



Soil Water Responses to Wood Ash Addition to Acidic Upland Soils: Implications for Combatting Calcium Decline in Lakes

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Abstract Calcium (Ca) concentrations in lakes have declined in many regions, and concerns have been expressed that Ca levels are falling below biologically significant thresholds. Wood ash additions to soil are typically used to combat soil acidification, and it is unclear whether wood ash additions to upland soils will lead to higher Ca leaching to surface waters. In this study we applied fly ash or bottom ash at 4 Mg ha⁻¹ and 8 Mg ha⁻¹ to upland soils at replicated plots in Haliburton Forest in central Ontario and measured soil water chemistry at 3 depths over 4 years. Increases in soil water Ca concentration following application were

quite modest and occurred primarily in the fly ash treatments in the upper depth (0.3 m) during the first 2 years following application. There was no concomitant increase in pH or acid-neutralizing capacity primarily because of the high sulphate leaching associated with the fly ash treatments. Overall, these results show that wood ash addition to soils at moderate doses will have little impact on soil export to lakes.

Keywords Calcium · Lakes · Wood ash · Alkalinity · Soil base cations

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1 Introduction

Calcium (Ca) concentrations in surface waters have fallen throughout many parts of Europe and eastern North America (Alewell et al., 2000; Keller et al., 2011; Likens et al., 1998; Stoddard et al., 1999). In some regions, Ca levels are approaching or have passed critical biological thresholds (Hessen et al., 2017; Jeziorski & Smol, 2017; Keller et al., 2011), and paleolimnological studies suggest that current Ca concentrations are below those that existed prior to industrialization (Jeziorski et al., 2008). While recent experimental studies have reported no short-term (<10 year) to medium-term (< 20 year) effects of forest harvesting on soil Ca levels (McLaughlin, 2014; Morris et al., 2019), it is important to identify specific sites that may be susceptible to Ca depletion and surface water impacts. Modeling studies have suggested that continued or increased timber harvesting in the catchments of

“sensitive lakes”—lakes with Ca values below or close to reported critical biological thresholds (i.e., $>1.5 \text{ mg Ca L}^{-1}$ for *Daphnia* reproduction and survival) (Ashforth & Yan, 2008)—in central Ontario will lead to substantial further declines in lake Ca levels (Reid & Watmough, 2016; Watmough et al., 2003); a feature that has been termed “aquatic osteoporosis” (Jeziorski et al., 2008). For the most part, the declines in surface water Ca can be attributed to the substantial decreases in acid deposition that have occurred over the past 3 decades, although continued soil acidification may further exacerbate lake Ca decline (Likens et al., 1996; Watmough et al., 2016).

Complementary studies have shown that upper soil Ca concentrations at acid sensitive forested sites were declining up to the early 2000s (Warby et al., 2009; Watmough & Dillon, 2003), but base cation mass balance estimates suggest that in many regions Ca losses have decreased, and some sites are now showing signs of soil recovery as soils become less acidic (Lawrence et al., 2015). Kirchner and Lydersen (1995) demonstrated that the acid buffering capacity of soils is a function of the size of the soil exchangeable pool, and that there is a linear relationship between the sum of strong base cations and the sum of strong acid ions [F-Factor], and the slope of this relationship depends on soil Ca (or base cation) concentrations. If soil Ca concentrations fall then the F-Factor will decrease and vice versa (Kirchner & Lydersen, 1995); hence soil water chemistry has been extrinsically linked to surface water chemistry in regions dominated by shallow, base poor soils.

Wood ash from industrial sources has been commonly used as a soil amendment to combat soil acidification in Europe (Augusto et al., 2008), but less so in eastern North America (Elliot & Mahmood, 2015; Hannam et al., 2018). The elemental composition of wood ash varies depending on the source of the material, tree species, type of plant tissue used and temperature of the burn (Pitman, 2006). Generally, industrial wood ash has a high neutralizing capacity, with pH values ranging from 8.9 to 13.5 (Demeyer et al., 2001), and Ca is usually present as calcium carbonate (CaCO_3), which gives the ash its liming effect (Stenari & Lindqvist, 1997). A review on wood-ash use in forestry by Pitman (2006) showed the elemental concentrations of ash from industrial sources to be, in order of decreasing concentration, Ca, potassium (K), magnesium (Mg), aluminum (Al), iron (Fe), and phosphorus (P), but there may be potentially toxic trace metals present such as

zinc (Zn), lead (Pb), and cadmium (Cd). Industrial wood ash is separated into fly ash and bottom ash in boilers. Fly ash is finer ($\sim 200 \mu\text{m}$), more reactive and generally contains higher concentrations of dioxins and metals than bottom ash (Pitman, 2006).

Currently, there are a number of wood ash trials taking place in Canada (AshNet, 2020), which focus primarily on the potential benefits (e.g., tree and soil nutrition; tree growth) (Emilson et al., 2020) and potential harm (increased trace metal availability) (Deighton et al., *in press*; Deighton & Watmough, 2020) of wood ash application to forests. These and other studies overwhelmingly show that the addition of wood ash leads to an increase in soil pH and soil Ca concentrations (Brais et al., 2015; Domes et al., 2018; Bieser & Thomas, 2019). Studies in other countries have shown short term (<10 years) increases in base cation concentrations in soil and surface water after ash applications (Park et al., 2004; Ring et al., 2006) but this aspect has not been evaluated in the context of “aquatic osteoporosis” in Canadian ecosystems.

The objective of this study was to evaluate changes in soil water chemistry sampled at 3 depths (0.3 m, 0.5 m, and 1.0 m) over a 4-year period following the application of either loose fly ash or bottom ash as treatment levels of 4 Mg ha^{-1} or 8 Mg ha^{-1} . In this region water flow has been shown to occur primarily vertically through the soil profile and then laterally along the soil-bedrock interface (Buttle & McDonald, 2002). In this context, our lysimeter depths are representative of the major flow path from the surface soil to surface waters. We expected that soil pH and base cations in soil would be elevated following ash application and that water Ca (and other base cations) concentrations would increase following wood ash application. We expected that the response would initially be greatest in the higher treatments and at the shallow soil depth, but over time, we hypothesized that increase in Ca would also occur at the deeper soil depths and that all treatments would exhibit an increase in F-factor [buffering capacity] as the Ca in the ash is mobilized.

2 Methods

2.1 Study Site

The study site is located in the Muskoka-Haliburton region of central Ontario in an upland, mixed-

deciduous forest near the southern border of the Boreal ecozone, a region considered very sensitive to acid deposition (Fig. 1). The site is within the Kennisis watershed, encompassing 17,400 ha and extending into Haliburton Forest and Wildlife Reserve and is within 500 m of Kennisis Lake, a deep (mean depth 23.4 m) cold-water lake low in nutrients (The Kennisis Lake Planning Steering Committee, 2007). In 2012, Kennisis Lake Ca levels ranged from 2.0 to 2.1 mg L⁻¹ (Ontario Lake Partner, 2020). Upland soils in the area are acidic (pH ranging from 4.0 to 5.5) (Gorgolewski et al., 2016), medium-to-coarse sandy loams (Chapman & Putnam, 1984), and belong to the Eluviated Dystric Brunisol subgroup (Soil Classification Working Group, 1998). The study site was harvested using the single tree selection silviculture system (Ontario Ministry of Natural Resources (OMNR), 2000) in 2003 and, subsequently, salvage logged for American beech (*Fagus grandifolia* Ehrh.) due to the arrival of beech bark disease in the stand. Mean basal area in the study site in 2013 for trees >8 cm diameter at breast height (DBH, 1.3 m) was 16.4 m² ha⁻¹, which has been estimated to remove 7.0 to 15.4 kg ha⁻¹ Ca yr⁻¹ (approximately 340 kg ha⁻¹ Ca per 20- to 25-year cycle). The forest site is dominated by uneven-aged sugar maple (*Acer saccharum* Marsh.) and American beech, with lesser amounts of yellow birch

(*Betula alleghaniensis* Britton.) and eastern hemlock (*Tsuga Canadensis* (L.) Carr). In the summer of 2013, dominant understory vegetation (total height of less than 2 m and diameter at breast height < 1 cm) included sugar maple, beech (*Fagus* spp.), and raspberry (*Rubus* spp.). Long-term mean annual precipitation is 1074 mm and long-term mean annual temperature is 5.0 °C (1981–2010; Environment Canada 2019). From 2013 to 2017 mean annual precipitation and air temperature were 1171 mm and 5.2 °C, respectively.

