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

Kangho Jung\(^a,b\), Woo-Jung Choi\(^c,*\), Scott X. Chang\(^a,**\), M.A. Arshad\(^a\)

\(^a\) Department of Renewable Resources, 442 Earth Sciences Building, University of Alberta, Edmonton, Alberta, Canada T6G 2E3  
\(^b\) Department of Agricultural Environment, National Academy of Agricultural Science, 150 Saimuro, Kweonseonku, Suwon 441-707, Republic of Korea  
\(^c\) Department of Rural & Biosystems Engineering, Chonnam National University, Gwangju 500-757, Republic of Korea

**Article history:**  
Received 19 February 2012  
Received in revised form 5 October 2012  
Accepted 8 October 2012

**Keywords:**  
Tree ring chemistry  
Soil chemistry  
Air pollution  
\(\delta^{13}C\)  
\(\delta^{15}N\)  
Oil sands region  
Tree growth

**Abstract**  
The impact of chronic air pollution such as increased CO\(_2\) and NO\(_x\) emissions on forest ecosystems in the Athabasca oil sands region in Alberta, Canada, was investigated in *Pinus banksiana* (jack pine) and *Populus tremuloides* (trembling aspen, aspen) stands in two watersheds (NE7 and SM8) located at different distances from the main emission sources of oil sands mining and upgrading facilities, using \(\delta^{13}C\), \(\delta^{15}N\), and Ca/Al of soil and tree ring samples as indicators. Watershed NE7 was exposed to greater amounts of acid deposition due to its closeness to the mining and upgrading area. The \(\delta^{15}N\) in the forest floor was lower (\(p<0.05\)) in NE7 (ranged from \(-1.42\) to \(-0.87\)%) than in SM8 (\(-0.54\) to \(-1.43\)%), implying a greater amount of recent deposition of \(^{15}\)N-depleted N in NE7. Tree ring \(\delta^{13}C\) gradually decreased over time for both tree species/watersheds, indicating the influence of \(^{13}\)C-depleted CO\(_2\) emitted from industrial sources. Tree ring N concentration and \(\delta^{15}N\) were not different between watersheds and did not significantly change with time. Interestingly, however, the difference between watersheds (NE7–SM8) that is expressed as Diff_N (for N) increased with concomitant decreases in Diff_{\delta^{15}}N over time, implying greater increases in \(^{15}\)N-depleted N input in NE7 than in SM8. Such trends were stronger in aspen stands (\(R^2 = 0.64\) and \(p<0.001\) for Diff_N and \(R^2 = 0.44\) and \(p<0.01\) for Diff_{\delta^{15}}N between 1964 and 2009) than in jack pine stands. We conclude that \(^{15}\)N in the forest floor and differences in N and \(\delta^{15}N\) of tree rings between watersheds are useful indicators reflecting the impact of spatial variations of air pollution on forest stands in the Athabasca oil sands region in western Canada.

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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 is one of the industrial activities that cause atmospheric pollution and threaten forest health (Aberne 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 sands mining and associated 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 (Fig. 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 sands region. Specifically, NO\(_x\) (nitrogen oxides, NO\(_x\) = NO + NO\(_2\)) 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 (Hazenewinkel et al., 2008) due to SO\(_2\) curtailment policies and technical improvement (Morrison, 2006). As boreal forests in general are N-limited (Hari and Kulmala, 2008), chronic N deposition has been expected to alleviate N limitation and to increase tree growth (Jung and Chang, 2012).  

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 (\(\delta^{13}C\)) and N (\(\delta^{15}N\)) 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., 2003a; Sauer et al., 2004; Watmough et al., 1999). For example, $\delta^{13}$C of tree tissues can be affected by $\delta^{13}$CO$_2$ of air as well as carbon isotope discrimination during photosynthesis (Farquhar et al., 1982):

$$\delta^{13}C_{\text{plant}} = \delta^{13}CO_2 - (a - b) \frac{C_i}{C_a}$$

(1)

where $\delta^{13}$C$_{\text{plant}}$ and $\delta^{13}$CO$_2$ are the carbon isotope abundances of plant and atmospheric CO$_2$, $C_i$ and $C_a$ are intercellular and atmospheric CO$_2$ concentrations, $a$ (normally ~4.4%) is the fractionation coefficient during CO$_2$ diffusion through stomata, and $b$ (normally ~27%) is the net fractionation coefficient by carboxylation. For numerical convenience, carbon isotope discrimination ($\Delta^{13}$C) was proposed by Farquhar and Richards (1984):

$$\Delta^{13}C = \frac{\delta^{13}CO_2 - \delta^{13}C_{\text{plant}}}{1 + \delta^{13}C_{\text{plant}}/1000} = a + (b - a) \frac{C_i}{C_a}$$

(2)

