

1 **WOOD ASH AND N FERTILIZATION IN THE CANADIAN BOREAL FOREST: SOIL PROPERTIES AND RESPONSE OF**
2 **JACK PINE AND BLACK SPRUCE**

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16 **ABSTRACT**

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

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

37 **Keywords:** Wood ash, N fertilization, boreal forest, soil properties, jack pine, relative growth.

38 **INTRODUCTION**

39 Interest in bioenergy, including the use of forest biomass as a fuel, is increasing in response to
40 concerns over climate change, growing oil prices and energy security (EU, 2009; Titus, et al., 2010).
41 As a result, an increased production of ash from forest biomass combustion is predicted (James, et al.,
42 2012). Wood ash is recycled as a fertilizer by the farming industry, but this represents only a small
43 portion of the total ash produced and thus, most is buried in landfills (Hébert and Breton, 2008; James,
44 et al., 2012). Because of the limited availability of landfills in close proximity of wood-fired power
45 plants and in turn, the large handling and transporting costs, recycling options in the vicinity of these
46 power plants need to be considered.

47 Wood ash fertilization in Canadian boreal forests has yet to be investigated. Nonetheless, the
48 use of ash as a fertilizer in forest ecosystems has been researched for more than eighty years in
49 Fennoscandia (Lundström, et al., 2003; Pitman, 2006). Ashes generated from wood products contain
50 variable amounts of most nutrients required for tree growth, with the exception of nitrogen (N) because
51 of its low heat of vaporization. The acid neutralizing capacity of ash stems from its high content of
52 calcium (Ca), magnesium (Mg) and potassium (K) hydroxides (Saarsalmi, et al., 2001). Early benefits
53 of ash application on the soil acid-base status, when they occurred, are observed in the forest floor and
54 involve exchanges of protons (H^+) by the mobile monovalent cations K and sodium (Na), while effects
55 on the mineral soil often take place more gradually (Augusto, et al., 2008; Pitman, 2006; Reid and
56 Watmough, 2014). The effects of ash application on forest soil acidity have been shown to last for as
57 much as 30 years (Saarsalmi, et al., 2012). Besides macro- and micro-nutrients present as oxides or
58 hydroxides, wood ash also contains low amounts of transition metals and metalloids such as cadmium
59 (Cd), barium (Ba), manganese (Mn) and arsenic (As) (Dahl, et al., 2010) that may become phytotoxic

60 (St-Clair and Lynch, 2005). The chemical composition of ash depends on tree species, fuel composition
61 (wood, bark, branches, etc.), boiler type (Pugliese, et al., 2014), heat of combustion and possible
62 sources of contamination (e.g. construction and demolition wood, bottom vs fly ash) (Pitman, 2006).

63 Wood ash has the potential to affect soil N availability through different mechanisms, but
64 mostly by increasing soil pH and dissolved organic carbon (DOC) (Jokinen, et al., 2006; Molina, et al.,
65 2007). Changes in soil acidity affect microbial communities and activity, generally resulting in more N
66 mineralization (Bååth and Arnebrant, 1993; Mahmood, et al., 2003; Perkiömäki and Fritze, 2002).
67 However, neither the increase in soil mineral forms of N or increases in foliar concentrations of P, K
68 and Ca following ash application (Augusto, et al., 2008) led to improved tree growth on poor mineral
69 soils (Jacobson, 2003; Saarsalmi, et al., 2004). Yet, the limited number of long-term studies precludes
70 any definitive conclusions regarding tree response to improved soil conditions (Reid and Watmough,
71 2014).

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

78 We report on a large scale replicated factorial experiment initiated in 2005 on a mature boreal
79 jack pine stand subjected to increasing loads of wood ash with and without N fertilization. Our
80 objective is to assess the initial response of forest stands to ash fertilization in the Canadian boreal
81 forest. We hypothesized that: (1) soil base cation concentrations, pH and N net mineralization would

82 increase with increasing ash loading, (2) increases in soil alkalinity would first take place in the forest
83 floor and would later appear in the mineral soil, and (3) tree foliar nutrition and growth would respond
84 positively within the first five years of wood ash application when being combined with N fertilization
85 (Jacobson, 2003; Saarsalmi, et al., 2006).

86 **APPROACH AND METHODS**

87 *Study area*

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

99 *Experimental design and sampling*

100 The 43 ha field trial was set up in October 2005 in a mature jack pine (*Pinus banksiana* Lamb)
101 stand of fire origin (approximately 53 years) that had been commercially thinned in 1999. The stand
102 had an average basal area of 22.3 m² ha⁻¹ with 20.0 m² ha⁻¹ of jack pine stems (average diameter = 16
103 cm) and the remainder composed of black spruce (*Picea mariana* (Mill.) BSP) stems (average diameter

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* | 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** | 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** | 31 | | Ni | 12 | 80 |
| Fineness | 92 | | Pb | 10 | 38 |
| OM (%) | 22 | | Zn | 286 | 3300 |

*Nitric acid (HNO₃) or HNO₃ and hydrochloric acid (HCl) extraction. **CCE = calcium carbonate equivalence, fineness = particles < 2 mm; OM = organic matter; **Ba was estimated in 2011 on a single sample.

105 = 10 cm). The experiment was designed as completely random with four replications (1 ha each) of five
106 ash treatments (0, 1, 2, 4 and 8 dry Mg ha⁻¹ of loose unstabilized fly ash.; see Table 1 for ash elemental
107 composition) with and without urea (CO(NH₂)₂) fertilization (280 kg N ha⁻¹) for a total of 40
108 experimental units. Ash and urea were applied with a farm spreader using harvesting trails.

109 Prior to ash and urea application and in each experimental unit, three permanent circular
110 sampling plots (PSP) of 200 m² were delineated. All jack pine and black spruce stems greater than 5.0
111 cm of diameter at breast height (DBH) were tagged, identified by species, and measured for DBH.
112 These were measured again five years later (2010) to obtain an estimate, for each stem, of the five-year
113 relative growth rate:

$$114 \quad \left[\frac{(DBH_{2010} - DBH_{2005})}{DBH_{2005}} \right].$$

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

120 One and two years (2006 - 2007) after treatments, current-year pine needles were collected
121 within the same PSPs where soils were sampled. To limit seasonal variability in nutrient
122 concentrations, foliar samples were taken in the fall after tree hardening. In each PSP, twigs in the
123 upper tier of the crown of three dominant jack pines were brought down with a shotgun and pooled in a
124 single sample for each experimental unit (n=24). Black spruce foliage was not sampled.

125

126 *Laboratory analyses*

127 Subsamples of the forest floor and mineral soil were air dried and sieved (2 mm) prior to
128 chemical analyses. Exchangeable base cations (Ca_{exch} , Mg_{exch} , K_{exch} , Na_{exch}) and acidity (Al^{+3} and H^{+})
129 were extracted with $\text{NH}_4\text{Cl}-\text{BaCl}_2$ (Amacher, et al., 1990) on subsamples from 2006, 2007 and 2010.
130 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
131 for the mineral soil. Exchangeable base cations were analyzed by inductively coupled plasma atomic
132 emission (ICP) (Perkin-Elmer Optima 4300DV), whereas exchangeable acidity was analyzed by
133 titration (848 Titrino plus, Metrohm). Effective cation exchange capacity (CEC_{eff}) was estimated by
134 adding base cations and exchangeable acidity ($\text{acidity}_{\text{exch}}$). Base saturation was defined as the ratio of
135 $\text{Ca}_{\text{exch}}+\text{Mg}_{\text{exch}}+\text{K}_{\text{exch}}+\text{Na}_{\text{exch}}$ over CEC_{eff} . Ratios of individual cations over CEC_{eff} were also calculated
136 for each base cation (e.g. Ca saturation). Available phosphorus ($\text{P}_{\text{Mehlich-3}}$) was assessed only on 2007
137 and 2010 subsamples using the Mehlich-3 procedure (Ziadi and Sen Tran, 2008). Forest floor and
138 mineral soil subsamples were ground to pass through a 250 μm mesh and analyzed for organic carbon
139 (C_{org}) concentration by lost on ignition (McKeague, 1976) and digested in a $\text{HSO}_4 - \text{H}_2\text{O}_2$ mixture
140 (Parkinson and Allen, 1975) for Kjeldahl N (Bremner and Mulvaney, 1982). Forest floor and mineral
141 soil subsamples collected in 2013 were analyzed for Ca_{exch} , Mg_{exch} , K_{exch} , Na_{exch} , Al_{exch} as well as
142 exchangeable barium (Ba_{exch}) and manganese (Mn_{exch}) which were found in relatively high
143 concentrations relative to microelements in wood ash (see Table 1). Elements were extracted with 0.1
144 M NH_4Cl (Bélanger, et al., 2007) instead of $\text{NH}_4\text{Cl}-\text{BaCl}_2$ in order to include Ba in the analysis.
145 Concentrations were determined by ICP mass spectrometry (Varian 820MS).

