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Short-term changes in spruce foliar nutrients and soil properties in response to wood ash application in the sub-boreal climate zone of British Columbia

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ABSTRACT

Utilization of wood ash as a forest soil amendment in British Columbia could have numerous benefits, including potentially increasing tree growth. Two wood-derived bottom ashes (low carbon gasifier ash and high carbon boiler ash) were applied at 5000 kg ha⁻¹ (dry weight equivalent) with urea (100 kg N ha⁻¹), in a two-way factorial randomized block design across two (18- and 24-year-old) hybrid spruce (*Picea glauca* X *engelmannii* Parry x Engelm.) plantations in interior British Columbia. Changes in spruce foliar nutrients and selected soil properties were evaluated. After one growing-season, foliar Ca and S significantly increased in plots treated with ash, and foliar N significantly increased while foliar Mg and P significantly decreased in spruce treated with urea. In LFH horizons, soil pH, exchangeable base cations (Ca, Mg, K), strong acid extractable B and Ca significantly increased ($p < 0.05$) with ash treatments; soil pH was greatest in plots treated with urea plus gasifier ash. No significant treatment effects were observed in underlying mineral soil. We conclude that gasifier and boiler ash derived from clean wood applied at 5000 kg ha⁻¹ are effective soil amendments as expressed within one year by changes in nutrient status of LFH horizons and spruce foliage.

Key words: bottom ash, Gray Luvisol, gasifier, forest soil, soil amendment, waste management

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Worldwide, bioenergy production is expanding to offset and reduce consumption of fossil fuels for heat and power (Hannam et al. 2016). The combustion of wood by-products can provide an efficient, renewable energy source, but as bioenergy power generation increases, so does the amount of ash produced as a by-product (Helle et al. 2009; Hannam et al. 2016, 2017). In some European countries and some Canadian provinces, ash produced through bioenergy combustion is commonly recycled in forest ecosystems (Hannam et al. 2016, 2017). In British Columbia, however, most of the wood ash produced in pulp and paper mills, sawmills and bioenergy plants is considered a waste, and is landfilled (Nishio 2016; Hannam et al. 2017).

Potential benefits of wood ash application to ecosystems include amelioration of soil acidity and increased concentrations of macro- and micronutrients (Campbell 1990; Pitman 2006; Huotari et al. 2015; Vance 1996). Elements are recycled, allowing for continued biogeochemical cycling in the biosphere. Reduced acidity may increase availability of P, % base saturation (% BS) and pH-dependent cation exchange capacity (CEC) of soils (Augusto et al. 2008; Pitman 2006; Pugliese et al. 2014). Increased pH has been associated with increased rates of microbial activity, organic matter mineralization, ammonification and nitrification (Zimmerman and Frey 2002; Saarsalmi et al. 2014). Wood ash typically contains most plant macronutrients, such as Ca, Mg, K and P, with lesser quantities of micronutrients such as B (Campbell 1990; Demeyer 2001; Vance 1996; Zhou 2003), but is lacking in nitrogen (N), which is largely volatilized during the combustion process (Pitman 2006; Saarsalmi et al. 2001; Helmisaari et al. 2008). Addition of N via commercial fertilizers or N-rich organic amendments (e.g. biosolids, manures, N-rich sludges) can help overcome this limitation. Motivations for ash application to forest ecosystems include

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potential enhancement of tree biomass, replenishment of harvested ecosystems with nutrients and base cations, and the emulation of natural disturbances such as wildfire (Hannam et al. 2016, 2017).

Chemical properties of wood ash vary widely, depending on composition of biomass residue, type of combustion system, and the point of collection (e.g. bottom or grate ash versus fly ash) (Pitman 2006; Hannam et al 2017). Wood ash is often more soluble and has a higher pH than agricultural limestone, typically ranging from pH 9-13. Calcium carbonate equivalent (CCE) ranges from <15 to >90% (Demeyer et al. 2001; Campbell 1990; Vance 1996). Some industrial boilers produce high-C ash that range between 7% to more than 50% total C (Pitman 2006; Hannam et al. 2016), much of which is in the form of charcoal (Karlton et al. 2008). In contrast, ash from modern pellet plants and gasifiers typically contain <5% organic C (Park et al. 2012; James et al. 2014). High C contents (usually associated with high C/N ratios) of readily decomposable organic substrates result in N immobilization. Deenik et al. (2010) concluded that adding charcoal (C/N ratio = 189 – 197) to an Andisol and a highly weathered Ultisol resulted in soil N immobilization, with the greatest immobilization associated with the charcoal having the highest volatile matter content. Omil et al. (2013) concluded that addition of wood charcoal (C/N about 200) reduced N mineralization in a sandy loam soil growing Monterey pine (*Pinus radiata* D.Don) in Spain. A recent meta-analysis has reported that biochar addition to soil generally reduces short-term concentrations of NH_4^+ -N and NO_3^- -N (Nguyen et al. 2017).

Wood ash, in some circumstances, may contain elevated concentrations of trace elements, which raises concerns regarding its use as a soil amendment (Aronsson and Ekelund 2004; Augusto et

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al. 2008; Bramryd and Fransman 1995; Lodenius et al. 2002). Most jurisdictions have established criteria to evaluate the suitability of wood ash intended for use as soil amendments (Hannam et al. 2016; Haglund 2008; Ribbing and Bjurström 2011). Although concentrations of some elements (e.g. Ca, Mg, K) are similar in fly ash and bottom ashes, other elements (e.g. Cd, Cu, Cr, Hg, Pb, Zn and As) may be enriched in fly ash (Pitman 2006; Reimann et al. 2008; Park et al. 2012). Due to lower metal content, bottom ash is generally preferred over fly ash as a soil amendment (Pitman 2006; Knapp and Insam 2011). Some jurisdictions recommend “hardening” of ash prior to land applications (Hannam et al. 2016). “Hardened” wood ash has been wetted and allowed to react with atmospheric CO₂ for several months, thereby converting hydroxides of base metals into carbonate forms. Subsequent drying results in a weakly cemented material that can be crushed into aggregates; hardened ash exhibits lower solubility of some plant nutrients (Jacobson 2003; Rehl 2014; Steenari and Lindqvist 1997) and is less prone to becoming air borne upon handling. Because many nutrients are more readily released from loose ash, the effects of loose ash applications tend to be more pronounced in the short-term compared to hardened ash applications (Augusto et al. 2008).

In sites where N is not the dominant limiting factor for tree growth, wood ash can enhance tree biomass and/or nutrient uptake over both the short- and long-term. Application of loose and hardened wood ash to organic soils in Finland have yielded growth increases in Scots pine (*Pinus sylvestris* L.) seedlings (Hytonen 2003) and have alleviated deficiencies in B, K, and P in Scots pine and Norway spruce (*Picea abies* (L.) Karst.) (Moilanen et al. 2005). A meta-analysis by Augusto et al. (2008) found that, over the long-term, the application of wood ash to

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coniferous stands growing on organic soils significantly increased foliar K, Ca, Fe and B, although it significantly decreased foliar Mn.

On mineral soils, where N is often the dominant limiting factor for tree growth, the application of wood ash alone does not normally increase tree growth (Jacobson et al. 2014). Although ash applications produce variable changes in foliar nutrient content of conifers growing on mineral soils (e.g. Saarsalmi et al. 2004, 2006; Jacobson 2003; McDonald et al. 1993), Augusto et al. (2008) reported that application of wood ash to mineral soils typically increased foliar P, K, and Ca concentrations in conifers. Increases in foliar B levels have also been documented soon after wood ash applications ($1000\text{--}9000\text{ kg ha}^{-1}$) to 30-60-year-old Scots pine and Norway spruce growing on N-limited mineral soil in sites across Sweden and Finland (Saarsalmi et al. 2004; Jacobson 2003). Short-term increases in foliar concentrations of some nutrients such as B (Saarsalmi et al. 2004, 2005, 2006) and Ca (Arvidsson and Lundkvist 2002) are often sustained over the long-term, but foliar concentrations of other nutrients such as K and P may respond in a slower fashion to ash application and may not be prevalent until several years after treatment (Arvidsson and Lundkvist, 2002).

Applying N fertilizer along with wood ash to mineral soils has been shown to somewhat compensate for N deficiencies, and to facilitate the uptake of nutrients from ash (Jacobson 2003; Saarsalmi et al. 2004). Addition of wood ash with N fertilizers has been shown to increase growth of conifers on mineral soil sites more than N treatments on their own, over both the short- and the long-term (Saarsalmi et al. 2006; Brockley 1989, 1990). Saarsalmi et al. (2014) argued that wood ash additions can prolong the growth response to N fertilizer treatments.