Therefore, tree rings formed under atmospheric conditions with $^{13}$C-depleted CO$_2$ released by fossil fuel combustion may develop more negative $\delta^{13}$C$_{\text{plant}}$ unless other factors that affect carbon isotope discrimination via modification of stomatal conductance and carboxylation rate such as rainfall, air pollutants, and nutrient availabilities have greater effects on $\delta^{13}$C$_{\text{plant}}$ than the effect of $^{13}$C-depleted CO$_2$ released by fossil fuel combustion (Bert et al., 1997; Choi et al., 2005b; Farmer and Baxter, 1974). On the other hand, if carbon isotope discrimination effect prevails over $^{13}$C effect or at least the first is compatible to the latter, there may not be a meaningful relationship between plant $^{13}$C and $\delta^{13}$CO$_2$.

The $\delta^{15}$N of tree rings can serve as another indicator of atmospheric environmental change (Savard et al., 2009; Norby, 1998) as anthropogenic NO$_x$, which is emitted from fossil fuel combustion and an atmospheric N source 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., 2003b; 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 decrease 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 progression of air pollution in an area have been demonstrated in industrial (Kwak et al., 2009b) and rural areas (Kwak et al., 2011); however, the response 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), different preference for NH$_4^+$ and NO$_3^-$ (Choi et al., 2005c; Kronzucker et al., 1997; Min et al., 2000), leaf morphology (Cole and Rapp, 1981), and soil characteristics such as pH (Augusto et al., 2002; Staelens et al., 2008).

In this study, we tested two hypotheses: (1) the impact of increasing air pollutants such as CO$_2$ and NO$_x$ can be reflected by changes in soil and tree ring chemistry such as $\delta^{13}$C, $\delta^{15}$N, and Ca/Al, with greater changes over time in the watershed closer to emission sources in the AOSR, and (2) N deposition would increase tree growth and deciduous stands would have a greater response than conifer stands due to faster N recycling in deciduous stands and nitrate discrimination by conifer roots. The responses of trees to air pollution can be studied by changes in growth rates and tree ring chemistry.

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 having coarse textured soils that have 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 (Fig. 2). As mining areas are mostly located north of Fort McMurray and the prevailing wind direction in the area is east to southeast, NE7 would have been exposed to greater rates of acid deposition (Jung et al., 2011a); annual depositions of SO$_4^{2-}$ and NO$_3^-$ were 4.1 kg ha$^{-1}$ and 2.2 kg 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. Based on data collected between 1960 and 1990, the mean annual temperature was 0.7°C with a mean relative humidity of 66–67%, 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 (Fig. 3); however, winter climate data were not collected at those stations.

Both watersheds were dominated by approximately 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 Brunisolic soils and Luvisolic soils in the Canadian system of soil classification (Soil Classification Working Group, 1998) or Boralf in US Soil Taxonomy (Soil Survey Staff, 1994). Five 20 m × 20 m plots were established in each watershed in 2005. Three plots were jack pine dominated stands and the other two were aspen dominated stands in each watershed. 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).

![Fig. 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.](image-url)
2.2. Collection of soil and tree ring samples

Soil samples were collected from two layers from eight points randomly selected in each plot in October 2009 and a composite sample was formed for each layer in each plot: 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. Wood cores were collected from four dominant trees with similar growth conditions such as age and exposure to light in each plot for tree ring analysis; therefore, four jack pine trees were selected in each jack pine dominated plot and four aspen trees were selected in each aspen dominated plot. Selected trees in each plot were similar in height but variable in diameter. Differences in intraspecific competition, exposure to light and spatial soil nutrient and water availabilities can lead to trees with similar age but different diameters. Therefore it was critical to include trees of different diameters to represent the average site condition. Two tree cores per tree 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 −18 °C before the analyses. Tree rings were dated and each ring width was measured using a tree ring measuring system with a 0.001 mm resolution (TA System, Velmex, USA). Basal area increment (BAI) in each year was calculated as following:

\[
BAI = \pi \times \left( \frac{d_i}{2} \right)^2 - \left( \frac{d_{i-1}}{2} \right)^2
\]

(4)

where \(i\) is year and \(d_i\) is the ring diameter of the year \(i\). Wood samples for 3-year growth ring bands between 1964 and 2008 (the 2009 growth ring was included in the band between 2006 and 2008) were taken from each core. Three-year band samples in the same period were composited for the four trees in each plot to obtain enough sample amounts for chemical analysis. For chemical analysis, all tree ring samples were dried at 70 °C for 72 h in a drying oven and 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 samples