146 Subsamples from 2006 were also analyzed for potential net N mineralization rate (Bundy and
147 Meisinger, 1994). Fresh forest floor (10 g) and mineral soil (5 g) samples were incubated under

148 anaerobic conditions at 23°C for two weeks in 50 ml deionized water. Samples were then extracted
149 with 50 ml 2 M KCl. Initial NH_4^+ concentrations were determined on equivalent subsamples extracted
150 with 100 ml 1 M KCl. Extracts were analyzed for NH_4^+ by colorimetry using an autoanalyzer (FIA
151 Quikchem 4000). The potential net N mineralization rate is the difference between final and initial
152 subsamples NH_4^+ concentrations over a 14 day period.

153 First-year needles collected in 2006 and 2007 were dried at 65° C for 48 hours, weighed,
154 ground and digested in the same $\text{HSO}_4 - \text{H}_2\text{O}_2$ mixture as above. Total Ca, Mg, K and P concentrations
155 were measured by ICP (Perkin-Elmer Optima 4300DV), while total N was measured using the Kjeldahl
156 method. Simple nutrient concentration ratios were computed.

157 *Statistical analyses*

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

170 and Mn measured from samples collected in 2013 were analyzed separately and only the linear effect
171 of ash was tested.

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

176 RESULTS

177 *Effects of ash loading over five years on soil acid-base status*

178 Forest floor K_{exch} concentration increased linearly with ash loading (Table 2, Fig. 1). One year
179 after application, concentration was 61 % higher in the 8 Mg ha⁻¹ treatment than in the control. The
180 effect of ash on K_{exch} concentrations remained constant over time as no significant interactions between
181 ash loading and time were found. Forest floor K saturation also increased linearly with ash loading
182 (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
183 following application. However, this effect decreased linearly with time. Five years after application, K
184 saturation under the different ash loads was similar to the control (5.2 %; SE = 0.3). Over the five year
185 period, forest floor Na_{exch} (results not shown) accounted for less than 1.2 % of base saturation,
186 independently of ash load.

187 Forest floor Ca_{exch} and Mg_{exch} concentrations also increased with ash loading (Fig. 1). However,
188 the difference between the 2 and 8 Mg ha⁻¹ treatments was generally weak, accounting for the
189 significant linear and quadratic effects of ash on forest floor Ca_{exch} and Mg_{exch} concentrations (Table 2).
190 The effect of ash remained constant over time for Mg_{exch} . Five years after treatment application, Mg_{exch}
191 concentration was 81 % higher in the 8 Mg ha⁻¹ treatment than in the control. Significant linear and

192 quadratic relationships between Mg saturation and ash loading were observed as well as significant
193 interactions between ash loading and linear and quadratic time effects (Table 2). Over the 5 year
194 period, forest floor Mg saturation ranged from 5.7 to 6.8 % (SE = 0.5) in the control. Saturation was the
195 highest in the 2 and 8 Mg ha⁻¹ treatments in the first year following ash application with respective
196 values of 9.1 % (SE = 0.4) and 10.9 % (SE = 0.6). Thereafter, saturation decreased but remained
197 similar between the two ash treatments with values of 7.5 % (SE = 0.3 – 0.5) five years after
198 application.

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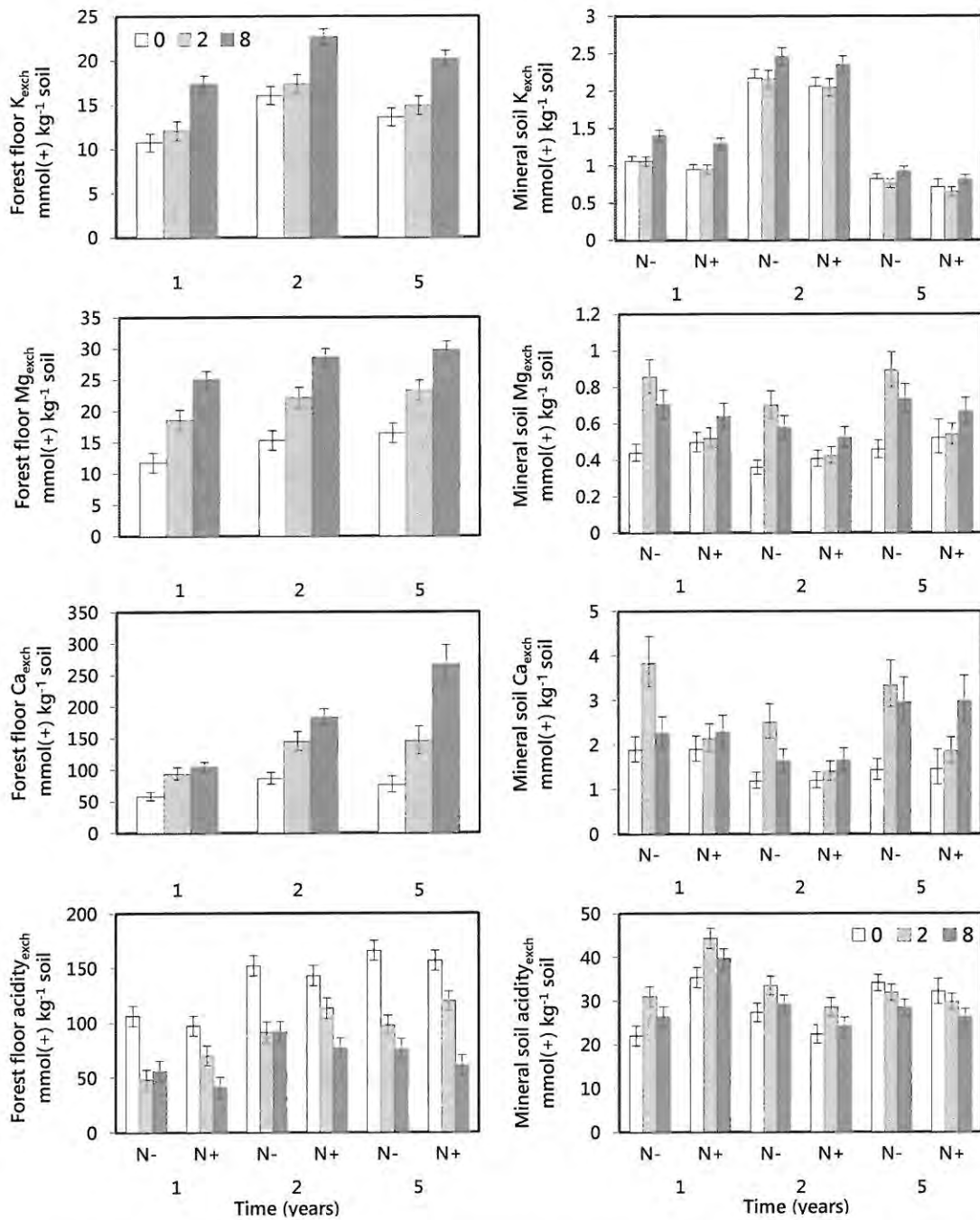
Table 2: Effects of ash loading and nitrogen (N) fertilization on soil acid-base status of a boreal coarse textured soil, one, two and five years after application. The significance of ash, N, time since treatment application and two-way interactions were tested using a mixed linear model and are based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

| Forest floor | | | | | | | | | | |
|---------------------------|--------|-------------------|------------------|--------------------|-------------------|----------------------|-------------------|----------------------|--------------------|------------|
| Response variables | pH | K _{exch} | K _{sat} | Mg _{exch} | Mg _{sat} | Ca _{exch} * | Ca _{sat} | Acid _{exch} | CEC _{eff} | Base sat.* |
| 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 | | | | | | | | | | |

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 treatment 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.

| 0 – 10 cm mineral soil | | | | | | | | | | |
|------------------------|--------|-------------------|------------------|---------------------------------|--------------------------------|---------------------------------|-------------------|----------------------|--------------------|------------------------|
| Response variables | pH | K _{exch} | K _{sat} | Mg _{exch} [*] | Mg _{sat} [*] | Ca _{exch} [*] | Ca _{sat} | Acid _{exch} | CEC _{eff} | Base sat. [*] |
| 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 |

*: Log transformed; **: NA; not applicable.