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Returning wood ash to British Columbian forests could have numerous benefits, including the replacement of nutrients removed through tree harvesting and related biomass removals from the site, amelioration of soil acidity and potential increases in stand yields. Numerous studies have examined the effects of wood ash application on coarse- and medium-textured soils, particularly in Scandinavia (e.g. Bramryd and Fransman 1995; Zimmerman and Frey 2002; Saarsalmi et al. 2012), but there is a need for more research in forested ecosystems on finer textured soils in the sub-boreal climatic zone. Response of trees and soil properties to ash (or lime) addition is highly variable; application of these materials to forest ecosystems is not universally beneficial (Reid and Watmough 2014). Although bottom ash is widely used as a soil amendment in other jurisdictions, bottom ash is not clearly recognized as a soil amendment under the current Code of Practice for Soil Amendments (Hannam et al. 2016; Government of B.C. 2007). There is a need to assess value-added uses for bottom ash, including use as soil amendments to forest ecosystems in British Columbia.

Short-term responses may influence long-term outcomes, but such responses may be eliminated over longer times and no longer be evident. Consequently, this short-term assessment was motivated by the following questions. 1) Are there short-term differences in the way contrasting ashes (low carbon bottom gasifier ash versus high carbon bottom boiler ash) influence soil chemistry and concentrations of plant nutrients? 2) Do differences in site preparation and stand age alter short-term responses of spruce to ash and urea-N treatments? 3) Is there short-term net N immobilization due to a large addition of C-rich and high C/N ratio ash? 4) Is there a short-term increase in trace elements of concern in soil after bottom ash application? Such short-term

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increases may in part be due to redistribution at the site following ash application, but they may be eliminated by chemical transformations over longer terms.

METHODS

Site Description and Trial Establishment

The experimental plots used in this study were established to allow long-term monitoring of the response of the forest ecosystem at the stand level to ash and fertilizer amendments. As this paper also reports on the initial establishment of these long-term research plots, we have provided significant detail on ash properties and baseline site and soil conditions.

In summer 2014, plots were staked out at the Aleza Lake Research Forest (ALRF), located 60 km northeast of Prince George, B.C. in the Sub-Boreal Spruce (SBS) Biogeoclimatic Zone and wk1 Subzone. The ALRF is characterized by glaciolacustrine fine-textured soils with forests dominated by hybrid spruce (*Picea glauca* X *engelmannii* Parry x Engelm.) and subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.). Two sites were used, located ~2.5km apart, and designated as the North Site and the South Site, which both contain Gray Luvisolic soils with associated Luvic Gleysolic soils (Soil Classification Working Group 1998) having < 1.0 cm to 11.5 cm LFH horizon depths, averaging ~5.2 cm in depth. The North Site (54.086 deg. N x 122.090 deg. W) was clearcut harvested in 1997 and planted to hybrid spruce the same year with no site preparation, and is classified as a 'Swx Oak Fern' mesic site series (Delong 2003). The South Site (54.071 deg. N x 122.080 deg. W) was clearcut harvested and broadcast burned in 1990 and planted to hybrid spruce in 1991, and is classified as a 'Swx Oak Fern' mesic site series transitioning to somewhat moister 'Sws - Twinberry - Oak Fern' site series (Delong 2003). Soil

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samples were collected from the forest floor (LFH) and upper 10 cm of underlying mineral soil in the fall of 2014 to establish baseline soil properties at the two sites. The two sites differed in their historic site preparation and stand age, and these differences were captured as random effects in our statistical model (described below).

Two types of wood ash were used in this study: boiler ash and gasifier ash. The boiler ash obtained from Canfor Pulp Limited was bottom ash produced in a fixed-bed industrial boiler (PG Pulp Boiler #2) from the combustion of wood residues (chips, bark and sawdust); it was collected in early spring 2015, and was stored in a covered bin until used in the trial. Gasifier ash was bottom ash produced by the UNBC 4.4 MW bioenergy plant, a Nexterra updraft gasifier that uses softwood sawmill residues as fuel. Gasifier ash was collected from the ash handling system in early fall 2014; the ash was wetted and mixed, and was then stored in a covered bin until used here. The UNBC bioenergy plant also produces fly ash, but no fly ash was included in this study. In early May 2015, three composite samples were collected from each of the boiler and gasifier ash storage bins and were submitted for chemical characterization.

A randomized block design was employed at the ALRF. At each site, there are 3 ash treatments x 2 urea treatments x 3 replicates, yielding 18 individual plots (i.e. 36 plots overall at both sites). Each plot was circular with an 8 m radius (0.0201 ha). Ash treatments were applied to the surface of the vegetated forest floor using shovels at 5000 kg ash ha⁻¹ (dry ash equivalent). Urea treatments were then immediately broadcast using hand scoops at 100 kg pelleted urea-N ha⁻¹. Treatments were applied to the plots between May 25 and 29, 2015, when tree leader extension was beginning. The ash application rate was selected based on unpublished greenhouse-pot trials

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conducted at UNBC, and can be considered moderate compared to other rates in North America and Europe, which range from <1 to >10 Mg ha⁻¹ (Hannam et al. 2016; Knapp and Insam 2011).

Sample Collection and Analyses

Soil and foliar samples were collected October 18th and 25th, 2015, five months after treatment applications, and after one growing-season. Soil samples (including 2014 baseline sampling) were collected from three locations within a 5.64 m-radius (0.0100 ha) sub-plot at the center of each 8.0 m-radius plot. At each location, the understory vegetation was removed along with the upper ~ 2 mm of the LFH (i.e. upper portion of litter was removed). This was done to avoid inclusion of any residual surface ash in LFH samples, which would alter some soil chemical analyses (e.g. CEC and % BS). Then, the underlying LFH was sampled down to the interface of the LFH with the mineral soil (LFH thickness averaged 5.2 cm, Table 1). Next, the upper 10 cm of the underlying mineral soil was sampled. Soil samples were air-dried at room temperature for two weeks and homogenized into one three-sample composite per plot. The composites were passed through a 2 mm sieve; mineral aggregates and smaller organic matter particles were broken down using a mortar and pestle until they passed through. Coarse mineral fragments (i.e. gravel, cobbles) were rare in soil samples collected at either site.

Methods for foliar sample collection and processing were adapted from standardized foliar sampling guidelines established by Brockley (2001). One foliar sample was collected from each of six healthy, dominant or co-dominant, planted hybrid spruce trees growing within each 5.64 m radius sub-plot. Samples consisted of the terminal and first-order lateral shoots of the last 30 cm of branches located between the top quarter and bottom half of the south-facing live crown.

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Fresh foliar samples were stored at 4°C in sealed plastic bags, and dried in a forced-air convection oven at 70°C for 24 hours within four days of collection. Needles were ground to <1 mm and homogenized into composites: each plot was represented by two composites, each made up of three homogenized samples.

Except when noted below, foliar and soil samples were analyzed at the BC Ministry of Environment Analytical Chemistry Laboratory (Victoria, BC). Based on Brockley (2012), the foliar nutrients chosen for inclusion in this study were B, Ca, Cu, K, Mg, Mn, P, S, and Zn, which were digested with VHP closed vessel microwave acid digestion (concentrated HNO₃) followed by ICP-OES analysis. Concentrations of C and N were analyzed using combustion elemental analysis (C not reported here). Concentrations of As, B, Ca, Cd, Co, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se and Zn were determined in LFH and mineral soil samples following strong acid digestion using concentrated HCl + HNO₃, followed by ICP-OES analysis (US EPA Method 3051A) (US EPA 2007). In this paper, we refer to strong acid soluble elemental concentrations (in ash or soil) as being “total”; but it should be noted that this technique does not liberate elements chemically bound within the mineral structure of some aluminosilicates (US EPA 1996, 2007; Austin 2015). Electrical conductivity (EC) was determined on < 2mm air-dried soil using a fixed ratio (g soil: mL water) of 1:2 (mineral soil) or 1:5 (LFH). Soil pH was determined at UNBC on air-dried < 2 mm soil, using a fixed ratio of 1:2 (mineral soil) or 1:4 (LFH) (Kalra and Maynard, 1991). Exchangeable cations, effective CEC and % BS were determined using the barium chloride method as described by Hendershot et al. (2008). “Available” elements (2014 baseline soil samples, only) were measured using the Mehlich-III extraction according to Ziadi and Tran (2008).

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Statistical Analyses

Linear mixed effects models were used for the analysis of both spruce foliar nutrients and soil chemical data. Categorical ash and urea treatments were crossed in a two-way experimental design; with soil chemical properties analyzed separately for the two depth categories (i.e. within LFH or within mineral soil). Ash and urea treatments were input as fixed effects; to account for potential differences between sites (e.g. different site preparation and stand age), we included site (North or South) as a random effect. An interaction term between ash and urea treatments was included in all models. Tukey's HSD tests were performed *a posteriori* to determine differences between treatment means ($p < 0.05$). Relative concentrations for foliar nutrients were calculated by comparing means for spruce treated with boiler ash, and spruce treated with gasifier ash, to means for spruce that received no ash treatment; means for spruce treated with urea were compared to means for spruce that received no urea treatment. The normality of the data was evaluated using Shapiro-Wilk test and visual interpretations of normal-probability plots. Statistical analyses were performed using the package nlme (Pinheiro et al. 2015) in R, a language and environment for statistical computing (version 3.1.3, R Core Team 2014). Each model was fit using log-likelihood maximization.