Soil pH was measured in deionized water using 10 g of air-dried soil in 40 mL of water for the forest floor and 20 mL of water for the surface mineral soil samples with an AR20 pH meter (Fisher Scientific Ltd., US). Soil exchangeable cations (\(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+\) and \(\text{Al}^{3+}\)) were determined with an ICP-MS (Elan 6000 quadrupole, Perkin-Elmer, Inc., CT, US) after extractions with 1 mol L\(^{-1}\) NH\(_4\)Cl at a ratio of 5 g soil to 100 mL extractant and after shaking for 1 h. Total C and N concentrations and their corresponding δ\(^{13}\)C and δ\(^{15}\)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 international standards of Pee Dee Belemite (PDB) for δ\(^{13}\)C and atmospheric N\(_2\) for δ\(^{15}\)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\(_2\)O\(_2\) on a digestion block at 125 °C for 4 h (Campbell 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 climate, tree growth, and tree ring chemistry, depending on the purpose of the analysis as described below. The autoregressive model was used to remove
an autocorrelation structure in the time series and to enhance common signals for most variables of which Durbin Watson statistics were less than 1.5 (positively autocorrelated error terms) or greater than 2.5 (negatively autocorrelated error terms) (Ott and Longnecker, 2008). The stepwise autoregression method was used to select the order (p) of the autoregressive model and the simplest autoregressive model (p = 0) was selected for most variables. A simple regression model was used for variables including tree growth, C, Al, and Ca/Al as Durbin Watson statistics for those parameters were between 1.5 and 2.5. 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 (Fig. 1). A multiple correlation analysis was conducted to examine the relationships between climate variables (summer temperature and precipitation) and tree ring data such as area and chemistry. As tree chemistry was analyzed with 3-year bands, average of climate variables for each 3-year band was used for correlation analysis.

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 the impact of atmospheric pollution (Savarid, 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 and the chemical parameter of interest (Tables 1 and 2). For example, pH in the forest floor was affected by tree species (p < 0.001, Table 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 1). However, pH in surface mineral soils 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 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 (Tables 1 and 2).

The δ13C in the forest floor and mineral soil was not different between watersheds or stand types (Tables 1 and 2). However, δ15N 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, δ13C and δ15N were not affected by watersheds or tree species, with their values greater (p < 0.001) than that in the forest floor. Exchangeable base cations and Ca/Al ratios were greater (p < 0.05) in aspen than in jack pine stands in both soil layers.

3.2. Climate change and tree growth

Summer temperature and precipitation did not show any significant trends in both watersheds except for an increasing trend (p < 0.001) of summer precipitation in SM8 between 1982 and 2009 (Fig. 3). Temperature and precipitation in the summer seasons were negatively correlated (r = −0.69 and p < 0.001) in SM8 while no relationship between them was found in NE7 (data not shown). In both watersheds, annual growth ring width of both species decreased over time (p < 0.001) between 1963 and 2009 (Fig. 4a). The BAI of jack pine trees ranged from 2.3 to 4.2 cm² year⁻¹ tree⁻¹ in NE7 and from 0.8 to 4.7 cm² year⁻¹ tree⁻¹ in SM8 and did not show any temporal trends (Fig. 4b). Meanwhile, BAI of aspen increased over time (p < 0.001) in both watersheds and ranged from 0.7 to 4.8 cm² year⁻¹ tree⁻¹ in NE7 and from 0.3 to 9.4 cm² year⁻¹ tree⁻¹ in SM8 (Fig. 4b). No significant relationship was found between climate variables and BAI in NE7 while BAI was positively correlated with the summer temperature (r = 0.61 and p < 0.001 for jack pine and r = 0.98 and p < 0.001 for aspen) but was negatively correlated with summer precipitation (r = 0.49 and p < 0.01 for jack pine and r = 0.70 and p < 0.001 for aspen) in SM8.