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Figure 1: Forest floor and 0 – 10 cm mineral 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.

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

212 Forest floor acidity_{exch} followed the inverse pattern of exchangeable base cations.
213 However, the difference between the 2 and 8 Mg ha⁻¹ treatments became significant only
214 five years after application (Fig. 1). Forest floor pH increased in the first year following
215 ash application, but remained constant in the following years (Fig. 2). As indicated by the
216 significant quadratic effect of ash on forest floor pH (Table 2), the largest proportional
217 increase (0.4 unit) was caused by the 2 Mg ha⁻¹ treatment compared with an increase of
218 0.6 unit following the 8 Mg ha⁻¹ treatment.

219 The effect of ash on forest floor CEC_{eff} enlarged with time since application
220 (Table 2, Fig 2). No significant effect of ash on CEC_{eff} was observed the year following
221 application, while increases of 15 and 61 % were observed five years after ash
222 applications of 2 and 8 Mg ha⁻¹, respectively. Forest floor base saturation initially
223 followed the same pattern as pH with a proportionally larger increase one to two years
224 after 2 Mg ha⁻¹ of ash were applied. However, the effect became more pronounced in the

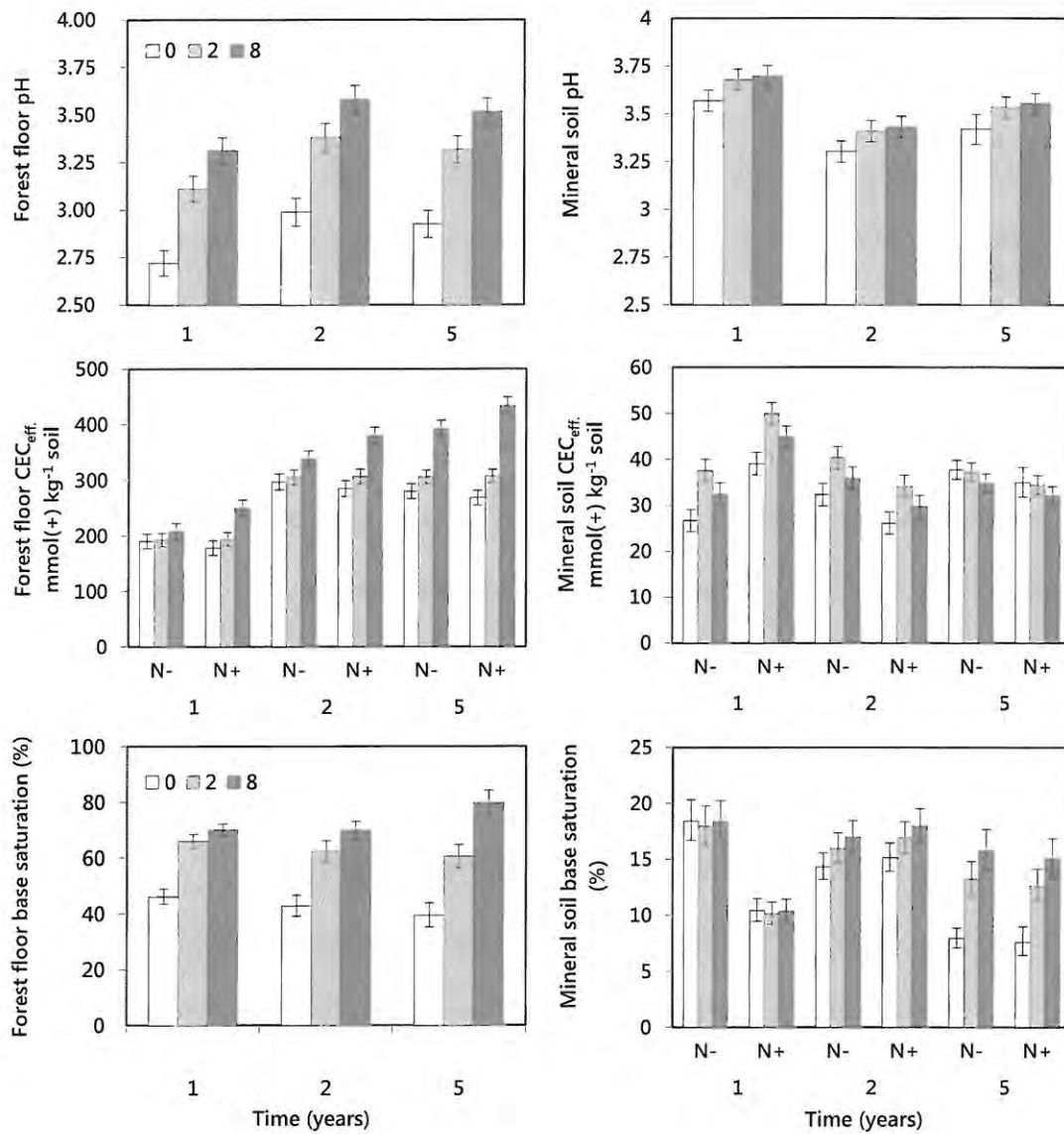


Figure 2: Forest floor and 0 – 10 cm mineral pH, effective CEC, and base saturation, one, two and five years after ash loading (0, 2, 8 Mg ha⁻¹) and N fertilization (280 kg N ha⁻¹) in a boreal jack pine stand. Predicted values and their standard error (bars) according to models of Table 2.

226 8 Mg ha⁻¹ treatment five years after application, representing an increase of 102 % in
227 forest floor base saturation relative to the control.

228 In the upper mineral soil (0 – 10 cm), K_{exch} concentration increased only in the 8
229 Mg ha⁻¹ treatment (Table 2, Fig. 1). The effect decreased linearly with time: in relation to
230 the control, the first year increase was 32 %, but the increase was only 13 % in the second
231 and fifth years after application. Ash application had a small significant but durable effect
232 on mineral soil K saturation (Table 2). Five years after ash application, K saturation was
233 2.5 % in the 8 Mg ha⁻¹ treatment compared with 2.1 % in the control (SE = 0.2). The
234 maximum Ca_{exch} and Mg_{exch} concentrations were observed with the 2 Mg ha⁻¹ ash
235 treatment. One year after ash applications of 2 and 8 Mg ha⁻¹, Mg_{exch} concentrations were
236 respectively 95 and 61% higher than that in the control and remained above the control
237 for the five year period (Fig. 1). The linear effect of ash loading on Mg saturation
238 increased linearly with time (Table 2). Five years after application, values ranged from
239 1.3 % in the control to 2.8 % (SE = 0.2) in the 8 Mg ha⁻¹ treatment. The differences in
240 Ca_{exch} concentration among treatments also increased over time, accounting for the
241 significant ash – time interaction (Table 2, Fig. 1). One, two and five years after ash
242 application of 2 Mg ha⁻¹, Ca_{exch} concentrations were respectively 104, 111 and 133 %
243 higher than the control. Changes in Ca_{exch} concentrations were less pronounced with the 8
244 Mg ha⁻¹ treatment, with values being 20, 37 and 105 % higher than the control after one,
245 two and five years, respectively. The linear effect of ash loading on mineral soil Ca
246 saturation increased linearly with time (Table 2) and was detectable five years after
247 application. Calcium saturation was 6.2 % (SE = 2.0) in the control and 13.0 % (SE = 1.5

248 - 1.7) in the 8 Mg ha⁻¹ treatment five years following application. Mineral soil Na_{exch}
249 (results not shown) represented less than 2.2 % of base saturation.

