

Trace metal biogeochemical responses following wood ash addition in a northern hardwood forest

Holly D. Deighton, Shaun A. Watmough, Nathan Basiliko, Paul W. Hazlett, Carolyn R. Reid, and Adam Gorgolewski

Abstract: Wood ash may be useful as a forest soil amendment in Canada, but trace metals can have detrimental effects if they accumulate in, or are transported from, forest ecosystems. Metal concentrations in soil water and sugar maple (*Acer saccharum* Marsh.) seedling tissue chemistry were measured in a north temperate hardwood forest over 4 years following a biomass boiler ash addition field trial. Twenty plots (3 m × 3 m) were established in Haliburton Forest with both fly and bottom ash treatments of 0, 4, and 8 Mg·ha⁻¹ with four replicates, and tension lysimeters were positioned in each plot at 30, 50, and 100 cm depths. Over the 4 years, soil water metal concentrations in treated plots were not significantly different from those of the control plots. No differences in metal concentrations in foliage of sugar maple seedlings could be detected, but there were significantly higher concentrations of some metals (Al, Fe, Zn, Pb, Ni, and Sr) in roots of treated plots. Simulated drought mobilized several metals in upper mineral soil, but this mobilization occurred similarly in controls and ash-treated soils. These results suggest that doses below 8 Mg·ha⁻¹ industrial wood ash with trace metal concentrations below Canadian regulatory limits do not cause an increase in trace metal mobility or availability in northern hardwood forests with acidic soils during the first 5 years after application.

Key words: fly ash, bottom ash, sugar maple, metal toxicity, forest soil amendments.

Résumé : On peut utiliser la cendre de bois pour amender les sols au Canada mais les métaux-traces peuvent avoir des effets néfastes s'ils sont exportés des écosystèmes forestiers ou s'y accumulent. La concentration des métaux dans l'eau du sol et les propriétés chimiques des tissus des semis d'érable à sucre (*Acer saccharum* Marsh.) ont été mesurées dans une forêt feuillue nordique tempérée pendant quatre années suivant l'apport de cendres de chaudières alimentées en biomasse dans le cadre d'un essai sur le terrain. Vingt placettes (3 m × 3 m) ont été établies dans la forêt Haliburton et traitées avec des cendres volantes et résiduelles à raison de 0, 4 et 8 Mg·ha⁻¹ avec quatre répétitions. Des lysimètres à tension ont été placés dans chaque placette à 30, 50 et 100 cm de profondeur. Au cours des quatre années, la concentration des métaux dans l'eau du sol des placettes traitées n'était pas significativement différente de celle des placettes témoins. Aucune différence dans la concentration des métaux n'a pu être détectée dans le feuillage des semis d'érable à sucre mais la concentration de certains métaux (Al, Fe, Zn, Pb, Ni et Sr) était significativement plus élevée dans les racines des placettes traitées. Une sécheresse simulée a entraîné la mobilisation de plusieurs métaux dans la partie supérieure du sol minéral, mais cette mobilisation est survenue de façon similaire dans les sols témoins et les sols traités avec la cendre. Ces résultats indiquent que des doses inférieures à 8 Mg·ha⁻¹ de cendre de bois industrielle avec des concentrations de métaux-traces inférieures aux limites permises au Canada n'entraînent pas d'augmentation de la mobilisation ou de la disponibilité de métaux-traces dans les forêts feuillues nordiques sur des sols acides durant les premières cinq années après une application. [Traduit par la Rédaction]

Mots-clés : cendre volante, cendre résiduelle, érable à sucre, toxicité des métaux, amendement du sol en forêt.

Introduction

Concerns over soil acidification and associated ecological impacts has promoted the potential use of wood ash as an amendment to increase soil pH and nutrient levels. Increased production of wood ash from a growing bioenergy sector (Pugliese et al. 2014) as well as increasing costs of landfill disposal and difficulties in finding new landfill sites (Demeyer et al. 2001) have sparked interest in using wood ash as a fertilizer in eastern North America (Hannam et al. 2018). However, more research is needed on the fate of trace metals

in wood ash and the detrimental effects these metals may have if they accumulate in forest ecosystems.

Regulation of wood ash is done at the provincial and territorial levels in Canada, and many of these areas require ash to be analyzed for trace element concentrations of arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn) prior to application (Hannam et al. 2016). Alberta is the only province in Canada with guidelines for the use of wood ash as a soil amendment (Alberta Environment 2002). In Ontario, the use of wood ash as a

Received 2 July 2020. Accepted 29 October 2020.

H.D. Deighton and C.R. Reid. Environmental and Life Sciences Graduate Program, Trent University, Peterborough, ON K9J 7B8, Canada.

S.A. Watmough. School of the Environment, Trent University, Peterborough, ON K9J 7B8, Canada.

N. Basiliko. Vale Living with Lakes Centre and the Department of Biology, Laurentian University, 935 Ramsey Lake Road, Sudbury, ON P3E 2C6, Canada.

P.W. Hazlett. Natural Resources Canada, Canadian Forest Service, Great Lakes Forestry Centre, 1219 Queen Street East, Sault Ste. Marie, ON P6A 2E5, Canada.

A. Gorgolewski. Graduate Department of Forestry, University of Toronto, 33 Willcocks Street, Toronto, ON M5S 3B3, Canada.

Corresponding author: Holly Deighton (email: hdeighton@trentu.ca).

Copyright remains with the author(s) or their institution(s). Permission for reuse (free in most cases) can be obtained from copyright.com.

soil amendment is governed by the Environmental Protection Act and the Nutrient Management Act, and no specific guidelines have yet been developed for its use on agricultural and forest soils (Hannam et al. 2016).

Wood ash has been shown to increase soil pH and mitigate the effects of soil acidification (Reid and Watmough 2014), and applying wood ash at rates equivalent to liming requirements should not cause any environmental risk (Campbell 1990). Sugar maple (*Acer saccharum* Marsh), an economically important and dominant species in eastern North America, has been shown to benefit from liming and calcium (Ca) additions (Long et al. 1997; Moore et al. 2012; Juice et al. 2006), with increases in soil pH, foliar Ca concentration, and tree growth metrics (Reid and Watmough 2014), and thus could also benefit from wood ash addition. However, specific concerns with wood ash must be addressed before it is used widely as a forest soil amendment in Canada (Hannam et al. 2018).

Wood ashes with high trace metal concentrations can be detrimental to forest ecosystems if applied at high dosages (Pitman 2006; Augusto et al. 2008). Industrial wood ashes are typically separated into fly ash and bottom ash waste streams in boilers. Fly ash is more lightweight and reactive than bottom ash and generally contains higher levels of metals such as Cd, Zn, Cu, and Pb (Huang et al. 2004). The initial increase in soil pH brought about by soil amendments such as wood ash generally results in a decreased availability of Zn, Cd, Pb, Cu, Ni, and other metals (Sommers 1980), through either the precipitation of insoluble phases (such as metal hydroxides) or promoting metal sorption via surface complexation processes (Querol et al. 2006). When the effects of wood ash on soil pH begin to decrease with acid additions from rain or other sources, metals retained in the soil become solubilized and mobilized (Zhan et al. 1996), which may result in leaching and subsequent groundwater contamination (Chirenje 2000). Additionally, concern over forest ecosystem pollution from trace metals in wood ash may be exacerbated due to increased occurrences of drought caused by climate change. Following summer drought events, declines in soil water pH associated with oxidization of sulfur (S) stored in upland organic soil can cause significant increases in dissolved metal concentrations (Landre et al. 2010).

Wood ash may be a useful product to lessen the effects of acidification and nutrient losses in eastern North American soils, but concern with trace metal accumulation and enrichment must be addressed before it can be used as a regular forest management practice (Huotari et al. 2015). Experiments have focused on changes in soil pH and the exchangeable base cation pool and tree growth rather than investigations of soil solution to measure the effectiveness of wood ash applications in forest ecosystems. It is widely accepted that ash application on peatlands promotes tree growth (Moilanen et al. 2012; Saarsalmi et al. 2014); however, on upland forest soils, ash application generally does not increase tree growth (Jacobson 2003). Ash application is still recommended on upland forest soils for nutrient cycling, particularly in Sweden (Olsson et al. 2017), and has been shown to have a positive effect on Jack pine (*Pinus banksiana* Lamb.) growth in upland forest sites in Canada (Emilsson et al. 2020). Currently, field studies are being conducted across Canada to help policy makers address provincial and territorial restrictions regarding wood ash regulation (Hannam et al. 2017). Investigations of soil solution chemistry have shown increased concentrations of Ca, Mg, NO₃, and SO₄ in soil water following ash application to acidic forest podzols (Kahl et al. 1996; Williams et al. 1996; Norström et al. 2012), and a review by Lundström et al. (2003) concluded that wood ash application generally increased dissolved organic carbon leaching and decreased soil solution pH.

Currently in Canada, wood ash field trials are being conducted in British Columbia, Saskatchewan, Manitoba, Ontario, and Quebec

to examine the effects of wood ash on forest ecosystems (Hannam et al. 2017). Recent publications from research conducted at these sites found that some concentrations of metals (Cu, molybdenum (Mo), and Zn) increased in forest floor (LFH) soil following ash application (Domes et al. 2018), and further research is needed on the potentially detrimental effects wood ash may have on understory vegetation communities and seedling growth, such as increases in plant tissue metal concentrations (Bieser and Thomas 2019; Emilsson et al. 2020; Hart et al. 2019; Deighton and Watmough 2020).