Table 1

<table>
<thead>
<tr>
<th>Water-shed</th>
<th>Tree species</th>
<th>pH</th>
<th>Total C (g kg⁻¹)</th>
<th>Total N (g kg⁻¹)</th>
<th>C/N</th>
<th>Δ13C (%)</th>
<th>Δ15N (%)</th>
<th>Exchangeable cations (cmol c⁻¹ kg⁻¹)</th>
<th>Ca/Al</th>
</tr>
</thead>
<tbody>
<tr>
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<td><strong>Forest floor</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NE7</td>
<td>Jack pine</td>
<td>4.30</td>
<td>367</td>
<td>12.9</td>
<td>29.1</td>
<td>−27.7</td>
<td>−1.4</td>
<td>9.14  1.50  0.81  0.43  51.2</td>
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<td></td>
<td></td>
<td>(0.08)</td>
<td>(31.9)</td>
<td>(2.6)</td>
<td>(3.98)</td>
<td>(0.05)</td>
<td>(0.1)</td>
<td>(3.37)  (0.52) (0.09) (0.30) (51.9)</td>
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</tr>
<tr>
<td></td>
<td>Aspen</td>
<td>5.58</td>
<td>335</td>
<td>16.7</td>
<td>21.0</td>
<td>−28.7</td>
<td>−0.9</td>
<td>17.6  3.37  1.13  0.03 1090</td>
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<tr>
<td></td>
<td></td>
<td>(0.19)</td>
<td>(20.9)</td>
<td>(5.5)</td>
<td>(5.73)</td>
<td>(0.13)</td>
<td>(0.2)</td>
<td>(2.58)  (0.54) (0.35) (0.01) (426)</td>
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<tr>
<td>SM8</td>
<td>Jack pine</td>
<td>4.15</td>
<td>323</td>
<td>10.9</td>
<td>30.6</td>
<td>−29.2</td>
<td>−0.5</td>
<td>5.90  1.47  0.81  0.59 20.1</td>
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<tr>
<td></td>
<td></td>
<td>(0.04)</td>
<td>(28.6)</td>
<td>(2.9)</td>
<td>(4.85)</td>
<td>(0.19)</td>
<td>(0.6)</td>
<td>(1.87)  (0.47) (0.30) (0.25) (17.7)</td>
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<td>4.79</td>
<td>361</td>
<td>18.8</td>
<td>19.6</td>
<td>−27.7</td>
<td>1.4</td>
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<td></td>
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<td>(0.45)</td>
<td>(2.3)</td>
<td>(3.6)</td>
<td>(3.88)</td>
<td>(0.15)</td>
<td>(1.1)</td>
<td>(1.75)  (0.33) (0.25) (0.003) (52.2)</td>
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<td><strong>Surface mineral soil</strong></td>
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<tr>
<td>NE7</td>
<td>Jack pine</td>
<td>4.03</td>
<td>7.78</td>
<td>0.32</td>
<td>25.3</td>
<td>−25.7</td>
<td>3.1</td>
<td>0.26     0.07  0.07  0.17 2.99</td>
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<tr>
<td></td>
<td></td>
<td>(0.30)</td>
<td>(1.27)</td>
<td>(0.11)</td>
<td>(5.72)</td>
<td>(0.50)</td>
<td>(0.7)</td>
<td>(0.12)  (0.02) (0.02) (0.10) (2.13)</td>
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<tr>
<td></td>
<td>Aspen</td>
<td>4.01</td>
<td>7.95</td>
<td>0.37</td>
<td>22.0</td>
<td>−27.1</td>
<td>4.6</td>
<td>0.93     0.23  0.11  0.10 14.3</td>
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<tr>
<td></td>
<td></td>
<td>(0.14)</td>
<td>(0.06)</td>
<td>(0.08)</td>
<td>(4.90)</td>
<td>(0.03)</td>
<td>(0.9)</td>
<td>(0.21)  (0.02) (0.02) (0.03) (5.90)</td>
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</tr>
<tr>
<td>SM8</td>
<td>Jack pine</td>
<td>4.40</td>
<td>11.9</td>
<td>0.41</td>
<td>29.4</td>
<td>−26.3</td>
<td>2.5</td>
<td>0.33     0.10  0.10  0.73 1.05</td>
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<tr>
<td></td>
<td></td>
<td>(0.33)</td>
<td>(2.51)</td>
<td>(0.09)</td>
<td>(2.53)</td>
<td>(0.01)</td>
<td>(1.4)</td>
<td>(0.21)  (0.05) (0.03) (0.62) (1.01)</td>
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<tr>
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<td>Aspen</td>
<td>4.33</td>
<td>25.3</td>
<td>1.93</td>
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<td>−27.3</td>
<td>3.9</td>
<td>1.56     0.35  0.18  1.17 2.01</td>
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<tr>
<td></td>
<td></td>
<td>(0.07)</td>
<td>(2.45)</td>
<td>(0.18)</td>
<td>(2.49)</td>
<td>(0.12)</td>
<td>(1.1)</td>
<td>(0.57)  (0.03) (0.04) (0.08) (0.75)</td>
<td></td>
</tr>
</tbody>
</table>

a Ca/Al was calculated based on exchangeable Ca⁺ and Al³⁺ on molar unit.
3.3. Tree ring chemistry

Carbon concentrations in tree rings were relatively stable while N concentration increased sharply toward the outermost tree rings formed between 2006 and 2009 (Fig. 5a and b), without differences between watersheds (Table 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 ($r^2 = 0.52$, $p < 0.05$) (Table 4 and Fig. 6b).