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

254 The maximum CEC_{eff} was observed with the 2 Mg ha⁻¹ treatment for up to two
255 years following ash application. Five years after application, CEC_{eff} decreased linearly
256 with ash loading. The quadratic effect of ash loading and its interaction with time (linear)
257 on CEC_{eff} were both significant (Table 2). The effect of ash application on mineral soil
258 base saturation increased with ash loading and with time since application. However, the
259 2 Mg ha⁻¹ ash treatment proportionally caused the largest effect five years after
260 application, increasing base saturation by 66 % relative to the control (compared to 99 %
261 with the 8 Mg ha⁻¹ treatment).

262 *Effects of ash loading over five years on soil C, N and P*

263 A decrease in forest floor C_{org} concentration was observed with increasing loading
264 for up to two years after ash application (Table 3, Fig. 3). Five years after application,
265 however, the 2 Mg ha⁻¹ treatment had a higher C_{org} concentration than the control and the
266 8 Mg ha⁻¹ treatment. A significant linear effect of ash loading on forest floor C_{org}
267 concentration as well as a significant time and ash quadratic interaction were found
268 (Table 3). Ash application had linear and quadratic effects on forest floor N_{Kjeldahl}
269 concentration (Table 3, Fig. 3). Ash application at 2 and 8 Mg ha⁻¹ respectively increased

270 and decreased N_{Kjeldahl} concentration relative to the control. This curvilinear pattern
271 became more apparent with time as indicated by the significant interaction between ash
272 treatment (quadratic) and time (Table 3). Forest floor C/N followed a quadratic and linear
273 pattern in relation to ash loading that remained stable over the five year period.

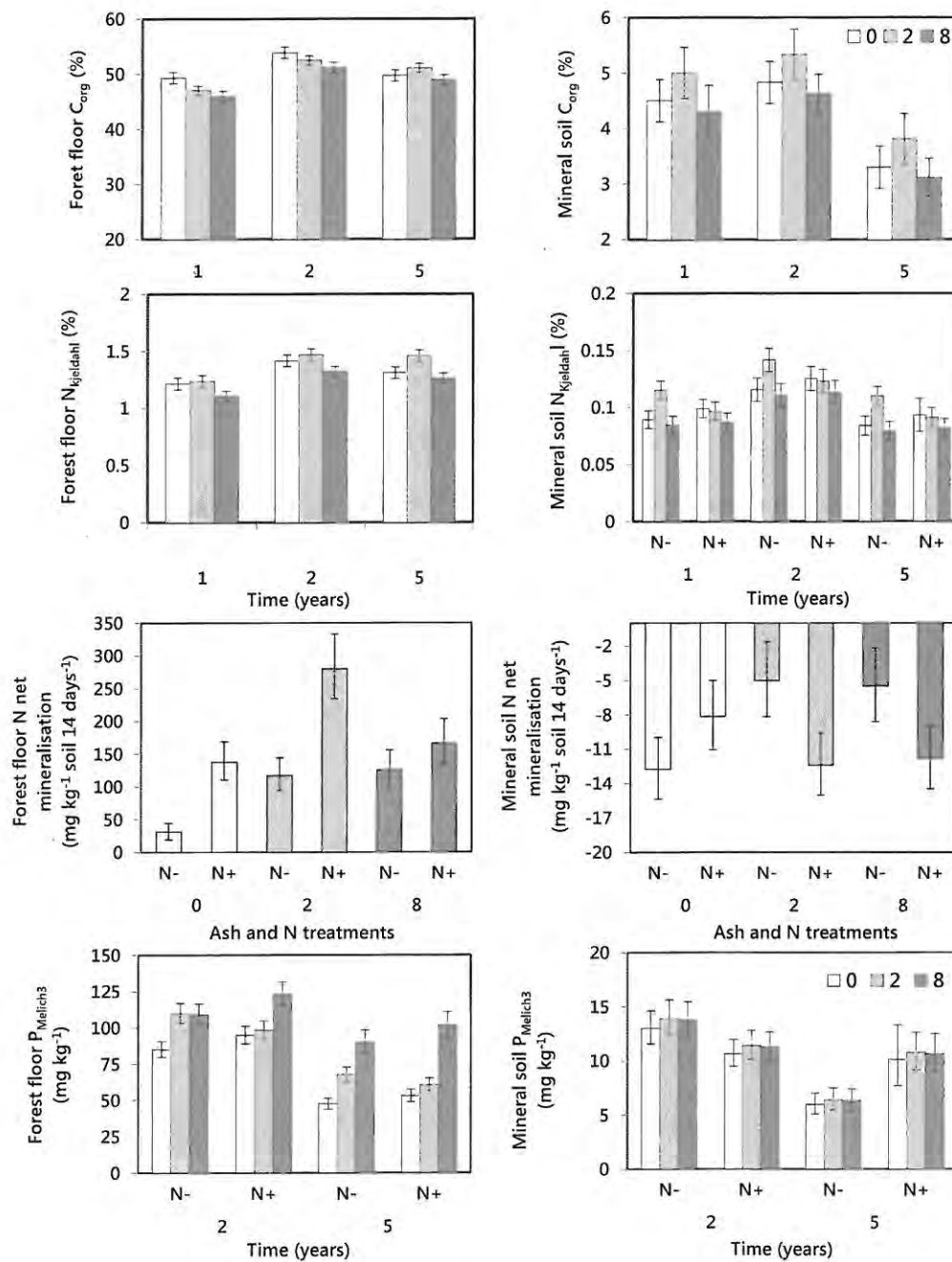


Figure 3: Forest floor and 0 – 10 cm mineral soil organic C, Kjeldhal N, one, two and five years after ash loading (0, 2, 8 tons ha⁻¹) and N fertilization (280 kg N ha⁻¹) in a boreal jack pine stand. Potential N net mineralisation rate measured one year after treatment application and Melich-3 P measured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

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

277 In the first year following ash application, forest floor potential net N
278 mineralization showed a similar increase under the 2 and 8 Mg ha⁻¹ treatments,
279 accounting for the significant linear and quadratic effects (Table 3). Net N mineralization
280 in the 8 Mg ha⁻¹ treatment was 300 % higher than in the control (Fig. 3). Forest floor
281 P_{Mehlich-3} concentration increased linearly with ash loading and the effect became more
282 pronounced with time as supported by the significant interaction between ash loading and
283 time (Table 3). Five years following ash application, forest floor P_{Mehlich-3} concentrations
284 in the 2 and 8 Mg ha⁻¹ treatments were respectively 43 and 90 % higher than in the
285 control.

286 Ash application had no significant effect on C_{org} and P_{Mehlich-3} concentrations
287 (Table 3) or potential net N mineralization in the upper mineral soil. The increase and
288 decrease in mineral soil C_{org} concentration observed respectively under the 2 and 8 Mg
289 ha⁻¹ treatments relative to the control were not significant because of large variations
290 within the treatments (Table 3, Fig. 3). Mineral soil N_{Kjeldahl} concentration followed a
291 similar pattern to that in the forest floor with the highest concentration observed under the
292 2 Mg ha⁻¹ treatment (Table 3, Fig. 3). The relationship between ash loading and mineral
293 soil C/N varied with time since ash treatment, but only the interaction between time and
294 ash (quadratic) was significant. Carbon/N ratio in the 2 Mg ha⁻¹ ash treatment first
295 increased and then decreased relative to the two other ash treatments. Five years after ash

296 application, mineral soil C/N was 41.0 (SE = 2.5), 35.3 (SE = 1.9) and 38.9 (SE = 1.9) in
297 the control and 2 and 8 Mg ha⁻¹ treatments, respectively.