RESULTS

The majority of soil chemical properties were similar at the two sites prior to the imposition of treatments (Table 1 and 2). Forest floor (LFH) samples collected from the North Site were slightly higher in electrical conductivity (EC) and concentrations of "total" (i.e. strong acid extractable) B, Cr, Mg, and Na, but were lower in concentrations of "total" Cd, Cu, Mn, Pb and

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Mehlich III “available” extractable P (Ziadi and Tran 2008) as compared to samples collected from South Site (Table 2). Mineral soil (upper 10 cm of mineral soil) collected from North Site exhibited higher clay content and slightly greater concentrations of total N, Mehlich III extractable Mg, “total” Mg, K, and Pb, but lower sand content, as compared to mineral soil collected from South Site (Table 2).

Although both ashes exhibited similar pH (~ 12) and electrical conductivity (EC) ($\sim 11 \text{ dS m}^{-1}$), most other chemical properties were different (Table 3). Most notably, the boiler ash exhibited a much higher total C concentration (297 g kg^{-1}) than the gasifier ash (73 g kg^{-1}), much of the C in the former being in charred organic (i.e. charcoal) form. Calcium carbonate equivalent was greater in the gasifier ash (56 %) than the boiler ash (30 %). Concentrations of total N were very low in both ashes, which is typical for wood ash (Pitman 2006). In general, concentrations of “total” (i.e. strong acid extractable) macronutrients were greater in gasifier ash (Ca, K, Mg, P), but total S was greater in boiler ash. Although “total” Ca was 2.9-fold greater in gasifier, compared to boiler ash, ammonium acetate extractable Ca (considered “available”) was 1.7-fold greater in the latter ash. Both hot water extractable and strong acid extractable B were greater in gasifier ash. Concentrations of some environmentally sensitive trace elements were greater in the gasifier ash (i.e. As, Cr, Co, Cu, Ni, Se), while others were greater in boiler ash (Cd, Hg, Mo, Pb); Zn concentrations did not differ (Table 3). Concentrations of these 11 environmentally sensitive elements fell below the maximum allowable concentrations referenced under the B.C. Code of Practice for Soil Amendments (Government of B.C. 2007) (Table 3).

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The application of bottom ash and urea resulted in a number of changes to soil chemical properties of the LFH, relative to non-amended controls; however, no significant ($p < 0.05$) treatment effects (or treatment interactions) were observed for underlying mineral soil samples (with the exception of a slight increase in exchangeable Na; data not shown). Tables 4 and 5 present soil chemical parameters which exhibited significant ($p < 0.05$) changes in the LFH in response to ash and/or urea fertilization treatments. Data from both sites in Table 4 were combined as the site effect was minimal. Compared to non-ash treated controls, LFH samples collected from gasifier ash treated plots exhibited significantly ($p < 0.05$) greater soil pH, CEC, % BS, exchangeable cations (Ca, Mg, K, Na) as well as total Ca and B. Significant interaction effects were observed for soil pH and total Ca. Forest floor samples collected from plots treated with both gasifier ash and urea had the greatest soil pH and total Ca concentrations (i.e. interaction effects were significant, $p < 0.05$). Forest floor samples collected from boiler ash treated plots also tended to have greater means for these parameters, relative to non-ash treated controls, but differences were only statistically significant for soil pH, % BS, total B and total Ca. Soil pH (across both sites and all treatments) was positively correlated with CEC (Pearson product-moment correlation: $r(34) = 0.51$, $p = 0.0014$), % BS ($r(34) = 0.75$, $p < 0.0001$), exchangeable Ca ($r(34) = 0.54$, $p = 0.0006$), exchangeable Mg ($r(34) = 0.57$, $p = 0.0003$), exchangeable K ($r(34) = 0.35$, $p = 0.035$) and exchangeable Na ($r(34) = 0.60$, $p = 0.0001$). Interestingly, LFH samples collected from gasifier ash treated plots had significantly lower concentrations of total Pb than non-ash treated plots. However, ash or urea treatments had no significant effects on total concentrations of other elements in LFH or mineral soil samples. Treatments had no significant effects on soil electrical conductivity.

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Tables 6 and 7 show mean concentrations of spruce foliar nutrients (and N/S ratio), and a summary of the linear mixed effects models, in response to ash and urea treatments. One season of growth after ash treatments, there was a tendency for increased concentrations of most measured foliar nutrients, except N, relative to non-ash treatments (Figure 1), but significant increases ($p < 0.05$) were only observed for Ca and S (Tables 6 and 7). Data from both sites in Table 6 were combined as the site effect was minimal. Foliar Ca concentrations were significantly higher for spruce in plots treated with boiler ash than for spruce in plots that received no ash. However, these levels were not significantly higher than those for spruce in plots treated with gasifier ash, and there was no significant difference between foliar Ca concentrations of spruce in plots treated with gasifier ash compared to those that received no ash. Foliar S concentrations were significantly higher for gasifier ash treatment as compared to boiler ash or no ash treatments ($p < 0.05$). There was no significant difference between foliar S concentrations of spruce within boiler ash and no ash treatments. All significant differences between ash treatments were independent of urea treatments.

After one season of growth, foliar N levels were significantly higher for spruce treated with urea than for spruce that received no urea (Figure 1). In contrast to the nutrient response to the ash treatments, urea treatments appeared to decrease the levels of most foliar nutrients, with significant ($p < 0.05$) decreases in Mg and P (Tables 6 and 7). Both ash and urea fertilization treatments tended to alter foliar N/S ratios (Tables 6 and 7). Urea fertilizer significantly increased the ratio, but gasifier ash addition significantly decreased the N/S ratio relative to non-ash treatments (Figure 1).

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DISCUSSION**Ash Fertilization**

The application of either boiler or gasifier bottom ash tended to increase foliar concentrations of all analyzed nutrients to some degree, except N (Figure 1); however, significant ($p < 0.05$) increases were only observed for Ca and S (Table 6 and 7). Given the short time frame of this study (treatments were applied in late May 2015 and samples were collected in mid-October the same year), large increases in foliar concentrations of most nutrients were not anticipated.

Following ash application, increases in soil pH, CEC, % BS and exchangeable Ca, Mg, K and Na, were expected (Augusto et al. 2008; Pugliese et al. 2014; Pitman 2006), but were actually only significant in LFH samples. Increases tended to be greater following gasifier ash application, as compared to boiler ash, likely due to its higher CCE and mineral content. We surmise that, over time, the chemical properties of the underlying mineral soil layers will be influenced by the surface ash treatments, as soluble components migrate downward into the soil profile through soil processes and biological activity (Pitman 2006; Reid and Watmough 2014; Brais et al. 2015). We expect the increased soil pH and exchangeable cations due to ash addition to last for many years as they have in other studies (Saarsalmi et al. 2012; Brais et al. 2015). It is not clear why LFH samples in plots receiving urea plus ash exhibited relatively high soil pH, particularly in plots that received gasifier ash with urea. Urea application is known to raise soil pH in the short-term, due to the hydrolysis of the compound via urease (Johnson 1992); however, urea did not raise soil pH in plots of the current study that did not receive ash. This observation prompts further study of possible interaction effects between urea and ash.

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It is interesting to note the increase in foliar Ca resulting from the boiler ash treatment, but not from the gasifier ash treatment. The total Ca added through the gasifier ash application was 194 kg ha⁻¹, while that from the boiler treatment was only 67 kg ha⁻¹. It is possible that Ca originating from the boiler ash was more available for plant uptake than that contained within the gasifier ash; interestingly, available Ca, as determined by ammonium acetate extraction, was greater in the boiler ash (14.4 g kg⁻¹) as compared to the gasifier ash (8.69 g kg⁻¹). This might be due the fact that the gasifier ash was wetted and allowed to react with atmospheric CO₂-C for over six months prior to use in this study. Wetted ash will absorb CO₂ over time, slowly converting CaO and Ca(OH)₂ mineral forms to carbonated forms, which reduces solubility of some ash constituents (Steenari and Lindqvist 1997; Rehl 2014). If this was the case, one would expect lower concentrations of exchangeable Ca in LFH samples from gasifier ash treated plots, as compared to boiler ash treated plots, but the opposite was true. This may be due in part to the fact that soil samples were collected at the end of the growing season and not during the time of active plant uptake.

The increase in foliar Ca after boiler ash application is consistent with some other studies, although results vary widely. In white spruce (*Picea glauca*) seedlings growing on clay loam in northern Saskatchewan, Staples and van Rees (2001) observed an increase in shoot Ca two years after treatment with ash generated from combustion of wood plus pulp mill sludge (5.7:1 mass ratio), and found that Ca was the most responsive element to the treatment. Rates of Ca application in their study were 84.2 kg total Ca ha⁻¹, which is much less than the total Ca loadings of the current study (Table 3). Similarly, Arvidsson and Lundkvist (2002) found an increase in foliar Ca in two to nine-year-old Norway spruce one and five years after application

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of hardened bark ash (891 and 486 kg total Ca ha⁻¹) on sites in Sweden, and comparable results were found in 38-year-old Scots pine growing on glaciofluvial sands in Lithuania (Ozolinčius et al. 2005). The rates of Ca application in these two trials, however, were somewhat higher than the boiler ash treatment (335 kg total Ca ha⁻¹), but less than the gasifier ash application (970 kg total Ca ha⁻¹) in the current study. In other studies, foliar Ca increases following ash applications were only apparent after 6-16 years (Augusto et al. 2008), or were not apparent at all (Genenger et al. 2003; Helmisaari et al. 2008; Saarsalmi et al. 2004, 2006). In 35- to 65-year-old Scots pine and Norway spruce stands on mesic tills located across Sweden, Jacobson (2003) found no increase in Ca after various wood ashes of different origin and constitution were applied either with or without N at rates of up to 2430 kg total Ca ha⁻¹. A recent systematic meta-analysis found that foliar Ca appeared more responsive to liming than to wood ash application (Reid and Watmough 2014).