The aim of this study was to investigate the fate of various trace metals in wood ash as a function of soil water and plant tissue concentrations in the 5 years post ash application. We also conducted a laboratory drought experiment to investigate the potential for metal mobilization to occur in upland forest soils following summer drought events and whether this response was greater in ash-treated soils. We predicted that an increase in soil and soil water metal concentrations would occur in the ash treatments, with the largest changes in the upper soil horizons (0–30 cm) during the first year following ash application. We also predicted that sugar maple seedling foliar metal concentrations would increase following wood ash application and that differences would be more pronounced in fly ash treatments at a higher application rate. It was also predicted that soil water metal concentrations would be highest following simulated drought and that the impact of drought would be lessened in ash-amended soils despite larger metal pools due to alkalinity associated with the ash buffering acidity generation.

Materials and methods

Site location

The study site was located in Haliburton Forest and Wildlife Reserve (45°11N, 78°35W), a mixed-deciduous forest underlain by granitic gneiss Precambrian Shield Bedrock (Neary et al. 1987). Dominant canopy trees included sugar maple (*Acer saccharum* Marsh.) and American beech (*Fagus grandifolia* Ehrh.), but there was also a heavy presence of yellow birch (*Betula alleghaniensis* Britton.) and eastern hemlock (*Tsuga canadensis* (L.) Carr). Stem density was approximately 450 stems·ha⁻¹ and basal area was 28.3 m²·ha⁻¹. In the summer of 2013, dominant understory vegetation (total height of less than 2 m and diameter at breast height of <1 cm) included sugar maple, beech (*Fagus* spp.), and raspberry (*Rubus* spp.). Climate is north temperate — south boreal (Reid and Watmough 2016), with a long-term mean annual precipitation of 1074 mm and a long-term mean annual temperature of 5.0 °C (1981–2010; Environment Canada 2019). During the study period of 2013–2017, the mean annual precipitation was 1324, 1146, 977.3, 1080, and 1330 mm, respectively (Environment Canada 2020), and the mean annual temperature was 5.0, 3.9, 5.1, 6.4, and 5.8 °C, respectively (Environment Canada 2020). Soils were shallow, acidic (pH ranging from 4.0 to 5.5) (Gorgolewski et al. 2016), medium- to coarse-textured sandy loams (Chapman and Putnam 1984) belonging to the Eluviated Dystric Brunisol subgroup based on the Canadian System of Soil Classification (Soil Classification Working Group 1998). Soil horizon thickness averaged 8 cm (LF), 12 cm (H), and 10 cm (Ah). The site was managed using single tree selection silviculture (Gorgolewski et al. 2016), which maintains an uneven-aged stand by removing about 30% of the stand every 20- to 25-year cycle. Phillips and Watmough (2012) estimated that tree harvesting could remove 7.0 to 15.4 kg·ha⁻¹·year⁻¹ (approximately 340 kg·ha⁻¹ per 20- to 25-year cycle).

Experimental design

Haliburton Forest in situ

An area of forest was selected and twenty 3 m × 3 m study plots were established, each with a 2.5 m buffer, in the summer of 2012

Table 1. Elemental concentration of fly and bottom ash applied in Haliburton Forest and Wildlife Reserve in August 2013.

	Fly ash concn. ^a	Bottom ash concn. ^a	NASM limits ^b	
			CM1	CM2
pH	8.6	9.7		
LOI (g·kg ⁻¹)	204.2	4.3		
C (g·kg ⁻¹)	175.7	5.2		
N (g·kg ⁻¹)	0.9	nd		
S (g·kg ⁻¹)	42.2	2.9		
Ca (g·kg ⁻¹)	101.1	43.6		
Mg (g·kg ⁻¹)	8.7	8.4		
K (g·kg ⁻¹)	30.7	14.3		
P (g·kg ⁻¹)	3.8	1.7		
Na (g·kg ⁻¹)	36.4	16.3		
Mn (g·kg ⁻¹)	8	3.2		
Al (g·kg ⁻¹)	23.3	44.7		
Fe (g·kg ⁻¹)	15.4	28.2		
Mo (mg·kg ⁻¹)	3	1	5	94
As (mg·kg ⁻¹)	10	12	13	170
Cd (mg·kg ⁻¹)	6	1	3	34
Zn (mg·kg ⁻¹)	691	140	500	4200
Cu (mg·kg ⁻¹)	52	38	100	1700
Pb (mg·kg ⁻¹)	21	15	150	1100
Cr (mg·kg ⁻¹)	28	33	210	2800
Co (mg·kg ⁻¹)	10	13	34	340
Ni (mg·kg ⁻¹)	16	20	62	420
Se (mg·kg ⁻¹)	10	3	2	34
Be (mg·kg ⁻¹)	nd	1		
V (mg·kg ⁻¹)	40	63		
Sr (mg·kg ⁻¹)	387	218		
Ba (mg·kg ⁻¹)	1.7	0.9		
La (mg·kg ⁻¹)	10	18		
Li (mg·kg ⁻¹)	12	22		

Note: Values are the mean of 3 replications. nd, not detected.

^aGorgolewski et al. (2016).

^bNutrient and Management Act (Government of Ontario 2002). Ontario Regulation 267/03 of the Nutrient Management Act limits for unrestricted (CM1) and restricted (CM2) use of wood ash for land application as a non-agricultural non-aqueous source material are also shown.

(Gorgolewski et al. 2016). The site was naturally regenerated, with no site preparation, and the plots and buffer zones were free from saplings and large trees (diameter at breast height (DBH) > 2.5 cm). Treatment blocks were identified based on moisture content and light availability and were randomized within blocks to reduce variability not caused by treatment effects. The five treatments were controls (no ash), untreated loose bottom ash (applied at either 4 or 8 Mg·ha⁻¹), and untreated loose fly ash (applied at either 4 or 8 Mg·ha⁻¹). Each 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 and 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. Ash chemistry is described in Table 1.

Bottom and fly ashes were produced from bark residues recovered from a large Babcock and Wilcox RotoStoker VGC biomass boiler system (for 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 (×3), 0.5 m (×2), and

1 m (×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 µm pore size (Model B02M2, Soil Moisture Equipment Corp., Santa Barbara, California). Prior to installation the lysimeters were acid washed with 1 mol·L⁻¹ HCl and then rinsed repeatedly with deionized water. Rinsing was complete when the pH, conductivity, and base cation and trace metal 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 prior to analysis.

Soil and sugar maple seedling samples were collected in the study plots in August 2017. Soil and seedling were not disturbed where the lysimeters collected soil water. From each plot, soil grab samples were sampled using a trowel to a depth of 30 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). Self-regenerated sugar maple seedlings (DBH < 2.5 cm, *n* ≤ 6 per plot) were removed carefully (keeping the roots intact) from treatment and control plots. Soil and seedling samples were sealed in plastic bags and stored at 4 °C until analysis.

Laboratory drought experiment ex situ

A 30-day simulated drought experiment was established in February 2019. Two treatments, with four replicates, were established: a 30-day drought treatment and a 30-day continually 'wet' treatment adapted from Juckers and Watmough (2014). For each treatment, approximately 70 g of homogenized, field moist soil (sampled from experimental treatment plots 4 years after ash application, including upper organic (LF) and lower organic (H) soil horizons from the 0–20 cm depth) (Soil Classification Working Group 1998) was added to 120 cm³ plastic containers and placed in an incubator (Thermo Scientific Precision Economy Incubator 3522) at 27 °C. Lids were left ajar in both treatments to allow air exchange. The mass of each sample was recorded at the beginning of the experiment and recorded every three days to maintain field moist conditions of the 'wet' treatments by adding back the mass of water lost from samples using deionized water. After 30 days, the mass of water lost in the drought treatment was added back using deionized water, and the samples were homogenized using a glass stirring rod and left for 24 h.

Chemical analysis

Wood ash

Ash chemistry was determined prior to addition. Carbon (C), nitrogen (N), and S were determined with a CNS combustion analyzer (Vario EL III, Elementar Americas, Mt. Laurel, New Jersey) and Ca, magnesium (Mg), potassium (K), phosphorous (P), sodium (Na), manganese (Mn), aluminum (Al), iron (Fe), Mo, As, Cd, Zn, Cu, Pb, Cr, Co, Ni, Se, beryllium (Be), vanadium (V), strontium (Sr), barium (Ba), lanthanum (La), and lithium (Li) were measured with an inductively coupled argon plasma spectrometer (Varian

Analytical Instruments, Walnut Creek, California) following high temperature microwave acid digestion (EPA standard method 3052; www.epa.gov) (Gorgolewski et al. 2016).

Soil and sugar maple seedlings

Soil cores were weighed, dried at 105 °C for 24 h, and then weighed again to calculate bulk density. Five grams of oven-dried soil was transferred to a muffle furnace at 450 °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 °C for 24 h, and reweighing. The remainder of the grab samples were left to air-dry for 2 weeks then sieved (<2 mm). A 1:5 soil to 0.01 mol·L⁻¹ CaCl₂ slurry and a 1:5 soil to reverse osmosis water slurry was used to measure pH and electrical conductivity, respectively, by allowing the slurries to be stirred every 2 min for 10 min and left to rest for 10 min before taking readings with an OAKTON pH 510 series multimeter (Oakton Instruments, Vernon Hills, Illinois, USA). The probe was calibrated every 15 samples. Sugar maple seedlings were washed with deionized water to remove excess soil particles and oven-dried at 60 °C for 48 h. The seedlings were separated into roots, stem, and foliage; weighed to the nearest 0.0001 g; and ground using a ball-mill. Replicate samples of roots stem and foliage from the same plots were pooled plotwise prior to chemical analysis.

Soil and seedling chemistry was determined using a CNS combustion analyzer (Elementar vario MACRO cube CNS) for total C, N, and S, and using inductively coupled plasma optical emission spectrometry (ICP-OES) following nitric acid digestion (Aristar® Plus, CAS 7697-37-2) for Ca, Mg, K, P, Na, Mn, Al, Fe, As, Cd, Zn, Cu, Pb, Ni, and Sr. 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. Precision of CNS analysis was confirmed using standard soil samples (EnviroMAT SS-2). Samples for ICP-OES were weighed (~0.2 g each) and placed in 50 mL DigiTUBE[®]s (SCP Science, Quebec, Canada), 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 a 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 samples 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.