The $\delta^{13}C$ gradually decreased over time for both stands in both watersheds, coinciding with the commencement of oil sands mining activities (Fig. 5c). Between 1982 and 2009, $\delta^{13}C$ in tree rings decreased linearly ($p < 0.001$ for both tree species) at rates of $-0.053\% \text{year}^{-1}$ for jack pine and $-0.054\% \text{year}^{-1}$ 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 $\delta^{13}C$ of tree ring was negatively correlated with summer precipitation with correlation coefficients

### Table 2

<table>
<thead>
<tr>
<th>Soil layer</th>
<th>Factor</th>
<th>pH</th>
<th>Total C</th>
<th>Total N</th>
<th>C/N</th>
<th>$\delta^{13}C$</th>
<th>$\delta^{15}N$</th>
<th>Exchangeable cations</th>
<th>Ca/Al$^b$</th>
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<tr>
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</tr>
<tr>
<td>Forest Floor</td>
<td>Species (S)</td>
<td>&lt;0.01</td>
<td>0.87</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>-0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>Watershed (W)</td>
<td>0.20</td>
<td>0.60</td>
<td>0.99</td>
<td>1.00</td>
<td>0.03</td>
<td>0.03</td>
<td>0.09</td>
<td>0.14</td>
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<tr>
<td></td>
<td>$S \times W^b$</td>
<td>0.12</td>
<td>0.08</td>
<td>0.41</td>
<td>0.65</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.90</td>
<td>0.88</td>
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<tr>
<td>Surface mineral soil</td>
<td>Species (S)</td>
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<td>&lt;0.01</td>
<td>0.02</td>
<td>0.01</td>
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<td></td>
<td>Watershed (W)</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>0.16</td>
<td>0.52</td>
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</tr>
<tr>
<td></td>
<td>$S \times W^b$</td>
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<td>&lt;0.01</td>
<td>0.08</td>
<td>0.65</td>
<td>0.56</td>
<td>0.17</td>
<td>0.02</td>
</tr>
</tbody>
</table>

$^a$ Ca/Al was calculated based on exchangeable Ca$^{2+}$ and Al$^{3+}$ on molar unit.
$^b$ $S \times W$ indicates tree species × watershed interaction.

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**Fig. 4.** (a) Annual ring width increment and (b) basal area increment (BAI) of jack pine (▲) and trembling aspen (●) in NE7 and SM8. Closed marks represent watershed NE7 that was closer to mining and upgrading areas and open marks represent watershed SM8. The bold solid line in (b) is the regression curves for trembling aspen. Error bars indicate standard errors of the mean; $n = 3$ for jack pine stands and $n = 2$ for aspen stands.
Fig. 5. 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 (▲) and trembling aspen (●) in NE7 and SM8. Closed marks represent watershed NE7 that was closer to mining and upgrading areas and open marks represent watershed SM8. The bold solid line in (c) is the regression curve for each tree species from 1982 to 2009. Error bars indicate standard errors of the mean; n = 3 for jack pine stands and n = 2 for aspen stands.

Table 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.

<table>
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<tr>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
<td>DiffC(^1)</td>
</tr>
<tr>
<td>Species (S)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Jack pine</td>
<td>&lt;0.01</td>
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<tr>
<td>Aspen</td>
<td>0.05</td>
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<td>0.01</td>
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<tr>
<td>Watershed (W)</td>
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<td>NE7</td>
<td>0.05</td>
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<td>SM8</td>
<td>0.07</td>
<td>0.79</td>
<td>0.01</td>
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<td>&lt;0.01</td>
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<td><strong>p</strong> &lt; 0.05.</td>
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Table 4
The \(R^2\) values for the time effect on tree ring chemistry using a simple regression model for C and an autoregressive model for other parameters.

<table>
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<tr>
<th>Period</th>
<th>Tree species</th>
<th>Water-shed</th>
<th>C</th>
<th>N</th>
<th>DiffC(^1)</th>
<th>DiffC(^1)</th>
<th>(\delta^{13})C</th>
<th>(\delta^{15})N</th>
<th>Ca/Al</th>
<th>DiffC/Al(^3)</th>
<th>(\delta^{15})N</th>
<th>1964–2009</th>
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</thead>
<tbody>
<tr>
<td>1964–1981 Jack pine</td>
<td>NE7</td>
<td>0.64**</td>
<td>0.56*</td>
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<td>0.10</td>
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<td>0.23</td>
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<td>0.003</td>
<td>0.33</td>
<td>0.003</td>
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<tr>
<td></td>
<td>SM8</td>
<td>0.05</td>
<td>0.54</td>
<td>0.01</td>
<td>0.21</td>
<td>0.22</td>
<td>0.06</td>
<td>0.01</td>
<td>0.001</td>
<td>0.49</td>
<td>0.54</td>
<td>0.26</td>
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<tr>
<td>1982–2009 Jack pine</td>
<td>NE7</td>
<td>0.01</td>
<td>0.52**</td>
<td>0.50</td>
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<td>0.77***</td>
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<td></td>
<td>SM8</td>
<td>0.43</td>
<td>0.61**</td>
<td>0.003</td>
<td>0.61**</td>
<td>0.85***</td>
<td>0.001</td>
<td>0.06</td>
<td>0.17</td>
<td>0.11</td>
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<tr>
<td>1964–2009 Aspen</td>
<td>NE7</td>
<td>0.05</td>
<td>0.61**</td>
<td>0.003</td>
<td>0.61**</td>
<td>0.85***</td>
<td>0.001</td>
<td>0.06</td>
<td>0.17</td>
<td>0.11</td>
<td>0.11</td>
<td>0.09</td>
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<tr>
<td></td>
<td>SM8</td>
<td>0.04</td>
<td>0.25</td>
<td></td>
<td>0.78***</td>
<td>0.85***</td>
<td>0.001</td>
<td>0.06</td>
<td>0.17</td>
<td>0.11</td>
<td>0.11</td>
<td>0.09</td>
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<tr>
<td><strong>p</strong> &lt; 0.05.</td>
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</table>