Site factors such as climate and soil properties will affect the uptake of nutrients, which is reflected in variability of foliar Ca response to wood ash applications. Calcium is an important regulator of growth and stress responses in trees (Lautner and Fromm 2010), and it is likely that trees growing on Ca-deficient sites will more readily take up the nutrient. However, an apparent nutrient uptake after ash application does not necessarily indicate a fertilization effect. For example, increases in Ca concentrations observed by Staples and Van Rees (2001) did not correspond with an increase in biomass, and were therefore attributed to luxury uptake. Based on foliar interpretive guidelines for spruce in interior British Columbia (Brockley 2012), the foliar nutrient concentrations of control trees (those that received neither ash nor urea) indicate that the ALRF sites are not Ca-deficient, and therefore the observed increase in Ca might also be

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attributed to luxury uptake. Without corresponding growth and biomass measurements, it is difficult to determine whether the significant increase in foliar Ca also indicate a fertilization effect. Growth and biomass measurements were not conducted in the current short-term study, but longer-term measurements are planned. These future measurements should allow us to better differentiate luxury and non-luxury nutrient uptakes.

Sulphur values are less commonly reported in the literature than Ca values for wood ash fertilization trials. Sulphur is largely released from ash particles in the first two years after application (Nieminen et al. 2005). However, in contrast to the significant increase in foliar S concentration observed in the first growing season of the ALRF trial, previous studies have reported a lack of response in foliar S over both short- and long-term time scales. Arvidsson and Lundkvist (2002) found that foliar S concentrations did not increase one or five years after wood ash or wood ash plus N applications, even though the total S additions from the ashes used (42 and 87 kg S ha⁻¹) were much higher than the total S additions from the boiler and gasifier ashes of the current study (15 and 9 kg total S ha⁻¹, respectively). Genenger et al. (2003) found similar results two years after application of wood chip ash (26 kg S ha⁻¹) to 70-year-old Norway spruce on Dystric Cambisol sites in Switzerland, and in 60-year-old Scots pine stands on N-poor mineral soil sites in northern Finland. Saarsalmi et al. (2006) also found no change in foliar S concentrations 23 years after treatment with wood ash or bark ash, although the S content of the ashes was not reported. The influence of atmospheric S on the results of these European studies is worth considering. Exposure to SO₂ has been shown to increase foliar S in Norway spruce in laboratory conditions (Tausz et al. 1996) and in experimental stands in England (Shaw and McLeod 1995), and the influence of acidifying deposition has been considered as a site factor in

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ash fertilization effects in Finland (Saarsalmi et al. 2004). The environmental effects of S deposition in Europe have been widely documented (Engardt and Langner 2013; Makipaa 1995; Ruoho-Airola et al. 1998; Syri et al. 2004). While it is speculative to attribute differences in results between the ALRF trial and European studies to the influence of airborne pollutants, the question warrants attention, and highlights the need for further research on the effects of ash fertilization in British Columbia forests that have low atmospheric SO₂ inputs.

Sulphur is an essential macronutrient and plays an important role in the manufacturing of chloroplasts and in electron transport during photosynthesis. In coniferous stands in interior British Columbia, however, S deficiencies have been documented (Swift and Brockley 1994; Wang and Klinka 1997). The interaction between S and N is important in conifers, with the potential for S to have a strong controlling influence on the uptake of N (Swift and Brockley 1994), and N fertilization to induce S deficiency and reduce growth (Brockley and Sheran 1994). The mean foliar N/S ratio for spruce in the ALRF trial control plots was 12.8 for the North Site and 11.8 for the South Site (values are normalized for inter-laboratory comparisons, Brockley 2012), and a foliar N/S ratio of less than 15 has been suggested to imply no deficiency for spruce in interior British Columbia (Brockley 2012). Based on this threshold, the spruce growing in the ALRF trial are not S-deficient. Based on S concentration, the control trees at the ALRF sites were moderately to severely S-deficient (in range of 0.6 to 0.8 g S kg⁻¹), but the same interpretive guide indicates N/S ratios have a higher interpretive value than S concentration (Brockley 2012). Spruce growing on these sites may be susceptible to induced S-deficiency following N fertilization. In our study, the foliar N/S ratios of the spruce treated with urea were significantly less favorable than those that received no urea (Figure 1, Table 6), while the foliar N/S ratios of

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the spruce treated with gasifier ash were significantly more favorable than those that received no ash. The significant increase in spruce foliar S concentration following ash addition in the current study suggests that an ash-N fertilizer combination may be more effective than a N-only fertilizer on similar sites; this is supported by the more favorable N/S ratios observed in the ash-treated sites. In a serial batch extraction analysis designed to emulate long-term weathering, Rehl (2014) observed a 27% total mass loss of S from the same gasifier ash used in this study, and also more sustained SO_4^{2-} concentrations in the ash leachate relative to other anion concentrations over time; this supports the hypothesis that wood ash amendments can be used as a source of plant-available S. Although no significant ash x urea interaction effects were observed for foliar S over one growing-season, it would be worthwhile to determine if interaction effects develop over time.

The general trend for increased foliar B following ash addition (Figure 1), although not statistically significant, is also notable. Numerous studies have reported increases in foliar B after wood ash applications, although the total B applied through ash in these trials was typically higher than B application via boiler ash ($0.34 \text{ kg total B ha}^{-1}$) or the gasifier ash ($0.93 \text{ kg total B ha}^{-1}$) in the current study. It is notable that the total B concentration within the LFH tended to increase following ash application (though only significantly ($p < 0.05$) in the case of gasifier ash addition). Boron is largely released from ash particles during the first two years after application (Nieminen et al. 2005) and, in Swedish coniferous stands growing on mineral soil, Jacobson (2003) found a significant increase in Scots pine and Norway spruce foliar B three to five years after treatment with various hardened wood ashes (0.13 to $2.74 \text{ kg B ha}^{-1}$). In Scots pine growing on peat sites in central Finland, Hytonen (2003) found a similar increase in B from wood ash

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fertilization (1.7 kg B ha^{-1}) only one year after treatment. Other Finnish studies have shown the effects of B fertilization from wood ash application to coniferous stands can be long-lasting. Three different studies of coniferous stands on mineral soils in central and northern Finland showed that the application of various wood ashes or wood ashes plus N increased foliar B concentrations 5, 10, 12 and 23 years after treatment (Saarsalmi et al. 2004, 2005, 2006). Twenty-three years after loose wood ash plus N application ($1.35 \text{ kg B ha}^{-1}$, 185 kg N ha^{-1}), B was the only foliar nutrient that remained significantly higher than the control values (Saarsalmi et al. 2006).

Boron is an important micronutrient for maintaining tree growth. Widespread B deficiencies have been documented in British Columbia (Brockley 1990). Swift and Brockley (1994) found that hybrid spruce in interior British Columbia showed an increase in foliar B concentrations one year after a complete fertilization treatment (2.2 kg B ha^{-1}). Pre-existing B deficiencies may limit the effectiveness of N fertilizer applied to lodgepole pine stands in interior British Columbia (Brockley 1989, 1990). Based on Brockley's (2012) interpretive nutrient guidelines for spruce growing in interior British Columbia, the control spruce of the current study are not B-deficient ($>12 \text{ mg kg}^{-1}$). However, Brockley (2003) found that N fertilization increased the severity of B deficiencies in some lodgepole pine stands, resulting in reduced growth and top dieback. Although the increase in foliar B in the ALRF trial was not significant one growing-season after ash application, it is likely that wood ash fertilization could be effective in mitigating B deficiencies in British Columbia, particularly in stands treated with N. It would be worthwhile to monitor both relative changes in foliar B concentrations and if significant interaction effects between the ash and urea treatments develop over a longer-term.

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Also worth noting is the lack of significant change in either foliar K or P concentrations one growing-season after wood ash treatments. These results are consistent with what was found by Ozolinčius et al. (2005) in 38-year-old Scots pine growing on sandy soil in Lithuania, but increases in these nutrients have been reported in similar studies (Arvidsson and Lundkvist 2002; Jacobson 2003; Saarsalmi et al. 2004). Time between ash application and sample collection is likely a factor in regard to differences between the results of the ALRF trial and other studies. For example, Arvidsson & Lundkvist (2002) found no increase in either K or P concentrations in Norway spruce needles one year after ash application, but did find an increase in both nutrients five years after application. Discrepancies in study results may also be related to other factors, including ash composition and site nutrient levels. Ashes used in trials that reported increases in foliar P tended to have a much higher P content than either the ashes used in the current study, and based on Brockley's (2012) guidelines, the foliar K and P values of the ALRF controls are adequate.

