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Wood ash and N fertilization in the Canadian boreal forest: Soil properties and response of jack pine and black spruce

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ABSTRACT

Wood ash fertilization has yet to be investigated in Canadian boreal forests. Ash often improves soil acid–base status, but without N addition it seldom increases tree growth on poor mineral soils. We report results of a large scale experiment conducted in a boreal jack pine (*Pinus banksiana* Lamb) stand growing on sandy acidic soil in Northeastern Canada. The experiment was completely random with four replications (1 ha each) of five treatments (0, 1, 2, 4 and 8 dry Mg ha^{-1}) of loose fly ash with and without urea (280 kg N ha^{-1}). Soils were sampled in the 0, 2, and 8 Mg ha^{-1} treatment up to eight years after application. Foliar nutrition and stand growth were assessed in all treatments one and two years and five years after treatment, respectively.

Even under low ash loading, forest floor exchangeable base cations, pH, and base saturation increased within a year of application. Ash application also resulted in a swift decrease in forest floor organic C and an increase in N potential net mineralization rate. The initial dominant pattern of upper mineral soil properties in relation to ash loading was a curvilinear relationship with the highest values observed in the 2 Mg ha^{-1} treatment. Eight years after ash application, significant linear relationships were found between ash loading and base cations and base saturation in the forest floor and mineral soil (0–10 cm, 10–20 cm). Contrary to N fertilization, ash had no effect on jack pine foliar nutrition and on its five-year growth. However, a decrease of 30% in relative growth rate was observed between the control and the 8 Mg ha^{-1} ash treatment for large ($\geqslant$10 cm DBH) black spruces (*Picea mariana* (Mill.) BSP). Black spruce is the dominant commercial species of Canadian eastern boreal forests and thus, additional studies are needed to validate the deleterious effect of ash on spruce growth and to elucidate the mechanisms involved.

1. Introduction

Interest in bioenergy, including the use of forest biomass as a fuel, is increasing in response to concerns over climate change, growing oil prices and energy security (EU, 2009; Titus et al., 2010). As a result, an increased production of ash from forest biomass combustion is predicted (James et al., 2012). Wood ash is recycled as a fertilizer by the farming industry, but this represents only a small portion of the total ash produced and thus, most is buried in landfills (Hébert and Breton, 2008; James et al., 2012). Because of the limited availability of landfills in close proximity of wood-fired power plants and in turn, the large handling and transporting costs, recycling options in the vicinity of these power plants need to be considered.

Wood ash fertilization in Canadian boreal forests has yet to be investigated. Nonetheless, the use of ash as a fertilizer in forest ecosystems has been researched for more than eighty years in Fennoscandia (Lundström et al., 2003; Pitman, 2006; Huotari et al., in press). Ashes generated from wood products contain variable amounts of most nutrients required for tree growth, with the exception of nitrogen (N) because of its low heat of vaporization. The acid neutralizing capacity of ash stems from its high content of calcium (Ca), magnesium (Mg) and potassium (K) hydroxides (Saarsalmi et al., 2001). Early benefits of ash application on the soil acid–base status, when they occurred, are observed in the forest floor and involve exchanges of protons (H^+) by the mobile monovalent cations K and sodium (Na), while effects on the mineral soil often take place more gradually (Augusto et al., 2008; Pitman,

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2006; Reid and Watmough, 2014). The effects of ash application on forest soil acidity have been shown to last for as much as 30 years (Saarsalmi et al., 2012). Besides macro- and micro-nutrients present as oxides or hydroxides, wood ash also contains low amounts of transition metals and metalloids such as cadmium (Cd), barium (Ba), manganese (Mn) and arsenic (As) (Dahl et al., 2010) that may become phytotoxic (St-Clair and Lynch, 2005). The chemical composition of ash depends on tree species, fuel composition (wood, bark, branches, etc.), boiler type (Pugliese et al., 2014), heat of combustion and possible sources of contamination (e.g. construction and demolition wood, bottom vs fly ash) (Pitman, 2006).

Wood ash has the potential to affect soil N availability through different mechanisms, but mostly by increasing soil pH and dissolved organic carbon (DOC) (Jokinen et al., 2006; Molina et al., 2007). Changes in soil acidity affect microbial communities and activity, generally resulting in more N mineralization (Bååth and Arnebrant, 1993; Mahmood et al., 2003; Perkiömäki and Fritze, 2002). However, neither the increase in soil mineral forms of N or increases in foliar concentrations of P, K and Ca following ash application (Augusto et al., 2008) led to improved tree growth on poor mineral soils (Jacobson, 2003; Saarsalmi et al., 2004). Yet, the limited number of long-term studies precludes any definitive conclusions regarding tree response to improved soil conditions on these sites (Reid and Watmough, 2014). However, increased growth was reported following wood ash application on N-rich but K and P deficient drained peatlands (Huotari et al., in press).

Canadian and Fennoscandian boreal environments share numerous characteristics which should contribute to similar soils, including similar climates, geological formations (Vogel et al., 1998) and recent glacial history (Kleman and Hättestrand, 1999). However, variations between and within regions in tree species composition, forest management history (Östlund et al., 1997) and environmental stressors (Scheffer et al., 2012) preclude direct inference of research findings from one region to the other without proper investigation.

We report on a large scale replicated factorial experiment initiated in 2005 on a mature boreal jack pine stand subjected to increasing loads of wood ash with and without N fertilization. Our objective is to assess the initial response of forest stands to ash fertilization in the Canadian boreal forest. We hypothesized that: (1) soil base cation concentrations, pH and N net mineralization would increase with increasing ash loading, (2) increases in soil alkalinity would first take place in the forest floor and would later appear in the mineral soil, and (3) tree foliar nutrition and growth would respond positively within the first five years of wood ash application when being combined with N fertilization (Jacobson, 2003; Saarsalmi et al., 2006).

2. Approach and methods

2.1. Study area

The study was conducted in the Abitibi-Témiscamingue region of northwestern Québec, Canada (48°31′24″N, 76°37′42″W). The region is included in the Superior geologic province of the Canadian Precambrian Shield. The topography is relatively flat and the elevation ranges from 300 to 350 m. Most of the bedrock is covered by quaternary deposits (Veillette et al., 2000). The climate is continental with an average annual temperature of 0.5 °C and a mean annual precipitation of 973 mm, with 64% falling inclusively between May and October (Governement of Canada, 2014). The region is part of the Canadian boreal forest (Rowe, 1972). It is located within the balsam fir (*Abies balsamea* L. Miller) – white birch (*Betula papyrifera* Marshall) bioclimatic domain (Saucier et al., 2011). Soils developed from well drained loamy sands to sandy loams and consist of Dystric Eluviated Brunisols (Dystrochrepts, Cryochrepts) with a 10–15 cm organic layer (LFH) originating from feathermoss (Agriculture Canada Expert Commitee on Soil Survey, 1998).

2.2. Experimental design and sampling

The 43 ha field trial was set up in October 2005 in a mature jack pine (*Pinus banksiana* Lamb) stand of fire origin (approximately 53 years) that had been commercially thinned in 1999. The stand had an average basal area of 22.3 m^2 ha^{-1} with 20.0 m^2 ha^{-1} of jack pine stems (average diameter = 16 cm) and the remainder composed of black spruce (*Picea mariana* (Mill.) BSP) stems (average diameter = 10 cm). The experiment was designed as completely random with four replications (1 ha each) of five ash treatments (0, 1, 2, 4 and 8 dry Mg ha^{-1} of loose unstabilized fly ash; see Table 1 for ash elemental composition) with and without urea ($CO(NH_2)_2$) fertilization (280 kg N ha^{-1}) for a total of 40 experimental units. Ash and urea were applied with a farm spreader using harvesting trails.

Prior to ash and urea application and in each experimental unit, three permanent circular sampling plots (PSP) of 200 m^2 were delineated. All jack pine and black spruce stems greater than 5.0 cm of diameter at breast height (DBH) were tagged, identified by species, and measured for DBH. These were measured again five years later (2010) to obtain an estimate, for each stem, of the five-year relative growth rate:

$$\left[\frac{(\mathrm{DBH}_{2010} - \mathrm{DBH}_{2005})}{\mathrm{DBH}_{2005}}\right]$$

In each PSP, soils were sampled one, two and five years (2006, 2007 and 2010, respectively) after application of 0, 2 and 8 Mg ha^{-1} of ash with and without urea. Bulk soil samples were taken from the forest floor and the 0–10 cm mineral soil. Eight years (2013) following treatment application, the forest floor as well as the 0–10 cm and 10–20 cm mineral soils were sampled once more in three replications in the 0, 2 and 8 Mg ha^{-1} ash treatments with and without urea.

One and two years (2006–2007) after treatments, current-year pine needles were collected within the same PSPs where soils were

Table 1
Characteristics of fly ash from Boralex wood residue thermal power plant during the year preceding field application (median, *n* = 8). The plant mostly uses softwood bark residues from nearby sawmills. Characteristics of fly ash (median, *n* = 4–10) of comparable origin published by the Wood ash database (WAD) (Swedish University of Agricultural Sciences, http://woodash.slu.se/eng/) are also provided.

