	93.6				
		Ae	0-12	3.90	4.9	0.4	0.2	0.1	0.1	0.0	1.5	2.0	20.9	0.73	0.24	0.03	LS
		Bm	12-48	4.98	2.0	0.3	0.1	0.0	0.1	0.0	0.3	0.6	40.7	0.95	0.02	0.03	S
		Bt1	48-72	5.51	2.2	0.4	7.5	3.3	0.4	0.1	0.4	11.7	96.3	0.61	0.17	0.22	SCL
		Bt2	72-100	5.76	2.5	0.4	9.2	3.8	0.4	0.1	0.1	13.7	98.6	0.60	0.16	0.24	SCL
	7	LFH	+12-0	3.31	296.7	8.8	12.0	2.1	2.3	0.2	2.1	19.7	83.5				
		Ae	0-5	3.82	12.2	0.8	0.4	0.1	0.2	0.0	3.3	4.2	16.4	0.42	0.53	0.05	SiL
		Bm	5-27	5.43	0.3	0.2	0.1	0.0	0.0	0.0	0.2	0.3	46.4	0.96	0.01	0.03	S
		Bt	27-65	4.98	7.3	0.7	0.8	0.4	0.2	0.0	3.9	5.3	26.0	0.26	0.54	0.20	SiL
		BC	65-100	5.69	0.2	0.2	0.2	0.1	0.0	0.0	0.1	0.4	75.0	0.96	0.01	0.03	S
		C	100+	5.72	2.0	0.2	0.2	0.1	0.0	0.0	0.1	0.5	80.0	0.97	0.01	0.02	S
	8	LFH	+10-0	4.48	359.2	21.3	30.2	6.5	4.5	0.1	0.3	43.5	94.7				
		Ae	0-10	4.33	11.2	0.9	1.0	0.3	0.2	0.0	3.8	5.6	27.5	0.43	0.50	0.07	SL
		Bt1	10-30	4.66	7.5	0.8	4.9	2.9	0.4	0.1	10.2	18.6	44.7	0.27	0.34	0.38	CL
		Bt2	30-50	4.68	4.9	0.6	4.8	2.9	0.4	0.1	10.2	18.6	44.4	0.23	0.35	0.42	C
		Btgj	50-80	4.69	5.2	0.7	6.5	4.0	0.5	0.2	9.8	21.1	53.3	0.19	0.36	0.44	C
		CII	80+	5.53	0.6	0.2	0.8	0.4	0.0	0.0	0.1	1.4	89.6	0.93	0.02	0.05	S
	9	LFH	+13-0	3.91	362.4	16.2	24.5	6.7	2.8	0.1	0.4	35.8	95.3				
		Ae	0-17	4.48	2.3	0.3	0.2	0.1	0.1	0.0	0.2	0.6	61.0	0.89	0.08	0.02	S
		Bt1	17-32	4.68	11.0	0.9	4.5	1.7	0.4	0.0	7.3	14.2	46.4	0.38	0.31	0.31	CL
		Bt2	32-65	4.83	3.9	0.5	7.3	3.5	0.4	0.1	5.2	16.5	68.0	0.39	0.27	0.33	CL
		CIIgj	65+	5.18	2.4	0.3	2.6	1.0	0.1	0.0	0.9	4.7	79.4	0.38	0.49	0.13	SL
	10	LFH	+4-0	3.54	318.7	9.6	11.5	2.7	2.3	0.2	2.2	20.4	82.4				
		Ae	0-8	4.27	3.6	0.3	0.0	0.0	0.0	0.0	1.0	1.3	10.5	0.87	0.09	0.03	S
		Bt1	8-25	4.94	3.1	0.4	0.4	0.0	0.1	0.0	1.3	1.9	25.6	0.86	0.07	0.08	LS
		Bt2	25-40	5.58	1.7	0.3	0.7	0.1	0.0	0.0	0.3	1.2	70.4	0.87	0.06	0.06	LS
		BC	40-57	5.73	0.6	0.2	0.2	0.0	0.0	0.0	0.1	0.5	63.7	0.96	0.01	0.03	S
		Cgj	57+	5.90	0.4	0.2	0.2	0.0	0.0	0.0	0.1	0.4	73.0	0.96	0.01	0.03	S

Appendix III. Basic information of research blocks of the simulated deposition study

Block	Location		Ecological unit	Soil type	Texture	
	Latitude (N)	Longitude (W)			Surface soil (0-15 cm)	Deep soil (35-50 cm)
NE	56.1596	110.8562	BM-d1.9	Orthic Gray Luvisol	Sandy loam	Loam
NW	56.1603	110.8502	BM-d1.9	Orthic Gray Luvisol	Silt loam	Sandy loam
SE	56.1364	110.8751	BM-d1.8	Orthic Gray Luvisol	Sandy loam	Loam
SW	56.1359	1108740	BM-d1.2	Orthic Gray Luvisol	Silt loam	Sandy clay loam