2.2 Experimental Design

Twenty study plots were established using a modified stratified random block two-way factorial design in the summer of 2012. An area of forest was selected, and twenty 3 m × 3 m plots were established, each with a 2.5-m buffer. The site was naturally regenerated, with no site preparation, and the plots and buffer zones were free from saplings and large trees (DBH > 2.5 cm). Treatments were assigned to plots to maximize variability within groups in moisture content and light availability (Noyce et al., 2017). The five treatments were controls (no ash), untreated loose bottom ash (applied at either 4 Mg ha⁻¹ or 8 Mg ha⁻¹) and untreated loose fly ash (applied at either 4 Mg ha⁻¹ or 8 Mg ha⁻¹). Each

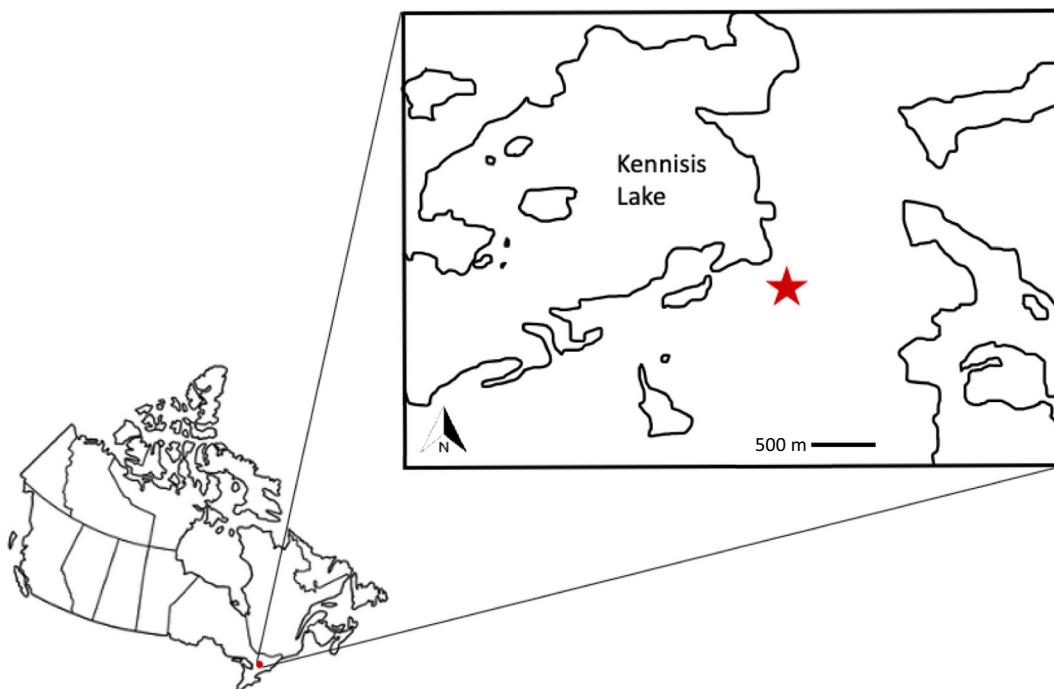


Fig. 1 Location of the study region in south-central Ontario, Canada

treatment was replicated four times. Ash application rates were determined with respect to an estimated 340 kg ha^{-1} Ca that is removed through tree harvesting (Phillips & Watmough, 2012). Fly ash (containing 101 g kg^{-1} Ca) applied at a rate of 4 or 8 Mg ha^{-1} would add 404 and 808 Mg ha^{-1} Ca, respectively, and bottom ash (containing 44 g kg^{-1} Ca) applied at a rate of 4 or 8 Mg ha^{-1} would add 176 or 352 Mg ha^{-1} Ca, respectively.

Fly and bottom ashes were produced from bark residues from the Maritimes and were recovered from a large Babcock and Wilcox RotoStoker VGC biomass boiler system. The pH of both the fly (8.6) and bottom (9.7) ashes were low compared to previously reported averages (Pitman, 2006; Vance, 1996), and fly ash had about two times the amount of Ca (101.1 g kg^{-1}), K (30.7 g kg^{-1}) and Na (36.4 g kg^{-1}) than the bottom ash (43.6 , 14.3 , and 16.3 g kg^{-1} for Ca, K, and Na, respectively). Fly and bottom ashes had similar concentrations of Mg (8.7 and 8.4 g kg^{-1} , respectively) and all metals were under Ministry of Environment and Climate Change limits for land application (Nutrient and Management Act, 2002) (for full ash composition details, see Gorgolewski et al., 2016). In mid-August 2013, bottom and fly ashes were weighed, carried to plots in plastic buckets and hand distributed as evenly as possible by sectioning each plot into quarters. Both ashes were applied to plots as untreated, loose ash.

Six porous cup tension lysimeters were installed vertically from the soil surface in each plot at 0.3 m ($\times 3$), 0.5 m ($\times 2$), and 1 m ($\times 1$) depths. The lysimeters were installed at least 0.5 m away from the edge of the plot, with at least 0.5 m between each lysimeter. Lysimeters were constructed with 2-bar standard ceramic cups with $1.3\text{-}\mu\text{m}$ pore size (Soil Moisture Equipment Corp., Santa Barbara, California). Prior to installation the lysimeters were acid washed with 1 M HCl and then rinsed repeatedly with deionized water. Rinsing was complete when the pH, conductivity, and base cation concentrations of solution passing through each lysimeter had reached the value of the deionized water. Each lysimeter was left to equilibrate for 2 weeks prior to initial sampling. Lysimeters were sampled three times with the solutions being discarded (Soil Moisture Equipment Corp., Santa Barbara, California) and allowed to equilibrate prior to the initiation of sampling in August 2013. Lysimeters were sampled monthly from August 2013 to November 2017 (excluding events where the ground was frozen) and evacuated to 50 kPa and left to

accumulate solution for the subsequent month. Lysimeters were largely still under suction when visited for the next monthly sampling. There were three sampling occasions in 2013, nine in 2014, ten in 2015, nine in 2016, and seven in 2017 (frequency varied depending on rainfall events). Subsamples within each replicate treatment plot (at the same lysimeter depth and sampling occasion) were pooled (if necessary) prior to analysis.

Soil samples were collected in the study plots in August 2017. From each plot, soil grab samples were sampled using a trowel to a depth of 10 cm . Soil samples were taken from three soil horizons, upper organic (LF), lower organic (H), and mineral (Ah). Additionally, soil cores were taken from each horizon using a soil corer, mallet, and wooden block to estimate bulk density (0.12 , 0.54 , and 0.93 g cm^{-3} for LF, H, and Ah soil horizons, respectively) used in nutrient content calculations required for estimating soil water input-output mass balance rates.

2.3 Chemical Analysis

2.3.1 Wood Ash

Ash chemistry was determined prior to application. Ca, Mg, K, P, sodium (Na), and manganese (Mn) were measured using an inductively coupled argon plasma spectrometer (Varian Analytical Instruments, Walnut Creek, CA) following high temperature microwave acid digestion (EPA standard method 3052) (Gorgolewski et al., 2016).

2.3.2 Soil Chemistry

Soil cores were weighed, dried at $105 \text{ }^\circ\text{C}$ for 24 h then weighed again to calculate bulk density. Five grams of oven-dried soil were transferred to a muffle furnace at $450 \text{ }^\circ\text{C}$ for 16 h to determine percent organic matter using loss-on-ignition. Soil grab samples were analyzed for moisture content by drying 5 g of wet soil at $105 \text{ }^\circ\text{C}$ for 24 h , and reweighing. The remainder of the grab samples were left to air dry for 2 weeks then sieved ($<2 \text{ mm}$). A 1:5 soil to 0.01 M CaCl_2 slurry and a 1:5 soil to reverse osmosis water slurry was used to measure pH and electrical conductivity (EC), respectively, by allowing the slurries to be stirred every 2 min for 10 min and left to rest for 10 min before taking readings using an OAKTON pH 510 series multimeter (Oakton

Instruments, Vernon Hills, IL). The probe was calibrated every 15 samples.

Soil chemistry was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) following nitric acid digestion (Aristar® Plus, CAS 7697-37-2) for base cations. The nitric acid digestion was used to determine the total metal concentration in the soil to enable an assessment of the input-output mass balance, rather than as a measurement of the bioavailable or geochemically reactive metal concentrations. Samples for ICP-OES were weighed (~0.2 g each) and placed in a 50 mL DigiTUBEs (SCP Science, Quebec, CA), where 2.5 mL of 100% (v/v) nitric acid was added. Caps were loosely placed on the tubes to allow air exchange. The samples were cold digested at room temperature for 8 h, then left to digest on hot plate at 100 °C for 8 h, or until all of the sample had dissolved. The samples were then rinsed with deionized water three times while being transferred to a 25-mL volumetric flask through P8 Fast Flow Filter Paper. Then, the solution was adjusted to 25 mL using deionized water. Lastly, the sample were transferred to a 50-mL Falcon tube and stored in a refrigerator until analysis. Glassware was soaked in 5% (v/v) nitric acid overnight, rinsed with deionized water and left to air dry prior to use. Precision of analysis was confirmed using blanks and NIST-1515-SRM apple leaves every 25 samples.

2.3.3 Soil Water

Lysimeter soil water samples were analyzed at the Great Lakes Forestry Centre in Sault Ste. Marie, Ontario for conductivity, alkalinity, pH, major ions, nutrients, and metals. Conductivity, alkalinity, and pH were measured using a Man-Tech PC-Titrate (Mantech, Guelph, ON). Silica dioxide (SiO₂), nitrate (NO₃), ammonium (NH₄), total nitrogen (TN), and dissolved organic carbon (DOC) were measured with a Technicon Autoanalyzer II (SEAL Analytical Inc., Mequon, WI) by the ascorbic acid, cadmium reduction, sodium nitroprusside, autoclave digestion, and potassium persulfate methods, respectively. Sulphate (SO₄) and chloride (Cl) concentrations were determined by ion chromatography. Base cations and metals were analyzed using an Agilent 7700X Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent Technologies, Santa Clara, CA).

2.4 Data Analysis

Statistical analyses were performed with the R statistical software version 4.0.3 (RStudio Team, 2016). General linear mixed models (GLMMs), using the *lme* function in the package *nlme*, were used to determine the effects of treatment, depth, and time (sampling date) on soil water chemistry. Prior to analysis, normality was assessed using the Shapiro–Wilk normality test (*rstatix* package) and QQ plots (*ggpubr* package), and homogeneity of variances was assessed by Bartlett's Test. *P* values for GLMMs were calculated using a three-way repeated measures anova (ANOVA). Statistical significance was accepted at Bonferroni's adjusted alpha levels of $P < 0.0125$ and $P < 0.0167$ for simple two-way interactions. Main effects analyses (pairwise comparisons) were determined using the *emmeans* package.