	Boralex[a]	WAD		Boralex	WAD
Macroelements (mg g^{-1})			Microelements (µg g^{-1})		
N tot	<1		As	2	6
Ca	67	214	B	62	210
K total	9	74	Ba[c]	1300	2460
Mg	4	20	Cd	3	8
Mn	2	12	Co	10	10
Na	2	14	Cr	11	47
P total	1	11	Cu	20	80
			Fe	1216	9000
Physicochemical properties (%)			Hg	0	<1
			Mo	4	7
CCE[b]	31		Ni	12	80
Fineness	92		Pb	10	38
OM (%)	22		Zn	286	3300

[a] Nitric acid (HNO_3) or HNO_3 and hydrochloric acid (HCl) extraction.
[b] CCE = calcium carbonate equivalence, fineness = particles < 2 mm; OM = organic matter
[c] Ba was estimated in 2011 on a single sample.

sampled. To limit seasonal variability in nutrient concentrations, foliar samples were taken in the fall after tree hardening. In each PSP, twigs in the upper tier of the crown of three dominant jack pines were brought down with a shotgun and pooled in a single sample for each experimental unit ($n = 24$). Black spruce foliage was not sampled.

2.3. Laboratory analyses

Subsamples of the forest floor and mineral soil were air dried and sieved (2 mm) prior to chemical analyses. Exchangeable base cations (Ca_{exch}, Mg_{exch}, K_{exch}, Na_{exch}) and acidity (Al^{3+} and H^+) were extracted with $NH_4Cl–BaCl_2$ (Amacher et al., 1990) on subsamples from 2006, 2007 and 2010. Soil pH was determined in 0.01 M $CaCl_2$ using a ratio of soil:solution of 1:4 for the forest floor and 1:2 for the mineral soil. Exchangeable base cations were analyzed by inductively coupled plasma atomic emission (ICP) (Perkin–Elmer Optima 4300DV), whereas exchangeable acidity was analyzed by titration (848 Titrino plus, Metrohm). Effective cation exchange capacity (CEC_{eff}) was estimated by adding base cations and exchangeable acidity ($acidity_{exch}$). Base saturation was defined as the ratio of $Ca_{exch} + Mg_{exch} + K_{exch} + Na_{exch}$ over CEC_{eff}. Ratios of individual cations over CEC_{eff} were also calculated for each base cation (e.g. Ca saturation). Available phosphorus ($P_{Mehlich-3}$) was assessed only on 2007 and 2010 subsamples using the Mehlich-3 procedure (Ziadi and Sen Tran, 2008). Forest floor and mineral soil subsamples were ground to pass through a 250 μm mesh and analyzed for organic carbon (C_{org}) concentration by lost on ignition (McKeague, 1976) and digested in a $HSO_4–H_2O_2$ mixture (Parkinson and Allen, 1975) for Kjeldahl N (Bremner and Mulvaney, 1982). Forest floor and mineral soil subsamples collected in 2013 were analyzed for Ca_{exch}, Mg_{exch}, K_{exch}, Na_{exch}, Al_{exch} as well as exchangeable barium (Ba_{exch}) and manganese (Mn_{exch}) which were found in relatively high concentrations relative to microelements in wood ash (see Table 1). Elements were extracted with 0.1 M NH_4Cl (Bélanger et al., 2007) instead of $NH_4Cl–BaCl_2$ in order to include Ba in the analysis. Concentrations were determined by ICP mass spectrometry (Varian 820MS).

Subsamples from 2006 were also analyzed for potential net N mineralization rate (Bundy and Meisinger, 1994). Fresh forest floor (10 g) and mineral soil (5 g) samples were incubated under anaerobic conditions at 23 °C for two weeks in 50 ml deionized water. Samples were then extracted with 50 ml 2 M KCl. Initial NH_4^+ concentrations were determined on equivalent subsamples extracted with 100 ml 1 M KCl. Extracts were analyzed for NH_4^+ by colorimetry using an autoanalyzer (FIA Quikchem 4000). The potential net N mineralization rate is the difference between final and initial subsamples NH_4^+ concentrations over a 14 day period.

First-year needles collected in 2006 and 2007 were dried at 65° C for 48 h, weighed, ground and digested in the same $HSO_4–H_2O_2$ mixture as above. Total Ca, Mg, K and P concentrations were measured by ICP (Perkin–Elmer Optima 4300DV), while total N was measured using the Kjeldahl method. Simple nutrient concentration ratios were computed.

2.4. Statistical analyses

All statistical analyses were done using the MIXED and MEANS procedures of the SAS Institute (SAS Institute Inc., 2009). Data were analyzed according to a completely random experimental design with repeated measurements. For data collected from 2006 to 2010, the effects on response variables of ash, urea (N), time since application and two-way interactions between main effects were tested using a mixed linear model (Littell et al., 2006). We tested whether response variables increased or decreased with ash load. Time and ash treatments were also squared to test for second order polynomial (quadratic) effects, whereas we tested whether response variables reached a minimum/maximum value under the intermediate load. To simplify models, interactions were removed from the analyses when found not to be significant. Similar models were used for foliar nutrients and nutrient ratios. For relative tree growth rates, the model used all ash treatments (0, 1, 2, 4 8 Mg ha^{-1}) and was tested for large ($\geqslant$16 cm DBH) and small (DBH < 16 cm) jack pines and for large (DBH $\geqslant$ 10 cm) and small (DBH < 10 cm) black spruces. Soil exchangeable cations as well as exchangeable Ba and Mn measured from sampled collected in 2013 were analyzed separately and only the linear effect of ash was tested.

Random effects (samples or individual trees nested within PSP, and PSP nested within experimental unit) and repeated effects (year of sampling, i.e. 1, 2 and 5) were included in the analyses to account for the non-random structure of the sampling design. Variance estimates were based on the restricted maximum likelihood and significance of treatments effect on the Type 1 test of hypothesis.

3. Results

3.1. Effects of ash loading over five years on soil acid–base status

Forest floor K_{exch} concentration increased linearly with ash loading (Table 2, Fig. 1). One year after application, concentration was 61% higher in the 8 Mg ha^{-1} treatment than in the control. The effect of ash on K_{exch} concentrations remained constant over time as no significant interaction between ash loading and time where found. Forest floor K saturation also increased linearly with ash loading (Table 2) from 5.8% (SE = 0.4) in the control to 8.1% (SE = 0.4) in the 8 Mg ha^{-1} treatment one year following application. However, this effect decreased linearly with time. Five years after application, K saturation under the different ash loads was similar to the control (5.2%; SE = 0.3). Over the five year period, forest floor Na_{exch} (results not shown) accounted for less than 1.2% of base saturation, independently of ash load.

Forest floor Ca_{exch} and Mg_{exch} concentrations also increased with ash loading (Fig. 1). However, the difference between the 2 and 8 Mg ha^{-1} treatments was generally weak, accounting for the significant linear and quadratic effects of ash on forest floor Ca_{exch} and Mg_{exch} concentrations (Table 2). The effect of ash remained constant over time for Mg_{exch}. Five years after application, Mg_{exch} concentration was 81% higher in the 8 Mg ha^{-1} treatment than in the control. Significant linear and quadratic relationships between Mg saturation and ash loading were observed as well as significant interactions between ash loading and linear and quadratic time effects (Table 2). Over the 5 year period, forest floor Mg saturation ranged from 5.7% to 6.8% (SE = 0.5) in the control. Saturation was the highest in the 2 and 8 Mg ha^{-1} treatments in the first year following ash application with respective values of 9.1% (SE = 0.4) and 10.9% (SE = 0.6). Thereafter, saturation decreased but remained similar between the two ash treatments with values of 7.5% (SE = 0.3–0.5) five years after application.

Exchangeable Ca concentration in the 8 Mg ha^{-1} treatment was still increasing in relation to the other treatments five years after application (Fig. 1). By year five, Ca_{exch} concentration was 3.5 higher in the 8 Mg ha^{-1} treatment than in the control. Over the five year period, Ca saturation ranged from 29.0% to 34.5% (SE = 2.9–3.1) in the control and from 50.4% to 51.5% (SE = 2.8–3.1) in the 2 Mg ha^{-1} treatment. However, in the 8 Mg ha^{-1} treatment, values increased from 54.5% in the first year after application to 58.1% in the second year and 68.4% (SE = 3.0–3.1) in the fifth year, accounting for significant linear and quadratic effects of ash loading and a highly significant interaction between time (linear) and ash loading (Table 2).

Table 2
Effects of ash loading and nitrogen (N) fertilization on soil acid–base status of a boreal coarse textured soil, one, two and five years after application. The significance of ash, N, time since application and two-way interactions were tested using a mixed linear model and are based on a Type 1 test of hypothesis. Time and ash loading were treated as numerical variables.

Response variables	pH	K_{exch}	K_{sat}	Mg_{exch}	Mg_{sat}	Ca_{exch}[a]	Ca_{sat}	$Acid_{exch}$	CEC_{eff}	Base sat.[a]
Forest floor										
Fixed factors										
Time linear	0.013	0.043	0.001	<0.001	<0.001	<0.001	0.154	<0.001	<0.001	0.410
Time quadratic	0.001	<0.001	0.268	0.114	<0.001	<0.001	0.953	<0.001	<0.001	0.427
Ash linear	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ash quadratic	0.001	0.723	0.592	0.017	<0.001	<0.001	<0.001	<0.001	0.855	<0.001
Nitrogen (N)	0.767	0.863	0.459	0.116	0.161	0.930	0.768	0.914	0.313	0.657
Ash linear ∗ N						0.076		0.335	0.030	
Ash lin. ∗ time lin.			<0.001		0.018	<0.001	<0.001	<0.001	<0.001	<0.001
Ash lin ∗ time quad.					0.015					
Time lin. ∗ N										
Ash quad. ∗ N								0.037		
Ash quad. ∗ time lin.										
Time quad. ∗ N										
0–10 cm mineral soil										
Fixed factors										
Time linear	0.156	<0.001	<0.001	0.150	0.694	0.440	0.200	0.346	0.228	0.000
Time quadratic	<0.001	<0.001	<0.001	0.008	0.071	<0.001	0.002	0.001	0.009	0.001
Ash linear	0.055	<0.001	0.044	0.004	0.013	0.032	0.251	0.539	0.815	0.011
Ash quadratic	0.127	0.176	0.350	0.003	0.046	0.004	0.050	0.014	0.002	0.161
Nitrogen (N)	0.108	0.049	0.789	0.044	0.020	0.098	0.041	0.197	0.495	0.024
Ash linear ∗ N				0.828		0.476				
Ash lin. ∗ time lin.		0.038			<0.001	0.027	0.002	0.020	0.110	<0.001
Ash lin. ∗ time quad.										
Time lin. ∗ N			0.052		0.006			<0.001	0.001	0.001
Ash quad. ∗ N				0.002		0.020				
Ash quad. ∗ time lin.								0.004	0.008	0.005
Time quad. ∗ N			0.002		0.003			<0.001	<0.001	<0.001

NA: not applicable.
[a] Log transformed.