298 *Effects of N fertilization over five years on overall soil properties, and interactions*
299 *with ash loading*

300 Nitrogen fertilization with urea had no significant direct effects on chemical
301 properties of the forest floor (Table 2), including C/N (Table 3). However, one year after
302 N fertilization, a strong positive effect on forest floor potential net N mineralization
303 (Table 3) rate was observed. This corresponded to an increase of 342 % in the N
304 fertilized – ash control treatment relative to the full control (Fig. 3). A significant N × ash
305 interaction was also observed (Table 3), whereas the linear increase in potential net N
306 mineralization with ash loading was less pronounced in N fertilized plots. Significant
307 interactions between N and ash loading were also found for forest floor CEC_{eff},
308 acidity_{exch}, and P_{Mehlich-3}, whereas N fertilization increased the divergence between ash
309 treatments (Fig. 2 and 3).

310 Similarly, N fertilization alone had little direct lasting effects on chemical
311 properties of the upper mineral soil (Table 2), including C/N (Table 3). Nitrogen
312 fertilization initially increased mineral soil acidity_{exch} (Fig. 1) and CEC_{eff} (Fig. 2) and
313 decreased individual cations (results not shown) and total base saturation (Fig. 2). The
314 effects of N fertilization on these variables fluctuated with time from two to five years
315 after application as indicated by the significant linear and quadratic time × N interaction
316 (Table 2). When N fertilization was applied in combination with ash, mineral soil N_{Kjeldahl}
317 concentration decreased, while Mg_{exch} and Ca_{exch} concentrations linearly increased with

318 increasing ash loading. This effect contrasted with the quadratic effect of ash loading on
 319 $N_{Kjeldahl}$, Mg_{exch} and Ca_{exch} in the absence of N fertilization.

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

328 *Effects of ash loading and N fertilization over five years on foliar nutrients and*
 329 *five-year relative tree growth*

330 No significant effect of ash was found on individual foliar nutrient concentrations
 331 (i.e. N, P, K, Ca and Mg) and nutrient ratios of jack pine one to two years after
 332 application, with the exception of K/P ($p = 0.053$). The 2006 – 2007 average K/P was
 333 3.09 (SE = 0.08) in the control and 3.36 in the 8 Mg ha⁻¹ treatment. The average 2006 –
 334 2007 foliar N concentration of N fertilized plots (1.09 %, SE = 0.02) was 7.1 % higher (p
 335 = 0.001) than the control (1.02 %).

336 Ash had no effect on the five-year relative growth rates of large (≥ 10 cm DBH, n
 337 = 1293, relative growth rate = 5.0%) and small (< 10 cm DBH, $n = 536$) jack pines and of
 338 small black spruces ($n = 211$). However, the five-year relative growth rate of large black
 339 spruces (≥ 10 cm DBH, $n = 269$) decreased linearly ($p = 0.002$) with ash loading (Fig. 4),

340 a difference in growth rate of -30 % between the control and the 8 Mg ha⁻¹ ash treatment.
341 Only large jack pines were affected by N fertilization ($p < 0.001$); their relative five-year
342 growth rate increased by 21 % due to N fertilization. No significant interaction was found
343 between ash treatment and N fertilization concerning the growth rate of any of the
344 species-size classes.
345

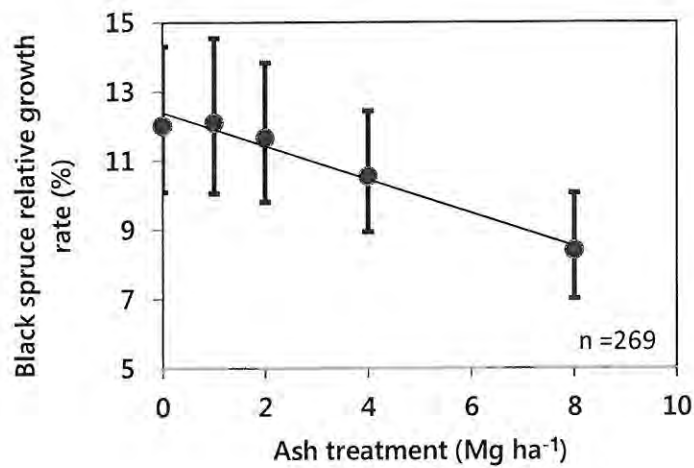


Figure 4: Black spruce (diameter at breast height ≥ 10 cm) relative growth rate 1 to 5 years following ash loading (0, 1, 2, 4, 8 Mg ha⁻¹) in a boreal jack pine stand.

346 *Effects of ash loading over eight years on soil acid-base status*

347 Soil extraction with NH_4Cl alone yielded exchangeable cation concentrations
348 within the range of those observed following the NH_4Cl - BaCl_2 extraction (Figs. 1 and 5).
349 Eight years after ash application, significant linear relationships were found between ash
350 loading and K_{exch} , Ca_{exch} , Mg_{exch} in the forest floor and upper (0 – 10 cm) and lower (10 –
351 20 cm) mineral soil (Table 3). However, the relationship between ash loading and Ca_{exch}
352 in the lower mineral soil was marginally significant ($p = 0.085$). Relative to the control,
353 increases in K_{exch} , Mg_{exch} and Ca_{exch} under the 8 Mg ha^{-1} ash treatment were respectively
354 40, 103 and 180 % in the forest floor, 61, 121 and 120 % in the upper mineral soil, and
355 49, 73 and 60 % in the lower mineral soil (Fig. 5).

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 | Mn^* | 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 |