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 with a Man-Tech PC-Titrate system (Mantech, Guelph, Ontario). Silica dioxide (SiO₂), nitrate (NO₃), ammonium (NH₄), total nitrogen (TN), and dissolved organic carbon (DOC) were measured with a Technicon Autoanalyser II (SEAL Analytical Inc., Mequon, Wisconsin) by the ascorbic acid, cadmium reduction, sodium nitroprusside, autoclave digestion, and potassium persulfate methods, respectively. Sulfate (SO₄) and chloride (Cl) concentrations were determined by ion chromatography. Base cations and metals were analyzed with an Agilent 7700X Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent Technologies, Santa Clara, California).

Soil water from the simulated drought experiment was extracted for chemical analysis by centrifuging approximately 40 mL of the soil-water suspension at 5000 r·min⁻¹ for 15 min. Soil water samples were analyzed at the Trent Environmental Research Lab with an OAKTON pH 510 Series meter (Oakton Instruments, Vernon Hills, Illinois) then filtered with a 0.45 µm nylon syringe filter for further analysis. Dissolved organic carbon concentrations were determined using a Shimadzu TOC-V instrument (5 mL sample and 15 mL deionized water) and concentrations of SO₄ and NO₃ were measured using ion chromatography (0.5 mL sample). Base cation (Ca, Mg, K, Na) and dissolved metal (Mn, Al, Fe, As, Cd, Zn, Cu, Pb, Co, Ni) concentrations were determined with an inductively coupled argon plasma spectrometer (Varian Analytical Instruments, Walnut Creek, California).

Statistical analysis

Soil water chemistry was modelled using a two-way mixed-model analysis of variance (ANOVA) with interaction effects. Concentration of analyte in soil water (repeated measures factor) was modelled as a function of treatment (fixed effect) and time (fixed effect). Separate models were created for each sampling depth. To control for the effect of differences among replicate plots within the same treatment type, a blocking treatment (random effect) was added to the ANOVA; however, it was not included in the final model, as it did not affect how much variation in the dependent variable they explain (low sum-of-squares and high *p* value). To check whether the model fits the assumption of homoscedasticity, quantile-quantile plots were used. Principal components analysis (PCA) was used to investigate relationships in soil water chemistry within each sampling depth. A correlation analysis (Pearson's *R*) was performed before PCA to remove analytes with no or low correlations. Outliers were identified (<1% of the dataset) using a quantile-quantile plot and removed prior to PCA. Non-normal data (according to Levene's test) were log transformed prior to PCA and ANOVA calculations.

To test the null hypothesis that ash has no effect on soil and sugar maple seedling tissue chemistry 4 years after application, comparisons were made between treated and control plots using a one-way ANOVA. Dunnett's post hoc test was used to compare treatment plots with control plots, and Tukey's honestly significant difference test was used to determine pairwise comparisons. The post hoc tests were completed only on those variables for which a significant treatment effect was determined by one-way ANOVA.

All statistical analysis was performed using RStudio, version 1.1.383 (RStudio Team 2016), and all results were significant at *p* < 0.05 unless otherwise stated.

Results

Wood ash chemistry

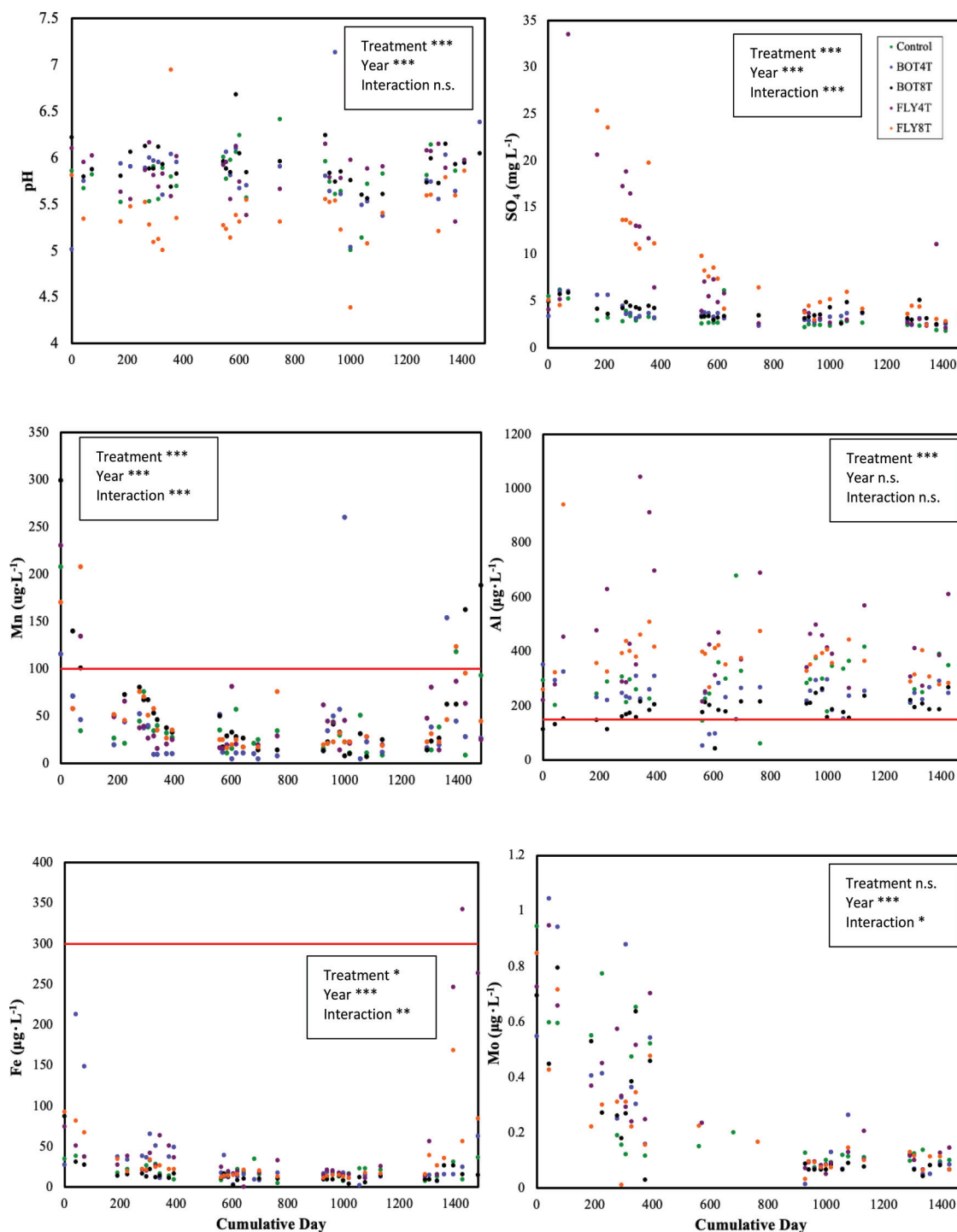
Metal concentrations in fly and bottom ashes were within non-agricultural source material limits for restricted land application of wood ash, but concentrations of Cd, Se, and Zn in fly ash breached limits for unrestricted land application (Nutrient and Management Act, 2002) (Table 1). Fly ash had much higher (15–30 times) C and S concentrations than bottom ash, and concentrations of Ca, Na, K, and P were approximately double those in bottom ash. Nitrogen concentrations were low in fly ash and not detected in bottom ash. Concentrations of metals were similar in both bottom ash and fly ash, with the exception of Zn and Cd, which were 4–6 times higher in fly ash.

Soil water chemistry (2013–2017)

Soil water chemistry at all three depths varied considerably over time (Supplementary Tables S1–S5¹). There was a significant

¹Supplementary data are available with the article at <https://doi.org/10.1139/cjfr-2020-0320>.

Fig. 1. Mean concentrations for lysimeter (30 cm) soil water concentrations of pH, SO_4 , Mn, Al, Fe, Mo, B, As, Cu, Cd, Zn, Pb, Cr, Co, Ni, Se, Sr, and Ba. Day 0 represents first sampling day in August 2013. Red line represents Canadian Council of Ministers of the Environment (CCME 1987) long-term water quality guidelines for fresh water ($\mu\text{g}\cdot\text{L}^{-1}$). Updated CCME guidelines for B (2009), As (1997), Cd (2014), Zn (2018), and Cr (1997) were used. Limits for sulfate (500 $\text{mg}\cdot\text{L}^{-1}$), Mo (73 $\mu\text{g}\cdot\text{L}^{-1}$), B (1500 $\mu\text{g}\cdot\text{L}^{-1}$), and Ni (25 $\mu\text{g}\cdot\text{L}^{-1}$) are not shown. No data were available for Ba. No guidelines were available for Sr or Mn, so Guidelines for Canadian Drinking Water Quality (Health Canada 2016, 2019) were used. Statistical significance: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$; n.s., no significance.

