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

Kangho Jung[a, 1], Scott X. Chang[a, *], and M.A. (Charlie) Arshad[a, b]

[a] *Department of Renewable Resources, 442 Earth Sciences Building, University of Alberta, Edmonton, Alberta, Canada T6G 2E3;* [b] *Agriculture and Agri-Food Canada, Beaverlodge Research Farm, Beaverlodge, AB, T0H 0C0, Canada*

E-mail address: kangho@ualberta.ca (K. Jung), scott.chang@ualberta.ca (S. X. Chang), and Charlie.Arshad@ales.ualberta.ca (M. A. (Charlie) ARSHAD)

Text pages: 27 Tables: 2 Figures: 4

Submitted to: *Environmental Pollution*

* Corresponding author.

Email address: scott.chang@ualberta.ca (S.X. Chang), tel: 1-780-492-6375, fax: 1-780-492-1767

[1] Permanent address: Department of Agricultural Environment, National Academy of Agricultural Science, 150 Suinro, Kweonseonku, Suwon, Republic of Korea 441-707

Jung, K., Chang, S. X., & Arshad, M. A. (2011). 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. Environmental Pollution, 159(5), 1327-1333. doi:10.1016/j.envpol.2011.01.012

ABSTRACT

Soil acidification has been of concern in the oil sands region in Alberta due to increased acid deposition. Using the canopy budget model, and accounting for H^+ canopy leaching by organic acids, we determined sources and sinks of H^+ in throughfall in jack pine (*Pinus banksiana*) and trembling aspen (*Populus tremuloides*) stands in two watersheds from 2006 to 2009. In pine stands, H^+ deposition was greater in throughfall than in bulk precipitation while the opposite was true in aspen stands. The annual H^+ interception deposition was 148.8-193.8 and 49.7-70.0 $mol_c\ ha^{-1}$ in pine and aspen stands, respectively; while the annual H^+ canopy leaching was 127.1-128.7 and 0.0-6.0 $mol_c\ ha^{-1}$, respectively. The greater H^+ supply in pine stands was caused by greater interception deposition of SO_4^{2-} and organic acids released from the pine canopy. Such findings have significant implications for establishing critical loads for various ecosystems in the oil sands region.

Keywords:

Soil acidification

Acid deposition

Canopy budget model

Throughfall

Canopy leaching

Capsule:

A modified canopy budget model was developed and organic acid leaching from jack pine canopies was a significant source of H^+ in the oil sands region of Alberta

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 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 (Inaki 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. Material 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):

$$TF_x = BD_x + ID_x + CE_x \tag{1}$$

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:

$$IDF_{Na} = (TF – BD)_{Na} / BP_{Na} \tag{2}$$

$$ID_x = BD_x \times IDF_{Na} \tag{3}$$

$$CL_x = TF_x – BD_x – ID_x \tag{4}$$

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).

$$\sum CL_{BC} = [CU_H + CU_{NH4}] + CL_{WA\_BC} \tag{5}$$

$$a = [CU_H + CU_{NH4}] / \sum CL_{BC} \tag{6}$$

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

$$CU_{NH4} = a \times \sum CL_{BC} - CU_H \tag{8}$$

where CL 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):