Forest floor acidity$_{exch}$ followed the inverse pattern of exchangeable base cations. However, the difference between the 2 and 8 Mg ha^{-1} treatments became significant only five years after application (Fig. 1). Forest floor pH increased in the first year following ash application, but remained constant in the following years (Fig. 2). As indicated by the significant quadratic effect of ash on forest floor pH (Table 2), the largest proportional increase (0.4 unit) was caused by the 2 Mg ha^{-1} treatment compared with an increase of 0.6 unit following the 8 Mg ha^{-1} treatment.

The effect of ash on forest floor CEC$_{eff}$ enlarged with time since application (Table 2, Fig. 2). No significant effect of ash on CEC$_{eff}$ was observed the year following application, while increases of 15% and 61% were observed five years after ash application of 2 and 8 Mg ha^{-1}, respectively. Forest floor base saturation initially followed the same pattern as pH with a proportionally larger increase one to two years after 2 Mg ha^{-1} of ash were applied. However, the effect became more pronounced in the 8 Mg ha^{-1} treatment five years after application, representing an increase of 102% in forest floor base saturation relative to the control.

In the upper mineral soil (0–10 cm), K$_{exch}$ concentration increased only in the 8 Mg ha^{-1} treatment (Table 2, Fig. 1). The effect decreased linearly with time: in relation to the control, the first year increase was 32%, but the increase was only 13% in the second and fifth years after application. Ash application had a small significant but durable effect on mineral soil K saturation (Table 2). Five years after ash application, K saturation was 2.5% in the 8 Mg ha^{-1} treatment compared with 2.1% in the control (SE = 0.2). The maximum Ca$_{exch}$ and Mg$_{exch}$ concentrations were observed with the 2 Mg ha^{-1} ash treatment. One year after ash application of 2 and 8 Mg ha^{-1}, Mg$_{exch}$ concentrations were respectively 95% and 61% higher than that in the control and remained above the control for the five year period (Fig. 1). The linear effect of ash loading on Mg saturation increased linearly with time (Table 2). Five years after application, values ranged from 1.3% in the control to 2.8% (SE = 0.2) in the 8 Mg ha^{-1} treatment. The differences in Ca$_{exch}$ concentration among treatments also increased over time, accounting for the significant ash - time interaction (Table 2, Fig. 1). One, two and five years after ash application of 2 Mg ha^{-1}, Ca$_{exch}$ concentrations were respectively 104%, 111% and 133% higher than the control. Changes in Ca$_{exch}$ concentrations were less pronounced with the 8 Mg ha^{-1} treatment, with values being 20%, 37% and 105% higher than the control after one, two and five years, respectively. The linear effect of ash loading on mineral soil Ca saturation increased linearly with time (Table 2) and was detectable five years after application. Calcium saturation was 6.2% (SE = 2.0) in the control and 13.0% (SE = 1.5–1.7) in the 8 Mg ha^{-1} treatment five years following application. Mineral soil Na$_{exch}$ (results not shown) represented less than 2.2% of base saturation.

Mineral soil acidity$_{exch}$ was initially higher in the 2 Mg ha^{-1} treatment one and two years following application. However, five years following the application of 2 and 8 Mg ha^{-1} of ash, acidity$_{exch}$ decreased respectively by 7% and 17% compared to the control. Ash application had little effect on upper mineral soil pH (Table 2, Fig. 2).

The maximum CEC$_{eff.}$ was observed with the 2 Mg ha^{-1} treatment for up to two years following ash application. Five years after application, CEC$_{eff.}$ decreased linearly with ash loading. The quadratic effect of ash loading and its interaction with time (linear) on CEC$_{eff}$ were both significant (Table 2). The effect of ash application on mineral soil base saturation increased with ash loading and with time since application. However, the 2 Mg ha^{-1} ash treatment proportionally caused the largest effect five years after application, increasing base saturation by 66% relative to the control (compared to 99% with the 8 Mg ha^{-1} treatment).

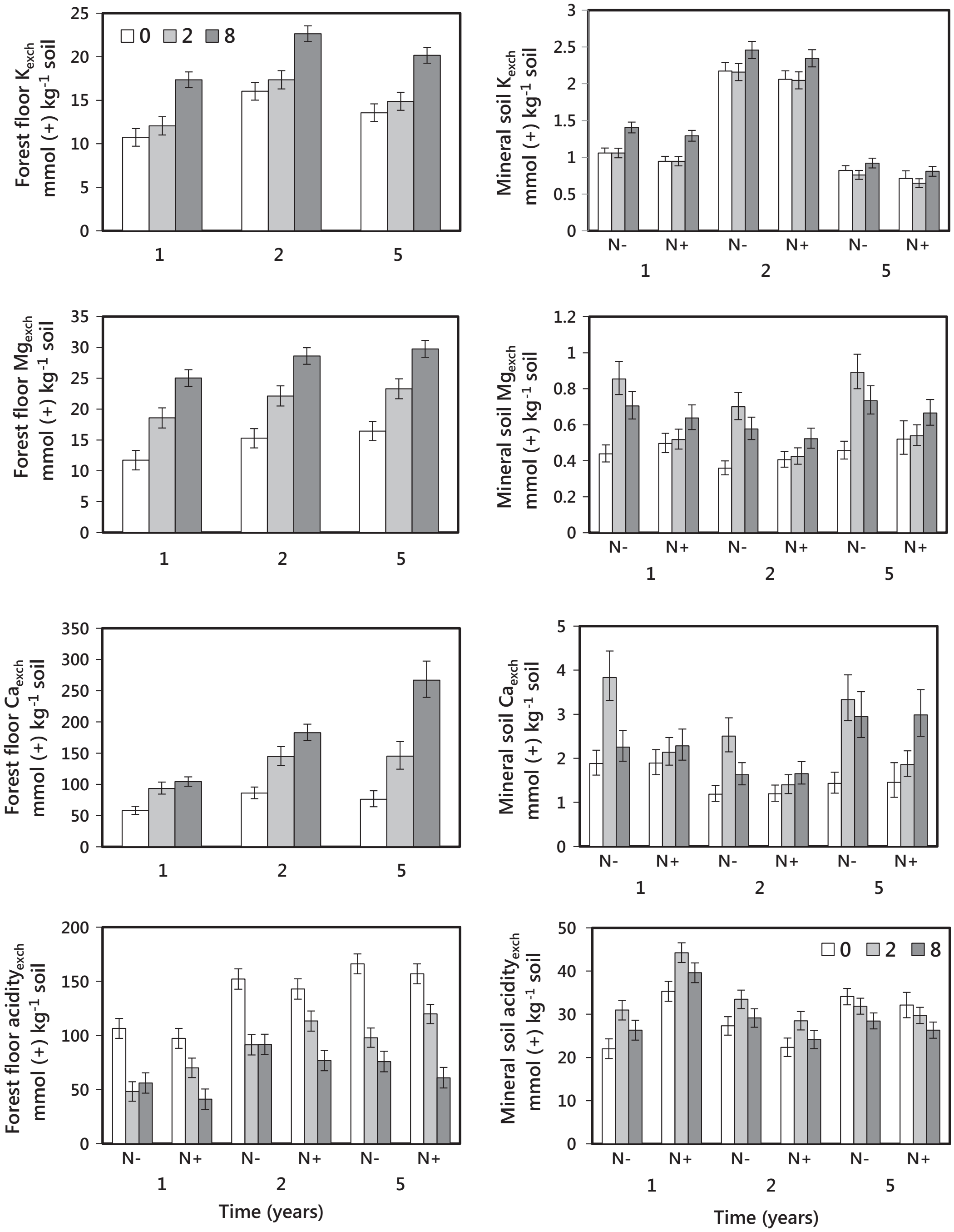

Fig. 1. Forest floor and 0–10 cm mineral soil exchangeable cation concentrations and acidity one, two and five years after ash loading (0, 2, 8 Mg ha^{-1}) and N fertilization (280 kg N ha^{-1}) in a boreal jack pine stand. Predicted values and their standard error (bars) according to models of Table 2.

3.2. Effects of ash loading over five years on soil C, N and P

A decrease in forest floor C_{org} concentration was observed with increasing loading for up to two years after ash application (Table 3, Fig. 3). Five years after application, however, the 2 Mg ha^{-1} treatment had a higher C_{org} concentration than the control and the 8 Mg ha^{-1} treatment. A significant linear effect of ash loading on forest floor C_{org} concentration as well as a significant time and ash quadratic interaction were found (Table 3). Ash application had linear and quadratic effects on forest floor $N_{Kjeldahl}$ concentration (Table 3, Fig. 3). Ash application at 2 and 8 Mg ha^{-1} respectively increased and decreased $N_{Kjeldahl}$ concentration relative to the control. This curvilinear pattern became more apparent with time as indicated by the significant interaction between ash treatment (quadratic) and time (Table 3). Forest floor C/N followed a quadratic and linear pattern in relation to ash loading that remained stable over the five year period.