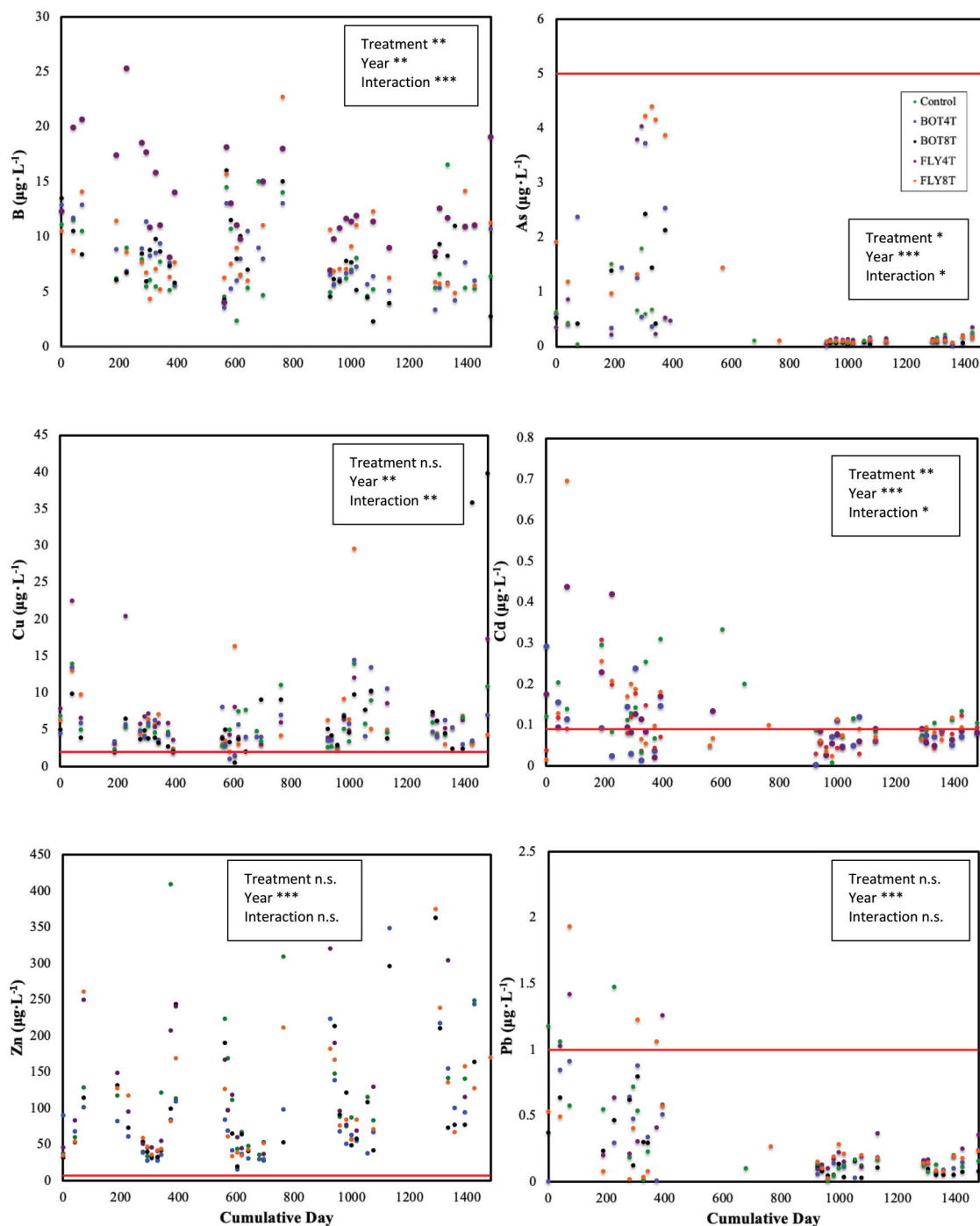


treatment effect on soil water pH and SO_4 concentrations following ash addition ($p < 0.05$). Soil water pH was significantly lower in fly ash (8 $\text{Mg}\cdot\text{ha}^{-1}$) plots than in control plots from 2014 to 2017 at the 30 cm depth. The response of SO_4 following ash application was opposite that of pH in soil water, with significantly higher

concentrations of SO_4 in fly ash (4 and 8 $\text{Mg}\cdot\text{ha}^{-1}$) plots at all depths from 2013 to 2017.

Concentrations of some metals at the 30 cm depth (Fe, Mo, As, Cd, Pb, Cr, Se, and Sr) were higher in all treatments and controls for the first year following ash addition compared with

Fig. 1 (continued).



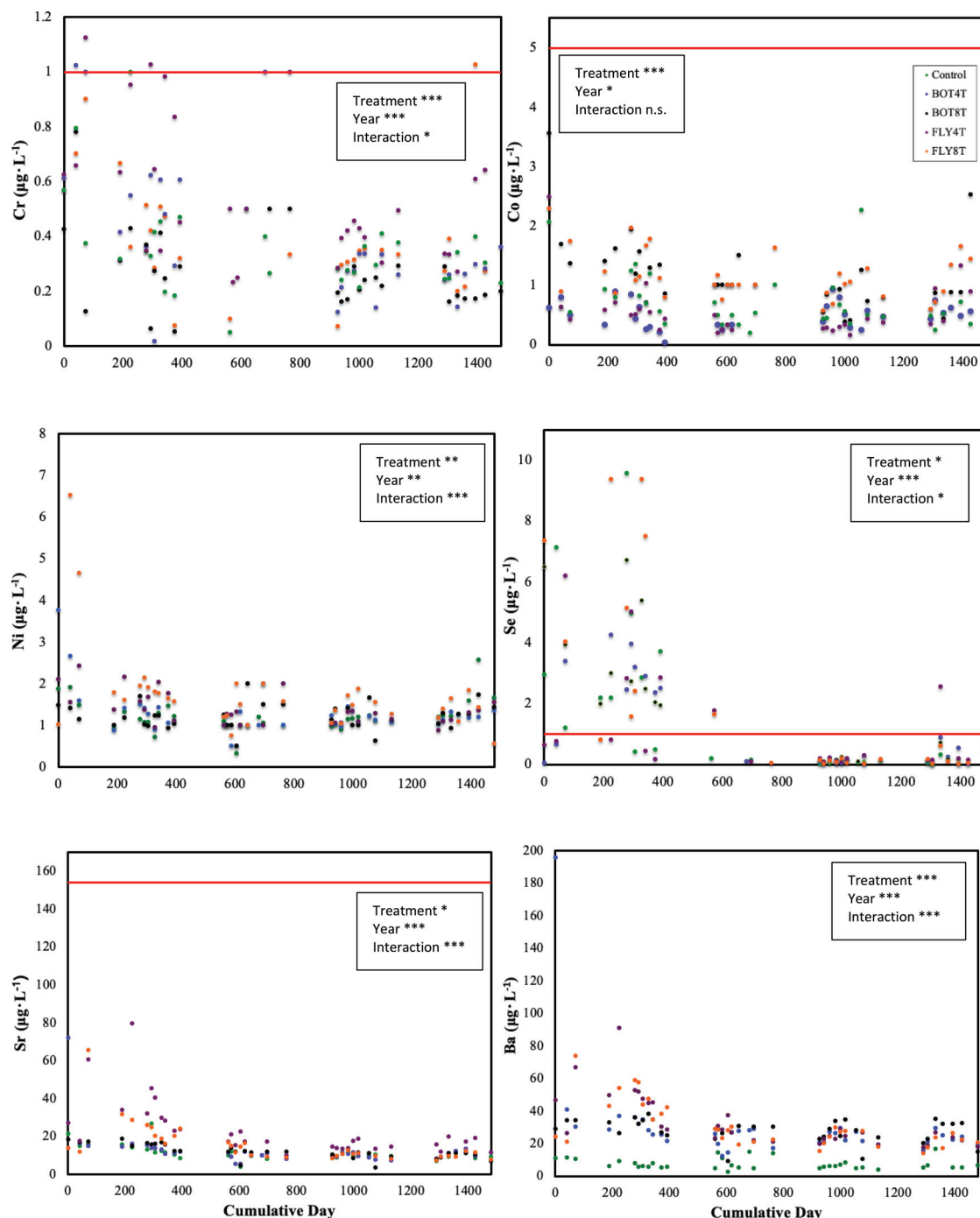
subsequent years (Fig. 1). For other metals (Mn, Al, boron (B), Cu, Co, Ni, and Ba), concentrations at the 30 cm depth were generally consistent through the sampling period, except for Zn concentrations, which tended to increase over time in all treatments and controls. This pattern was also seen at the 50 and 100 cm depths (Supplementary Tables S1–S5¹).

There was also a significant treatment effect on the soil water Mn, Al, Fe, B, As, Cd, Cr, Co, Ni, Sr, and Ba concentrations ($p < 0.05$; Fig. 1). However, most of these significant differences were among the ash-treated plots, and ash treatments were generally not significantly different from the control plots (Supplementary Tables S6–S8¹). Significant differences between treatment and

control plots were only found for Co, Ni, and Se; however, Se concentrations were significantly lower compared with control plots in all cases, and Co concentrations were higher or lower depending on depth and year and did not seem to follow any pattern. Concentrations of Ni at 30 cm were higher in treatment plots compared with control plots in 2013, 2014, 2015, and 2016, but this result was only significant in fly ash plots (Supplementary Tables S1–S5¹).

Concentrations of some metals differed by depth, irrespective of treatment. For example, Mn, Fe, As, Cu, Cr, and Zn concentrations tended to decrease with depth in all treatments and controls, whereas Sr and Ba concentrations tended to increase with depth (Supplementary Tables S1–S5¹).

Fig. 1 (concluded).



Concentrations of metals in soil water were generally low, but several metals exceeded provincial or Canadian Council of Ministers of the Environment (CCME 1987) surface or drinking water quality guidelines (even in control plots) (Fig. 1). For example, short-term concentrations of Cd in freshwater should not exceed $1.0 \mu\text{g}\cdot\text{L}^{-1}$ (CCME 1987); however, this limit was exceeded 45 times in control plots and 26–44 times in treatment plots from 2013 to 2017 (Table 2).