\(^{1,2,3,4}\text{Diff}_\text{x}\) means the difference of parameter \(x\) between watersheds as \(x\) in NE7–\(x\) in SM8.

\(^1p < 0.05.\)

\(^2p < 0.01.\)

\(^3p < 0.001.\)
ranging from −0.32 to −0.53 while summer temperature was not related with δ^{13}C of tree rings. The δ^{15}N in tree rings did not show any difference between tree species nor did it change with time (Fig. 5d); however, Diff_δ^{15}N (δ^{15}N in NE7–δ^{15}N in SM8) in aspen stands decreased over time (p < 0.05) (Fig. 6d). The δ^{15}N in tree rings did not show any significant relationship with summer temperature and precipitation.

Calcium concentrations in tree rings decreased over time (p < 0.05) in aspen (range: 0.16–0.85 g kg^{-1}) but did not change over time in jack pine trees (range: 0.06–0.25 g kg^{-1}) (data not shown). Aluminum concentration in tree rings (range: 0.007–0.041 g kg^{-1}) did not show any pattern of change with time in both tree species (data not shown). The molar ratio of Ca/Al was significantly lower (p < 0.01) in jack pine (range: 4.0–13.7) than in aspen (range: 4.5–40.3) (Table 3 and Fig. 5e). 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

We found that soil chemistry was affected by tree species rather than the distance from the pollution source (Tables 1 and 2), rejecting our first hypothesis. For example, 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 1); those differences were likely affected by litter amount and quality (e.g., decomposability and the initial N concentration), as litter from broadleaf trees are more decomposable and have higher N concentrations than those from conifer trees (Johansson, 1995; Van Hees et al., 2002). The faster decomposition of aspen litters than that of jack pine and the inherently high N concentration in the litter of aspen trees caused the lower C/N ratio of the forest floor in aspen stands (Table 1), implying higher N availability as well as greater nitrification rates and nitrate leaching in aspen stands (Lovett et al., 2002). 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 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). As these processes result in ^{15}N enrichment of the remaining N in the soil (Högberg, 1997), the higher soil N availability in aspen stands would eventually lead to a higher δ^{15}N in the forest floor (Table 1).

The higher Ca/Al in the forest floor and mineral soils in aspen than in jack pine stands (Table 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 in both soil layers was higher (p < 0.01) in NE7 than in SM8 (Table 1), contrary to our initial hypothesis, because the whole
soil profile in NE7 had greater Ca/Al than that in SM8 (Jung et al., 2011a).

Effects of atmospheric pollution were indicated by δ^{15}N of the forest floor, partially supporting our first hypothesis. The lower (p < 0.001) δ^{15}N of the forest floor in NE7 than that in SM8 reflected the greater amount of δ^{15}N-depleted N deposition in NE7 than in SM8, with the former closer to N emission sources and thus a greater rate of N deposition than the latter (Jung et al., 2011a). On the other hand, no difference in δ^{15}N in the surface mineral soil was found between watersheds. As δ^{15}N of the surface mineral soil is affected by N from forest floor and further influenced by N isotopic fractionation in the mineral soil layers (Evans, 2007), the δ^{15}N of the surface mineral soil (range: 2.5–4.6‰) was greater than that of the forest floor (range: −1.4 to 2.2). This implies that δ^{15}N in the surface mineral soil would be less affected by anthropogenic N deposition than that in the forest floor due to variations of N isotopic fractionation from site to site. Furthermore, the δ^{15}N in the mineral soil in this study was slightly higher than those in other studies, e.g., from 2.2 to 2.8‰ in Pinus taeda stands (Choi et al., 2005a), from 0.6 to 2.5‰ in P. mariana–Larix laricina stands (Choi et al., 2007), and from 0.4 to 2.1‰ in Picea jezoensis, Abies ephelops, and Betula ermanii stands (Cheng et al., 2010), indicating a relatively high N isotopic fractionation potential in our study sites.

These results suggest that most soil chemistry was affected more by tree species or site-specific physicochemical conditions rather than distance from the pollution source, indicating that soil chemistry alone may not be a reliable indicator of the magnitude of exposure of forest stands to atmospheric pollution. Therefore, we need to select proper indicators to assess the impact of environmental change on soil chemistry. Based on our data, δ^{15}N in the forest floor could be a sensitive indicator to study the differential effect of N deposition on the two watersheds when it was compared for stands with the same tree species.