Five years after ash was applied, C/N was 38.3, 35.1 and 40.2 (SE = 1.2) in the control and 2 and 8 Mg ha^{-1} treatments, respectively.

In the first year following ash application, forest floor potential net N mineralization showed a similar increase under the 2 and 8 Mg ha^{-1} treatments, accounting for the significant linear and quadratic effects (Table 3). Net N mineralization in the 8 Mg ha^{-1} treatment was 300% higher than in the control (Fig. 3). Forest floor $P_{Mehlich\text{-}3}$ concentration increased linearly with ash loading and the

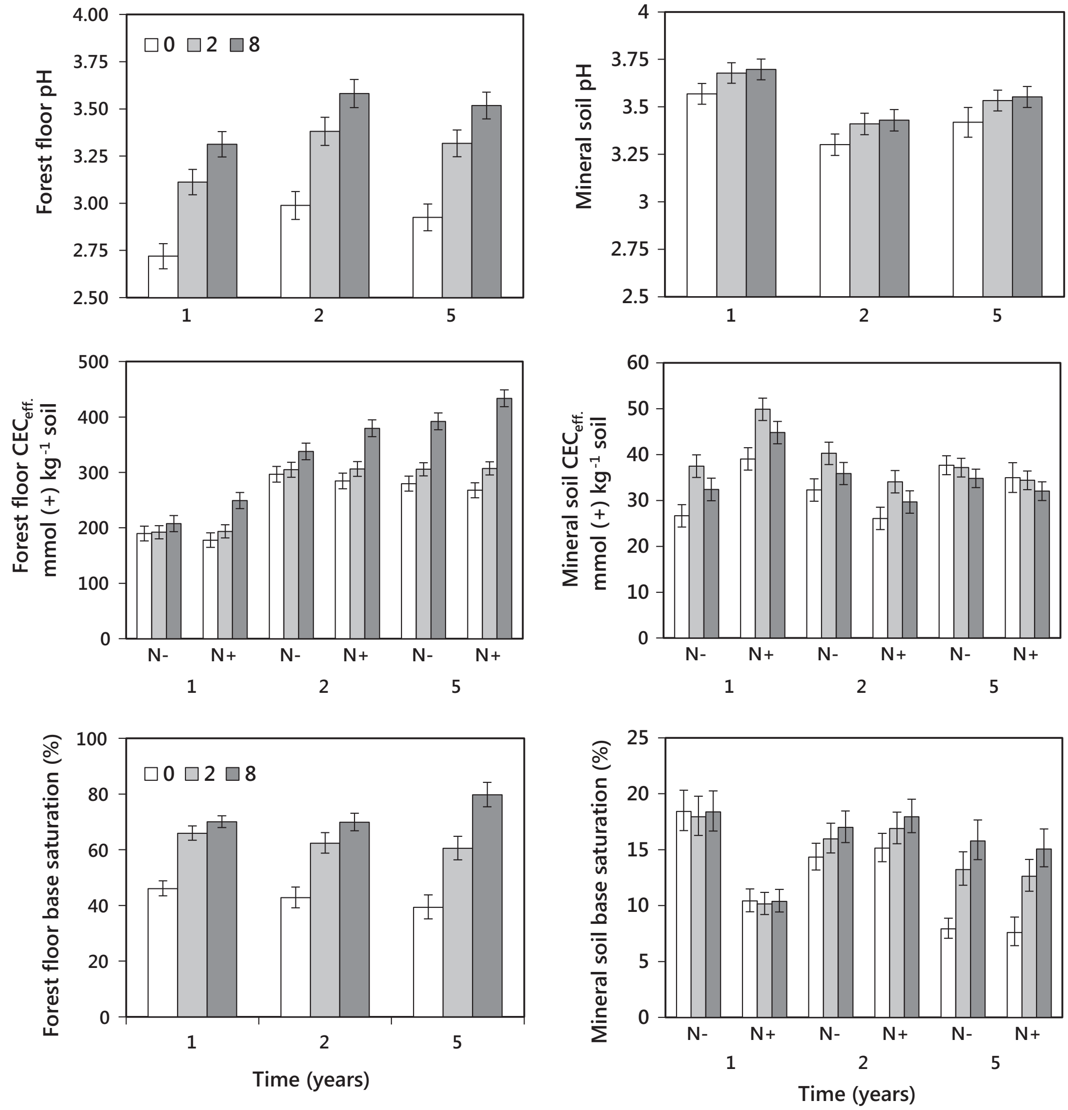

Fig. 2. Forest floor and 0–10 cm mineral soil pH, effective CEC, and base saturation, one, two and five years after ash loading (0, 2, 8 Mg ha^{-1}) and N fertilization (280 kg N ha^{-1}) in a boreal jack pine stand. Predicted values and their standard error (bars) according to models of Table 2.

Table 3

Effects of ash loading and nitrogen (N) fertilization on a boreal coarse textured soil organic C, Kjeldahl N, Mehlich-3 P concentrations and potential net N mineralization rate (Net N min.), one, two and five years after application. The significance of ash, N, time since application and two-way interactions were tested using a mixed linear model and are based on a Type 1 test of hypothesis. Time and ash loading were treated as numerical variables.

Response variables	Forest floor					Mineral soil				
	C_{org}	$N_{Kjeldahl}$	Net N min.[a]	$P_{Mehlich-3}$[a]	C/N	Corg	$N_{Kjeldahl}$	Net N min[a]	$P_{Mehlich-3}$[a]	C/N
Fixed factors										
Time linear	0.100	<0.001	NA[b]	<0.001	0.001	<0.001	0.062	NA	<0.001	0.001
Time quadratic	<0.001	<0.001	NA	NA	0.216	0.125	0.001	NA	NA	0.001
Ash linear	0.013	0.032	0.014	<0.001	0.036	0.312	0.076	0.560	0.706	0.405
Ash quadratic	0.819	0.055	0.001	0.144	0.007	0.118	0.039	0.578	0.610	0.561
Nitrogen (N)	0.869	0.121	0.001	0.431	0.095	0.395	0.713	0.144	0.201	0.902
Ash linear ∗ N			0.008	0.499			0.923	0.085		
Ash lin. ∗ time lin.	0.305	0.682		0.001				NA		0.397
Time lin. ∗ N			NA					NA	0.002	
Ash quad. ∗ N				0.047			0.050	0.038		
Ash quad. ∗ time lin.	0.039	0.043	NA					NA		0.002
Time quad. ∗ N			NA	NA				NA	NA	

[a] Log transformed.

[b] NA: not applicable.