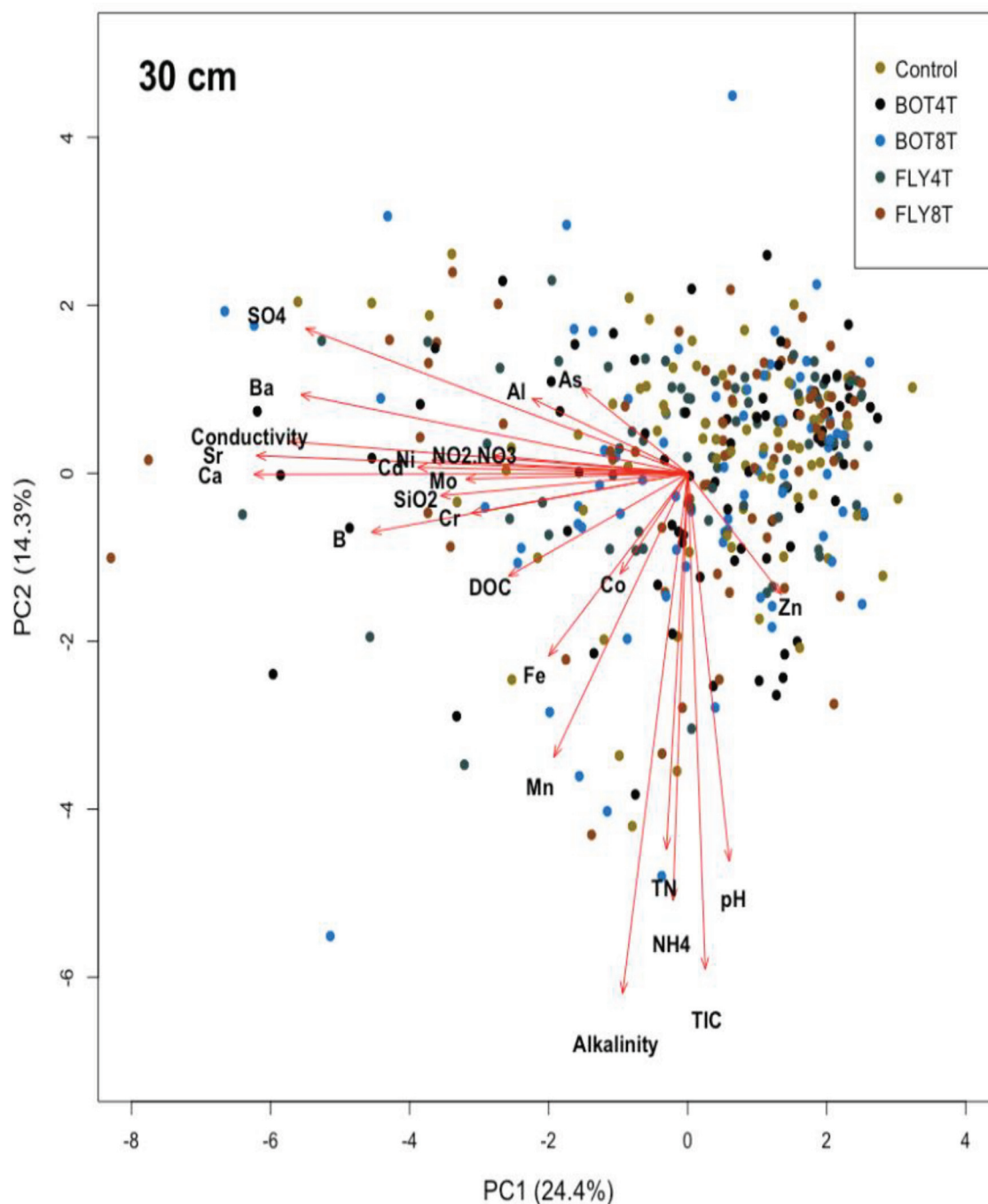
PCA analysis revealed pH, alkalinity, SO_4 , and conductivity to be major factors explaining the variability in metal concentrations at all depths. At the 30 cm depth, 39% of the variability in soil water chemistry could be explained by the first two axes of a PCA (Fig. 2).

The first PCA was negatively loaded with SO_4 , B, conductivity, and metals such as Mo, Cd, Cr, Ni, Sr, and Ba. The second axis reflected variability in pH and alkalinity but few metals. Similar patterns were found at 50 cm, where SO_4 was the major factor explaining variability in metal concentrations (Supplementary Fig. S1¹), but this was less evident at 100 cm, where much less of the variability could be explained by the first two axes of the PCA (Supplementary Fig. S2¹).

Soil physical and chemical properties

Four years after ash addition, there was no significant difference in pH among treatments in the upper organic horizon (Table 3).

Fig. 2. Principal component analysis for volume-based concentration data at lysimeter (30 cm) soil water depths. BOT4T and BOT8T, bottom ash at 4 and 8 Mg·ha⁻¹, respectively; FLY4T and FLY8T, fly ash at 4 and 8 Mg·ha⁻¹, respectively. DOC, dissolved organic carbon; TN, total nitrogen; TIC, total inorganic carbon.



In the lower organic horizon, the 8 Mg·ha⁻¹ ash treatments tended to have higher pHs than their corresponding 4 Mg·ha⁻¹ treatments; however, this pH difference was only significantly different from the control in fly ash (8 Mg·ha⁻¹) plots. Mineral soil pH in all treatments was 0.3–0.6 units higher than that in the control after 4 years, but no significant treatment effect was found. Fly and bottom ash addition had no significant effect on soil organic matter and moisture in both organic horizons and the mineral soil horizon; however, organic matter and soil moisture tended to be higher in mineral soil in all treatments. For example, soil organic matter

was about 2% higher in treatment plots compared with control plots in all horizons. Similarly, soil moisture was 3%–14% higher in treatment plots compared with control plots in the lower organic horizon and 1%–3% higher in treatment plots compared with control plots in the mineral horizon 4 years after ash addition.

Four years after ash application, significant differences in some nutrient and metal concentrations were observed in the lower organic and mineral soil horizons (Table 4). Concentrations of S, P, Ca, Mg, and K in the ash treatments were generally much higher

Table 2. Total number of lysimeter (30 cm) soil water samples from 2013 to 2017 that were above Canadian Council of Ministers of the Environment (CCME 1987) long-term water quality guidelines for fresh water ($\mu\text{g}\cdot\text{L}^{-1}$).

	Control	Bottom ash		Fly ash	
		4 $\text{Mg}\cdot\text{ha}^{-1}$	8 $\text{Mg}\cdot\text{ha}^{-1}$	4 $\text{Mg}\cdot\text{ha}^{-1}$	8 $\text{Mg}\cdot\text{ha}^{-1}$
Mn ^a	7	10	19	15	8
Al	75	89	79	90	101
Fe	0	2	0	3	0
Cd	45	26	35	37	44
Zn	95	101	106	85	98
Cu	94	97	95	93	98
Pb	8	6	4	5	8
Cr	3	6	3	5	1
Se	20	15	17	11	21

^aGuidelines for Canadian Drinking Water Quality (Health Canada 2016) were used.

(2–3 times), and significantly greater for the 4 $\text{Mg}\cdot\text{ha}^{-1}$ treatments than control plots when measured 4 years after wood ash addition. There were fewer significant differences in soil metal concentrations, although Al and Sr tended to be higher in treatment than control plots, and As and Ni tended to be lower in treatment than control plots. For example, Sr concentrations were 1.4–3 times higher in treatment plots than control plots. Cadmium and Zn concentrations were also significantly higher than control plots in the fly ash (4 $\text{Mg}\cdot\text{ha}^{-1}$) plots.

Sugar maple seedling tissue chemistry

There were few significant differences between treatment and control plots in sugar maple seedling foliar chemistry measured 4 years after ash application (Table 5). The only significant differences in foliar chemistry between treatment and control plots were observed in fly ash (8 $\text{Mg}\cdot\text{ha}^{-1}$) seedlings that had significantly lower levels of Zn and Sr and in fly ash (4 and 8 $\text{Mg}\cdot\text{ha}^{-1}$) seedlings that had significantly higher levels of Fe. In general, fly-ash-treated seedlings had higher levels of foliar Fe than bottom-ash-treated seedlings (Table 5).

There were significant differences among treatments in sugar maple root and stem chemistry measured in 2017, but responses were quite variable (Supplementary Table S9¹). Many root metal concentrations (Mn, Al, Zn, Pb, and Ni) were significantly higher in the fly ash (8 $\text{Mg}\cdot\text{ha}^{-1}$) seedlings compared with the control. Bottom ash (4 $\text{Mg}\cdot\text{ha}^{-1}$) seedlings had significantly higher Fe, Al, Zn, and Sr concentrations in roots compared with the control. Stem Cu concentrations were significantly higher in all ash-treated plots compared with the control 4 years following application. Fly ash (8 $\text{Mg}\cdot\text{ha}^{-1}$) seedlings also had significantly higher concentrations of Cd and Pb compared with the control. Generally, Al, Fe, Zn, Pb, and Ni were found in higher concentrations in root biomass, whereas Cu and Sr concentrations were higher in the stems.

Soil water response to simulated drought

Base cation concentrations (Ca, Mg, K, and Na) and pH tended to be higher in treatment plots relative to control plots for soil water sampled from the ‘wet’ treatment that was not exposed to simulated drought (Table 6). Soil water SO_4 concentrations were significantly higher in fly (4 and 8 $\text{Mg}\cdot\text{ha}^{-1}$) and bottom ash (8 $\text{Mg}\cdot\text{ha}^{-1}$) plots when compared with the control. Baseline metal concentrations, however, were low and very similar among all treatments.

Simulated drought resulted in a decrease in soil water pH and DOC concentrations (Fig. 3) and an increase in SO_4 and NO_3 in all treatments (Fig. 4). The response to simulated drought was not always significant, but patterns were consistent among

Table 3. Soil organic matter, moisture, and pH in control and treatment plots for organic (LF and H) and mineral (Ah) soil horizons 4 years after ash application.