The lack of significant change in foliar N concentrations after wood ash application is consistent with what has been observed in other studies (Arvidsson & Lundkvist 2002; Jacobson 2003; Hytonen 2003; Saarsalmi et al. 2004). Brais et al. (2015) reported no significant effect of ash addition (up to 8 Mg ha⁻¹) on foliar N concentrations of mature jack pine (*Pinus banksiana* Lamb.) one to two years after application, even though potential mineralizable N was increased 3-fold during a laboratory incubation of forest floor soil. It is notable that addition of high carbon boiler ash (30% total C, with a C:N ratio of >300) at an application rate of 5000 kg ha⁻¹ did not influence foliar N concentrations in our study. Some charcoals may reduce N availability

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to plants through net N immobilization (Deenik 2011). Pugliese et al. (2014) reported a small reduction of NH_4^+ -N, but an increase in NO_3^- -N concentration, following addition of high carbon (~ 16% total C) ash (equivalent to 5 Mg ha^{-1}) to soils in laboratory incubations. Omil et al. (2013) reported slightly reduced N mineralization rates in sandy loam soil following additions of high carbon ash, but foliar N concentrations in mature Monterey pine stands (1 to 2 years following one or three annual doses at 4.5 Mg ha^{-1}) were not changed by ash addition. The influence of ash addition on net N mineralization-immobilization is in part dictated by the N status of the site (Rosenberg et al. 2010; Omil et al. 2013).

One concern about wood ash application to forest systems is the potential risk of metal loading to forest soils. As such, most jurisdictions have criteria to evaluate ash quality in terms of its suitability for use as soil amendments (Hannam et al. 2016; Haglund 2008; Ribbing and Bjurström 2011). Both bottom ashes used in this study exhibited trace element concentrations which were relatively low compared to the maximum allowable concentrations identified within British Columbia regulations (Government of B.C. 2007). Of the 11 elements targeted by the regulation, most elements in these two ashes had concentrations that were lower than, or similar to, the baseline (untreated) soils used in this study; only Cu (gasifier ash), Mo and Zn exhibited elevated concentrations compared to baseline soils. Ash treatments did not significantly increase the “total” (i.e. strong acid soluble) concentrations of any trace elements within LFH or mineral soil samples. We cannot explain the significant decrease in total Pb within gasifier treated LFH soil (relative to non-ash treated control) and recommend further monitoring of these plots.

Urea Fertilization

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Urea fertilization significantly increased the foliar N concentration of spruce one growing-season after application (Table 1, Figure 1). In contrast to results from the ash fertilization, the urea fertilization also appeared to decrease foliar Ca, Mg, Mn, P, and Zn concentrations. A significant ($p < 0.05$) decrease was observed for foliar P, and for foliar Mg, although just barely ($p = 0.049$).

The significant increase in foliar N concentration observed in the spruce is not surprising, and other studies in British Columbia and Central Europe have reported similar results one to two years after treatment with N fertilizer, with or without wood ash (Brockley and Sheran 1994; Genenger et al. 2003; Ozolinčius et al. 2005; Swift and Brockley 1994); however, the effect may only exist in the short-term. Jacobson (2003) found that increased concentrations of foliar N following wood ash plus N applications (150 kg N ha^{-1}) were no longer apparent five to seven years after treatment. Likewise, Saarsalmi et al. (2004), Helmisaari et al. (2008), and Saarsalmi et al. (2006) found that the addition of wood ash plus N ($120\text{--}185 \text{ kg N ha}^{-1}$) had no effect on needle N concentrations of Scots pine and Norway spruce growing on mineral soils 5 and 10, 10, and 23 years after treatment, respectively. It would be worthwhile to re-measure foliar N in the plots no more than five years after treatment to determine a timeline for foliar N response.

Nitrogen is a major limiting nutrient in terrestrial ecosystems (Vitousek and Howarth 1991), and N deficiency is common in coniferous stands throughout British Columbia (Ballard and Carter 1986). Because coniferous stands growing on mineral soil are generally N-deficient, co-application of N fertilizer with ash has been widely studied as a means of increasing plant uptake of nutrients released from ash (e.g. Genenger et al. 2003; Jacobson et al. 2003; Ozolinčius et al. 2005; Saarsalmi et al. 2004, 2006). Similarly, the effectiveness of N fertilization in increasing

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coniferous tree growth can be limited if other nutrients are not sufficiently available (consistent with Liebig's Law of the Minimum) (Brockley 1989, 1990; Brockley and Sheran 1994; Swift and Brockley 1994), which might be mitigated by the addition of wood ash (Brockley et al. 1989, 1990; Saarsalmi et al. 2006). The mean foliar N values of 1.08% and 1.18% for control spruce in the North Site and South Site, respectively, have been suggested to represent severe N deficiency for hybrid spruce growing in the SBS Zone (Swift and Brockley 1994); this is consistent with the foliar interpretive guidelines from Brockley (2012). The observed increase in foliar N concentration, however, may be attributed to luxury consumption (Swift and Brockley 1994), and without corresponding observations of increased growth, does not indicate a fertilizer effect on its own. Subsequent measurements in the plots should examine potential interaction effects of ash and urea treatments on foliar nutrient concentrations, with complementary growth data, to better assess the effectiveness of the combination wood ash plus N fertilization treatments in coniferous stands in British Columbia.

Reasons for the significant decreases in foliar Mg and P concentrations following urea application are less immediately apparent. It is possible that the change is due to a dilution effect and that the values do not reflect lower total nutrient levels, but rather lower relative nutrient levels resulting from an increase in needle mass. Swift and Brockley (1994) observed a decrease in foliar K concentration following N application to hybrid spruce in the SBS Zone, which they hypothesized could be due to a dilution effect, and similar decreases in foliar Mn following applications of wood ash (3000 kg ha⁻¹) plus N (120-150 kg ha⁻¹) to Scots pine and Norway spruce stands on sandy sites across Finland have been reported (Saarsalmi et al. 2004). The rationale of an N-induced dilution effect contributing to the observed decreases in Mg and P is

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supported by corresponding, although non-significant, decreases in Ca, Mn, and Zn concentrations. In comparison, none of these nutrients decreased as a result of ash applications. Huotari et al. (2015) recommend accounting for a dilution effect in foliar nutrient analyses by calibrating nutrient values with the relative mass of individual needles. However, because of variation in the needle biomass distribution between different trees, reliably calibrating changes in foliar nutrients to changes in needle mass would be a challenging task.

Another possible explanation for the observed decrease in foliar Mg and P concentrations is an antagonistic interaction between the addition of N and the bio-availability of these nutrients, which Swift and Brockley (1994) also suggested could have caused the decreases in foliar K they observed. Soil nutrient availability can also be affected by changes in pH (Pitman 2006), which is increased in the range of 0.5-3 units following ash application (Huotari et al. 2015). However, a decrease in foliar concentrations of these nutrients was not observed in plots treated with ash, and there was no significant ash-urea treatment interaction effects for these nutrients. If an N-induced dilution effect is occurring in spruce, it should dissipate over time, as increases in foliar N concentrations attenuate. Monitoring the N fertilization effect and the ash-urea treatment interaction effect on Ca, Mg, Mn, P, and Zn over time, particularly over the next five to seven years, would help to better assess whether the decrease in nutrients that were observed in this study should be attributed to a dilution effect or to other factors.

It is notable that changes in foliar nutrient concentrations were not significantly affected by ash-urea treatment interactions (Table 6 and 7). In similar studies, the application of wood ash plus N to coniferous stands on N-limited sites has been shown to be more effective as a fertilizer, by

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increasing both foliar nutrient levels and tree growth more significantly than the application of wood ash alone (Jacobson 2003; Saarsalmi et al. 2004, 2006). Treatment interaction effects may become apparent over time as more nutrients are released from the ash and made available for uptake. Wang and Klinka (1997) warn against using foliar nutrient concentrations on their own as indicators of nutrient deficiencies, and treatment interaction effects can provide useful information on the nutrient status of the sites and the trees. It would be interesting, for example, to determine if the increase in foliar S concentration following gasifier ash application is related to a more sustained increase in N uptake for trees that received both gasifier ash and urea treatments.

CONCLUSIONS

From this short-term field study, conducted within the Sub-Boreal Spruce biogeoclimatic zone in B.C., we conclude the following. 1) Application of either boiler or gasifier bottom ash tended to increase foliar concentrations of all analyzed nutrients to some degree, except N; however, significant ($p < 0.05$) increases were only observed for Ca and S. In general, the addition of gasifier ash (low C) resulted in more pronounced increases in soil pH and exchangeable cations within LFH soil than boiler ash; however, these trends were not always statistically significant. We expect these enhancements to soil properties to last for many years; over time we expect to observe similar trends in underlying mineral soil. 2) Differences in site preparation and stand age present in this study had minimal influence on the short-term responses of spruce to ash and urea-N treatments. 3) There was no evidence of short-term N immobilization due to the large addition of C-rich and high C/N ratio boiler ash. 4) The addition of either ash type did not significantly increase concentrations of environmentally sensitive trace elements in LFH (or

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mineral) soil as compared to the non-amended control. Trace element concentrations in these ashes fell below regulatory limits set by the B.C. Code of Practice for Soil Amendments.