To test the null hypothesis that ash has no effect on soil pH, OM (organic matter), percent moisture and base cation (Ca²⁺, Mg²⁺, K⁺, and Na⁺) concentrations 4 years after application, comparisons were made between treated and control plots ($n = 4$) using a one-way analysis of variance (ANOVA). Dunnett's post hoc test was used to compare treatment plots to control plots, and Tukey's HSD test was used to determine pairwise comparisons. The post hoc tests were completed only on those variables where a significant treatment effect was determined by one-way ANOVA.

F factors were calculated using Eqs. (1) and (2):

$$F_1 = FCa/FSAA \quad (1)$$

$$F_2 = FSBC/FSAA \quad (2)$$

where *FCa* is the average annual concentration (meq L⁻¹) of Ca at a certain soil water depth, *FSBC* is the average annual concentration (meq L⁻¹) of the sum of base cations (Ca²⁺ + Mg²⁺ + K⁺ + Na⁺) at a certain soil water depth, and *FSAA* is the average annual concentration (meq L⁻¹) of the sum of the acid anions (SO₄²⁻ + NO₃⁻ + DOC + OH⁻) at a certain soil water depth.

Concentration of OH⁻ was calculated by multiplying alkalinity (as meq L⁻¹ CaCO₃) by 0.34 and valency of ion and charge associated with DOC was calculated using the Oliver Equation (Oliver et al., 1983).

Base cation pools (g m⁻²) were calculated using an input–output mass balance, where concentration in wood ash (mg m⁻²) and bulk deposition (mg m⁻²) contributed to inputs and runoff and average concentration

in soil water contributed to outputs. Base cation inputs were calculated by adding bulk deposition values recorded at nearby forest catchments (see Watmough et al., 2007) to mass of the element in fly and bottom ash that was applied at various treatments (see Gorgolewski et al., 2016). Outputs were calculated by using an average runoff value of $400 \text{ L m}^{-2} \text{ yr}^{-1}$ multiplied by average concentrations ($\text{mg L}^{-1} \text{ yr}^{-1}$) of the element in soil water at 30-cm depth. The assumed runoff value was based on records at Plastic Lake ($45^{\circ} 11 \text{ N}$, $78^{\circ} 50 \text{ W}$). Estimates of the total amount of base cations lost over the study period for each treatment were determined by summing annual output values and subtracting by control values as a percent of total pool losses. Total pool size was calculated by multiplying average concentrations of base cations in the soil (mg m^{-2}) by the average bulk density of the H (0.54 g cm^{-3}) and Ah (0.93 g cm^{-3}) and depth (10 or 30 cm). Potential base cation accumulation in biomass was excluded so this estimate may be considered conservative. Mass balance calculations have uncertainty from the assumption that Plastic Lake subcatchment is representative of the study area.

3 Results

3.1 Soil Water Chemistry

For most chemical parameters measured in soil water there was a significant treatment, time, and treatment \times time interaction effect (Table A1). Significant ($P < 0.05$) treatment \times time interaction effects occurred only in the upper (0.3 and 0.5 m) soil depths in the first 2 years of study (the first sixteen sampling dates) for all variables. An exception to this was for pH, where there were significant treatment \times time interaction effects in the final 2 years of study in the upper soil depths.

The chemical response in soil water was generally greatest in the two fly ash treatments (4 and 8 Mg ha^{-1}), in the upper (0.3 m and 0.5 m) soil depths in the first 2 years of study. For example, Ca concentrations in soil solution at the 0.3 m depth increased from around 2 mg L^{-1} to greater than 4 mg L^{-1} in the year immediately following application (Fig. 2). By the third year following application, Ca concentrations in soil water at 0.3 m in the two fly ash treatments were again close to 2 mg L^{-1} and were indistinguishable from controls and bottom ash treatments (Fig. 2). Similar responses were

noted for Mg, K, and Na, whereby concentrations in soil water in the two fly ash treatments were elevated, primarily in the first 2 years and in the 0.3 m and 0.5 m soil depths (Figs. 2 and 3).

Despite the increase in base cation concentrations that were observed in soil solution at 0.3 m and 0.5 m in the fly ash treatments in the first 2 years, there was no significant increase in soil water pH or ANC (Figs. 2 and 3), except for two sampling dates (June 17th, 2016 and November 17th, 2017) which yielded significantly higher ($P < 0.01$) pH values in 4 Mg ha^{-1} bottom ash treatment plots compared with all other treatments. In fact, soil water pH at the high fly ash treatment was lower than the other treatments at every sampling period (except one instance) in the first 2 years at the 0.3-m depth (Fig. 2). The lack of a positive increase in pH or ANC can be attributed to large increases in SO_4 and to a lesser extent NO_3 in the two fly ash treatments in the first 2 years at the 0.3-m and 0.5-m depths (Figs. 2 and 3). For example, immediately following applications SO_4 concentrations increased from around 5 mg L^{-1} to more than 20 mg L^{-1} , at the 0.3-m depth and declined steadily over the first 2 years after application (Fig. 2). Similar responses were found at the 0.5-m depth, whereas soil water responses at 1.0 m were muted in comparison to the upper depths (Figs. 3 and 4).

3.2 Soil Buffering Capacity [F-Factor]

Because the amount of acid leaching will affect the concentrations of base cations in solution, one way of assessing whether soils have a greater buffering capacity is to compare F-Factors, which reflects the relative amount of base cations relative to acid anions in soil water. Two-way analysis of variance (ANOVA) revealed no statistically significant interaction between the effects of treatment and year on the buffering capacity of the soils [F-Factors], and no significant main effect of wood ash treatment at any soil depth (Table 1). For example, over the 4-year average annual F-Factors [FCa/SAA] in the control plots at 0.3 m were between 0.25 and 0.31, compared with 0.14 and 0.30 in the 8 Mg ha^{-1} fly ash treatment (Table 1). The low Ca F-Factor (FCa/SAA) in the 8 Mg ha^{-1} treatment occurred in the first year following treatment and was due to a greater proportion of acid buffering provided by Na and K (Fig. 2) in the year immediately following application. The F-Factors at the deeper soil depths were higher than

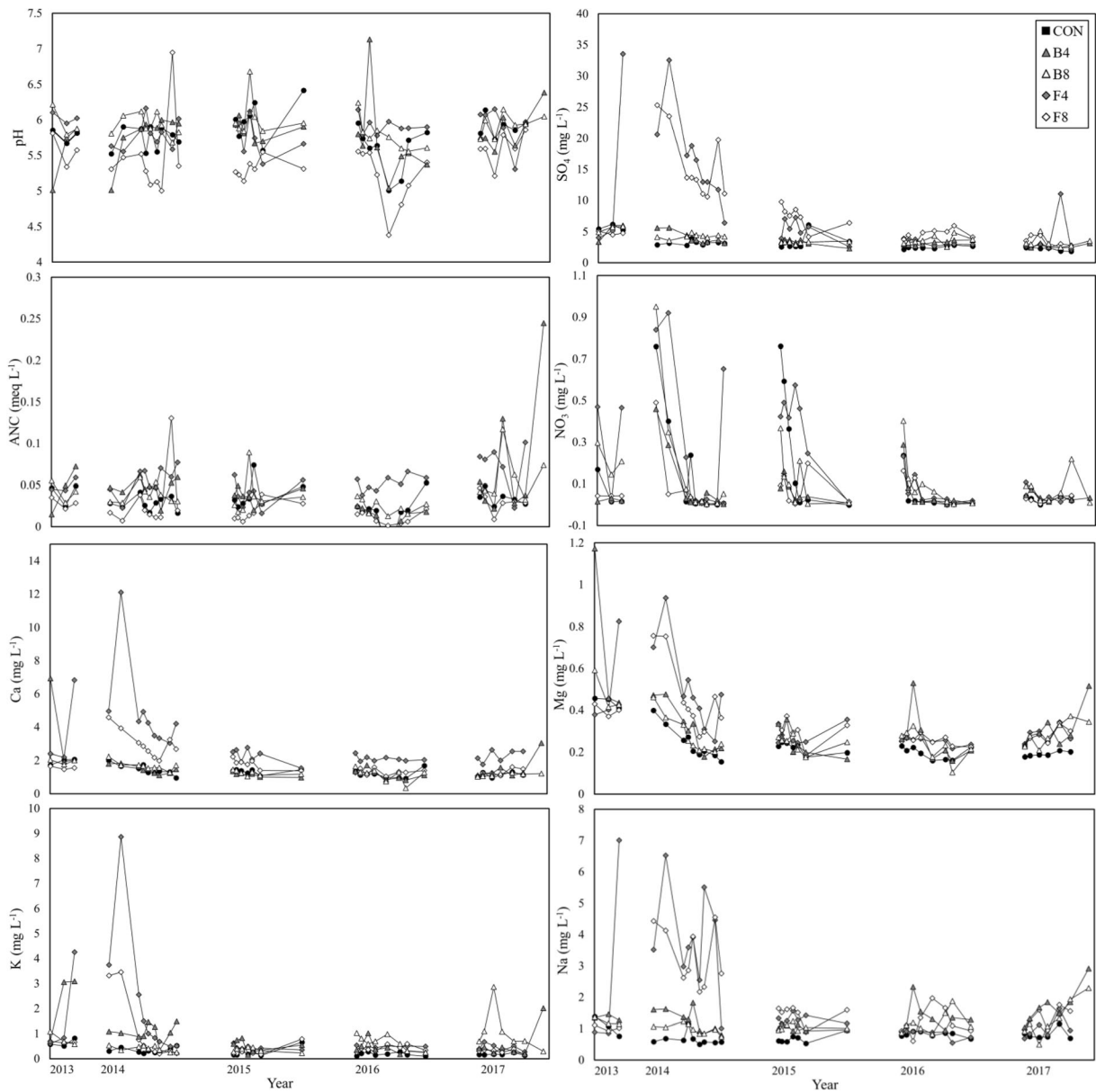


Fig. 2 Mean lysimeter (0.3 m) soil water concentrations of pH, SO₄, ANC, NO₃, Ca, Mg, K, and Na from August 2013 to November 2017

values measured at 0.3 m reflecting the increased buffering effect of soils, but again there was no significant effects of wood ash treatment on soil buffering (Table 1). There was a significant main effect of year on F-Factor (FSBCA/SAA) at the 30-cm, 50-cm, and-100 cm lysimeter soil water depths; however, post hoc analysis showed few significant differences and only two significant differences between treatment and control plots (Table 1).