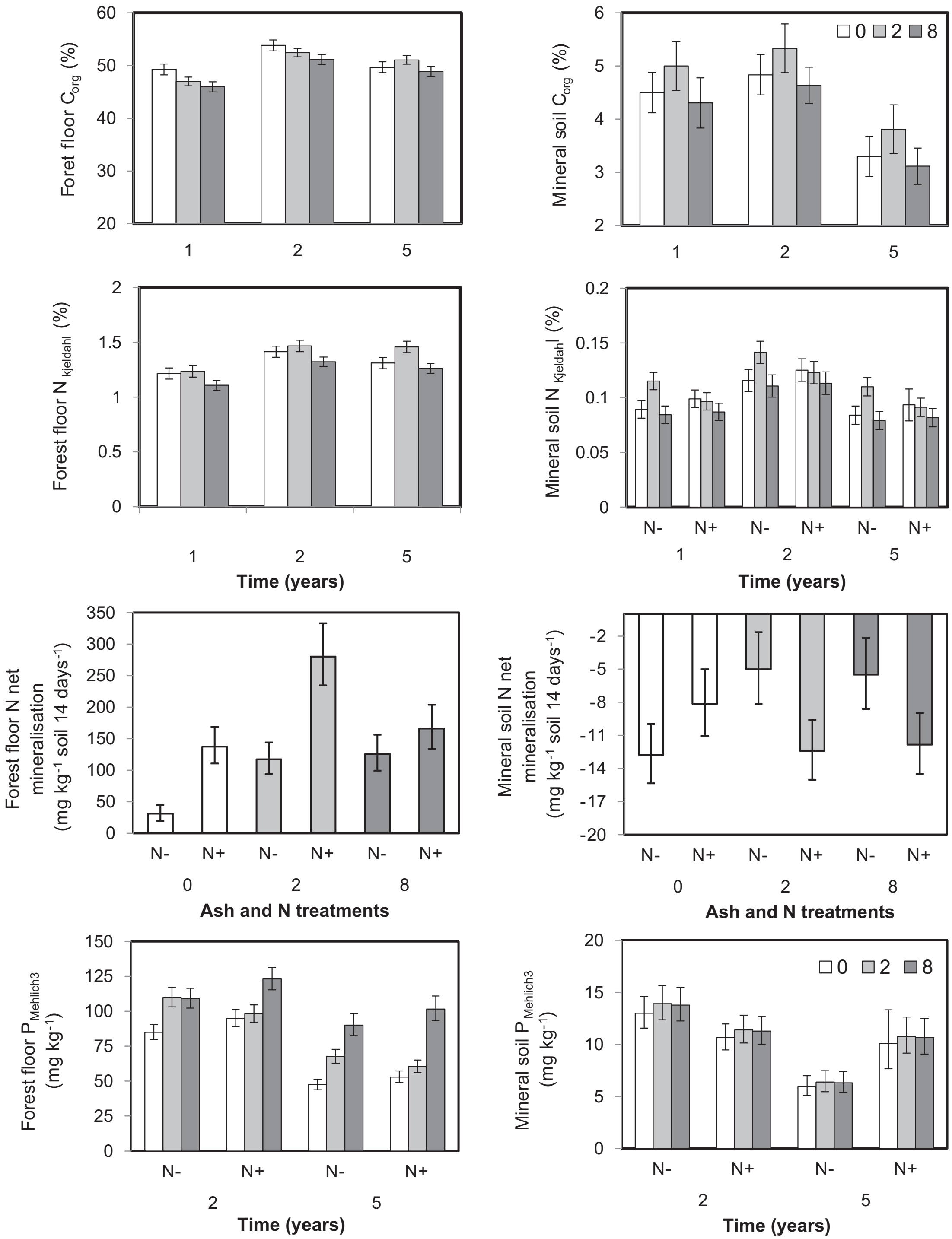

Fig. 3. Forest floor and 0–10 cm mineral soil organic C, Kjeldhal N, one, two and five years after ash loading (0, 2, 8 tons ha^{-1}) and N fertilization (280 kg N ha^{-1}) in a boreal jack pine stand. Potential N net mineralization rate measured one year after application and Mehlich-3 P measured two and five years after application. Predicted values and standard error (bars) according to mixed linear models of Table 3.

effect became more pronounced with time as supported by the significant interaction between ash loading and time (Table 3). Five years following ash application, forest floor $P_{Mehlich-3}$ concentrations in the 2 and 8 Mg ha^{-1} treatments were respectively 43% and 90% higher than in the control.

Ash application had no significant effect on C_{org} and $P_{Mehlich-3}$ concentrations (Table 3) or potential net N mineralization in the upper mineral soil. The increase and decrease in mineral soil C_{org} concentration observed respectively under the 2 and 8 Mg ha^{-1} treatments relative to the control were not significant because of large variations within the treatments (Table 3, Fig. 3). Mineral soil $N_{Kjeldahl}$ concentration followed a similar pattern to that in the forest floor with the highest concentration observed under the 2 Mg ha^{-1} treatment (Table 3, Fig. 3). The relationship between ash loading and mineral soil C/N varied with time since ash treatment, but only the interaction between time and ash (quadratic) was significant. Carbon/N ratio in the 2 Mg ha^{-1} ash treatment first increased and then decreased relative to the two other ash treatments. Five years after ash application, mineral soil C/N was 41.0 (SE = 2.5), 35.3 (SE = 1.9) and 38.9 (SE = 1.9) in the control and 2 and 8 Mg ha^{-1} treatments, respectively.

3.3. Effects of N fertilization over five years on overall soil properties, and interactions with ash loading

Nitrogen fertilization with urea had no significant direct effects on chemical properties of the forest floor (Table 2), including C/N (Table 3). However, one year after N fertilization, a strong positive effect on forest floor potential net N mineralization (Table 3) rate was observed. This corresponded to an increase of 342% in the N fertilized–ash control treatment relative to the full control (Fig. 3). A significant N × ash interaction was also observed (Table 3), whereas the linear increase in potential net N mineralization with ash loading was less pronounced in N fertilized plots. Significant interactions between N and ash loading were also found for forest floor CEC$_{\mathrm{eff}}$, acidity$_{\mathrm{exch}}$, and P$_{\text{Mehlich-3}}$, whereas N fertilization increased the divergence between ash treatments (Figs. 2 and 3).

Similarly, N fertilization alone had little direct lasting effects on chemical properties of the upper mineral soil (Table 2), including C/N (Table 3). Nitrogen fertilization initially increased mineral soil acidity$_{\mathrm{exch}}$ (Fig. 1) and CEC$_{\mathrm{eff}}$ (Fig. 2) and decreased individual cations (results not shown) and total base saturation (Fig. 2). The effects of N fertilization on these variables fluctuated with time from two to five years after application as indicated by the significant linear and quadratic time × N interaction (Table 2). When N fertilization was applied in combination with ash, mineral soil N$_{\mathrm{Kjeldahl}}$ concentration decreased, while Mg$_{\mathrm{exch}}$ and Ca$_{\mathrm{exch}}$ concentrations linearly increased with increasing ash loading. This effect contrasted with the quadratic effect of ash loading on N$_{\mathrm{Kjeldahl}}$, Mg$_{\mathrm{exch}}$ and Ca$_{\mathrm{exch}}$ in the absence of N fertilization.

Contrary to the forest floor, the mineral soil led to net N immobilization (Fig. 3). One year following N fertilization, no simple effect of N on mineral soil potential net N mineralization was observed (Table 3). However, a significant interaction was noted between ash (quadratic) and N fertilization (Table 3). In the absence ash loading, N fertilization decreased mineral soil net N immobilisation, while the opposite trend was observed in plots receiving ash (Fig. 3). A significant linear and quadratic interaction between N fertilization and time was found for P$_{\text{Mehlich-3}}$; P$_{\text{Mehlich-3}}$ of N fertilized plots was initially lower and then higher than in the unfertilized plots (Fig. 3).

3.4. Effects of ash loading and N fertilization over five years on foliar nutrients and five-year relative tree growth

No significant effect of ash was found on individual foliar nutrient concentrations (i.e. N, P, K, Ca and Mg) and nutrient ratios of jack pine one to two years after application, with the exception of K/P ($p = 0.053$). The 2006–2007 average K/P was 3.09 (SE = 0.08) in the control and 3.36 in the 8 Mg ha^{-1} treatment. The average 2006–2007 foliar N concentration of N fertilized plots (1.09%, SE = 0.02) was 7.1% higher ($p = 0.001$) than the control (1.02%).

Ash had no effect on the five-year relative growth rates of large ($\geqslant$10 cm DBH, $n = 1293$, relative growth rate = 5.0%) and small (<10 cm DBH, $n = 536$) jack pines and of small black spruces ($n = 211$). However, the five-year relative growth rate of large black spruces ($\geqslant$10 cm DBH, $n = 269$) decreased linearly ($p = 0.002$) with ash loading (Fig. 4), a difference in growth rate of −30% between the control and the 8 Mg ha^{-1} ash treatment. Only large jack pines were affected by N fertilization ($p < 0.001$); their relative five-year growth rate increased by 21% due to N fertilization. No significant interaction was found between ash treatment and N fertilization concerning the growth rate of any of the species-size classes.

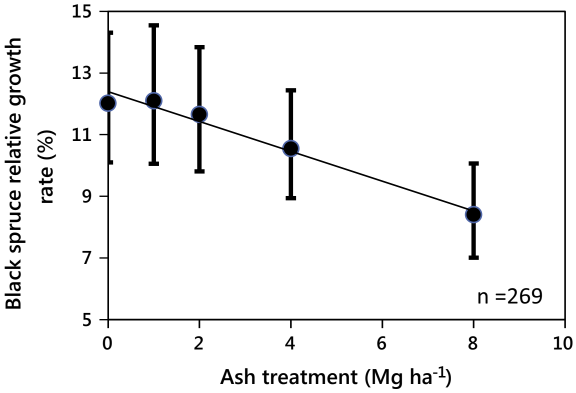

Fig. 4. Black spruce (diameter at breast height $\geqslant$10 cm) relative growth rate 1–5 years following ash loading (0, 1, 2, 4, 8 Mg ha^{-1}) in a boreal jack pine stand.

3.5. Effects of ash loading over eight years on soil acid–base status

Soil extraction with NH$_4$Cl alone yielded exchangeable cation concentrations within the range of those observed following the NH$_4$Cl–BaCl$_2$ extraction (Figs. 1 and 5). Eight years after ash application, significant linear relationships were found between ash loading and K$_{\mathrm{exch}}$, Ca$_{\mathrm{exch}}$, Mg$_{\mathrm{exch}}$ in the forest floor and upper (0–10 cm) and lower (10–20 cm) mineral soil (Table 3). However, the relationship between ash loading and Ca$_{\mathrm{exch}}$ in the lower mineral soil was marginally significant ($p = 0.085$). Relative to the control, increases in K$_{\mathrm{exch}}$, Mg$_{\mathrm{exch}}$ and Ca$_{\mathrm{exch}}$ under the 8 Mg ha^{-1} ash treatment were respectively 40%, 103% and 180% in the forest floor, 61%, 121% and 120% in the upper mineral soil, and 49%, 73% and 60% in the lower mineral soil (Fig. 5).

Eight years following ash loading, no difference among treatments was observed for forest floor K saturation (Fig. 6; control = 7.0%, SE = 0.8), whereas Mg and Ca saturation increased (Table 4, Fig. 6) with ash loading. Forest floor Mg saturation increased from 11.0% (SE = 0.6) in the control to 13.6% (SE = 0.8) in the 8 Mg ha^{-1} treatment, whereas Ca saturation increased from 42.2% (SE = 5.8) to 71.8% (SE = 6.1).