$$ID_H = ID_{SO4} + ID_{NO3} – ID_{NH4} \tag{9}$$

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

$$\sum CL_{WA} = CL_{WA\_H} + CL_{WA\_BC} \tag{10}$$

$$\sum CL_{WA\_H\_OA} = CL_{WA\_H} - CL_{WA\_H\_CO3} \tag{11}$$

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 $CL_{WA\_H\_OA}$ and the contribution factor of ion exchange (a in equation 7), regression equations were developed using estimated $CL_{WA\_H\_OA}$ at CU100, CU75, CU50, and CU25 for jack pine and aspen stands, respectively. The $CL_{WA\_H\_OA}$ 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 ($p=0.002$) but was not different in the mineral soil (Table 1). In mineral soils, total C and N were similar between watersheds (Table 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 1). Exchangeable Al concentrations in the forest floor were greater in jack pine than in aspen ($p=0.016$), but the highest exchangeable Al concentration was found in mineral soils in aspen stands in SM8 (Table 1). The BC:Al ratios were significantly greater in aspen than in jack pine stands in both watersheds ($p=0.006$ in the forest floor, $p<0.001$ in the surface mineral soil, and $p=0.002$ 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 (Fig. 1a). Bulk depositions of SO_4^{2-} and NO_3^- were as much as 4.10 kg S ha and 2.15 kg N ha^{-1} yr^{-1}, respectively, in NE7, and 3.21 and 1.84 kg 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 (Fig. 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 (Fig. 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 (Fig. 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 (Fig. 1b). Sulfate deposition in throughfall was greater ($p=0.040$) in NE7 than in SM8 and greater ($p=0.011$) in jack pine than in aspen stands (Fig. 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 (Fig. 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 ($p=0.014$, 0.017, and 0.045, respectively) in jack pine than in aspen stands in NE7 but no species effect was observed in SM8 (Fig. 2). Interception depositions of SO_4^{2-}, Ca^{2+}, and Mg^{2+} were greater ($p=0.021$, 0.005, and 0.011, respectively) in NE7 than in SM8 in jack pine stands only (Fig. 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 (Fig. 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 (Fig. 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 (Fig. 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 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 ($p=0.042$) 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 (Fig. 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 193.8 and 86.6 mol_c ha^{-1} yr^{-1}, respectively, in jack pine, and 70.0 and 272.2 mol_c ha^{-1} yr^{-1}, respectively, in aspen stands in NE7 and 148.8 and 75.5 mol_c ha^{-1} yr^{-1}, respectively, in jack pine and 49.7 and 342.8 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 (Fig. 1). Base causing materials were also emitted from industrial areas in AOSR, causing greater base cation deposition in NE7 than in SM8 (Fig. 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; Environment Canada, 2010).

In this study, the canopy leaching of base cations was greater in aspen than in jack pine stands (Fig. 3) and aspen stands had greater concentrations of base cations and BC:Al ratios in the soils than jack pine stands (Table 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 (Fig. 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 (Fig. 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 (Fig. 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 (Fig. 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.

Acknowledgements

This study was carried out in the framework and financial support of the NO_x & SO_2 Management Working Group (NSMWG) in the Cumulative Environmental Management Association (CEMA). The project also received financial and logistic support from Alberta Environment. The Natural Sciences and Engineering Research Council of Canada (NSERC) also supported part of the research.

References

Aherne, J., Shaw, P., 2010. Impacts of sulphur and nitrogen deposition in western Canada. Journal of Limnology 69 (Suppl. 1), 1-3.

AMEC. 2009. Properties of sensitive soils in the Athabasca oil sands area, Alberta. CEMA, Alberta.

Augusto, L., Ranger, J., Binkley, D., Rothe, A., 2002. Impact of several tree species of European temperate forests on soil fertility. Annals of Forest Science 59, 233–253.

Bohn, H.L., McNeal, B.L., O'Connor, G.A., 2001. Soil chemistry, third ed. Wiley, New

Work.

Chiwa, M., Miyake, T., Kimura, N., Sakugawa, H., 2008. Organic acids and aldehydes in throughfall and dew in a Japanese pine forest. Journal of Environmental Quality 37, 2397-2402.

Cole, D.W., Rapp, M., 1981. Elemental cycling in forest ecosystems, in: Reichle, D.E. (Ed.), Dynamic properties of forest ecosystems. Cambridge University Press, Cambridge.

Cronan, C.S., Reiners, W.A., 1983. Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. Oecologia 59, 216–223.

Draaijers, G.P.J., Erisman, J.W., 1995. A canopy budget model to estimate atmospheric deposition from throughfall measurement. Water, Air, and Soil Pollution 85, 2253-2258.

Draaijers, G.P.J., Erisman, J.W., Sparnger, T., Wyers, G.P., 1996. The application of throughfall measurements for atmospheric deposition monitoring. Atmospheric Environment 30, 3349-3361.

Draaijers, G.P.J., Erisman, J.W., van Leeuwen, N.F.M., Romer, F.G., te Winkel, B.H., Veltkamp, A.C., Vermeulen, A.T., Wyers, G.P., 1997. The impact of canopy exchange on differences observed between atmospheric deposition and throughfall fluxes. Atmospheric Environment 31, 387–397.

Fujii, K., Funakawa, S., Hyakawa, C., Kaosaki, T., 2008. Contribution of different proton sources to pedogenetic soil acidification in forested ecosystems in Japan. Geoderma 144, 478-490.