3.3 Soil Chemistry and Base Cation Leaching Losses

Wood ash applications resulted in a significant increase in base cation concentrations in the upper mineral soil and soil pH, soil moisture and organic matter content also tended to be higher in the ash treatments compared with the controls, but the difference was not significant (Table 2). Based on the Ca concentrations measured in ash, we estimated that soil Ca, Mg, K, and Na

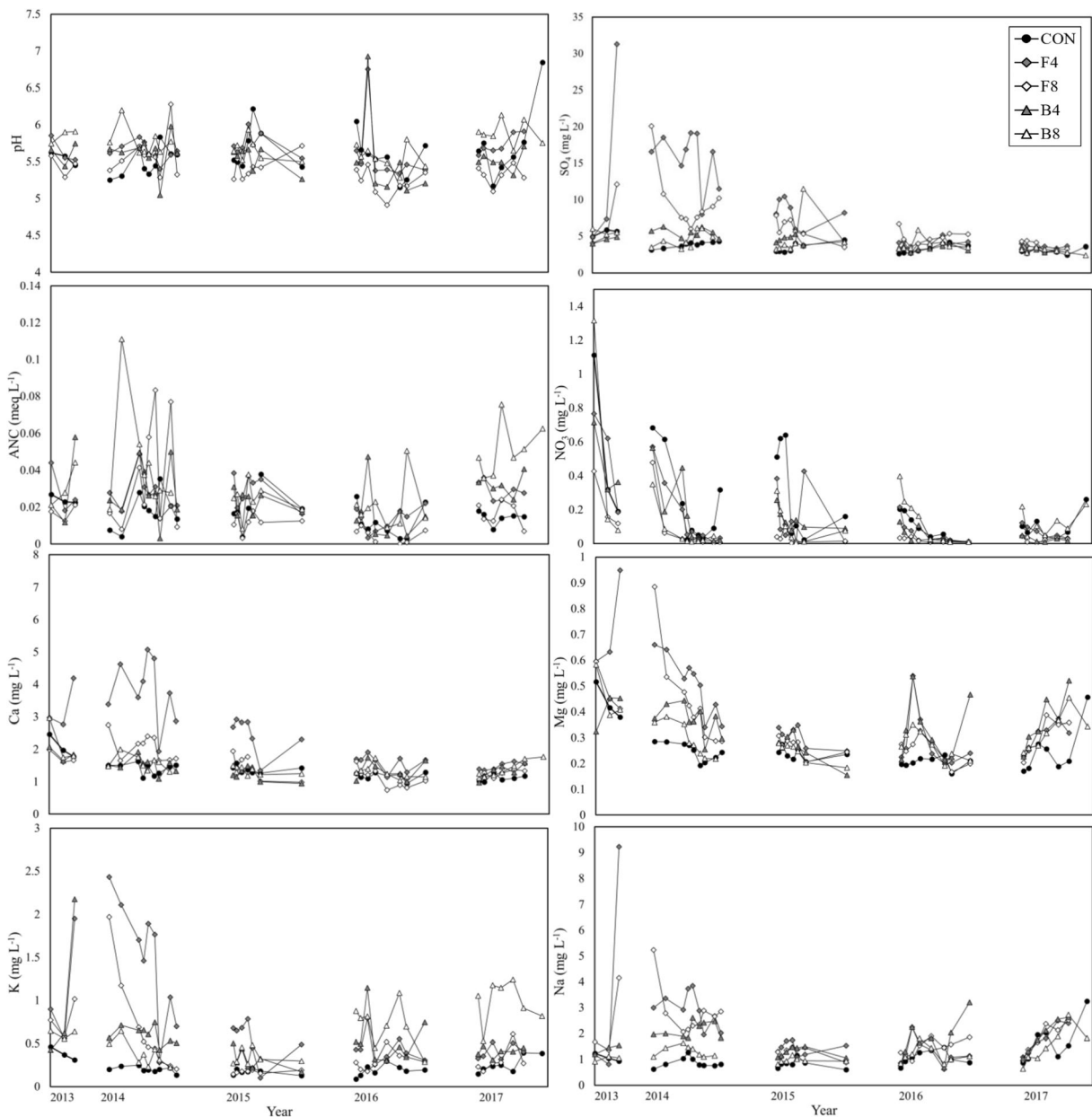


Fig. 3 Mean lysimeter (0.5 m) soil water concentrations of pH, SO_4 , ANC, NO_3 , Ca, Mg, K, and Na from August 2013 to November 2017

concentrations in the upper 10 cm would increase by between 8% (Mg: 4 Mg ha^{-1} (fly and bottom ash) and 99% (Na: 8 Mg ha^{-1} fly ash) (Table 3). Despite high variability in soil chemistry, the predicted increase in soil base cations is generally within the range of the measured differences in soil base cation concentrations (Table 2) indicating that much of the base cations applied in ash are retained in upper soil. When the base cation additions are expressed relative to the base cation

pools in the entire 0.3-m soil depth, which represents the uppermost depth of the lysimeters, more modest increases (3.5–45%) in base cation pools resulting from ash application are expected (Table 3). Furthermore, mass balance estimates suggest that over the 4-year period, between 6 and 17% of the Ca that was applied in ash leached below the 0.3-m soil depth (Table 3). Relative leaching losses of Mg, K, and Na were generally higher; for example, between 14 and 44% of the Na

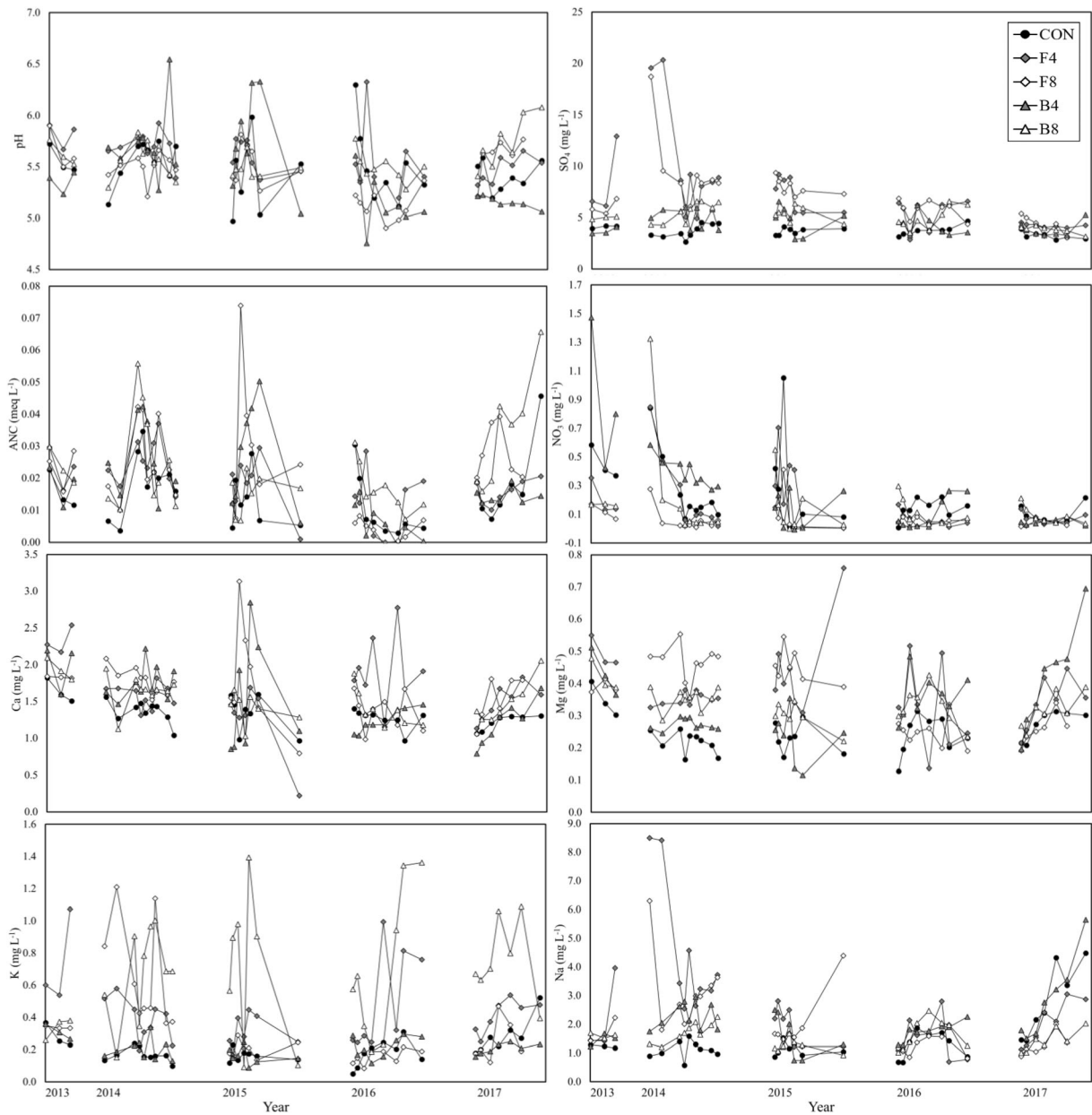


Fig. 4 Mean lysimeter (1.0 m) soil water concentrations of pH, SO₄, NO₃, ANC, Ca, Mg, K, and Na from August 2013 to November 2017

applied in ash was estimated to have leached below 30 cm over the 4-year period (Table 3).