*: Log transformed

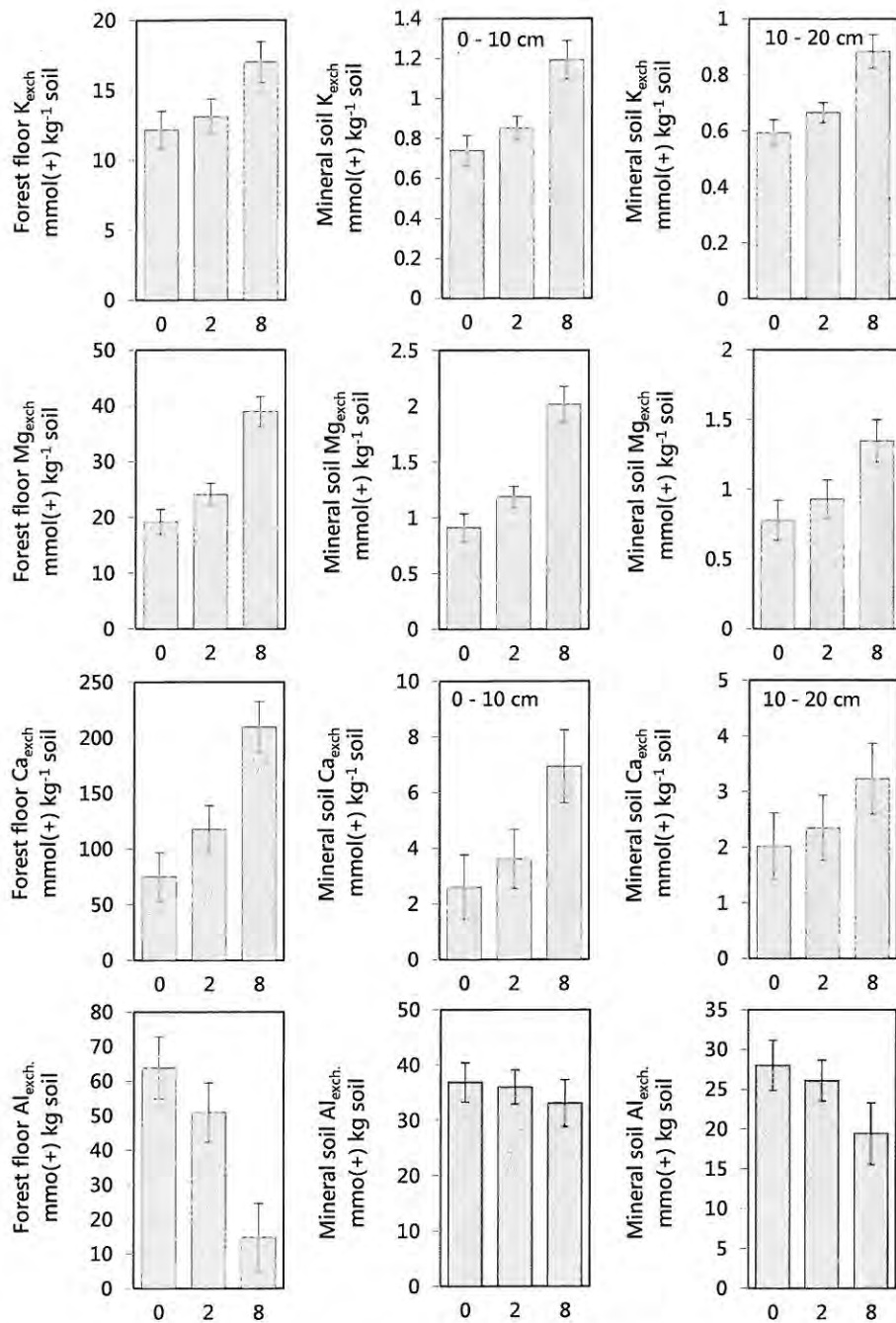
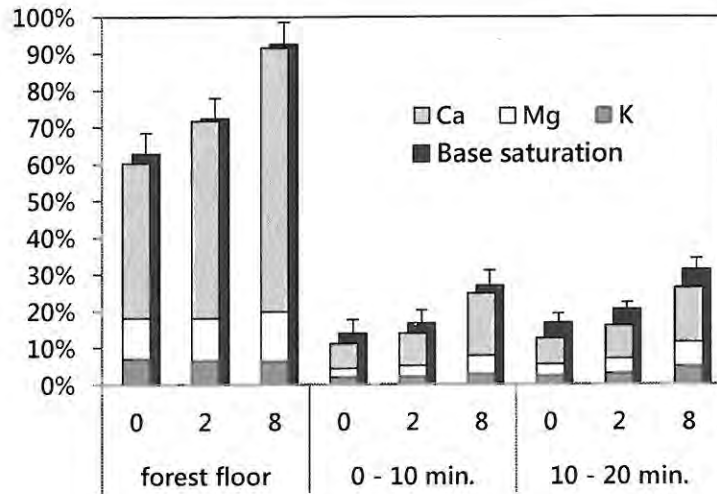


Figure 5: Forest floor, 0 – 10 and 10 – 20 cm mineral soil exchangeable cations and Al concentrations eight years after ash loading (0, 2, 8 Mg ha⁻¹) in a boreal jack pine stand. Predicted values and their standard error (bars) based on a mixed linear model. See Table 4 for a Type 1 test of hypothesis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



358

Figure 6: Forest floor, 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.

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

364 Potassium saturation (Table 4, Fig. 6) significantly increased with ash loading
365 from 1.9 (SE = 0.2) in the control to 2.8 % (SE = 0.2) in the 8 Mg ha⁻¹ treatment within
366 the 0 – 10 cm depth, and from 2.3 % (SE = 0.4) to 4.8 % (SE = 0.6) within the 10 – 20
367 cm depth. Magnesium saturation also increased from 2.4 % (SE = 0.4) in the control to
368 5.0 % (SE = 0.4) in the 8 Mg ha⁻¹ treatment within 0 – 10 cm, and from 3.1 % (SE = 0.5)
369 to 6.7 % (SE = 0.7) within 10 – 20 cm. Finally, Ca saturation within the 0 – 10 cm depth
370 increased with ash loading from 6.8 % (SE = 3.5) in the control to 17.0 % (SE = 3.7) in
371 the 8 Mg ha⁻¹ treatment. Within the 10 – 20 cm depth, Ca saturation increased from 7.1 %
372 (SE = 1.2) in the control to 14.8 % (SE = 1.5) in the 8 Mg ha⁻¹ treatment. For all soil
373 horizons, the increase in base saturation caused by ash loading was mostly associated to
374 Ca (Fig. 6).

375 Significant linear relationships between ash loading and Al_{exch} (Fig. 5) and CEC_{eff}
376 (Table 4) were found only for the forest floor. Forest floor CEC_{eff} was 175.3 (SE = 17.7)
377 mmol(+) kg⁻¹ in the control and 284.4 (SE = 18.9) mmol (+) kg⁻¹ in the 8 Mg ha⁻¹
378 treatment. Ash loading had no effect on Ba_{exch} (average forest floor = 1.24 mmol(+) kg⁻¹,
379 SE = 0.18). The log of Mn_{exch} significantly increased at all soil depths with ash loading.
380 In the forest floor, Mn_{exch} increased from 0.57 mmol(+) kg⁻¹ (SE = 0.11) in the control to

381 1.01 (SE = 0.16) and 5.54 (SE = 1.41) mmol(+) kg⁻¹ in the 2 and 8 Mg ha⁻¹ treatments,
382 respectively. This corresponded to increases of 76 and 862 %. Exchangeable Mn values
383 in the upper and lower mineral soils were much lower than those in the forest floor - with
384 values of 0.024 (SE = 0.004) and 0.029 (SE = 0.007) mmol(+) kg⁻¹ in the control of the 0
385 – 10 cm and 10 – 20 cm depths, respectively. Increases of 73 % and 105 % in Mn_{exch}
386 were observed at the 0 – 10 cm and 10 – 20 cm depths, respectively, after comparing the
387 control to the 8 Mg ha⁻¹ treatment.

388 DISCUSSION

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

397 Independently of treatments, large year to year variations on soil properties were
398 observed that might have been caused variation in soil moisture at sampling time. In
399 general, soil drying increases the concentration of solutes, which may cause precipitation
400 or an increased sorption of cations on soil exchange surfaces (Mengel, 1982). Potassium
401 is especially sensitive to soil drying. Exchangeable K levels generally decrease upon
402 drying for soils with low CEC (e.g. < 5 mmol kg⁻¹) (Erich and Hoskins, 2011) Higher

403 exchangeable K concentrations under the control at 2 years could therefore suggest lower
404 soil moisture during the sampling period. A similar explanation can be provided for Ca.
405 Soil drying may also increase soil acidity on exchange surface, which affects the
406 solubility of many nutrients, particularly metals (Dowding, et al., 2005). As a whole,
407 protonation of exchange sites would decrease CEC – however, this is not what was
408 observed in this study. Cation exchange capacity is also increased in year 2, which could
409 be attributed to a reduction of C mineralization (Borken and Matzner, 2008) or perhaps a
410 decrease in dissolved organic C leaching under dryer conditions (Borken, et al., 1999), or
411 both.

412 *Effects of ash loading over eight years on forest floor acid-base status*

413 Even under low ash loading, forest floor exchangeable base cation concentrations,
414 pH, and base saturation increased within a year of application. The unstable nature and
415 fineness of the ash particulates likely explain their high solubility and in turn, the rapid
416 soil response (Nieminen, et al., 2005; Perkiömäki and Fritze, 2002; Steenari, et al.,
417 1999a) despite the relatively low elemental composition of the applied ash compared to
418 published values (Augusto, et al., 2008). Also, the intrinsically low pH of the forest floor
419 may account for its significant response because a large proportion of acidity could be
420 replaced. The increased concentration of charge (or activity) in base cations in forest
421 floor solution after ash application has clearly favored a large mass effect which led to a
422 substantial displacement/replacement of H^+ adsorbed on exchange sites that arise from
423 the dissociation of carboxylic (COOH) and phenolic (COH) functional groups at the
424 surface of humic and fulvic acids (Evans, 1989).