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Fig. 1. Relative mean nutrient concentrations in current-year spruce needles, one growing-season after treatment of plots with ash and/or urea fertilizer. Values for spruce treated with boiler ash (Ab, n = 24) and spruce treated with gasifier ash (Ag, n = 24) are relative to means for spruce that received no ash treatment ($CO_{ASH} = 100\%$, n = 24); values for spruce treated with urea (N, n = 36) are relative to means for spruce that received no urea treatment ($CO_N = 100\%$, n = 36). S values are from the acid digestion method of analysis. N/S values are normalized for inter-laboratory comparison (Brockley 2012). Levels of significance compared to untreated control are denoted by *, $p < 0.05$ and **, $p < 0.001$ based on analysis of variance (Table 7). Relative mean values for foliar Cu are omitted because of large variance in results.

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Table 1. Selected initial properties (2014) of LFH horizons at North Site and South Site. Means with standard deviations. Ranges are shown when some data fell below detection. Concentrations expressed on an oven-dry mass basis.

Parameter	North Site (n=18) ^a	South Site (n=18) ^a	Overall (n=36) ^b
Forest Floor thickness (cm)	5.4 (2.0)	5.1 (1.7)	5.2 (1.9)
pH (1:1 H ₂ O:soil)	4.64 (0.18)	4.60 (0.13)	4.62 (0.15)
EC (dS m ⁻¹)	0.433** (0.067)	0.366 (0.053)	0.399 (0.068)
Total C (g kg ⁻¹)	220.7 (51.0)	232.6 (63.7)	226.7 (57.2)
Inorganic C (g kg ⁻¹)	<0.5 – 9.1	<0.5 – 8.7	<0.5 – 9.1
Total N (g kg ⁻¹)	7.13 (1.47)	7.78 (2.05)	7.45 (1.8)
Total S (g kg ⁻¹)	0.74 (0.16)	0.74 (0.17)	0.74 (0.16)
CEC (cmol _c kg ⁻¹)	32.93 (8.48)	34.60 (6.88)	33.77 (7.66)
Base saturation (%)	92.1 (2.6)	90.0 (4.5)	91.0 (3.9)
<i>Mehlich III Extractable “Available” Nutrients</i>			
B (mg kg ⁻¹)	<0.6 – 1.2	<0.6	<0.6 – 1.2
Ca (mg kg ⁻¹)	3430 (1110)	3440 (900)	3440 (1000)
Cu (mg kg ⁻¹)	2.23 (0.66)	2.60 (0.99)	2.42 (0.85)
Fe (mg kg ⁻¹)	681 (107)	693 (131)	687 (118)
K (mg kg ⁻¹)	450 (108)	498 (119)	474 (115)
Mg (mg kg ⁻¹)	597 (70)	597 (120)	597 (97)
Mn (mg kg ⁻¹)	377 (146)	452 (177)	415 (165)
P (mg kg ⁻¹)	152 (46)	208** (60)	180 (60)
S (mg kg ⁻¹)	48 (13)	50 (19)	49 (16)
<i>“Total” Concentration by Strong Acid Digestion followed by ICP-OES</i>			
As (mg kg ⁻¹)	<4 – 11.9	<4 – 10.3	<4 – 11.9
B (mg kg ⁻¹)	10.5** (1.8)	8.7 (1.7)	9.6 (1.9)
Ca (g kg ⁻¹)	7.60 (2.41)	7.59 (1.61)	7.59 (2.02)
Cd (mg kg ⁻¹)	3.1 (0.5)	3.6* (0.6)	3.3 (0.6)
Co (mg kg ⁻¹)	22.2 (3.7)	23.2 (6.3)	22.7 (5.2)
Cr (mg kg ⁻¹)	38.9* (5.7)	34.6 (5.2)	36.7 (5.8)
Cu (mg kg ⁻¹)	16.9 (4.1)	20.1* (4.2)	18.5 (4.4)
Hg (mg kg ⁻¹)	<3.0	<3.0	<3.0
K (g kg ⁻¹)	5.45*** (0.67)	4.10 (0.43)	4.77 (0.88)
Mg (g kg ⁻¹)	5.13** (0.79)	4.37 (0.79)	4.75 (0.87)
Mn (mg kg ⁻¹)	2090 (690)	3040** (1160)	2570 (1050)
Mo (mg kg ⁻¹)	<2	<2	<2
Na (mg kg ⁻¹)	426*** (57)	338 (49)	382 (69)
Ni (mg kg ⁻¹)	21.2 (3.9)	22.4 (4.3)	21.8 (4.1)
P (g kg ⁻¹)	1.25 (0.27)	1.40 (0.22)	1.32 (0.25)
Pb (mg kg ⁻¹)	8.7 (1.7)	10.0* (1.8)	9.4 (1.8)
Se (mg kg ⁻¹)	<6	<6	<6
Zn (mg kg ⁻¹)	110 (27)	109 (20)	110 (23)

Note: Bold text indicates significant differences between North and South Site; *, ** and *** indicate a significantly greater mean at $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

^a n = 12 for As, B (Mehlich III and total), Inorganic C, Hg and Se.

^b n = 24 for As, B (Mehlich III and total), Inorganic C, Hg and Se.

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Table 2. Selected initial properties (2014) of upper mineral soils (upper 10 cm mineral) at North Site and South Site. Means with standard deviations. Ranges are shown when some data fell below detection. Concentrations expressed on an oven-dry mass basis.

Parameter	North Site (n=18) ^a	South Site (n=18) ^a	Overall (n=36) ^b
Sand (%)	8.98 (4.97)	15.37** (5.52)	11.35 (5.97)
Silt (%)	53.57 (5.74)	54.88 (3.27)	54.04 (4.94)
Clay (%)	37.45** (5.42)	29.75 (5.52)	34.60 (6.55)
pH (1:1 H ₂ O:soil)	4.60 (0.12)	4.55 (0.10)	4.57 (0.11)
EC (dS m ⁻¹)	0.164 (0.035)	0.147 (0.029)	0.155 (0.033)
Total C (g kg ⁻¹)	21.5 (6.5)	18.4 (3.4)	20.0 (5.4)
Inorganic C (g kg ⁻¹)	<0.5 – 0.6	<0.5	<0.5 – 0.6
Total N (g kg ⁻¹)	1.42* (0.35)	1.22 (0.21)	1.32 (0.30)
Total S (g kg ⁻¹)	0.12 (0.03)	0.10 (0.02)	0.11 (0.03)
CEC (cmol _c kg ⁻¹)	10.20 (1.79)	10.16 (1.78)	10.18 (1.76)
Base saturation (%)	76.7 (6.2)	71.0 (5.2)	74.0 (6.2)
<i>Mehlich III Extractable “Available” Nutrients</i>			
B (mg kg ⁻¹)	<0.6	<0.6	<0.6
Ca (mg kg ⁻¹)	887 (209)	793 (139)	840 (181)
Cu (mg kg ⁻¹)	<1 – 1.73	1.32 (0.22)	<1 – 1.73
Fe (mg kg ⁻¹)	466 (42)	455 (59)	460 (51)
K (mg kg ⁻¹)	104 (23)	106 (17)	105 (20)
Mg (mg kg ⁻¹)	270* (57)	236 (37)	253 (50)
Mn (mg kg ⁻¹)	45 (23)	33 (16)	39 (20)
P (mg kg ⁻¹)	44.8 (8.6)	49 (13)	47 (11)
S (mg kg ⁻¹)	10 (3)	9 (2)	9 (3)
<i>“Total” Concentration by Strong Acid Digestion followed by ICP-OES</i>			
As (mg kg ⁻¹)	<4 – 16.6	<4 – 16.0	<4 – 16.6
B (mg kg ⁻¹)	<5 – 11.5	8.3 (2.1)	<5 – 13.9
Ca (g kg ⁻¹)	3.7 (0.4)	3.9* (0.3)	3.8 (0.4)
Cd (mg kg ⁻¹)	3.6 (0.7)	3.6 (0.7)	3.6 (0.7)
Co (mg kg ⁻¹)	32.7 (3.5)	30.0 (4.8)	31.4 (4.4)
Cr (mg kg ⁻¹)	55.8 (5.8)	54.7 (5.2)	55.2 (5.5)
Cu (mg kg ⁻¹)	21.9 (4.5)	24.3 (5.2)	23.1 (4.9)
Hg (mg kg ⁻¹)	<3	<3	<3
K (g kg ⁻¹)	5.98** (0.94)	5.04 (0.66)	5.51 (0.93)
Mg (g kg ⁻¹)	8.33* (0.93)	7.56 (0.85)	7.95 (0.96)
Mn (mg kg ⁻¹)	1542 (413)	1359 (534)	1450 (480)
Mo (mg kg ⁻¹)	<2	<2	<2
Na (mg kg ⁻¹)	524 (99)	514 (71)	519 (85)
Ni (mg kg ⁻¹)	31.6 (4.1)	30.1 (4.2)	30.8 (4.2)
P (g kg ⁻¹)	1.00 (0.10)	1.01 (0.13)	1.00 (0.11)
Pb (mg kg ⁻¹)	10.7* (1.4)	9.7 (1.4)	10.2 (1.5)
Se (mg kg ⁻¹)	<6	<6	<6
Zn (mg kg ⁻¹)	120 (17)	113 (17)	117 (17)

Note: Bold text indicates significant differences between North and South Site; *, ** and *** indicate a significantly greater site mean at $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

^a n = 12 for As, B (Mehlich III and total), Inorganic C, Hg and Se; n = 17 and 10 for North Site sand, silt, clay; n = 10 for South Site sand, silt, clay.