4.2. Tree ring δ^{13}C

The δ^{13}C in rings were lower in aspen than in jack pine trees by approximately 1% (Fig. 5c) 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 the location of the watershed, δ^{13}C in tree rings decreased over time, especially since the early 1980s (Fig. 5c), coincident with the increase of CO₂ emission caused by increased oil production in the AOSR (Suncor, 2010; Syncrude, 2009); emission of δ^{15}N-depleted CO₂ per volume of oil production typically ranged from 0.57 to 1.0 mg m⁻² (Furimsky, 2003). This result partially supports our first hypothesis that the δ^{13}C in tree rings reflects the changes in the δ^{13}C-depleted CO₂ emissions over time (February and Stock, 1999). The rate of decrease of δ^{13}C (−0.05% year⁻¹) in the tree rings observed in this study is similar to those reported for other areas that were moderately polluted (Sakata et al., 2001; Dongarrà and Varrica, 2002; Li et al., 2010), but much lower than those (−0.1% year⁻¹) reported for highly polluted areas (Kwak et al., 2009b).

Meanwhile, δ^{13}C in tree rings was not different between watersheds for each species (rejecting part of the first hypothesis) and the rate of decrease (−0.05% year⁻¹) of δ^{13}C was not different between tree species (Fig. 5c). There are several possible mechanisms for the similar patterns of tree ring δ^{13}C between the two watersheds. First, geographically, NE7 and SM8 might not be distant enough to reflect the different degrees of δ^{13}C-depleted CO₂ supply in the atmosphere, partly because of the mixing of CO₂ in the atmosphere in the local area, and increases in atmospheric CO₂ concentration has been a global trend (February and Stock, 1999). Second, plant physiologically in relation with environmental stresses, the similar δ^{13}C pattern suggests that atmospheric CO₂ emission is not a single factor that affects δ^{13}C in tree rings in the study sites. As indicated by Eq. (1), plant δ^{13}C is affected not only by the δ^{13}C of the atmospheric CO₂ but also by other factors associated with carbon isotope discrimination during photosynthesis such as rainfall (Roden et al., 2005), atmospheric pollution such as acid rain (Kwak et al., 2009a; Savard, 2010), air temperature (Warren and Dreyer, 2006), and soil water and nutrient availability (Choi et al., 2005a) via modification of stomatal conductance and/or carboxylation rate (Choi and Lee, 2012). In the present study, the δ^{13}C of tree ring was negatively (r = −0.69 and p < 0.001) correlated with summer precipitation in SM8, likely reflecting the effect of water availability on carbon isotope discrimination as improved water availability increases stomatal conductance that maintains a higher C/CO₂, leading to a greater carbon isotope discrimination (more negative δ^{13}C) (Becker et al., 1991; Werner and Máguas, 2010). Therefore, the greater summer precipitation in SM8 (371 mm) over time than in NE7 (248 mm) might induce a higher stomatal conductance of trees in SM8 that leads to more negative δ^{13}C and thus narrows plant δ^{13}C differences from that in NE7 which is likely to have a higher δ^{13}C-depleted CO₂ emission.

In the context of air pollutants, SO₂ and NOₓ co-emitted with CO₂ in the mining area would contribute partially to the similar δ^{13}C pattern between the two sites as these pollutants induce stomatal closure, leading to less negative δ^{13}C (Savard, 2010). Since NE7 is closer to and downwind from the mining and upgrading area, pollution-induced stomatal closure might decrease carbon isotope discrimination by lowering C/CO₂ (leading to a higher δ^{13}C), and thus somewhat reduce the δ^{13}C-depleted CO₂ effect on tree ring δ^{13}C. In addition, increases in atmospheric CO₂ concentration may further decrease stomatal conductance (Ainsworth et al., 2007), diluting the effect of increased CO₂ (with depleted δ^{13}C abundance) on decreasing the δ^{13}C signal in tree rings, diluting the effect of increased CO₂ (with depleted δ^{13}C abundance) on decreasing the δ^{13}C signal in tree rings. As such, tree ring δ^{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 δ^{13}C-depleted CO₂, pollution-induced stomatal closure, and changes in water availability on tree ring δ^{13}C. However, when the effects of δ^{13}C-depleted CO₂ are dominant over other factors, changes in annual tree ring width and tree ring δ^{13}C have implications for the effect of CO₂ emissions on tree growth and physiology.