Potassium saturation (Table 4, Fig. 6) significantly increased with ash loading from 1.9% (SE = 0.2) in the control to 2.8% (SE = 0.2) in the 8 Mg ha^{-1} treatment within the 0–10 cm depth, and from 2.3% (SE = 0.4) to 4.8% (SE = 0.6) within the 10–20 cm depth. Magnesium saturation also increased from 2.4% (SE = 0.4) in the control to 5.0% (SE = 0.4) in the 8 Mg ha^{-1} treatment within 0–10 cm, and from 3.1% (SE = 0.5) to 6.7% (SE = 0.7) within 10–20 cm. Finally, Ca saturation within the 0–10 cm depth increased with ash loading from 6.8% (SE = 3.5) in the control to 17.0% (SE = 3.7) in the 8 Mg ha^{-1} treatment. Within the 10–20 cm depth, Ca saturation increased from 7.1% (SE = 1.2) in the control to 14.8% (SE = 1.5) in the 8 Mg ha^{-1} treatment. For all soil horizons, the increase in base saturation caused by ash loading was mostly associated to Ca (Fig. 6).

Significant linear relationships between ash loading and Al$_{\mathrm{exch}}$ (Fig. 5) and CEC$_{\mathrm{eff}}$ (Table 4) were found only for the forest floor. Forest floor CEC$_{\mathrm{eff}}$ was 175.3 (SE = 17.7) mmol(+) kg^{-1} in the control and 284.4 (SE = 18.9) mmol (+) kg^{-1} in the 8 Mg ha^{-1} treatment. Ash loading had no effect on Ba$_{\mathrm{exch}}$ (average forest floor = 1.24 mmol(+) kg^{-1}, SE = 0.18). The log of Mn$_{\mathrm{exch}}$ significantly increased at all soil depths with ash loading. In the forest floor, Mn$_{\mathrm{exch}}$ increased from 0.57 mmol(+) kg^{-1} (SE = 0.11) in the control to 1.01 (SE = 0.16) and 5.54 (SE = 1.41) mmol(+) kg^{-1} in the 2 and 8 Mg ha^{-1} treatments, respectively. This corresponded to increases of 76% and 862%. Exchangeable Mn values in the upper and lower mineral soils were much lower than those in the forest floor – with values of 0.024 (SE = 0.004) and 0.029 (SE = 0.007)

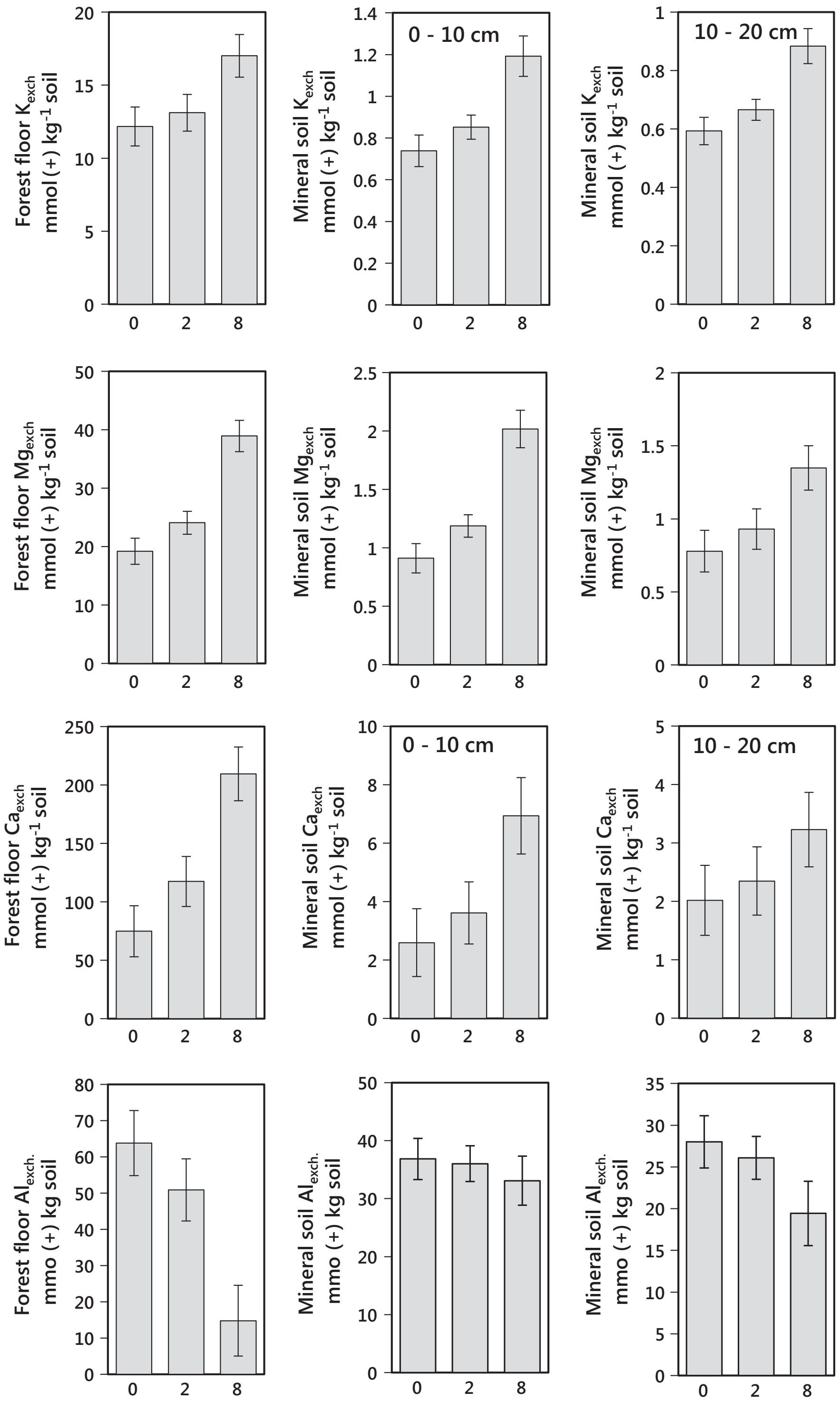

Fig. 5. Forest floor and 0–10 and 10–20 cm mineral soil exchangeable cations and Al concentrations eight years after ash loading (0, 2, 8 Mg ha^{-1}) in a boreal jack pine stand. Predicted values and their standard error (bars) based on a mixed linear model. See Table 4 for a Type 1 test of hypothesis for a linear effect of ash loading.

mmol(+) kg^{-1} in the control of the 0–10 cm and 10–20 cm depths, respectively. Increases of 73% and 105% in Mn_{exch} were observed at the 0–10 cm and 10–20 cm depths, respectively, after comparing the control to the 8 Mg ha^{-1} treatment.

4. Discussion

To our knowledge, this is the first large scale ash fertilization experiment conducted in the Canadian boreal forest despite a large legacy of research in comparable European ecosystems (Saarsalmi et al., 2012; Jacobson et al., 2014). Some of the results obtained in the course of this eight year research were anticipated. Our results also show that soils and trees do not always respond to ash application as predicted. For example, black spruce growth decreased with ash loading. As highlighted by Reid and Watmough's (2014) meta-analysis, large variations in soil and tree response to ash application are to be expected, stressing the need for regional studies.

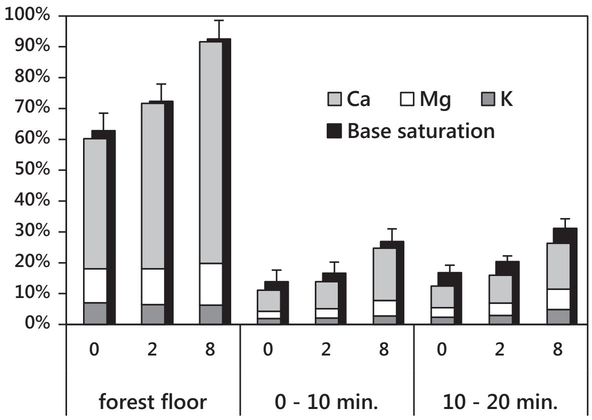

Fig. 6. Forest floor and 0–10 and 10–20 cm mineral soil individual base cation and total base saturation eight years after ash loading (0, 2, 8 Mg ha^{-1}) in a boreal jack pine stand. Predicted values and their standard error (bars) based on a mixed linear model. See Table 4 for a Type 1 test of hypothesis for a linear effect of ash loading.

Independently of treatments, large year to year variations on soil properties were observed, which might have been caused by variations in soil moisture at sampling time. In general, soil drying increases the concentration of solutes, which may cause precipitation or an increased sorption of cations on soil exchange surfaces (Mengel, 1982). Potassium is especially sensitive to soil drying. Exchangeable K levels generally decrease upon drying for soils with low CEC (e.g. <5 mmol kg^{-1}) (Erich and Hoskins, 2011). Higher exchangeable K concentrations under the control at year 2 could therefore suggest lower soil moisture during the sampling period. A similar explanation can be provided for Ca. Soil drying may also increase soil acidity on exchange surfaces, which affects the solubility of many nutrients, particularly metals (Dowding et al., 2005). As a whole, protonation of exchange sites would decrease CEC – however, this is not what was observed in this study. Cation exchange capacity is also increased in year 2, which could be attributed to a reduction in C mineralization (Borken and Matzner, 2008) or perhaps a decrease in dissolved organic C leaching under dryer conditions (Borken et al., 1999), or both.

4.1. Effects of ash loading over eight years on forest floor acid–base status

Even under low ash loading, forest floor exchangeable base cation concentrations, pH, and base saturation increased within a year of application. The unstable nature and fineness of the ash particulates likely explain their high solubility and in turn, the rapid soil response (Nieminen et al., 2005; Perkiömäki and Fritze, 2002; Steenari et al., 1999a) despite the relatively low elemental composition of the applied ash compared to published values (Augusto et al., 2008). Also, the intrinsically low pH of the forest floor may account for its significant response because a large proportion of acidity could be replaced. The increased concentration of charge (or activity) in base cations in forest floor solution after ash application has clearly favored a large mass effect which led to a substantial displacement/replacement of H$^+$ adsorbed on exchange sites that arise from the dissociation of carboxylic (COOH) and phenolic (COH) functional groups at the surface of humic and fulvic acids (Evans, 1989).