Fung, M.Y.P., Macyk, T.M., 2000. Reclamation of oil sands mining areas, in: Barnhisel, R.I., Darmody, R.G., Daniels, W.L. (Eds.), Reclamation of Drastically Disturbed Lands. ASA, CSSA and SSSA, Madison, pp. 755-774

Gee, G.W., Or, D., 2002. Particle size analysis, in: Dane, J.H., Topp, C. (Eds.), Methods of Soil Analysis. ASA, Wisconsin, pp. 255-293

Gower, S.T., Hunter, A., Campbell, J., Vogel, J., 2000. Nutrient dynamics of the southern and northern BOREAS boreal forests. Ecoscience 7, 491-490.

Houle, D., Ouimet, R., Paquin, R., Laflamme, J.G., 1999. Determination of sample size for estimating ion throughfall deposition under a mixed hardwood forest at the Lake Clair Watershed (Duchesnay, Quebec). Canadian Journal of Forest Research 29, 1935–1943.

Johansson, M.B., 1995. The chemical composition of needle and leaf litter from Scots pine, Norway spruce and white birch in Scandinavian forests. Forestry 68, 49-62.

Ignatova, N., Dambrine, E., 2000. Canopy uptake of N deposition in spruce (*Picea abies* L. Karst) stands. Annals of Forest Science 57, 113–120.

Inagaki, M, Sakai, M., Ohnuki, Y., 1995. The effects of organic carbon on acid rain in a temperate forest in Japan. Water, Air, and Soil Pollution 85, 2345-2350.

Kalra, Y.P., Maynard, D.G., 1991. Methods Manual for Forest Soil and Plant Analysis. Forestry Canada, Alberta.

Köhler, S., Laudon, H., Wilander, A., Bishop, K., 2000. Estimating organic acid dissociation in natural surface waters using total alkalinity and TOC. Water Resources Research 34, 1425-1434.

Lutgens, F.D., Tarbuck, E.J., 2007. The Atmosphere tenth ed. Pearson Prentice Hall, Inc., New Jersey.

Marion, G.M., Hendricks, D.M., Dutt, G.R., Fuller, W.H., 1976. Aluminum and silica solubility in soils. Soil Science 121, 76-85.

Mosello, R., Amoriello, T., Benham, S., Clarke, N., Derome, J., Derome, K., Genouw, G., Koenig, N., Orru, A., Tartari, G., Thimonier, A., Ulrich, E., Lindroos, A., 2008. Validation of chemical analyses of atmospheric deposition on forested sites in Europe: 2. DOC concentration as an estimator of the organic ion charge. Journal of Limnology 67, 1-14.

Mulder, J., van Grinsven, J.J.M., van Breemen, N., 1987. Impacts of acid atmospheric deposition on woodland soils in the Netherlands: III. Aluminum chemistry. Soil Science Society of America Journal 51, 1640-1646.

Neary, A.J., Gizyn, W.I., 1994. Throughfall and stemflow chemistry under deciduous coniferous forest canopies in south-central Ontario. Canadian Journal of Forest Research 24, 1089–1100.

New, M.G., Hulme, M., Jones, P.K., 1999. Representing twentieth-century space–time climate variability. Part I: Development of a 1961–90 mean monthly terrestrial climatology. Journal of Climate 12, 829–856.

Niemi, D., 2004. Emissions of pollutants related to acid deposition in North America, in: 2004 Canadian acid deposition science assessment. Meteorological Service of Canada, Ontario, pp 5-14.

NOAA. 2010. http://www.esrl.noaa.gov/gmd/ccgg/trends/

NO_x-SO_2 Management Working Group (NSMWG), 2004. A summary of work for the management of acid emissions in the oil sands: Background information for the dynamic modeling of acid emissions. Workshop 2. Cumulative Environmental

Management Association, Alberta.

Ok, Y.S., Chang, S.X., Feng, Y.S., 2007. Sensitivity to acidification of forest soils in two watersheds with contrasting hydrological regimes in the oil sands region of Alberta. Pedosphere 17, 747-757.

Schrijver, A.D., Geudens, G., Augusto, L., Staelens, J., Mertens, J., Wuyts, K., Gielis, L., Verheyen, K., 2007. The effect of forest type on throughfall deposition and seepage flux: a review. Oecolgia 153, 663-674.