4 Discussion

Wood ash application resulted in short-term increases in base cation concentrations in soil water, but these were

mostly restricted to the fly ash applications and were most pronounced during the first 2 years and in the 0.3-m soil depth. Base cation concentrations were higher in fly ash compared with bottom ash (101.1 vs. 43.6 g kg⁻¹ Ca, 30.7 vs. 14.3 g kg⁻¹ K, 8.7 vs. 8.4 g kg⁻¹ Mg and Na 36.4 vs. 16.3 g kg⁻¹ Na) which is likely why differences were mostly found in fly ash treatments. While the soil water response to wood ash application will vary due to a

Table 1 Annual *F* factor (\pm S.E.) over the course of the study period (2013–2017) at (a) 30-cm soil water depth, (b) 50-cm soil water depth, and (c) 100-cm soil water depth

	Year	<i>F</i> factor	CON	B4	B8	F4	F8	<i>P</i> value
(a)								
30 cm	2013	FSBC/SAA	0.60 (0.16)a	0.47 (0.26)a	0.62 (0.16)a	0.79 (0.24)ab	0.87 (0.17)b	0.491
		FCa/SAA	0.31 (0.13)	0.21 (0.20)	0.29 (0.13)	0.25 (0.17)	0.14 (0.09)	0.300
	2014	FSBC/SAA	0.55 (0.07)a	0.56 (0.04)a	0.68 (0.07)b	0.68 (0.26)ab	0.75 (0.15)b	0.287
		FCa/SAA	0.31 (0.06)	0.23 (0.03)	0.36 (0.06)	0.31 (0.20)	0.28 (0.11)	0.072
	2015	FSBC/SAA	0.47 (0.04)	0.73 (0.03)	0.73 (0.04)	0.49 (0.07)	0.65 (0.07)	0.287
		FCa/SAA	0.25 (0.03)	0.30 (0.02)	0.36 (0.03)	0.28 (0.05)	0.30 (0.05)	0.161
	2016	FSBC/SAA	0.49 (0.06)	0.66 (0.04)	0.80 (0.07)	0.52 (0.10)	0.60 (0.08)	0.427
		FCa/SAA	0.25 (0.05)	0.27 (0.03)	0.33 (0.05)	0.30 (0.08)	0.27 (0.07)	0.673
	2017	FSBC/SAA	0.60 (0.09)ab	0.77 (0.07)b	0.69 (0.09)ab	0.49 (0.11)a	0.68 (0.08)ab	0.003
		FCa/SAA	0.29 (0.08)	0.30 (0.06)	0.25 (0.06)	0.29 (0.09)	0.28 (0.06)	0.398
<i>P</i> value		FSBC/SAA	0.297	0.374	0.147	0.961	0.417	
		FCa/SAA	0.252	0.373	0.124	0.883	0.402	
(b)								
50 cm	2013	FSBC/SAA	0.74 (0.07)	0.86 (0.06)	0.80 (0.07)	0.82 (0.06)	0.89 (0.07)	0.568
		FCa/SAA	0.39 (0.04)	0.37 (0.04)	0.40 (0.04)	0.34 (0.04)	0.33 (0.03)	0.650
	2014	FSBC/SAA	0.73 (0.04)a	0.98 (0.08)b	0.91 (0.06)ab	0.85 (0.04)ab	0.91 (0.04)ab	0.022
		FCa/SAA	0.38 (0.02)	0.51 (0.03)	0.41 (0.02)	0.39 (0.02)	0.35 (0.02)	0.240
	2015	FSBC/SAA	1.00 (0.16)ab	1.37 (0.17)b	1.07 (0.10)ab	1.23 (0.07)ab	1.16 (0.08)a	0.041
		FCa/SAA	0.47 (0.05)	0.57 (0.03)	0.43 (0.06)	0.57 (0.13)	0.46 (0.09)	0.233
	2016	FSBC/SAA	0.88 (0.10)	1.15 (0.13)	0.98 (0.08)	0.95 (0.11)	0.92 (0.07)	0.345
		FCa/SAA	0.39 (0.03)	0.41 (0.04)	0.39 (0.02)	0.46 (0.05)	0.35 (0.03)	0.334
	2017	FSBC/SAA	0.96 (0.12)	0.97 (0.12)	0.94 (0.12)	0.95 (0.14)	1.02 (0.12)	0.994
		FCa/SAA	0.40 (0.04)	0.32 (0.03)	0.35 (0.04)	0.37 (0.03)	0.36 (0.03)	0.601
<i>P</i> value		FSBC/SAA	0.470	0.313	0.408	0.765	0.345	
		FCa/SAA	0.391	0.313	0.455	0.501	0.304	
(c)								
100 cm	2013	FSBC/SAA	1.03 (0.13)	1.24 (0.12)	1.22 (0.16)	1.22 (0.18)	0.97 (0.15)	0.054
		FCa/SAA	0.49 (0.05)	0.58 (0.07)	0.54 (0.04)	0.53 (0.07)	0.43 (0.04)	0.309
	2014	FSBC/SAA	0.91 (0.06)	1.07 (0.06)	1.10 (0.08)	1.55 (0.41)	1.03 (0.04)	0.187
		FCa/SAA	0.45 (0.02)	0.43 (0.04)	0.44 (0.02)	0.59 (0.23)	0.38 (0.03)	0.691
	2015	FSBC/SAA	1.59 (0.10)b	1.20 (0.22)ab	1.40 (0.04)ab	1.22 (0.04)ab	1.09 (0.08)a	0.009
		FCa/SAA	0.77 (0.09)	0.53 (0.18)	0.61 (0.05)	0.48 (0.05)	0.52 (0.06)	0.172
	2016	FSBC/SAA	1.00 (0.11)	1.14 (0.08)	1.14 (0.08)	1.15 (0.17)	0.86 (0.05)	0.179
		FCa/SAA	0.41 (0.03)	0.43 (0.03)	0.43 (0.03)	0.53 (0.05)	0.40 (0.02)	0.295
	2017	FSBC/SAA	1.31 (0.24)ab	1.52 (0.17)b	1.09 (0.09)ab	1.30 (0.17)ab	0.84 (0.05)a	0.018
		FCa/SAA	0.39 (0.5)	0.42 (0.03)	0.43 (0.03)	0.47 (0.03)	0.41 (0.03)	0.621
<i>P</i> value		FSBC/SAA	0.266	0.477	0.611	0.535	0.743	
		FCa/SAA	0.264	0.511	0.419	0.484	0.679	

Data that is in bold is significant ($P < 0.05$)

number of factors including ash composition, dosage, and site conditions (Arvidsson & Lundkvist, 2003; Eriksson,

1998; Kahl et al., 1996; Ludwig et al., 2002) most previous studies have similarly shown that ash application often

Table 2 Soil (weighted mean H and Ah horizons) pH, organic matter (OM), moisture, and total base cation concentrations (mean \pm S.E.) in control and treatment plots ($n=4$) 4 years after ash application. Significant differences ($P<0.05$) from pairwise

comparisons (Tukey) indicated with different letters. Significant differences to control (Dunnett) indicated by a*. The post hoc tests were completed only on those variables where a significant treatment effect was determined by one-way ANOVA

	CON	B4	B8	F4	F8
pH	4.4 (0.11)	4.7 (0.08)	4.7 (0.12)	4.5 (0.08)	4.8 (0.07)
OM (%)	15.1 (2.6)	17.1 (3.8)	20.4 (3.4)	22.5 (4.5)	16.4 (1.9)
Moisture (%)	40.4 (3.6)	44.1 (5.2)	47.6 (4.3)	42.3 (3.5)	45.5 (6.7)
Ca (g kg ⁻¹)	2.8 (1.2)a	5.9 (0.7)b*	4.3 (0.1)ab	8.6 (1.8)c*	3.6 (1.3)ab
Mg (g kg ⁻¹)	0.6 (0.1)a	0.9 (0.1)ab	1.0 (0.4)ab	1.3 (0.3)b*	0.8 (0.2)ab
K (g kg ⁻¹)	0.6 (0.1)a	1.2 (0.1)bc*	1.0 (0.1)a	1.4 (0.3)c*	0.8 (0.2)ab
Na (g kg ⁻¹)	0.4 (0.0)ab	0.3 (0.0)ab	0.3 (0.1)a	0.7 (0.3)b	0.3 (0.1)a

leads to a transitory response in soil water chemistry, even using additions greater than those in the present study. For example, Williams et al. (1996) investigated soil solution response to wood ash in a column study, as well as a field study using ash application rates of 11, 22, and