^b n = 24 for As, B (Mehlich III and total), Inorganic C, Hg and Se; n = 27 for sand, silt, clay.

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Table 3. Selected chemical properties of the two bottom ashes used in this trial, and upper concentration limits for trace elements under the BC CoPSA^a. Both ashes applied to research plots at 5000 kg ha⁻¹. Concentrations expressed on an equivalent oven-dry mass basis.

Analyte	Units	Gasifier ash	Boiler ash	CoPSA
pH (1:2 ash:water)	pH	11.7	12.0	
EC ^b (1:2 ash:water)	dS m ⁻¹	10.5	11.0	
CCE ^c	% CCE	55.8	30.4	
H ₂ O content	g H ₂ O 100g ⁻¹ solids	53.5	27.1	
Total C	g kg ⁻¹ (kg ha ⁻¹)	73.1 (366)	297 (1490)	
Total Organic C	g kg ⁻¹ (kg ha ⁻¹)	35.8 (179)	285 (1430)	
Total N	g kg ⁻¹ (kg ha ⁻¹)	0.80 (4.0)	0.90 (4.5)	
Total S	g kg ⁻¹ (kg ha ⁻¹)	1.8 (9.0)	2.8 (14.0)	
<i>“Available” (easily extractable^d) Nutrients</i>				
B	mg kg ⁻¹ (kg ha ⁻¹)	53.6 (0.268)	11.8 (0.059)	
Ca	g kg ⁻¹ (kg ha ⁻¹)	8.69 (43.5)	14.4 (72.0)	
K	g kg ⁻¹ (kg ha ⁻¹)	15.9 (79.5)	9.55 (47.8)	
Mg	g kg ⁻¹ (kg ha ⁻¹)	2.01 (10.1)	0.941 (4.71)	
NH ₄ ⁺ -N	mg kg ⁻¹ (kg ha ⁻¹)	<2	<2	
NO ₃ ⁻ -N	mg kg ⁻¹ (kg ha ⁻¹)	70 (0.35)	50 (0.25)	
P	mg kg ⁻¹ (kg ha ⁻¹)	46 (0.23)	23 (0.12)	
<i>“Total” Concentration by Strong Acid Digestion^e followed by ICP-OES</i>				
As	mg kg ⁻¹ (kg ha ⁻¹)	6.21 (0.0311)	1.23 (0.00615)	75
B	mg kg ⁻¹ (kg ha ⁻¹)	185.9 (0.930)	67.9 (0.340)	
Ca	g kg ⁻¹ (kg ha ⁻¹)	194 (970)	67 (335)	
Cd	mg kg ⁻¹ (kg ha ⁻¹)	2.08 (0.0104)	2.90 (0.0145)	20
Cr	mg kg ⁻¹ (kg ha ⁻¹)	23.9 (0.120)	14.5 (0.0725)	1060
Co	mg kg ⁻¹ (kg ha ⁻¹)	7.95 (0.0398)	4.61 (0.0231)	150
Cu	mg kg ⁻¹ (kg ha ⁻¹)	63.0 (0.315)	27.6 (0.138)	2200
K	g kg ⁻¹ (kg ha ⁻¹)	50.6 (253)	15.9 (79.5)	
Hg	mg kg ⁻¹ (kg ha ⁻¹)	0.026 (1.3x10 ⁻⁴)	0.045 (2.3x10 ⁻⁴)	5
Mg	g kg ⁻¹ (kg ha ⁻¹)	25.8 (129)	6.6 (33)	
Mn	g kg ⁻¹ (kg ha ⁻¹)	9.28 (46.4)	1.71 (8.55)	
Mo	mg kg ⁻¹ (kg ha ⁻¹)	4.58 (0.0229)	5.48 (0.0274)	20
Na	g kg ⁻¹ (kg ha ⁻¹)	7.4 (37)	1.8 (9.0)	
Ni	mg kg ⁻¹ (kg ha ⁻¹)	38.1 (0.191)	18.9 (0.0945)	180
P	mg kg ⁻¹ (kg ha ⁻¹)	6400 (32.0)	2680 (13.4)	
Pb	mg kg ⁻¹ (kg ha ⁻¹)	1.4 (0.0070)	3.0 (0.015)	500
Se	mg kg ⁻¹ (kg ha ⁻¹)	2.2 (0.011)	1.4 (0.0070)	14
Zn	mg kg ⁻¹ (kg ha ⁻¹)	435 (2.18)	439 (2.20)	1850

^a CoPSA – maximum allowable under B.C. Code of Practice for Soil Amendments (Government of B.C. 2007).^b EC – electrical conductivity (Miller and Curtin 2008).^c CCE – % calcium carbonate equivalent (Goh and Mermut 2008)^d Available B determined by hot water extraction- Azomethine-H (Hettiarachchi and Gupta 2008); available Ca and Mg by ammonium acetate extraction (Hendershot et al. 2008); available K and P by Modified Kelowna Method (Ashworth and Mrazek 1995); available ammonium -N and nitrate-N by KCl extraction (Maynard et al. 2008).^e Concentrated acid digestion (HCl and HNO₃) in either a digestion block or microwave; CoPSA listed elements in both ashes digested using BC SALM (Austin 2015) ; others using EPA 3050B or 3051A (US EPA 1996, 2007).

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Table 4. Mean (and SD) chemical properties of LFH soil samples (North Site and South Site combined) that showed statistically significant ($p < 0.05$) ash or urea treatment effects five months after imposition of treatments. Concentrations expressed on an equivalent oven-dry mass basis. See Table 5 for more information regarding statistical analyses.

	N Treatment	Ash Treatment			Mean of N Treatment
		No Ash	Boiler Ash	Gasifier Ash	
soil pH	No N	4.69 (0.26)	5.21 (0.36)	5.23 (0.43)	5.05b (0.42)
	N	4.62 (0.27)	5.36 (0.39)	6.21 (0.29)	5.40a (0.73)
	Mean (within ash)	4.66c (0.27)	5.29b (0.37)	5.72a (0.62)	
CEC ($\text{cmol}_c \text{ kg}^{-1}$)	No N	31.3 (7.4)	41.6 (9.9)	41.7 (11.7)	38.2 (10.5)
	N	30.4 (5.5)	35.6 (6.4)	44.5 (8.3)	36.8 (8.8)
	Mean (within ash)	30.9b (6.2)	38.6ab (8.6)	43.1a (9.8)	
BS (%)	No N	90.4 (5.7)	94.9 (3.3)	96.0 (2.3)	93.7b (4.5)
	N	92.8 (1.9)	97.1 (1.0)	98.5 (0.8)	96.1a (2.8)
	Mean (within ash)	91.6b (4.2)	96.0a (2.6)	97.3a (2.1)	
Exch Ca ($\text{cmol}_c \text{ kg}^{-1}$)	No N	21.9 (6.3)	31.1 (9.2)	29.4 (8.9)	27.5 (8.8)
	N	21.6 (5.0)	26.6 (5.9)	33.0 (6.0)	27.1 (7.2)
	Mean (within ash)	21.8b (5.4)	28.8ab (7.7)	31.2a (7.5)	
Exch Mg ($\text{cmol}_c \text{ kg}^{-1}$)	No N	5.0 (1.6)	6.6 (1.1)	8.5 (2.4)	6.7 (2.2)
	N	5.3 (1.0)	6.2 (0.6)	8.6 (1.3)	6.7 (1.7)
	Mean (within ash)	5.2b (1.3)	6.4b (0.9)	8.6a (1.9)	
Exch K ($\text{cmol}_c \text{ kg}^{-1}$)	No N	1.4 (0.5)	1.8 (0.4)	2.0 (0.8)	1.7 (0.6)
	N	1.2 (0.2)	1.6 (0.2)	2.0 (1.0)	1.6 (0.6)
	Mean (within ash)	1.3b (0.4)	1.7ab (0.3)	2.0a (0.9)	
Exch Na ($\text{cmol}_c \text{ kg}^{-1}$)	No N	0.08 (0.04)	0.13 (0.04)	0.24 (0.09)	0.15 (0.09)
	N	0.06 (0.03)	0.11 (0.02)	0.29 (0.11)	0.15 (0.12)
	Mean (within ash)	0.07b (0.04)	0.12b (0.03)	0.26a (0.10)	
B, total (mg kg^{-1})	No N	8.53 (4.67)	8.57 (2.31)	9.05 (2.73)	8.72 (3.20)
	N	5.52 (1.52)	6.48 (0.80)	10.9 (2.28)	7.63 (2.87)
	Mean (within ash)	7.03c (3.67)	7.53ab (1.9)	9.98a (2.59)	
Ca, total (g kg^{-1})	No N	7.36 (2.04)	9.16 (1.69)	8.71 (2.26)	8.41 (2.04)
	N	6.70 (1.03)	8.18 (0.90)	11.4 (1.86)	8.76 (2.37)
	Mean (within ash)	7.03b (1.58)	8.67a (1.39)	10.04a (2.42)	
Pb, total (mg kg^{-1})	No N	11.21 (4.22)	8.78 (2.69)	7.85 (2.40)	9.28 (3.35)
	N	10.57 (1.92)	8.65 (2.68)	8.15 (2.46)	9.12 (2.47)
	Mean (within ash)	10.89a (3.15)	8.72ab (2.56)	8.00b (2.32)	

Note: Significant ash: fertilizer interaction effects found for soil pH, and total Ca (Table 5); adjacent means (within ash or within N treat.) not significantly different ($p < 0.05$) from each other if no lower case letters are shown, or if they share the same letter within a row or column.