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

441 On the one hand, Ca is the most abundant base cation in ash (Augusto, et al.,
442 2008, Table 1). Its dominant form is Ca carbonate ($CaCO_3$), which forms from oxides
443 (CaO) when ashes are exposed to water and CO_2 (Steenari, et al., 1999a). The solubility
444 of $CaCO_3$ increases exponentially with decreasing pH meaning that solubilization of Ca
445 from $CaCO_3$ is promoted if solution pH in the vicinity of ash particulates decreases
446 sufficiently (Nieminen, et al., 2005; Steenari, et al., 1999b). On the other hand, Mg in ash

447 is mostly present as Mg oxides, which are chemically stable (Steenari, et al., 1999a).
448 Also, ash concentrations of Mg are generally much lower than those of Ca (Jacobson, et
449 al., 2004), more than 16 times in the case of our study (Table 1). Thus, the liming effect
450 of ash comes from its CaCO_3 and, to a lesser extent, MgCO_3 content (Pitman, 2006) and
451 takes place over a number of years (Reid and Watmough, 2014). In our study, Ca_{exch} and
452 Ca saturation in the forest floor increased over time in response to the progressive
453 dissolution of CaCO_3 but the lowest ash treatment initially caused a proportionally higher
454 increase in forest floor Ca_{exch} compared to the higher treatment. This nonlinear
455 relationship suggests some control of solution pH on Ca release from ash particulates
456 (Steenari, et al., 1999a) and under the 8 Mg ha^{-1} ash treatment, an increase in solution pH
457 may have initially reduced the rate of dissolution of carbonates in the ash. Ludwig et al.,
458 (2002) reported that most of the added Ca from ash in a German pine stand (*Pinus*
459 *sylvestris*) was still found in insoluble forms in the forest floor as much as nineteen
460 months following application.

461 A significant increase in forest floor Mg_{exch} was also observed with ash loading,
462 but its dominance on the exchange complex was expectedly much lower than Ca. In fact,
463 Mg_{exch} behaved more like K_{exch} in that it did not increase over time like Ca_{exch} , suggesting
464 Mg oxides are stable in this environment and acting as a small source of Mg^{2+} .

465 The progressive adsorption of Ca^{2+} on exchange sites in the forest floor was
466 accompanied by the displacement of $\text{acidity}_{\text{exch}}$ (i.e. H^+) and in turn, an increase in pH.
467 However, changes in forest floor pH in response to ash loading occurred more rapidly
468 (but also stabilized more quickly) than changes in Ca_{exch} , $\text{acidity}_{\text{exch}}$ and base saturation.

469 It is possible that pH initially changed in response to displacement by K and subsequently
470 in response to replacement by Ca. Conversely, Reid and Watmough (2014) reported that
471 base saturation is more susceptible to ash loading than pH and this regardless of soil
472 horizon. In our study, nonetheless, functional groups were deprotonated at high pH,
473 resulting in more negative charges and consequently high CEC_{eff} .

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

479 *Effects of ash loading over eight years on mineral soil acid-base status*

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

488 The upper mineral soil responds to changes in the chemical composition of the
489 solution coming from the forest floor and reaching the mineral soil via preferential flow
490 paths (Bundt, et al., 2001). Ash application normally leads to a major and rapid flush of

491 base cations (including Na) that displaces forest floor acidity in the form of H^+ and Al
492 (Ludwig, et al., 2002; Lundström, et al., 2003). This acidity is released in the soil
493 solution, whereas base cations decrease in the soil solution as they progressively react
494 with soil. Moreover, application of ash may result in an increase in soil solution SO_4^{2-} ,
495 caused by the dissolution of salts in the ash. It is thus possible that the acid neutralizing
496 capacity (ANC, i.e. the balance between alkalinity and acidity) of the soil solution
497 (inflow) under the 2 Mg ha⁻¹ treatment was too low within the first two years for it to
498 continue acting as a net source of alkalinity in the mineral soil (Norström, et al., 2012;
499 Geibe, et al., 2003; Ring, et al., 2006). In time, forest floor chemistry stabilized and its
500 incoming acidity decreased (Ludwig, et al., 2002), increasing ANC of the soil solution
501 reaching the mineral, and in turn allowing alkalinity to increase. This was reflected by the
502 increase in mineral soil Ca_{exch} , Mg_{exch} and base saturation with ash loading observed five
503 years after ash application. The 8 Mg ha⁻¹ ash treatment did not undergo any significant
504 increase in $acidity_{exch}$ in the mineral soil at any period of the study, likely because an
505 excess of base cations (alkalinity) in the forest floor solution that augmented its ANC.

506 Protons dissociate from the surfaces of Al and Fe hydrous oxides and from the
507 edges of clay minerals (Sposito, 2008). Soil particles of coarse Boreal Shield Podzols
508 such as the ones in this study are coated with Al and Fe hydrous oxides (Courchesne, et
509 al., 1996). This gives a pH-dependent negative charge that behaves like the functional
510 groups of organic acids, i.e. the number of negatively charged surfaces increases as pH
511 increases. An increase in alkalinity in the mineral soil is thus bound to an increase in
512 CEC_{eff} as seen with our results. Additionally, the curvilinear pattern of Ca_{exch} , Mg_{exch} , and

513 acidity_{exch} with ash loading in the upper mineral soil followed changes in organic matter
514 content at the same depth. This can also explain, in part, the increase in CEC_{eff} in the
515 mineral soil (Molina, et al., 2007)

516 The observed changes in the forest floor and mineral soil acid-base status caused
517 by ash application differed by their magnitude and rate from what was reported by
518 Augusto, et al., (2008) following a meta-analysis of 33 independent trials. According to
519 the analysis, only ash loading > 4 Mg ha⁻¹ induced a decline in soil acidity within the first
520 five years of ash application, and these modifications were mostly limited to the forest
521 floor. In a more recent meta-analysis, Reid and Watmough (2014) found that over 25 %
522 of the trials reported no effect of liming or ash application on soil base saturation, and 33
523 % of trials reported no effect on soil pH. Differences in loading, ash chemical
524 composition, soils and monitoring period likely explain the diverging results between
525 studies.

526

527 *Effects of ash loading over five years on soil C, N and P*

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

547 The decrease in soil acidity caused by ash application can also induce changes in
548 the microbial community composition (Bååth and Arnebrant, 1993) and stimulates its

549 activity (Jokinen, et al., 2006; Zimmermann and Frey, 2002). Thus, the elevated potential
550 net N mineralization rates observed in the forest floor immediately following ash
551 application were expected and consistent with previous findings (Jacobson, et al., 2004;
552 Khanna, et al., 1994). Longer term positive effects of ash application on forest floor
553 microbial activity and organic matter decomposition have been reported (Perkiömäki, et
554 al., 2004), but they cannot be generalized to all situations (Rosenberg, et al., 2010). We
555 do not expect that the effect of ash loading on potential net N mineralization after one
556 year of application was long lasting (Ring, et al., 2006) as the observed reduction in
557 forest floor C_{org} concentrations possibly caused by organic matter solubilization took
558 place within a year of ash application.

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

567 Phosphorus content of the applied ash was low compared to published values
568 (Table 1, see Augusto et al., (2008)). Phosphorus has very limited mobility in these
569 naturally acidic soils as $H_2PO_4^{3-}$ strongly adsorbs to positively charged surfaces of Fe and
570 Al hydroxides in the mineral soil or precipitates (to form new minerals) by reacting with

571 free Al and Fe in the soil solution (Bolan, et al., 2008). Phosphorus availability can also
572 increase if organic matter decomposition increases (also favored by an increase in pH),
573 thus releasing more P, or if organic acids produced from the decomposition act as
574 chelates for free Al and Fe in the soil solution, thus reducing P fixation and precipitation.
575 The observed increase in forest floor pH (CaCl₂) from 2.9 in the control to 3.5 in the 8
576 Mg ha⁻¹ treatment partly explains the increase in forest floor P_{Mehlich-3} concentrations with
577 ash loading observed five years following ash application. However, the mechanisms
578 leading to this change cannot be easily elucidated with the data available. No increase in
579 P availability was observed in the mineral soil where increases in soil pH were not
580 significant. Jacobson et al., (2004) have reported similar results for forest floor and
581 mineral soil P availability five years following ash application in a *P. sylvestris* forest
582 stand growing on acidic podzolic soils.