44 Mg ha⁻¹. They noted that soil water chemistry returned to pretreatment values after about 60 weeks and that the response of groundwater was very limited. Park et al. (2004) applied wood ash at rates of 10 Mg ha⁻¹ and 20 Mg ha⁻¹ to a coppiced willow stand in New York

Table 3 Soil base cation pools (g m⁻²) and total base cation leaching losses as a percent of pool size from 2013 to 2017 in control and treatment plots ($n=4$). Total pools calculated using

average concentration of base cation in control soil (at 10-cm and 30-cm depths) and average bulk density of H and Ah horizons

Treatment	Base cation	Total base cation content added via ash (g m ⁻²)	Total pool size (g m ⁻²)	Percent of total pool added from ash (%)		Estimated total leaching losses over four years from ash (%)
				10 cm	30 cm	
CON	Ca	0	450	0	0	0
	Mg	0	100	0	0	0
	K	0	200	0	0	0
	Na	0	70	0	0	0
B4	Ca	17.4	950	8.47	3.85	17.7
	Mg	3.4	150	7.61	3.46	36.5
	K	5.7	190	12.97	5.89	19.5
	Na	6.5	50	22.18	10.08	41.1
B8	Ca	34.9	700	16.95	7.70	8.4
	Mg	6.7	160	15.23	6.93	8.8
	K	11.4	160	25.94	11.79	7.6
	Na	13.0	50	44.35	20.16	14.3
F4	Ca	40.4	1390	19.65	8.93	15.4
	Mg	3.5	260	7.89	3.59	21.9
	K	12.3	210	27.84	12.66	23.2
	Na	14.6	110	45.54	22.51	43.1
F8	Ca	80.9	580	39.30	17.86	6.3
	Mg	7.0	130	15.78	7.16	18.0
	K	24.6	130	55.69	25.31	11.2
	Na	29.1	50	99.22	45.10	43.5

and found that base cation concentrations in soil solution increased and remained elevated for 2 years, but the chemical response at 40 cm was much lower than 20 cm. Norström et al. (2011) monitored stream water of plots in central Sweden receiving 3 Mg ha⁻¹ wood ash addition over a 3-year period and noted that differences in chemistry between the control and treated site were difficult to detect. A significant response was only noted when the authors compared cumulative losses that showed that the ash treated plot exported more base cations than the untreated plots. Overall, the findings in our study are consistent with previous research that shows soil water base cations increase following ash application, but increases are usually modest, and most pronounced in the years immediately following application and more apparent in upper soil horizons.

Despite the increase in base cation concentration, especially in the fly ash treatments there was no concomitant increase in soil water pH of ANC and there was a significant decrease in soil water pH at the highest fly ash treatment. This potentially adverse response was caused primarily by elevated leaching losses of SO₄ and, to a lesser extent, NO₃. Other studies have shown that SO₄ leaching losses immediately following ash application can be high and this can vary depending on the chemical composition of the ash (Deighton et al., *in press*; Kahl et al., 1996; Ludwig et al., 2002). The increase in NO₃ concentration in soil water may also have arisen from direct leaching from the ash, although the N content is typically low (Pitman, 2006). An alternate reason for the increase in NO₃ may be due to an increase in nitrification rates that may increase nitrate beyond biological demand (Ludwig et al., 2002). In both cases, the elevated concentrations in soil water had mostly disappeared by the third year of study. Furthermore, the decrease in pH did not lead to elevated trace metal levels in soil water, even during the first-year post ash application (Deighton et al., *in press*).

Because ash applications led to an increase in acid leaching, which in turn will impact base cation leaching, another way to evaluate whether ash application increase the buffering capacity of soils that will lead to higher Ca leaching is to compare the F-Factors. In this study we calculated the relative buffering of Ca because of the widespread concerns over Ca decline in the region (Jeziorski et al., 2008), as well as the sum of base cations that is important for reducing acidity. We found that there was no significant difference in FSBC/SAA among treatments or years indicating that the soil

buffering capacity was not significantly altered by ash application. In the first year of study the FCA/SAA was lower in the fly ash treatments [though not significantly] and this reflects the relatively higher leaching losses of Na and K immediately following ash application. Both Na and K are less strongly held on the soil exchange complex compared with divalent cations such as Mg and Ca, so greater losses of K, and especially Na are expected; indeed, Na has been used as a conservative element in forest biogeochemical studies (Bailey et al., 2003). High levels of Na and K can adversely impact aquatic biota (Arnott et al., 2020; Azan et al., 2019). Of direct relevance to this work, Azan et al. (2019) found that *Daphnia* growth and survival were heavily impacted by residential wood ash (ash from nonindustrial sources, such as from homes) addition with K the likely causal agent. In the study by Azan et al. (2019), however the ash was applied directly to surface water and concentrations were orders of magnitude higher (> 200 mg l⁻¹) than we recorded even at the peak, just following ash application.

Long-term monitoring of forested catchments in the region has shown that the buffering capacity of soils decreased over the past 30 years (Watmough et al., 2016) but has recently leveled off as SO₄ leaching has decreased, indicating that soils are no longer losing base cations (including Ca). However, these studies indicate that quite large changes in soil chemistry are needed to result in detectable changes in the F-Factor. For example, Watmough et al. (2003) reported that the FCa/SAA decreased by just 15% during a period in which the soil exchangeable Ca pool was estimated to have decreased by 40%. Overall, it appears that sizeable increases in soil base cation pools are required to produce measurable differences in soil buffering capacity.

We measured a significant difference in soil base cation concentrations in the upper 10 cm of soil, 4 years following application. The differences in base cation concentrations in the upper mineral soil are generally consistent with the expected increase in base cation content resulting from ash applications, even though there is considerable spatial variability in soil chemistry. Increases in mean base cation concentrations in the 0–10-cm soil horizon were typically between 0 and 100% compared with expected increases of 8–99% based on our mass balance estimates. The majority of studies that have applied wood ash to forest soils show that the majority of ash that is applied is retained in the upper mineral soil (Bramyrd &

Fransman, 1995; Saarsalmi et al., 2004). The increase in soil base cation concentration is typically associated with an increase in soil pH and improved nutrient content in vegetation (Deighton & Watmough, 2020; Ozolinčius et al., 2007). We similarly found that soil pH was higher in ash treated plots, and foliar concentrations of sugar maple had higher Ca concentrations (unpublished). We also noted that soil organic matter and soil moisture tended to be higher in ash treated plots, but again these differences were not statistically significant.

By subtracting estimated base cation leaching losses from control plots, we estimated that over the 4-year study less than 20% of the Ca that was applied in ash was leached below the 0.3-m soil depth. Estimated losses of Mg, K, and Na from ash were higher, with up to 44% of the Na applied in ash leached below the 0.3-m depth. As differences in soil water chemistry at the 0.3-m depth were no longer evident after 4 years, we assume that the remaining ash is incorporated within the 0–0.3-m soil horizon. We estimate that this would increase the base cation content of this layer by 3.5 to 45%, though typically <20%. This relatively small increase in base cation content of mineral soil would indicate that future increases in base cation leaching beyond the duration of this study are unlikely although longer-term studies beyond 4 years are required to confirm this observation. In our study, ash application rates were consistent with many studies in Europe and elsewhere and were chosen to replenish Ca losses associated with tree harvesting. Adding greater amounts of ash may also compensate for losses associated with historic acid deposition by increasing the soil base cation content. The greater increase in soil base saturation may increase base cation leaching losses, but the longer-term ecosystem benefits, as well as potential risks of enhanced trace metal mobility (Augusto et al., 2008; Kahl et al., 1996), would similarly need investigation.

The precipitous decline in lake Ca concentration that has been reported in central Ontario and elsewhere has led to concerns that lake ecosystems are becoming adversely impacted with the loss of more Ca-dependent species, such as daphniids (Jeziorski et al., 2008) and crayfish (Edwards et al., 2015). There are two, not necessarily mutually exclusive, reasons for the decline in lake Ca concentration. The first is caused by the large decline in acidic deposition (primarily SO_4), that leads a reduction in base cation [including Ca] leaching (Dillon & LaZerte, 1992;

Foster and Hazlett, 2002). This process is evident in this study, whereby changes in acidic leaching drive changes in base cation concentration. The second reason is soil acidification that is caused by the accelerated leaching of base cations due to acid deposition or possibly by timber harvesting, that may deplete soil Ca reserves slowly and gradually reduce the soil buffering capacity such that for a given amount of acid leaching, less base cations are leached (Likens, 2010; Watmough & Dillon, 2003, 2004; Yan et al., 2008). In central Ontario and elsewhere that are characterized by shallow soils with impermeable bedrock, surface water Ca concentrations have been directly related to soil exchangeable pools, such that regions with greater exchangeable soil Ca levels have higher Ca concentrations in surface waters draining these catchments (Houle et al., 2006; Kirchner & Lydersen, 1995; Watmough & Dillon, 2003). Replacing soil base cations through the application of wood ash (or lime) will certainly increase soil base cation pools and lead to several benefits to vegetation (and possibly other terrestrial biota) (Bieser & Thomas, 2019; Bramyrd & Fransman, 1995; Deighton & Watmough, 2020; Eriksson, 1998; Kahl et al., 1996), but this study indicates that these changes will not likely translate to measurable benefit to surface waters unless ash applications are higher than the moderate dosages used in this study and also applied at the catchment scale.