Schrijver, A.D., Nachtergale, L., Staelens, J., Luyssaert, S., Keersmaeker, L.D., 2004. Comparison of throughfall and soil solution chemistry between a high-density Corsican pine stand and a naturally regenerated silver birch stand. Environmental Pollution 131, 93-105.

Soil Classification Working Group, 1998. The Canadian system of soil classification. NRC Research Press, Ottawa.

Soil Survey Staff, 1994. Keys to soil taxonomy, sixth ed. NRCS, Washington, D.C.

Staelens, J., Daniel, H., Schrijver, A.D., Neirynck, J., Verheyen, K., 2008. Calculating dry deposition and canopy exchange with the canopy budget model: review of assumptions and application to two deciduous forests. Water, Air, and Soil Pollution 191, 149–169.

Sverdrup, H., de Vries, W., 1994. Calculating critical loads for acidity with the simple mass balance method. Water, Air, and Soil Pollution 72, 143-162.

Thimonier, A., Schmitt, M., Waldner, P. Rihm, B., 2005. Atmospheric deposition on Swiss long-term forest ecosystem research (LWF) plots. Environmental Monitoring and Assessment 104, 81–118.

UBA, 2004. Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends. Federal Environmental Agency, Berlin.

Ulrich, B., 1983. Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride, in: Ulrich, B., Pankrath, J., (Eds.), Effects of accumulation of air pollutants in forest ecosystems. Kluwer, Dordrecht, pp. 33-45.

van Breemen, N., Mulder, J., Driscoll, C.T., 1983. Acidification and alkalinization of soils. Plant and Soil 75, 283-308.

Van der Maas, M.P., Pape, Th., 1991. Hydrochemistry of two Douglas fir ecosystems and a heather ecosystem in the Veluwe, the Netherlands. Report no. 102.1-01, Dutch Priority Programme on Acidification, Utrecht.

Vanguelova, E.I., Nortcliff, S., Moffat, A.J., Kennedy, F., 2007. Short-term effects of manipulated increase in acid deposition on soil, soil solution chemistry and fine roots in Scots pine (*Pinus sylvestris*) stand on a Podzol. Plant and Soil 294, 41–54.

Vet, R., Brook, J., Ro, C., Shaw, M., Narayan, J., Zhang, L., Moran, M., Lusis, M., 2004. Atmospheric response to past emission control programs, in: 2004 Canadian acid deposition science assessment. Meteorological Service of Canada, Ontario, pp 15-98.

Whitfield, C.J., Adkinson, A., Eimers, M.C., Watmough, S.A., 2010a. The adsorption and release of sulfur in mineral and organic soils of the Athabasca oil sands region, Alberta, Canada. Journal of Environmental Quality 39, 1108-1112.

Whitfield, C.J., Aherne, J., Cosby, B.J., Watmough, S.A., 2010b. Modelling catchment response to acid deposition: a regional dual application of the MAGIC model to soils and lakes in the Athabasca Oil Sands Region, Alberta. Journal of Limnology 69

(Suppl. 1), 147-160.

Whitfield, C.J., Aherne, J., Watmough, S.A., McDonald, M., 2010c. Estimating the sensitivity of forest soils to acid deposition in the Athabasca Oil Sands Region, Alberta. Journal of Limnology 69 (Suppl. 1), 201-208.

World Meteorological Organization (WMO), 2005. Manual for the GAW Precipitation Chemistry Programme - GAW Report No. 160. WMO, Geneva.

Zeng, G.M., Zhang, G., Huang, G.H., Jiang, Y.M., Liu, H.L., 2005. Exchange of Ca^{2+}, Mg^{2+} and K^+ and uptake of H^+, NH_4^+ for the subtropical forest canopies influenced by acid rain in Shaoshan forest located in Central South China. Plant Science 168, 259–266.

Zhang, G., Zeng, G.M., Jiang, Y.M., Yao, J.M., Huang, G.H., Jiang, X.Y., Tan, W., Zhang, X.L., Zeng, M., 2006. Effects of weak acids on canopy leaching and uptake processes in a coniferous–deciduous mixed evergreen forest in central−south China. Water, Air, and Soil Pollution 172, 39–55.

Zimmermann, F., Plessow, K., Queck, R., Bernhofer, C., Matschullat, J., 2006. Atmospheric N- and S-fluxes to a spruce forest—Comparison of inferential modelling and the throughfall method. Atmospheric Environment 40, 4782–4796.