The relationship between ash loading and changes in individual nutrient concentrations varied with chemical kinetics and time since application. Potassium in wood ashes forms highly soluble salts and oxides (Steenari et al., 1999b). It is therefore quickly released following precipitation events (Nieminen et al., 2005). Hence, forest floor K_{exch} concentration increased linearly and rapidly following ash loading. Because of its lower energy of adsorption (it is monovalent and has a relatively large hydrated ionic radius), K$^+$ tends to compete less for exchange sites compared to the divalent and smaller radii base cations Ca^{2+} and Mg^{2+}, unless K$^+$ has a very high concentration of charge in the solution. Therefore, we expected K_{exch} concentration following ash application to recede, within the study period, to values similar to the control. However, differences in forest floor K_{exch} concentration among ash loads remained more or less stable over the eight year study. It is possible that a relatively tight cycling of K$^+$ by the stand helped maintain its activity in the soil solution to a level that was sufficient to preserve the initially rapid gains in K_{exch}. However, the proportion of exchangeable sites occupied by K$^+$ decreased rapidly as indicated by the comparable K saturation among treatments five years following application.

On the one hand, Ca is the most abundant base cation in ash (Augusto et al., 2008, Table 1). Its dominant form is Ca carbonate ($CaCO_3$), which forms from oxides (CaO) when ashes are exposed to water and CO_2 (Steenari et al., 1999a). The solubility of $CaCO_3$ increases exponentially with decreasing pH, meaning that solubilization of Ca from $CaCO_3$ is promoted if solution pH in the vicinity of ash particulates decreases sufficiently (Nieminen et al., 2005; Steenari et al., 1999b). On the other hand, Mg in ash is mostly present as Mg oxides, which are chemically stable (Steenari et al., 1999a). Also, ash concentrations of Mg are generally much lower than those of Ca (Jacobson et al., 2004), more than 16 times in the case of our study (Table 1). Thus, the liming effect of ash comes from its $CaCO_3$ and, to a lesser extent, $MgCO_3$ content (Pitman, 2006) and takes place over a number of years (Reid and Watmough, 2014). In our study, Ca_{exch} and Ca saturation in the forest floor increased over time in response to the progressive dissolution of $CaCO_3$ but the lowest ash treatment initially caused a proportionally higher increase in forest floor Ca_{exch} compared to the higher treatment. This nonlinear relationship suggests some control of solution pH on Ca release from ash particulates (Steenari et al., 1999a) and under the 8 Mg ha^{-1} ash treatment. An increase in solution pH may have initially reduced the rate of dissolution of carbonates in the ash. Ludwig et al. (2002) reported that most of the added Ca from ash in a German pine stand (*Pinus sylvestris*) was still found in insoluble forms in the forest floor as much as nineteen months following application.

A significant increase in forest floor Mg_{exch} was also observed with ash loading, but its dominance on the exchange complex

Table 4

Effects of ash load on NH_4Cl – extractable cation concentrations and saturation (sat.) of a boreal coarse textured soil eight years after ash loading. The significance of a linear ash loading effect on response variables was tested using a mixed linear model and is based on a Type 1 test of hypothesis.

Soil horizon	K_{exch}	K sat	Mg_{exch}	Mg sat	Ca_{exch}	Ca sat	Al_{exch}	Ba_{exch}	Mn_{exch}[a]	CEC_{eff}	Base sat.
Forest floor	0.004	0.419	<0.001	0.025	<0.001	<0.001	<0.001	NS	<0.001	<0.001	<0.001
0–10 cm mineral	0.002	0.006	<0.001	<0.001	0.006	0.010	NS	NS	0.015	NS	0.005
10–20 cm mineral	0.001	0.002	0.001	<0.001	NS	<0.001	NS	NS	0.016	NS	0.002

[a] Log transformed.

was expectedly much lower than Ca. In fact, Mg_{exch} behaved more like K_{exch} in that it did not increase over time like Ca_{exch}, suggesting Mg oxides are stable in this environment and acting as a small source of Mg^{2+}.

The progressive adsorption of Ca^{2+} on exchange sites in the forest floor was accompanied by the displacement of $acidity_{exch}$ (i.e. H^{+}) and in turn, an increase in pH. However, changes in forest floor pH in response to ash loading occurred more rapidly (but also stabilized more quickly) than changes in Ca_{exch}, $acidity_{exch}$ and base saturation. It is possible that pH initially changed in response to displacement by K and subsequently in response to replacement by Ca. Conversely, Reid and Watmough (2014) reported that base saturation is more susceptible to ash loading than pH, regardless of soil horizon. In our study, nonetheless, functional groups were deprotonated at high pH, resulting in more negative charges and consequently high CEC_{eff}.

Eight years after ash application, forest floor base cation concentrations and saturation all increased linearly with ash loading. However, the relationships were less pronounced than five years after application. The alkalinizing effects of ash on soil can be preserved for a long period (Saarsalmi et al., 2012) and further study is required to determine its lasting effect in the context of the Canadian boreal forest.

4.2. Effects of ash loading over eight years on mineral soil acid–base status

Compared to the forest floor, the response of the mineral soil to ash loading was more complex, if not slower. Up to five years after application, the dominant pattern of upper mineral soil properties in relation to ash loading was a curvilinear relationship with the highest values observed under the 2 Mg ha^{-1} treatment. This was the case for Ca_{exch} and Mg_{exch}. It was also the case for up to two years after application for CEC_{eff} and, unexpectedly, for $acidity_{exch}$. Such curvilinear relationships between ash loading and soil properties have been reported in other studies (Ring et al., 2006; Stuczynski et al., 1998a).

The upper mineral soil responds to changes in the chemical composition of the solution coming from the forest floor and reaching the mineral soil via preferential flow paths (Bundt et al., 2001). Ash application normally leads to a major and rapid flush of base cations (including Na) that displaces forest floor acidity in the form of H^{+} and Al^{3+} (Ludwig et al., 2002; Lundström et al., 2003). This acidity is released in the soil solution, whereas base cations decrease in the soil solution as they progressively react with soil. Moreover, application of ash may result in an increase in soil solution SO_4^{2-}, caused by the dissolution of salts in the ash. It is thus possible that the acid neutralizing capacity (ANC, i.e. the balance between alkalinity and acidity) of the soil solution (inflow) under the 2 Mg ha^{-1} treatment was too low within the first two years for it to continue acting as a net source of alkalinity in the mineral soil (Norström et al., 2012; Geibe et al., 2003; Ring et al., 2006). In time, forest floor chemistry stabilized and its incoming acidity decreased (Ludwig et al., 2002), increasing ANC of the soil solution reaching the mineral and in turn, allowing alkalinity to increase. This was reflected by the increase in mineral soil Ca_{exch}, Mg_{exch} and base saturation with ash loading observed five years after ash application. The 8 Mg ha^{-1} ash treatment did not undergo any significant increase in $acidity_{exch}$ in the mineral soil at any period of the study, likely because of an excess of base cations (alkalinity) in the forest floor solution that augmented its ANC.

Protons dissociate from the surfaces of Al and Fe hydrous oxides and from the edges of clay minerals (Sposito, 2008). Soil particles of coarse Boreal Shield Podzols such as the ones in this study are coated with Al and Fe hydrous oxides (Courchesne et al., 1996). This gives a pH-dependent negative charge that behaves like the functional groups of organic acids, i.e. the number of negatively charged surfaces increases as pH increases. An increase in alkalinity in the mineral soil is thus bound to an increase in CEC_{eff} as seen with our results. Additionally, the curvilinear pattern of Ca_{exch}, Mg_{exch}, and $acidity_{exch}$ with ash loading in the upper mineral soil followed changes in organic matter content at the same depth. This can also explain, in part, the increase in CEC_{eff} in the mineral soil (Molina et al., 2007).

The observed changes in the forest floor and mineral soil acid–base status caused by ash application differed by their magnitude and rate from what was reported by Augusto et al. (2008) following a meta-analysis of 33 independent trials. According to the analysis, only ash loading >4 Mg ha^{-1} induced a decline in soil acidity within the first five years of ash application, and these modifications were mostly limited to the forest floor. In a more recent meta-analysis, Reid and Watmough (2014) found that over 25% of the trials reported no effect of liming or ash application on soil base saturation, and 33% of trials reported no effect on soil pH. Differences in loading, ash chemical composition, soils and monitoring period likely explain the diverging results between studies.

4.3. Effects of ash loading over five years on soil C, N and P

Immediately following ash application, its Ca content and speciation can affect organic matter solubility. Calcium hydroxides in the soil solution can cause a chemically-mediated degradation of soil organic matter (Stuczynski et al., 1998b). This increases dissolved organic C (DOC) mobilization in the forest floor solution (Jokinen et al., 2006; Nilsson et al., 2001), which then leaches to and adsorbs in deeper soil horizons (Molina et al., 2007; Nilsson et al., 2001; Ring et al., 2006). Also, soluble forms of Ca^{2+} (CaO) can also briefly form insoluble complexes with humic structures, thus increasing C stabilization (Stuczynski et al., 1998a). In the longer term, in acidic soils with abundant organo-mineral complexes and high Al_{exch} concentrations, large inputs of Ca^{2+} may reduce the bioavailability of soil organic matter constituents (Condron et al., 1993). Dissolved organic C was not measured, but the decrease in forest floor C_{org} and $N_{Kjeldahl}$ concentrations the year following ash application was consistent with forest floor organic matter solubilization (Stuczynski et al., 1998a). However, no subsequent significant increase in mineral soil C_{org} was observed, while $N_{Kjeldahl}$ concentrations followed, with time, a curvilinear pattern with the highest concentrations observed under the 2 Mg ha^{-1} treatment. This curvilinear relationship between ash loading and forest floor $N_{kjeldahl}$ and C_{org}, and between ash loading and upper mineral soil $N_{Kjeldahl}$ and C/N, suggest a balance between selective processes that result in decreased mineral soil C/N, but only at low ash loading.