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Table 5. Results from linear mixed-effects models of LFH soil chemical properties, five months after plots were treated with ash and/or urea (n = 36), with treatments as fixed effects and site (North or South) as a random effect.

	Ash Treat		N Treatment		Ash Treat: N Treat		Random Effect SD	
	F-Value	p-value	F-value	p-value	F-value	p-value	Site	Residual
pH	29.5	<0.0001	9.54	0.0044	7.92	0.0018	3.71x10 ⁻⁶	0.311
CEC	6.78	0.004	0.246	0.623	0.867	0.431	1.88	7.51
BS	12.0	<0.0001	5.64	0.024	0.005	0.955	7.05x10 ⁻⁵	2.71
Exch Ca	5.97	0.007	0.034	0.854	1.01	0.377	1.24	6.35
Exch Mg	16.7	<0.0001	0.001	0.98	0.188	0.830	4.21x10 ⁻⁵	1.32
Exch K	3.63	0.039	0.424	0.52	0.068	0.935	0.112	0.55
Exch Na	29.1	<0.0001	0.046	0.831	1.14	0.333	0.015	0.058
B, total	4.30	0.0232	1.52	0.228	2.88	0.0725	0.376	2.41
Ca, total	9.42	0.0007	0.381	0.542	4.24	0.0243	2.77x10 ⁻⁶	0.156
Pb, total	3.90	0.0317	0.0335	0.856	0.0972	0.9077	0.906	2.41

Note: Only analyses showing significant differences between treatment means have been included and significant p values (p < 0.05) are in bold; for significant ash treatment effects; Tukey’s HSD test compared differences between treatment means. SD = standard deviation.

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Table 6. Mean (and standard deviation) foliar concentrations (and adjusted N/S concentration ratios) of current year spruce foliar samples (North Site and South Site combined) collected five months after imposition of treatments. Concentrations expressed on an oven-dry mass basis. See Table 7 for more information regarding statistical analyses.

	N Treatment	Ash Treatment			Mean (within N Treatment)
		No Ash	Boiler Ash	Gasifier Ash	
B (mg kg ⁻¹)	No N	13.50 (2.90)	15.34 (5.52)	13.21 (3.35)	14.02 (4.08)
	N	13.45 (2.98)	14.19 (2.85)	15.82 (3.18)	14.48 (3.09)
	Mean (within ash)	13.48 (2.88)	14.77 (4.33)	14.52 (3.46)	
Ca (g kg ⁻¹)	No N	7.11 (1.17)	7.87 (1.32)	7.45 (1.26)	7.48 (1.25)
	N	6.85 (0.88)	7.68 (0.68)	6.85 (1.23)	7.13 (1.01)
	Mean (within ash)	6.98c (1.02)	7.77a (1.03)	7.15ab (1.26)	
Cu (mg kg ⁻¹)	No N	4.44 (4.18)	5.30 (3.50)	6.10 (4.86)	5.28 (4.15)
	N	3.54 (1.53)	5.57 (4.17)	9.90 (11.94)	6.34 (7.63)
	Mean (within ash)	3.99 (3.11)	5.44 (3.77)	8.00 (9.12)	
K (g kg ⁻¹)	No N	6.38 (0.66)	6.86 (1.11)	6.38 (0.74)	6.54 (0.87)
	N	6.31 (0.72)	6.50 (0.64)	6.57 (0.89)	6.46 (0.75)
	Mean (within ash)	6.34 (0.67)	6.68 (0.90)	6.47 (0.81)	
Mg (g kg ⁻¹)	No N	0.97 (0.12)	1.08 (0.24)	1.08 (0.15)	1.04a (0.18)
	N	0.96 (0.09)	0.99 (0.08)	0.98 (0.12)	0.98b (0.10)
	Mean (within ash)	0.96 (0.10)	1.04 (0.18)	1.03 (0.15)	
Mn (mg kg ⁻¹)	No N	895 (218)	957 (279)	968 (255)	940 (247)
	N	881 (200)	894 (219)	885 (131)	887 (182)
	Mean (within ash)	888 (204)	926 (247)	926 (203)	
N (g kg ⁻¹)	No N	11.3 (0.8)	11.3 (1.0)	11.5 (0.7)	11.3b (0.8)
	N	12.7 (0.7)	12.1 (0.6)	12.7 (1.4)	12.5a (1.0)
	Mean (within ash)	12.0 (1.0)	11.7 (0.9)	12.1 (1.2)	
P (g kg ⁻¹)	No N	1.83 (0.16)	1.92 (0.29)	1.90 (0.17)	1.88a (0.21)
	N	1.68 (0.09)	1.68 (0.17)	1.78 (0.21)	1.72b (0.17)
	Mean (within ash)	1.76 (0.15)	1.80 (0.26)	1.84 (0.20)	
S (g kg ⁻¹)	No N	0.77 (0.09)	0.78 (0.11)	0.81 (0.10)	0.78 (0.10)
	N	0.75 (0.08)	0.79 (0.08)	0.84 (0.09)	0.79 (0.09)
	Mean (within ash)	0.76b (0.08)	0.78b (0.09)	0.83a (0.09)	
N/S ratio	No N	12.3 (0.8)	12.2 (1.5)	11.9 (1.1)	12.2b (1.1)
	N	14.0 (1.2)	12.6 (1.0)	12.5 (1.0)	13.0a (1.2)
	Mean (within ash)	13.1a (1.3)	12.4ab (1.3)	12.2c (1.1)	
Zn (mg kg ⁻¹)	No N	67.4 (10.5)	74.3 (11.8)	70.2 (12.0)	70.6 (11.5)
	N	64.9 (12.7)	66.8 (12.2)	67.3 (16.0)	66.3 (13.4)
	Mean (within ash)	66.2 (11.5)	70.5 (12.3)	68.7 (13.9)	

Note: No significant ash : fertilizer interactions were found (Table 7); adjacent means (within ash or within N treat.) not significantly different ($p < 0.05$) from each other if no lower case letters are shown, or if they share the same letter within a row or column; N/S values were normalized according to Brockley (2012).

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Table 7. Results from linear mixed-effects models of foliar nutrients in spruce needles, five months after plots were treated with ash and/or urea (n = 72), with treatments as fixed effects and site (North or South) as a random effect.

	Ash Treat		N Treatment		Ash Treat: N Treat		Random Effect SD	
	F-Value	p-value	F-value	p-value	F-value	p-value	Site	Residual
B	1.03	0.363	0.365	0.548	2.05	0.138	1.33	3.16
Ca	3.63	0.0319	1.92	0.170	0.251	0.779	0.0293	0.103
Cu	2.86	0.0644	0.577	0.450	1.04	0.358	1.13	5.63
K	1.72	0.187	0.269	0.606	1.12	0.332	0.0481	0.0609
Mg	1.94	0.151	4.01	0.0493	0.773	0.466	0.0021	0.0135
Mn	0.251	0.779	1.09	0.300	0.169	0.845	52.9	205.6
N	1.43	0.246	29.1	<0.0001	0.700	0.500	8.97x10 ⁻⁷	0.0871
N/S	4.58	0.0138	10.6	0.0018	2.31	0.108	2.65x10 ⁻⁵	1.08
P	1.15	0.323	13.8	0.0004	0.597	0.553	3.06x10 ⁻⁷	0.0182
S	3.29	0.0437	0.268	0.606	0.470	0.627	2.54x10 ⁻⁷	0.0087
Zn	1.19	0.310	3.45	0.0678	0.479	0.622	7.63	9.41

Note: All values reflect nutrient differences in current needles one season after ash and urea applications; significant values (p < 0.05) are in bold; for significant ash treatment effects; Tukey’s HSD test compared differences between treatment means; S values were determined by ICP-OES following strong acid digestion; N/S values are normalized according to Brockley (2012).

Figure 1