5 Conclusion

Wood ash application to upland forest soils resulted in modest short-term increases in base cation leaching in upper soil horizons. The response varied between ash types, with fly ash showing much greater responses than fly ash. Despite an increase in base cation concentration in soil water, there was no increase in pH or ANC because SO_4 and, to a lesser extent, NO_3 leaching also increased post ash application. Base cation concentrations in upper mineral soil were higher in ash treated plots consistent with estimated increases in base cation pools resulting from ash applications. The increase in soil base cations did not result in a measurable increase in soil buffering capacity indicating that while wood ash will likely have several beneficial impacts to terrestrial systems, moderate ash dosages are not likely to increase Ca concentrations in surface waters unless applications

are greater than used in this study and are applied at the catchment scale.

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Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent to Publication We confirm that all authors have read the manuscript and agree to its submission in *Water, Air, & Soil Pollution*.

Conflict of Interest The authors declare that they have no competing interests.

References

- Alewell, C., Manderscheid, H., Meesenburg, H., & Bittersohl, J. (2000). Is acidification still an ecological threat? *Nature*, *407*, 856–857. <https://doi.org/10.1038/35038158>.
- Arnott, S. E., Celis-Salgado, M. P., Valleau, R. E., DeSellas, A. M., Paterson, A. M., Yan, N. D., Mol, J. P., & Rusak, J. A. (2020). Road salt impacts freshwater zooplankton at concentrations below current water quality guidelines. *Environmental Science & Technology*, *54*, 9398–9407. <https://doi.org/10.1021/acs.est.0c02396>.
- Arvidsson, H., & Lundkvist, H. (2003). Effects of crushed wood ash on soil chemistry in young Norway spruce stands. *Forest Ecology and Management*, *176*, 121–132. [https://doi.org/10.1016/S03781127\(02\)00278-5](https://doi.org/10.1016/S03781127(02)00278-5).
- Ashforth, D., & Yan, N. D. (2008). The interactive and effects of calcium concentration and temperature on the survival of *Daphnia pulex* at high and low food concentrations. *Limnology and Oceanography*, *53*(2), 420–432. <https://doi.org/10.4319/lo.2008.53.2.0420>.
- AshNet. 2020. AshNet [online]. <https://www.nrcan.gc.ca/science-data/research-centres-labs/forestry-research-centres/great-lakes-forestry-centre/ashnet/20279>. Accessed 23 November 2020.
- Augusto, L., Bakker, M. R., & Meredieu, C. (2008). Wood ash applications to temperate forest ecosystems—Potential benefits and drawbacks. *Plant and Soil*, *306*, 181–198. <https://doi.org/10.1007/s11104-008-9570-z>.
- Azan, S. S. E., Yan, N. D., Celis-Salgado, M. P., Arnott, S. E., Rusak, J. A., & Sutey, P. (2019). Could a residential wood ash recycling programme be part of the solution to calcium decline in lakes and forests in Muskoka (Ontario, Canada)? *Facets*, *4*, 69–90. <https://doi.org/10.1139/facets-2018-0026>.
- Bailey, S. W., Buso, D. C., & Likens, G. E. (2003). Implications of sodium mass balance for 454 interpreting the calcium cycle of a forested ecosystem. *Ecology*, *84*(2), 471–484.
- Bieser, J., & Thomas, S. (2019). Biochar and high-carbon wood ash effects on soil and vegetation in a boreal clearcut. *Canadian Journal of Forest Research*, *49*, 1124–1134. <https://doi.org/10.1139/cjfr-2019-0039>.
- Brais, S., Bélanger, N., & Guillemette, T. (2015). Wood ash and N fertilization in the Canadian boreal forest: Soil properties and response of jack pine and black spruce. *Forest Ecology and Management*, *348*, 1–14. <https://doi.org/10.1016/j.foreco.2015.03.021>.
- Bramyrd, T., & Fransman, B. (1995). Silvicultural use of wood ashes—effects on the nutrient and heavy metal balance in a pine (*Pinus sylvestris*, L.) forest soil. *Water, Air, and Soil Pollution*, *85*, 1039–1044.
- Buttle, J. M., & McDonald, D. J. (2002). Coupled vertical and lateral preferential flow on a forested slope. *Water Resources Research*, *38*(5), 1060. <https://doi.org/10.1029/2001WR000773>.
- Chapman, L.J., & Putnam, D.F. (1984). The physiography of southern Ontario. 3rd ed. Ontario Geological Survey, Government of Ontario, Canada. Special Volume 2. Pp 270.

- Deighton, H. D., & Watmough, S. A. (2020). Effects of non-industrial wood ash (NIWA) applications on soil chemistry and sugar maple (*Acer saccharum*, marsh.) seedling growth in an acidic sugar bush in Central Ontario. *Forests*, 11(6), 693. <https://doi.org/10.3390/f11060693>.
- Deighton, H. D., Watmough, S. A., Basiliko, N., Hazlett, P., Reid, C. R., & Gorgolewski, A. S. (in press). Trace metal biogeochemical responses following wood ash addition in a northern hardwood forest. *Canadian Journal of Forest Research*. <https://doi.org/10.1139/cjfr-2020-0320>.
- Demeyer, A., Voundi Nkana, J. C., & Verloo, M. G. (2001). Characteristics of wood ash and influence on soil properties and nutrient uptake: An overview. *Bioresource Technology*, 77, 287–295. [https://doi.org/10.1016/S0960-8524\(00\)00043-2](https://doi.org/10.1016/S0960-8524(00)00043-2).
- Dillon, P. J., & LaZerte, B. D. (1992). Response of the plastic Lake catchment, Ontario, to reduced Sulphur deposition. *Environmental Pollution*, 77(2–3), 211–217. [https://doi.org/10.1016/0269-7491\(92\)90079-P](https://doi.org/10.1016/0269-7491(92)90079-P).
- Domes, K. A., de Zeeuw, T., Massicotte, H. B., Elkin, C., McGill, W. B., Jull, M. J., Chisholm, C. E., & Rutherford, P. M. (2018). 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. *Canadian Journal of Soil Science*, 98(2), 246–263. <https://doi.org/10.1139/CJSS-20177-0115>.
- Edwards, B. A., Jackson, D. A., & Somers, K. (2015). Evaluating the effect of lake calcium concentration on the acquisition of carapace calcium by freshwater crayfish. *Hydrobiologia*, 744, 91–100. <https://doi.org/10.1007/s10705-014-2059-2>.
- Elliot, A., & Mahmood, T. (2015). Generation and management of solid residues by Canadian pulp and paper mills in 2013. Confidential report prepared for FPIInnovations.
- Emilson, C. E., Bélanger, N., Brais, S., Chisholm, C. E., Diochon, A., Joseph, R., Markham, J., Morris, D., Van Rees, K., Rutherford, M., Venier, L. A., & Hazlett, P. W. (2020). Short-term growth response of jack pine and spruce spp. to wood ash amendment across Canada. *GCB Bioenergy*, 12, 158–167.
- Eriksson, H. M. (1998). Short-term effects of granulated wood ash on forest soil chemistry in SW and NE Sweden. *Scandinavian Journal of Forest Research*, 2(Suppl), 23–32.
- Foster, N.W., & Hazlett, P.W. (2002). Trends in water chemistry in a maple forest on a steep slope. *Water, Air, & Soil Pollution: Focus*, 2, 23–36. <https://doi.org/10.1023/A:1015830223037>.
- Gorgolewski, A., Caspersen, J., Hazlett, P., Jones, T., Tran, H., & Basiliko, N. (2016). Responses of eastern red-backed salamander (*Plethodon cinereus*) abundance 1 year after application of wood ash in a northern hardwood forest. *Canadian Journal of Forest Research*, 46(3), 402–409. <https://doi.org/10.1139/cjfr-2015-0230>.
- Hannam, K. D., Venier, L., Allen, D., Deschamps, C., Hope, E., Jull, M., Kwiaton, M., McKenney, D., Rutherford, P. M., & Hazlett, P. W. (2018). Wood ash as a soil amendment in Canadian forests: What are the barriers to utilization? *Canadian Journal of Forest Research*, 48(4), 442–450. <https://doi.org/10.1139/cjfr-2017-0351>.
- Hessen, D. O., Andersen, T., Tominaga, K., & Finstad, A. G. (2017). When soft water becomes softer: drivers of critically low levels of Ca in Norwegian lakes. *Limnology and Oceanography*, 26, 289–298. <https://doi.org/10.1002/lno.10394>.
- Houle, D., Ouimet, R., Couture, S., & Gagnon, C. (2006). Base cation reservoirs in soil control the buffering capacity of lakes in forested catchments. *Canadian Journal of Fisheries and Aquatic Sciences*, 63, 471–474. <https://doi.org/10.1139/F06-007>.
- Jeziorski, A., & Smol, J. P. (2017). The ecological impact of lakewater calcium decline on softwater boreal ecosystems. *Environmental Reviews*, 25, 245–253. <https://doi.org/10.1139/er-2016-0054>.
- Jeziorski, A., Yan, N. D., Paterson, A. M., DeSellas, A. M., Turner, M. A., Jeffries, D. S., Keller, B., Weeber, R. C., McNicol, D. K., Palmer, M. E., McIver, K., Arseneau, K., Ginn, B. K., Cumming, B. F., & Smol, J. P. (2008). The widespread threat of calcium decline in fresh waters. *Science*, 322, 1374–1377. <https://doi.org/10.1126/science.1164949>.
- Kahl, J., Fernandez, R., Rustad, L., & Peckenham, J. (1996). Threshold application rates of wood ash to an acidic forest soil. *Journal of Environmental Quality*, 25, 220–227. <https://doi.org/10.2134/jeq1996.00472425002500020003x>.
- Keller, W., Dixit, S. S., & Heneberry, J. (2011). Calcium declines in northeastern Ontario lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 58, 2011–2020. <https://doi.org/10.1139/cjfas-58-10-2011>.
- Kirchner, J. W., & Lydersen, E. (1995). Base cation depletion and potential long-term acidification of Norwegian catchments. *Environmental Science & Technology*, 29(8), 1953–1960. <https://doi.org/10.1021/es00008a012>.
- Lawrence, G. B., Hazlett, P. W., Fernandez, I. J., Ouimet, R., Bailey, S. W., Shortle, W. C., Smith, W. T., & Antidormi, M. R. (2015). Declining acidic deposition begins reversal of forest-soil acidification in the northeastern U.S. and eastern Canada. *Environmental Science & Technology*, 49, 13103–13111.
- Ludwig, B., Rumpf, S., Mindrup, M., Meiwes, K.-J., & Khanna, P. K. (2002). Effects of lime and wood ash on soil-solution chemistry, soil chemistry and nutritional status of a pine stand in northern Germany. *Scandinavian Journal of Forest Research*, 17, 225–227. <https://doi.org/10.1080/028275802753742891>.
- The Kennis Lake Planning Steering Committee. (2007). Kennis watershed and lakes management plan. The Kennis Lake Cottage Owners' Association. pp 152. Available <https://www.klcoa.org/wp-content/uploads/2018/01/Kennis-Watershed-and-Lakes-Plan-September-2007.pdf>. Accessed 20 July 2020.
- Likens, G. E. (2010). The role of science in decision making: Does evidence-based science drive environmental policy? *Frontiers in Ecology and the Environment*, 8, 1–9. <https://doi.org/10.1890/090132>.
- Likens, G. E., Driscoll, C. T., & Buso, D. C. (1996). Long-term effects of acid rain: Response and recovery of a forest ecosystem. *Science*, 272(5259), 244–246. <https://doi.org/10.1126/science.272.5259.244>.
- Likens, G., Driscoll, C., Buso, D., Siccama, T. G., Johnson, C. E., Lovett, G. M., Fahey, T. J., Reiners, W. A., Ryan, D. F., Martin, C. W., & Bailey, S. W. (1998). The biogeochemistry of calcium at Hubbard brook. *Biogeochemistry*, 41, 89–173. <https://doi.org/10.1023/A:1005984620681>.