The decrease in soil acidity caused by ash application can also induce changes in the microbial community composition (Bååth and Arnebrant, 1993) and stimulates its activity (Jokinen et al., 2006; Zimmermann and Frey, 2002). Thus, the elevated potential net N mineralization rates observed in the forest floor immediately following ash application were expected and consistent with previous findings (Jacobson et al., 2004; Khanna et al., 1994). Longer term positive effects of ash application on forest floor microbial activity and organic matter decomposition have been reported (Perkiömäki et al., 2004), but they cannot be generalized to all situations (Rosenberg et al., 2010). We do not expect that the effect of ash loading on potential net N mineralization after one year of application was long lasting (Ring et al., 2006) as the observed reduction in forest floor C_{org} concentrations possibly caused by organic matter solubilization took place within a year of ash application.

Ash application does not always result in changes in forest floor or mineral soil C_{org} content (Jacobson et al., 2004; Saarsalmi et al., 2001) and may reduce (Ozolinèius et al., 2007; Mandre et al., 2006) or have no significant effect (Jacobson et al., 2004; Saarsalmi et al., 2001; Arvidsson and Lundkvist, 2003) on total N concentrations of forest floor or mineral soil horizons. Reid and Watmough (2014) stressed the fact that the scientific literature lacks data on long-term organic matter dynamics following ash application. With increasing concerns over greenhouse gas emissions, more research is warranted (Maljanen et al., 2006; Huaotari et al., 2015).

Phosphorus content of the applied ash was low compared to published values (Table 1, see Augusto et al. (2008)). Phosphorus has very limited mobility in these naturally acidic soils as $H_2PO_4^{3-}$ strongly adsorbs to positively charged surfaces of Fe and Al hydroxides in the mineral soil or precipitates (to form new minerals) by reacting with free Al and Fe in the soil solution (Bolan et al., 2008). Phosphorus availability can also increase if organic matter decomposition increases (also favored by an increase in pH), thus releasing more P, or if organic acids produced from the decomposition act as chelates for free Al and Fe in the soil solution, thus reducing P fixation and precipitation. The observed increase in forest floor pH ($CaCl_2$) from 2.9 in the control to 3.5 in the 8 Mg ha^{-1} treatment partly explains the increase in forest floor $P_{Mehlich\text{-}3}$ concentration with ash loading observed five years following ash application. However, the mechanisms leading to this change cannot be easily elucidated with the data available. No increase in P availability was observed in the mineral soil where increases in soil pH were not significant. Jacobson et al. (2004) have reported similar results for forest floor and mineral soil P availability five years following ash application in a *P. sylvestris* forest stand growing on acidic podzolic soils.

4.4. Effects of N (urea) fertilization over five years on overall soil properties and interactions with ash loading

We decided to fertilize with urea to assess the potential of an increase in N availability to enhance tree response to ash application (Saarsalmi et al., 2006). However, effects of N fertilization and its interactions with ash on soil properties are also of interest. Similarly to ash application, fertilization of boreal soils with urea can increase forest floor pH and C_{org} mobility caused by urea hydrolysis, which consumes H^+ to form NH_4^+ in acid soils (Saarsalmi and Mälkönen, 2001; Camiré and Bernier, 1981). This effect on soil pH is quick and generally short-lived (Aarnio et al., 2003). In our study, few direct lasting effects of urea fertilization on forest floor properties were in fact observed in the five years following N fertilization. The notable exception was a predictable increase in forest floor potential net N mineralization (Camiré and Bernier, 1981; Aarnio and Martikainen, 1996). However, when applied in combination with ash and over the five year period, urea amplified the effect of the largest ash load on forest floor $acidity_{exch}$, CEC_{eff}, and $P_{Mehlich\text{-}3}$. In combination with ash, urea hydrolysis probably improved the soil acid–base status enough for deprotonation of functional groups to occur (thus, increasing CEC_{eff}) and for P availability to increase.

Mineral soil properties were affected by urea fertilization to a greater extent than the forest floor. Short-lived increases in mineral soil $acidity_{exch}$ and decreases in base saturation were observed following urea regardless of ash treatments. Simultaneous applications of ash and urea also nullified the previously discussed curvilinear relationship between ash load and mineral soil $N_{Kjeldahl}$, Ca_{exch} and Mg_{exch}. Studies on combined application of wood ash and urea rarely separate the effects of N and ash or their interaction on forest soil properties (Saarsalmi et al., 2004, 2006). However, in the mid and long terms, N fertilization of agricultural soils (including with urea) is well known to lower pH (Barak et al., 1997), exchangeable base cations and base saturation (Bouman et al., 1995; Liu et al., 1997), and augment exchangeable acidity (Liu et al., 1997). This is due to microbial oxidation of ammoniacal fertilizers, which despite initially being a base (e.g. urea) are involved in acid-forming reactions in soils. In the boreal soils studied, the acid-forming process was most likely the uptake of NH_4^+ by plant roots in exchange for H^+ (whereas nitrification would be a net source of H^+ in less acidic soils). The net effect of urea fertilization observed on forest floor potential net N mineralization (in the form of NH_4^+) has only increased that potential for acidity production.

4.5. Effects of ash loading and N (urea) fertilization on foliar nutrient status and on 5-year relative tree growth

Jack pine represented the largest overstory component of the studied stand. Despite a small increase in large jack pine relative growth rate following N fertilization and the fact that the stand had been recently thinned, the relative growth rate remained low. Similarly, ash application in boreal forests has had limited effects on tree growth in the absence of N fertilization (Jacobson et al., 2014; Saarsalmi et al., 2004; Jacobson, 2003). This remained surprising given the improved soil acid–base status and N availability of these generally poor forest soils. An exception to this general trend, Saarsalmi et al. (2006) reported an increase in the growth rate of a *P. sylvestris* boreal stand growing on a podzol 10 to 20 years following ash application and N fertilization when compared with N fertilization alone. In their meta-analysis of ash and lime application experiments, Reid and Watmough (2014) emphasized on the possible bias created by the short duration of studies. Half of the studies were less than 6 years in duration, whereas changes in mineral soil properties can take place over longer periods. In our study, the full effect of ash treatments on the upper mineral soil properties materialized between three and five years after application. The properties of the lower mineral soil were only measured eight years after treatments, but we can assume that changes at this depth occurred over a slightly longer period than those at the 0–10 cm depth. According to a recent study by Houle et al. (2014), jack pine acquires nutrients from mineral soil horizons rather than from the forest floor. Hence, the benefit of ash application for jack pine nutrition, if any, would be contingent on the response rate of the mineral soil. Longer term measurements will possibly yield different results. Unfortunately, the studied stand was harvested in 2013.

Black spruce is a shade tolerant species that establishes alongside jack pine following stand replacing fire. However, it grows at a slower rate. Because foliar nutrients were only measured on jack pine foliage, we can only speculate on causes behind the decreasing growth rate of black spruce with increasing ash loading. Contrary to jack pine, the forest floor is the main source of nutrients for black spruce (Houle et al., 2014). Ash contained large amounts of Mn when compared with other micronutrients, and eight years following application of 8 Mg ha^{-1} of ash, an increase of over 860% of forest floor Mn_{exch} was observed. In comparison, the corresponding increase was 180% for forest floor Ca_{exch}. As a micronutrient, Mn is involved in the water-splitting reaction of photosynthesis and as a cofactor in enzymatic reactions (Marschner, 2012). In soils, however, the affinity of Mn^{n+} for soil organic matter is relatively low (McGrath et al., 1988). The activity of free Mn^{n+} in the soil solution can thus be high, which raises questions relative to Mn toxicity or nutrient imbalance between Mn and other nutrients (notably Ca) following ash application. On the one hand, large amounts of Mn can accumulate in some tree species such as spruce spp. without showing toxicity symptoms (Zöttl, 1985) and ash has been shown to reduce Mn toxicity of tropical acid soils (Nkana et al., 1998). On the other hand, high foliage Mn concentrations have been shown to reduce needle chlorophyll concentrations of *Picea glauca* (Moench (Voss)) seedlings (St-Clair and Lynch, 2005) and growth of *P. sylvestris* L. and *Pinus nigra* (Arnold) seedlings (Kavvadias and Miller, 1999). The negative reaction of black spruce to ash application clearly needs further investigation before any large scale use of ash is implemented in eastern Canadian boreal forests.

5. Conclusion

Our results underline the need to thoroughly investigate the effect of ash application on forest soils, tree nutrition and stand growth in the context of Canadian boreal forests. The unforeseen interactions between organic matter dynamics and soil nutrient retention following ash application suggest a need for a better understanding of the effect of ash on soil organic constituents as well as their transformation and mobilization. Combined ash and urea application did not improve tree response to ash application over a 5 year period. Moreover, additional studies are needed to validate the deleterious effect of large ash loads on black spruce growth and to elucidate the mechanisms involved. Black spruce is the most important commercial species of eastern boreal forests and if confirmed, these results strongly limit the potential of ash fertilization.

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