	Organic matter (%)	Moisture (%)	pH (CaCO_3)
Upper organic (LF)			
Control	89.3 (3.3)	NA	4.7 (4.7–4.8)
Bottom ash			
4 $\text{Mg}\cdot\text{ha}^{-1}$	91.0 (2.1)	NA	4.8 (4.6–4.9)
8 $\text{Mg}\cdot\text{ha}^{-1}$	91.5 (1.3)	NA	4.6 (4.4–4.9)
Fly ash			
4 $\text{Mg}\cdot\text{ha}^{-1}$	90.7 (2.4)	NA	4.8 (4.6–4.9)
8 $\text{Mg}\cdot\text{ha}^{-1}$	92.8 (1.2)	NA	4.8 (4.5–5.3)
Lower organic (H)			
Control	18.6 (0.7)	50.5 (2.9)	4.3 (4.0–4.4)a
Bottom ash			
4 $\text{Mg}\cdot\text{ha}^{-1}$	20.2 (5.1)	56.8 (8.1)	4.3 (4.1–4.6)ab
8 $\text{Mg}\cdot\text{ha}^{-1}$	28.2 (5.2)	64.0 (1.9)	4.5 (4.3–4.6)ab
Fly ash			
4 $\text{Mg}\cdot\text{ha}^{-1}$	30.4 (7.5)	53.6 (5.2)	4.3 (4.1–4.7)a
8 $\text{Mg}\cdot\text{ha}^{-1}$	19.9 (1.6)	57.4 (5.6)	4.8 (4.6–5.2)b*
Mineral (Ah)			
Control	11.5 (2.4)	30.2 (4.2)	4.4 (4.1–5.0)
Bottom ash			
4 $\text{Mg}\cdot\text{ha}^{-1}$	13.9 (2.5)	31.3 (2.3)	5.0 (4.7–5.1)
8 $\text{Mg}\cdot\text{ha}^{-1}$	12.5 (1.6)	31.1 (6.7)	4.8 (4.0–5.2)
Fly ash			
4 $\text{Mg}\cdot\text{ha}^{-1}$	14.5 (1.4)	30.9 (1.8)	4.7 (4.5–4.9)
8 $\text{Mg}\cdot\text{ha}^{-1}$	12.8 (2.2)	33.5 (7.7)	4.8 (4.6–4.9)

Note: Values are the mean (\pm SE) of 4 replications; values in parentheses for pH are the range. Significant differences ($p < 0.05$) from pairwise comparisons (Tukey) are indicated with different lowercase letters. An asterisk (*) indicates a significant difference from the control at $p = 0.05$, unless otherwise stated, as determined by Dunnett's post hoc test. The post hoc tests were completed only on those variables where a significant treatment effect was determined by one-way ANOVA. NA, not applicable.

treatment and control plots. For example, all treatment and control plots showed a decrease in pH following simulated drought of approximately 0.5 pH units (Fig. 3).

The response of soil water Ca, Mg, K, Na, Mn, Fe, As, Cd, and Zn concentrations to drought were similar across all treatments (Fig. 4). Soil water concentrations of these elements increased following simulated drought; however, the magnitude of response differed among treatments. Concentrations of Al, Cu, and Pb in soil water behaved similarly to DOC following simulated drought, with concentrations lower in drought compared with the continually wet treatment (Fig. 5). Soil water Co and Ni concentrations showed little change following simulated drought (Fig. 4).

Discussion

This 4-year study examined trace metal behaviour in hardwood forest plots treated with bottom or fly ash at 4 and 8 $\text{Mg}\cdot\text{ha}^{-1}$ obtained from a biomass boiler in eastern Canada. Metal levels in ashes were low but were generally higher in fly ash. After 4 years, metal concentrations in soil were variable and a few metals (Al, Cd, Zn, and Sr) were higher in upper soil horizons in fly ash plots relative to control plots. Contrary to our expectations, there were few significant effects of treatment on sugar maple seedling foliar metal concentrations. Wood ash applications generally had minimal impact on soil water metal concentrations relative to control plots and simulated drought led to a decrease in soil pH and an increase in soil water metal concentrations, but this occurred in all treatments including control.

Table 4. Total elemental concentrations of Haliburton soil (weighted mean H and Ah horizons) in control and treatment plots 4 years after ash application.

	Control	Bottom ash		Fly ash	
		4 Mg·ha ⁻¹	8 Mg·ha ⁻¹	4 Mg·ha ⁻¹	8 Mg·ha ⁻¹
C (g·kg ⁻¹)	8.7 (3.1)	10.0 (4.5)	11.8 (5.0)	12.5 (1.3)	9.4 (1.6)
N (g·kg ⁻¹)	1.7 (0.3)	2.0 (0.2)	2.4 (0.4)	2.4 (0.5)	1.7 (0.4)
S (g·kg ⁻¹)	0.6 (0.2)a	1.5 (0.1)b*	1.3 (0.2)b*	1.0 (0.2)ab	1.0 (0.4)ab
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
P (g·kg ⁻¹)	0.4 (0.1)a	1.0 (0.1)b*	0.9 (0.1)b*	0.8 (0.1)b*	0.8 (0.4)b*
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
Mn (g·kg ⁻¹)	0.9 (0.6)	1.0 (0.5)	0.7 (0.2)	1.5 (0.6)	0.6 (0.0)
Al (g·kg ⁻¹)	2.7 (0.1)a	3.4 (1.2)ab	3.3 (2.1)ab	5.4 (1.4)b*	3.8 (0.8)ab
Fe (g·kg ⁻¹)	5.2 (1.5)ab	5.0 (1.0)a	4.8 (2.3)a	6.4 (0.8)ab	7.9 (1.0)b
As (mg·kg ⁻¹)	6.2 (2.3)b	2.4 (0.8)a*	5.2 (1.9)b	2.6 (1.5)a*	6.4 (1.9)b
Cd (mg·kg ⁻¹)	0.8 (0.3)a	1.0 (0.1)b	0.8 (0.4)a	2.3 (0.5)b*	0.3 (0.0)a
Zn (mg·kg ⁻¹)	49.9 (23.6)a	51.3 (3.6)a	56.4 (9.8)a	119 (46 b)	46.5 (15.4)a
Cu (mg·kg ⁻¹)	32.2 (0.3)ab	25.0 (1.6)a	30.4 (4.4)ab	32.7 (3.1)b	36.0 (1.2)b
Pb (mg·kg ⁻¹)	26.0 (5.1)ab	16.1 (4.7)a	15.5 (6.6)a	15.1 (1.4)a	32.0 (11.1)b
Ni (mg·kg ⁻¹)	9.9 (0.6)b	6.4 (0.8)a*	6.0 (0.5)a*	7.2 (0.8)a*	6.2 (0.2)a*
Sr (mg·kg ⁻¹)	19.4 (9.0)a	45.2 (3.5)b*	35.1 (0.7)a	59.4 (11.2)b*	27.5 (8.2)a

Note: Values are the mean \pm standard error of 4 replications. Significant differences ($p < 0.05$) from pairwise comparisons (Tukey) are indicated with different lowercase letters. An asterisk (*) indicates a significant difference from the control at $p = 0.05$, unless otherwise stated, as determined by Dunnett's post hoc test. The post hoc tests were completed only on those variables where a significant treatment effect was determined by one-way ANOVA.

Table 5. Sugar maple seedling foliar metal concentrations 4 years after addition of fly and bottom ash.

Ash type	Ash dosage		Mn (g·kg ⁻¹)	Fe (g·kg ⁻¹)	As (mg·kg ⁻¹)	Cd (mg·kg ⁻¹)	Zn (mg·kg ⁻¹)	Cu (mg·kg ⁻¹)	Pb (mg·kg ⁻¹)	Ni (mg·kg ⁻¹)	Sr (mg·kg ⁻¹)
	(Mg·ha ⁻¹)										
Control	0		0.56 (0.28)	0.04a (0.02)	5.45 (2.81)	0.24 (0.06)	19.30a (1.51)	26.23 (6.60)	2.15 (0.41)	0.71 (0.19)	51.15b (9.59)
Bottom	4		0.64 (0.18)	0.03a (0.08)	7.40 (3.23)	0.17 (0.08)	25.74a (3.17)	25.17 (5.48)	1.47 (0.34)	0.67 (0.32)	63.06b (7.90)
	8		0.37 (0.10)	0.02a (0.05)	4.44 (3.20)	0.30 (0.05)	21.86a (1.35)	27.01 (2.56)	1.73 (0.35)	0.63 (0.21)	50.33b (6.00)
Fly	4		0.66 (0.17)	0.10b* (0.03)	5.55 (4.22)	0.29 (0.05)	20.05a (3.64)	21.87 (2.61)	1.73 (0.45)	0.91 (0.22)	55.27b (6.96)
	8		0.55 (0.15)	0.07b* (0.03)	8.44 (5.89)	0.17 (0.08)	10.49b* (0.10)	23.69 (3.22)	1.43 (0.43)	0.86 (0.47)	24.21a* (2.02)

Note: Values are the mean \pm standard error of 4 replications. Significant differences from pairwise comparisons (Tukey) are indicated with different lowercase letters. An asterisk (*) indicates a significant difference from the control at $p < 0.05$, as determined by Dunnett's post hoc test. The post hoc tests were completed only on those variables where a significant treatment effect was determined by one-way ANOVA.

Ash properties

Possibly one of the largest concerns with using wood ash as a soil amendment is the potentially high trace metal content of wood ash (Pitman 2006). However, concentrations of metals in both ashes used in this study were low, and none exceeded the 2002 Nutrient Management Act guidelines for Category 2 non-agricultural source material. In addition, the pH of the ashes used in this experiment were 8.6 for fly ash and 9.7 for bottom ash, which are at the lower end of ranges for wood-fired boiler ashes of 7.8–13.1 reported by Vance (1996) and 8.9–13.5 reported by Demeyer et al. (2001).