- McLaughlin, J. W. (2014). Forest soil calcium dynamics and water quality: Implications for forest management planning. *Soil Science Society of America Journal*, 78(3), 1003–1020.
- Morris, D. M., Hazlett, P. W., Fleming, R. L., Kwiaton, M. M., Hawdon, L. A., Leblanc, J. D., Primavera, M. J., & Weldon, T. P. (2019). Effects of biomass removal levels on soil carbon and nutrient reserves in conifer-dominated, coarse-textured sites in northern Ontario: 20-year results. *Soil Science Society of America Journal*, 83, S116–S132.
- Norström, S. A., Bylund, D., Vestin, J. L. K., & Lundström, U. S. (2011). Water chemistry in a boreal catchment in Central Sweden. *Water, Air, and Soil Pollution*, 221, 123–136. <https://doi.org/10.1007/s11270-011-0775-z>.
- Noyce, G. L., Jones, T., Fulthorpe, R., & Basiliko, N. (2017). Phosphorus uptake and availability and short-term seedling growth in three Ontario soils amended with ash and biochar. *Canadian Journal of Soil Science*, 97(4), 678–691. <https://doi.org/10.1139/cjss-2017-0007>.
- Nutrient and Management Act (2002). Government of Ontario. O. Reg. 267/03: general under Nutrient and Management Act, 2002, S.O. 2002, c.4 Retrieved June 12, 2020, from <https://www.ontario.ca/laws/regulation/030267>
- Oliver, B. G., Thurman, E. M., & Malcom, R. L. (1983). The contribution of humic substances to the acidity of colored natural waters. *Geochimica et Cosmochimica Acta*, 47(11), 2031–2035. [https://doi.org/10.1016/0016-7037\(83\)90218-1](https://doi.org/10.1016/0016-7037(83)90218-1).
- Ontario Lake Partner (2020). Dorset environmental science centre: lake partner program. Available <https://desc.ca/programs/LPP>. Accessed 20 July 2020.
- Ozolinčius, R., Buožytė, R., & Varnagiryté-Kabašinskiėnė, I. (2007). Wood ash and nitrogen influence on ground vegetation cover and chemical composition. *Biomass and Bioenergy*, 31(10), 710–716. <https://doi.org/10.1016/j.biombioe.2007.06.015>.
- Park, B. B., Yanai, R. D., & Sahn, J. M. (2004). Wood ash effects on soil solution and nutrient budgets in a willow bioenergy plantation. *Water, Air, and Soil Pollution*, 159, 209–224. <https://doi.org/10.1023/B:WATE.0000049177.60761.37>.
- Phillips, T., & Watmough, S. A. (2012). A nutrient budget for a selection harvest: Impacts for long-term sustainability. *Canadian Journal of Forest Research*, 42(12), 2064–2077. <https://doi.org/10.1139/cjfr-2012-0024>.
- Pitman, R. M. (2006). Wood ash use in forestry—A review of environmental impacts. *Journal of Forestry*, 79(5), 563–588. <https://doi.org/10.1093/forestry/cpl041>.
- Reid, C., & Watmough, S. A. (2016). Spatial patterns, trends, and the potential long-term impacts of tree harvesting on lake calcium levels in the Muskoka River watershed, Ontario, Canada. *Canadian Journal of Fisheries and Aquatic Sciences*, 73(2), 382–393. <https://doi.org/10.1139/cjfas-2015-0231>.
- Ring, E., Jacobson, S., & Nohrstedt, H. Ö. (2006). Soil-solution chemistry in a coniferous stand after adding wood ash and nitrogen. *Canadian Journal of Forest Research*, 36(1), 153–163.
- RStudio Team (2016). RStudio: Integrated Development for R. RStudio, Inc. Available <http://www.rstudio.com/>.
- Saarsalmi, A., Malkonen, E., & Kukkola, M. (2004). Effects of wood ash fertilization on soil chemical properties and stand nutrient status and growth of some coniferous stands in Finland. *Scandinavian Journal of Forest Research*, 19(3), 217–233. <https://doi.org/10.1080/02827580410024124>.
- Soil Classification Working Group. (1998). The Canadian System of Soil Classification. 3rd ed. Agriculture and Agri-Food Canada Publication 1646. NRC Research Press. pp 187.
- Steenari, B.-M., & Lindqvist, O. (1997). Stabilization of biofuel ashes for recycling to forest soil. *Biomass and Bioenergy*, 13(1–2), 39–50. [https://doi.org/10.1016/S0961-9534\(97\)00024-X](https://doi.org/10.1016/S0961-9534(97)00024-X).
- Stoddard, J.L., Jeffries, D.S., Lükewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, B.L., Skjelkvåle, M., Stainton, M.P., Traaen, T., van Dam, H., Webster, K.E., Wieting, J., & Wilander, A. (1999). *Nature*, 401, 575–578. [doi:https://doi.org/10.1038/44114](https://doi.org/10.1038/44114).
- Vance, E. (1996). Land application of wood-fired and combination ashes: An overview. *Journal of Environmental Quality*, 25, 937–944. <https://doi.org/10.2134/jeq1996.00472425002500050002x>.
- Warby, R. A. F., Johnson, C. E., & Driscoll, C. T. (2009). Continuing acidification of organic soils across the northeastern USA: 1984–2001. *Soil Science Society of America Journal*, 73, 274–284.
- Williams, T. M., Hollis, C. A., & Smith, B. R. (1996). Forest soil and water chemistry following bark and boiler bottom ash application. *Journal of Environmental Quality*, 25(5), 955–961. <https://doi.org/10.2134/jeq1996.00472425002500050005x>.
- Watmough, S. A., & Dillon, P. J. (2003). Base cation losses and nitrogen budgets for seven forested catchments in Central Ontario, 1983–1999. *Forest Ecology and Management*, 177(1–3), 155–177. [https://doi.org/10.1016/S0378-1127\(02\)00320-1](https://doi.org/10.1016/S0378-1127(02)00320-1).
- Watmough, S. A., & Dillon, P. J. (2004). Major element fluxes from coniferous catchment in Central Ontario, 1983–1999. *Biogeochemistry*, 67, 369–398. <https://doi.org/10.1023/B:BIOG.0000015792.42624.57>.
- Watmough, S. A., Aherne, J., & Dillon, P. J. (2003). Potential impact of forest harvesting on lake chemistry in south-Central Ontario at current levels of acid deposition. *Canadian Journal of Fisheries and Aquatic Sciences*, 60, 1095–1103. <https://doi.org/10.1139/F03-093>.
- Watmough, S. A., Eimers, C., & Baker, S. (2016). Impediments to recovery from acid deposition. *Atmospheric Environment*, 146, 15–27. <https://doi.org/10.1016/j.atmosenv.2016.03.021>.
- Watmough, S.A., Aherne, J., Eimers, M.C., & Dillon, P.J. (2007) Acidification at Plastic Lake, Ontario: has 20 years made a difference? *Water, Air, & Soil Pollution: Focus*, 7(1-3), 301–306. <https://doi.org/10.1007/s11267-006-9064-z>.
- Yan, N., Paterson, A. M., Somers, K. M., & Scheider, W. A. (2008). Thirty years of aquatic science at the Dorset environmental science Centre: Transforming understanding of factors that regulate aquatic ecosystems on the southern Canadian shield. *Canadian Journal of Fisheries and Aquatic Sciences*, 65, 781–944. <https://doi.org/10.1139/F08-077>.

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