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

Inter-tree ring translocation of N in tree stems has been reported to make it difficult to use N concentrations in tree rings as an indicator of historical changes in N availability in ecosystems (Bukata and Kyser, 2005; Elhani et al., 2003; Poulsen et al., 1995; 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 anthropogenic impacts of δ^{15}N-depleted, recent N deposition (Kwak et al., 2009b; Choi et al., 2005b; Savard et al., 2009; Poulsen et al., 1995; Bukata and Kyser, 2007), although the δ^{15}N signal stored in the ring formed in a specific year might be affected by inter-tree ring translocation of N. Meanwhile, in this study, the δ^{15}N in tree rings did not show any temporal pattern regardless of tree species and watershed (Fig. 5d), which does not support part of the first hypothesis and suggests that the δ^{15}N of tree rings in the study sites has limited utility.
for indicating changes in atmospheric N deposition. This could be attributed to increased δ15N in the soil caused by greater rates of N transformation in association with increased N availability (Garten Jnr and Van Miegroet, 1994). The greater contribution of isotopic fractionation in recent years would mute the direct effect of the increased rate of deposition of 15N-depleted N.

The Diff-δ15N, however, showed decreasing trends in conjunction with increasing Diff_N over time, particularly in aspen stands (Fig. 6), indicating that NE7 has been exposed to 15N-depleted N deposition to a greater degree as compared with SM8. This is consistent with the greater rate of N deposition in NE7 than in SM8 (Jung et al., 2011a). Greater changes in Diff-δ15N and Diff_N over time were found in aspen stands than in jack pine stands. It could be due to different preference of tree species for N forms. Differences in δ15N between NH4+ and NO3− in the soil may produce species-specific signatures of N isotopes in tree rings due to different preference of tree species for N forms (McLaughlan and Craine, 2012). Conifer species such as Pinus contorta and Picea glauca show a clear preference for acquisition of NH4+ over NO3− while some deciduous species such as aspen have relatively high efficiency utilizing NO3− (Kronzucker et al., 1997; Min et al., 2000). As emitted NOx infiltrates into the soil as NO3−, the δ15N signature could be clearer in aspen than in jack pine tree rings. It could also explain the increased BA1 over time of aspen trees, however, the BA1 of jack pine trees did not increase over time (Fig. 4b); those results support part of the second hypothesis about the differential effects of N deposition on tree growth between species. Another possibility could be the difference in N cycling between stands dominated with different tree species. As N cycling is comparatively faster in deciduous than in evergreen stands (Augusto et al., 2002), aspen tree rings could show clear trends of Diff-δ15N and Diff_N over time as compared to jack pine tree ring. We suggest that Diff-δ15N and Diff_N rather than δ15N and N concentrations are more useful indicators of the impact of atmospheric N deposition between different locations because δ15N and N concentrations are affected by a number of site-specific conditions such as N availability and N transformation processes (Garten Jnr 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 (Vangeloula 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, again rejecting part of the first hypothesis. This implies that tree ring Ca/Al ratios have been affected not only by acid precipitation but also other factors such as precipitation pattern and parent material. For example, while NE7 has been exposed to greater rates of acid deposition than SM8 (Jung et al., 2011a), 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 1). Therefore, the Ca/Al may not be a reliable indicator for evaluating 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), δ13C, δ15N, 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; different mechanisms were at play in causing the trends we observed. The lower δ15N in the forest floor in NE7 than in SM8 indicated greater impacts of 15N-depleted N deposition in NE7 than in SM8. The δ15N in the forest floor appeared to be the most sensitive indicator for N deposition in different watersheds. Tree ring δ13C showed a decreasing pattern over time in both watersheds due to global increases in 13C-depleted CO2. Meanwhile, tree ring δ13C were not different between NE7 and SM8. We suggest that the counterbalancing effects of (1) other air pollutants increasing δ13C in polluted areas and (2) the increasing trend of summer precipitation in SM8 causing δ13C in that watershed to become more negative. Temporal changes in Diff_N and Diff-δ15N also reflected greater anthropogenic N deposition in NE7 than in SM8, consistent with results of δ15N in the forest floor. Diff_N and Diff-δ15N in aspen tree rings were believed to be more sensitive to N deposition by NOx emission than those in jack pine due to the preference of aspen for NO3− and faster N recycling in aspen stands. Nitrogen deposition increased the BA1 of aspen but not that of jack pine. We conclude that δ15N in the forest floor and Diff_N and Diff-δ15N of tree rings were useful indicators for the impact of N deposition on forest stands in the study area.

Acknowledgements

This study was carried out in the frame work of the NOx & SO2 Management Working Group (NSMWG) in the Cumulative Environmental Management Association (CEMA) and was financially supported by CEMA, Alberta Environment and Natural Science and Engineering Council of Canada (NSERC). We thank two anonymous reviewers for their comments that substantially improved an earlier version of the manuscript.

References


Energy

trees.

199,


indicators

soil

Lelarge,

Varrica,

Stock,

S.X.,

Influence

Isotopes

Chang,

Wolfe,

M.S.,

1541–1548.

Chemosphere

2008.

24,

birch

1636–1645.

Curtis,

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