Soil water chemistry

There is concern over contamination of surface and ground waters after application of wood ash to forest environments (Kahl et al. 1996). In this study, metal concentrations in soil water varied considerably over the 4-year period. Concentrations of several metals (Mn, Fe, Mo, As, Cd, Pb, Cr, Co, Ni, Se, and Sr) were higher during the first 1 to 2 years of study, but there was only a significant treatment effect on Mo, As, Co, Ni, and Se, and in general, these differences were not between wood ash treatment plots and control plots. Several studies have investigated the effects of trace metal inputs into forest ecosystems. No significant treatment effect was found in soil solution for most metals up to 2 years following ash application (Rumpf et al. 2001; Ozolinčius and Varnagiryte 2005; Saarsalmi et al. 2005).

Some studies found increased metal concentrations at 10–20 cm (Cd, Zn, and Pb) and 50 cm (Ni) depths; however, these values were either well within legal limits for drinking water or lower than the maximum recommended metal input (Rumpf et al. 2001; Ozolinčius and Varnagiryte 2005). Following ash addition, metals were bound in insoluble forms, mainly in the organic horizon, which is likely why no negative changes in soil solution chemistry were found (Bramryd and Fransman 1995; Eriksson 1998).

The high concentration for some metals measured during the first year after ash application could be related to the lysimeter installation. Hydrological anomalies as a result of soil disturbance associated with tension lysimeter installation can last anywhere from 2 months to 2 years (Titus and Mahendrappa 1996). Litaor (1988) observed extremely high levels of several trace metals in soil solution collected 3 weeks after lysimeter installation and found these anomalies to be due to root responses to soil and rhizosphere disturbance.

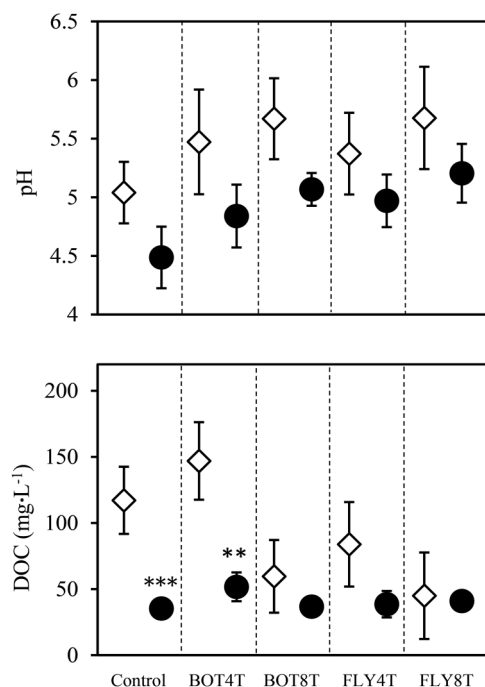
Soil solution pH remained relatively consistent throughout the study period, except in fly ash (8 Mg·ha⁻¹) plots where a 0.4 drop in pH units was observed across all depths 3 years following ash addition. A similar decrease of 0.3 pH units was seen after wood ash (2.4 Mg·ha⁻¹) application in a pine stand in northern Germany, which was attributed to soluble salts leaching from the ash leading to desorbed exchangeable protons (Rumpf et al. 2001). The PCA analysis indicates that increased soil water metal concentrations are associated with high SO₄ concentrations, and although

Table 6. Baseline pH, dissolved organic carbon (DOC), sulfate, nitrate, base cation, salt, and metal concentrations of soil water (0–20 cm) from Haliburton Forest experimental plots 4 years following wood ash addition.

	Control	Bottom ash		Fly ash	
		4 Mg·ha ⁻¹	8 Mg·ha ⁻¹	4 Mg·ha ⁻¹	8 Mg·ha ⁻¹
pH	3.8±0.1a	4.2±0.2a	4.4±0.2a	4.4±0.2a	4.6±0.3b*
DOC (mg·L ⁻¹)	7.1±0.9a	12.4±1.2b*	6.0±2.0a	7.8±4.0ab	6.5±0.8a
SO ₄ (mg·L ⁻¹)	2.8±0.1a	2.6±0.1a	3.4±0.2b*	5.4±0.2c*	4.9±0.3c*
NO ₃ (μg·L ⁻¹)	56.1±34.5	94.3±45.7	112.4±60.4	108.3±76.5	84.2±59.6
Ca (mg·L ⁻¹)	27.5±2.1a	42.5±12.8ab	41.9±3.8b*	42.5±6.7b*	44.8±6.2b*
Mg (mg·L ⁻¹)	5.1±0.7	7.0±1.5	8.4±0.8	6.6±2.3	8.0±1.1
K (mg·L ⁻¹)	6.2±0.7	9.8±2.3	8.9±0.8	7.3±2.3	10.8±1.1
Na (mg·L ⁻¹)	1.7±0.5a	2.8±0.9a	4.0±0.6ab	2.6±1.0a	6.0±0.7b*
Mn (mg·L ⁻¹)	3.5±0.8	4.3±1.1	4.7±0.1	3.7±1.0	4.1±1.0
Al (μg·L ⁻¹)	1140.3±172.2	914.0±61.1	848.1±76.8	815.2±115.5	727.0±31.4
Fe (mg·L ⁻¹)	1.1±0.5	0.4±0.2	0.4±0.2	0.2±0.1	0.2±0.1
As (μg·L ⁻¹)	9.8±5.7	9.7±4.7	12.2±3.9	11.4±2.4	16.7±4.0
Cd (μg·L ⁻¹)	2.1±0.4	2.5±0.8	1.8±0.1	1.6±0.3	1.7±0.4
Zn (μg·L ⁻¹)	159.9±28.8	156.8±40.3	135.8±23.9	138.0±20.6	184.5±39.4
Cu (μg·L ⁻¹)	12.0±8.9	4.0±2.5	4.5±2.9	3.6±2.8	2.0±1.2
Pb (μg·L ⁻¹)	8.8±1.5	8.6±0.7	7.3±0.9	8.1±1.9	5.9±0.8
Co (μg·L ⁻¹)	13.3±7.5	5.2±1.4	9.9±3.9	3.8±3.2	3.0±0.7
Ni (μg·L ⁻¹)	10.7±2.8	9.2±3.4	7.7±0.5	5.7±0.5	6.1±0.9

Note: Values are the mean ± standard error of 4 replications. An asterisk (*) indicates a significant difference from the control at $p < 0.1$, as determined by Dunnnett's post hoc test. The post hoc tests were completed only on those variables where a significant treatment effect was determined by one-way ANOVA.

Fig. 3. pH and dissolved organic carbon (DOC) concentrations (mean ± SE) in soil water (0–20 cm) extracted from Haliburton Forest wood ash experimental plots ($n = 4$) and subject to two treatments: 30-day drought (●) and wet (◇). Statistical significance: **, $p < 0.05$; ***, $p < 0.001$. BOT4T and BOT8T, bottom ash at 4 and 8 Mg·ha⁻¹, respectively; FLY4T and FLY8T, fly ash at 4 and 8 Mg·ha⁻¹, respectively.



this was most pronounced in the shallow soil depth (30 cm), similar patterns were observed at 50 and 100 cm. The S concentration of fly ash used in this study is high compared with the average for bark ashes (42.2 versus 6.5 g·kg⁻¹) (Pitman 2006) and is likely why there

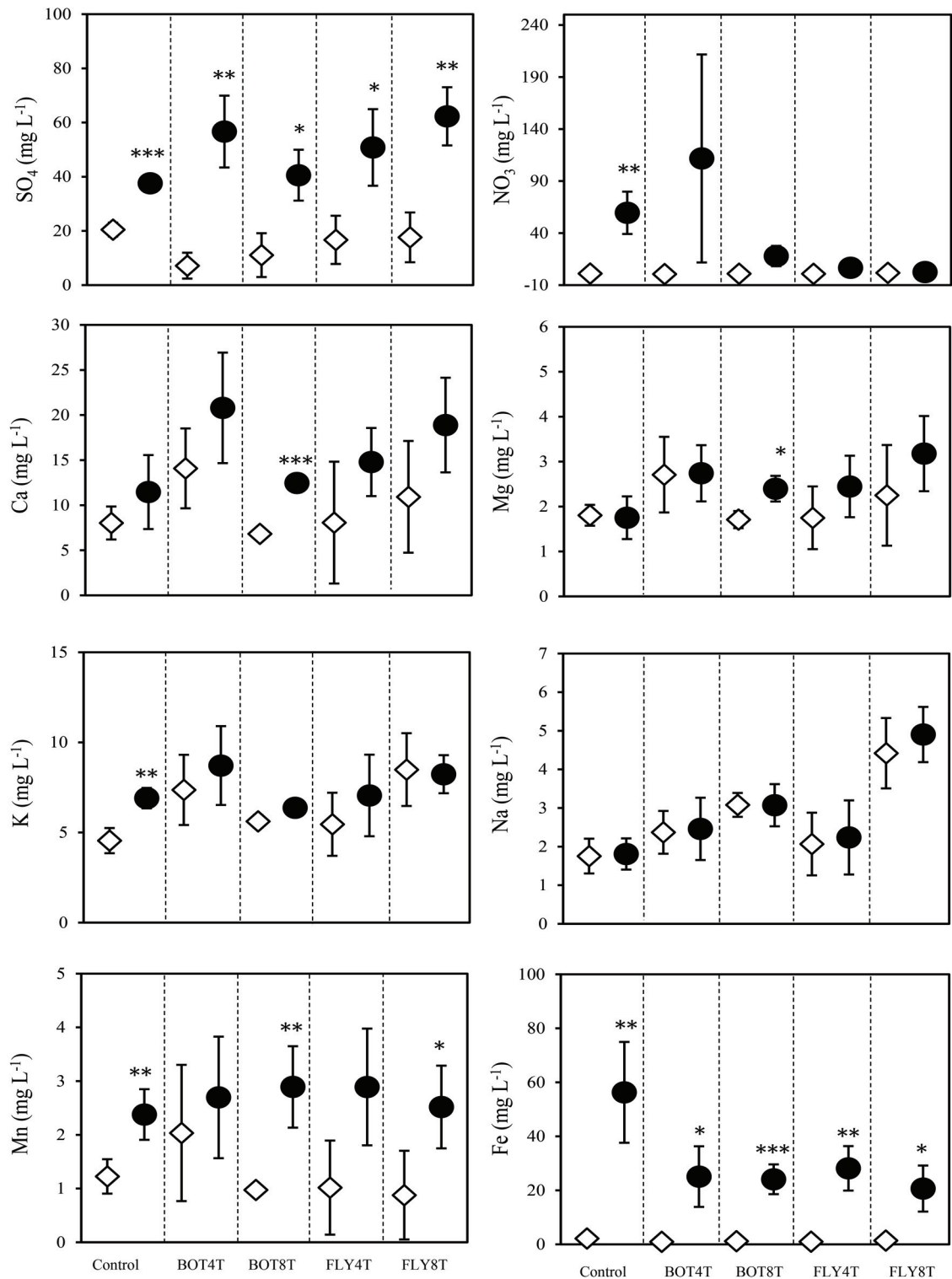
were high SO₄ concentrations in soil pore water following fly ash application. Sulfate concentrations remained significantly higher in fly-ash-amended plots up to 4 years after treatment. A study on an acidic forest Podzol (Kahl et al. 1996) amended with wood ash found a similar pattern with elevated SO₄ concentrations in soil solution following treatment. Increased SO₄ in soil solution was attributed to it being desorbed from the soil by the reduction of positively charged anion sites due to increased soil pH (Kahl et al. 1996). No changes in DOC due to ash addition were found, which is consistent with other studies (Rumpf et al. 2001), suggesting that variation in metal concentration is less impacted by changes in DOC.