583 ***Effects of N (urea) fertilization over five years on overall soil properties and***
584 ***interactions with ash loading***

585 We decided to fertilize with urea to assess the potential of an increase in N
586 availability to enhance tree response to ash application (Saarsalmi, et al., 2006).
587 However, effects of N fertilization and its interactions with ash on soil properties are also
588 of interest. Similarly to ash application, fertilization of boreal soils with urea can increase
589 forest floor pH and C_{org} mobility caused by urea hydrolysis, which consumes H⁺ to form
590 NH₄⁺ in acid soils (Saarsalmi and Mälkönen, 2001; Camiré and Bernier, 1981). This
591 effect on soil pH is quick and generally short-lived (Aarnio, et al., 2003). In our study,
592 few direct lasting effects of urea fertilization on forest floor properties were in fact

593 observed in the five years following N fertilization. The notable exception was a
594 predictable increase in forest floor potential net N mineralization (Camiré and Bernier,
595 1981; Aarnio and Martikainen, 1996). However, when applied in combination with ash
596 and over the five year period, urea amplified the effect of the largest ash load on forest
597 floor acidity_{exch}, CEC_{eff}, and P_{Melich-3}. In combination with ash, urea hydrolysis probably
598 improved the soil acid-base status enough for deprotonation of functional groups to occur
599 (thus, increasing CEC_{eff}) and for P availability to increase.

600 Mineral soil properties were affected by urea fertilization to a greater extent than
601 the forest floor. Short-lived increases in mineral soil acidity_{exch} and decreases in base
602 saturation were observed following urea regardless of ash treatments. Simultaneous
603 applications of ash and urea also nullified the previously discussed curvilinear
604 relationship between ash load and mineral soil N_{Kjeldahl}, Ca_{exch} and Mg_{exch}. Studies on
605 combined application of wood ash and urea rarely separate the effects of N and ash or
606 their interaction on forest soil properties (Saarsalmi, et al., 2004; Saarsalmi, et al., 2006).
607 However, in the mid and long terms, N fertilization of agricultural soils (including with
608 urea) is well known to lower pH (Barak, et al., 1997), exchangeable base cations and base
609 saturation (Bouman, et al., 1995; Liu, et al., 1997) and augment exchangeable acidity
610 (Liu, et al., 1997). This is due to microbial oxidation of ammoniacal fertilizers, which
611 despite initially being a base (e.g. urea) are involved in acid-forming reactions in soils. In
612 the boreal soils studied, the acid-forming process was most likely the uptake of NH₄⁺ by
613 plant roots in exchange for H⁺ (whereas nitrification would be a net source of H⁺ in less
614 acidic soils). The net effect of urea fertilization observed on forest floor potential net N

615 mineralization (in the form of NH_4^+) has only increased that potential for acidity
616 production.

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

619 Jack pine represented the largest overstory component of the studied stand.
620 Despite a small increase in large jack pine relative growth rate following N fertilization
621 and the fact that the stand had been recently thinned, the relative growth rate remained
622 low. Similarly, ash application in boreal forests has had limited effects on tree growth in
623 the absence of N fertilization (Jacobson, et al., 2014; Saarsalmi, et al., 2004; Jacobson,
624 2003). This remained surprising given the improved soil acid-base status and N
625 availability of these generally poor forest soils. An exception to this general trend,
626 Saarsalmi et al., (2006) reported an increase in the growth rate of a *Pinus sylvestris* boreal
627 stand growing on a podzol 10 to 20 years following ash application and N fertilization
628 when compared with N fertilization alone. In their meta-analysis of ash and lime
629 application experiments, Reid and Watmough (2014) emphasized on the possible bias
630 created by the short duration of studies. Half of the studies were less than 6 years in
631 duration, whereas changes in mineral soil properties can take place over longer periods of
632 time. In our study, the full effect of ash treatments on the upper mineral soil properties
633 materialized between three and five years after application. The properties of the lower
634 mineral soil were only measured eight years after treatments, but we can assume that
635 changes at this depth occurred over a slightly longer period than those at the 0 – 10 cm
636 depth. According to a recent study by Houle et al., (2014), jack pine acquires nutrients

637 from mineral soil horizons rather than from the forest floor. Hence, the benefit of ash
638 application for jack pine nutrition, if any, would be contingent on the response rate of the
639 mineral soil. Longer term measurements will possibly yield different results.
640 Unfortunately, the stand was harvested in 2013.

641 Black spruce is a shade tolerant species that establishes alongside jack pine
642 following stand replacing fire. However, it grows at a slower rate. Because foliar
643 nutrients were only measured on jack pine foliage, we can only speculate on causes
644 behind the decreasing growth rate of black spruce with increasing ash loading. Contrary
645 to jack pine, the forest floor is the main source of nutrients for black spruce (Houle, et al.,
646 2014). Ash contained large amounts of Mn when compared with other micronutrients,
647 and eight years following application of 8 Mg ha⁻¹ of ash, an increase of over 860 % of
648 forest floor Mn_{exch} was observed. In comparison, the corresponding increase was 180%
649 for forest floor Ca_{exch}. As a micronutrient, Mn is involved in the water-splitting reaction
650 of photosynthesis and as a cofactor in enzymatic reactions (Marschner, 2012). In soils,
651 however, the affinity of Mnⁿ⁺ for soil organic matter is relatively low (McGrath, et al.,
652 1988). The activity of free Mnⁿ⁺ in the soil solution can thus be high, which raises
653 questions relative to manganese toxicity or nutrient imbalance between Mn and other
654 nutrients (notably Ca) following ash application. On the one hand, large amounts of Mn
655 can accumulate in some tree species such as spruce spp. without showing toxicity
656 symptoms (Zöttl, 1985) and ash has been shown to reduce Mn toxicity of tropical acid
657 soils (Nkana, et al., 1998). On the other hand, high foliage Mn concentrations have been
658 shown to reduce needle chlorophyll concentrations of *Picea glauca*, (Moench, (Voss))

659 seedlings (St-Clair and Lynch, 2005) and growth of *Pinus sylvestris* L. and *Pinus nigra*
660 (Arnold) seedlings (Kavvadias and Miller, 1999). The negative reaction of black spruce
661 to ash application clearly needs further investigation before any large scale use of ash is
662 implemented in eastern Canadian boreal forests.

663 CONCLUSION

664 Our results underline the need to thoroughly investigate the effect of ash
665 application on forest soils, tree nutrition and stand growth in the context of Canadian
666 boreal forests. The unforeseen interactions between organic matter dynamics and soil
667 nutrient retention following ash application suggest a need for a better understanding of
668 the effect of ash on soil organic constituents as well as their transformation and
669 mobilization. Combined ash and urea application did not improve tree response to ash
670 application over the 8 year period. Moreover, additional studies are needed to validate the
671 deleterious effect of large ash loads on black spruce growth and to elucidate the
672 mechanisms involved. Black spruce is the most important commercial species of eastern
673 boreal forests and if confirmed, these results strongly limit the potential of ash
674 fertilization.

675 ACKNOWLEDGEMENT

676 This work was supported by the Natural Sciences and Engineering Research
677 Council of Canada (NSERC RDCPG, grant 450412-13, Resolute Forest Products, and the
678 Quebec Ministry of Forests, Wildlife and Parks (PMVRMF, Volet 1, Volet 2). We are
679 grateful to Sylvain Moreau (Resolute), the city of Senneterre and Boralex for their help
680 implementing the experiment, Alfred Coulomb, Emilie Robert, Suzie Rollin, Josée

681 Frennette and employees of Kinojevis-Abijevis Forest Coop for field assistance, and
682 Alain Brousseau, H el ene Lalande, Jacinthe Ricard-Pich e for laboratory work.

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