Concentrations of several metals in soil water exceeded federal and (or) provincial guidelines for surface or drinking water on numerous sampling days, but this occurred as frequently in controls as in treatment plots further indicating that wood ash application had limited effect on soil water metal values for up to 4 years post application. While we would not expect soil water concentrations to directly align with these surface water standards, they provide reference levels as a point of comparison. Landre et al. (2010) collected soil water from mineral soil horizons at a nearby upland forest site without ash applications and found similar soil water metal concentrations for all metals except Zn and Cu. Concentrations of Zn and Cu for control plots in this study (on average, 29–324 and 3.2–8.8 μg·L⁻¹, respectively) were much higher than those recorded by Landre et al. (2010), who found average soil water concentrations of 16 μg·L⁻¹ for Zn and 0.33 μg·L⁻¹ for Cu.

Soil chemistry

In this study, trace metal concentrations in ash were low compared with acceptable limits for land application in Ontario, and although not statistically significant, ash application tended to increase mineral soil pH by 0.3–0.6 units after 4 years. This is comparable to data found in a meta-analysis by Reid and Watmough (2014), who showed a mean increase in mineral soil pH of 0.36 units, with the greatest effects seen during the first 4 years after ash application. One year after application at the same site, ash treatments resulted in a large increase in pH (2 units) in

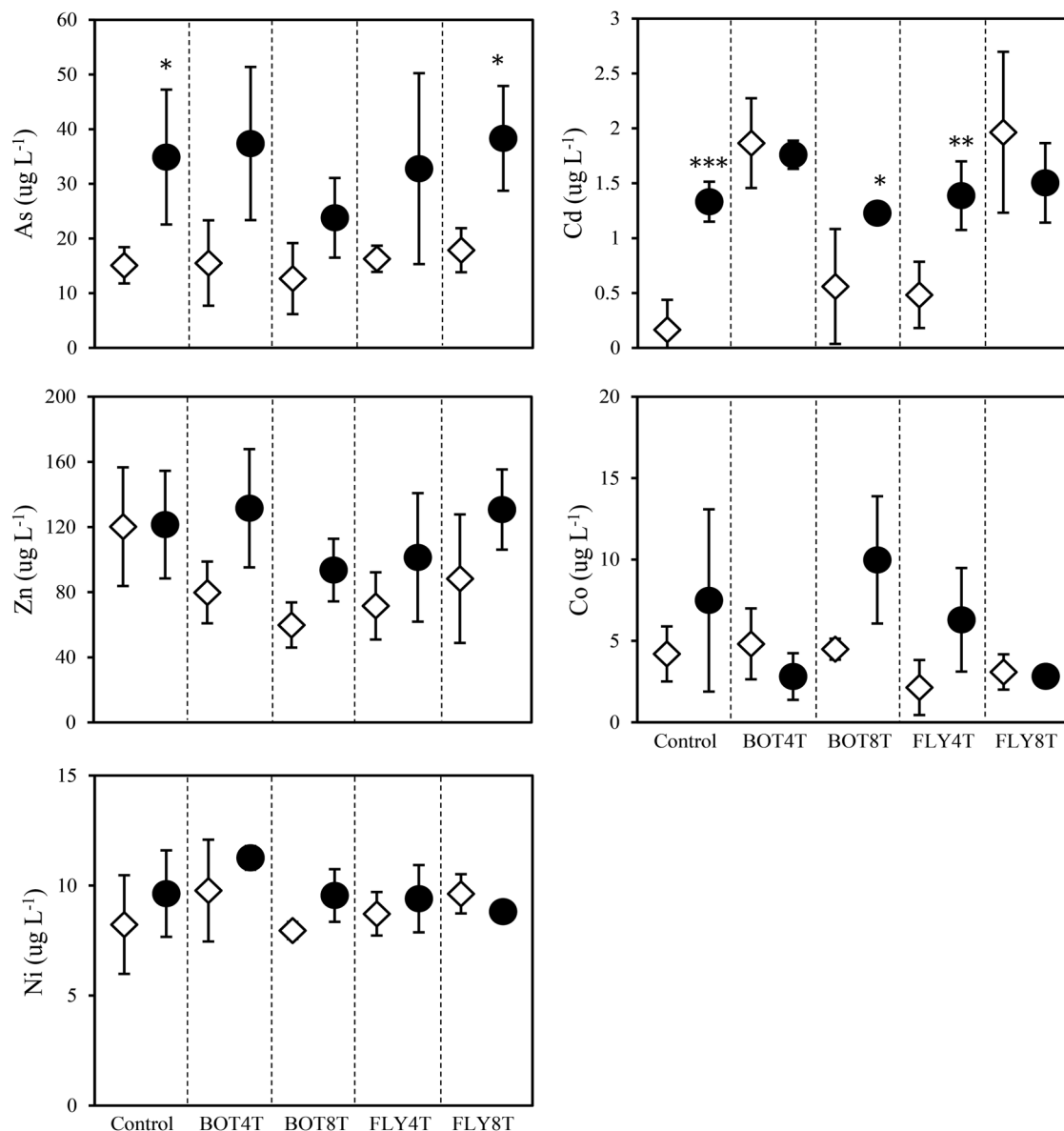
Fig. 4. Concentration (mean \pm SE) of SO_4 , NO_3 , Ca, Mg, K, Na, Mn, Fe, As, Cd, Zn, Co, and Ni in soil water (0–20 cm) extracted from Haliburton Forest wood ash experimental plots ($n = 4$) and subject to two treatments: 30-day drought (black circle) and wet (open diamond). Statistical significance: *, $p < 0.1$; **, $p < 0.05$; ***, $p < 0.001$. BOT4T and BOT8T, bottom ash at 4 and 8 $\text{Mg}\cdot\text{ha}^{-1}$, respectively; FLY4T and FLY8T, fly ash at 4 and 8 $\text{Mg}\cdot\text{ha}^{-1}$, respectively.



the organic soil horizons (Gorgolewski et al. 2016), but no effects were seen into the mineral soil, possibly because it takes longer for neutralization effects to be seen in deeper soil layers (Saarsalmi et al. 2001). An increase in soil pH resulting from ash application

can limit trace metal mobility (Sommers 1980), although it is possible that the effects of higher pH on metal mobility will eventually be reversed, and trace metals from the ash immobilized in the soil will become more mobile (Demeyer et al. 2001).

Fig. 4 (concluded).



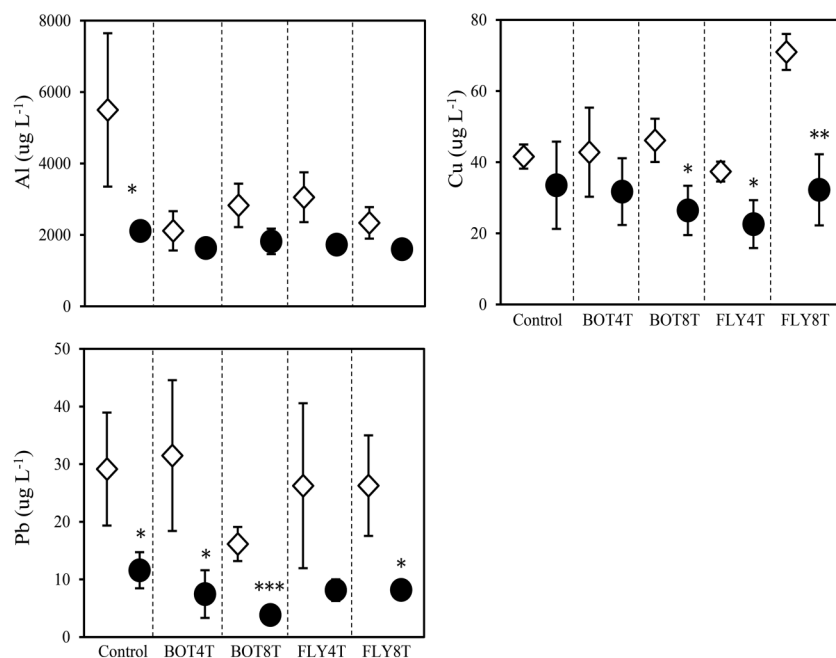
Significant increases in nutrients (S, Ca, Mg, K, and P) and significant decreases in Pb and Ni were also apparent in the fly ash plots. Increases in nutrients following fly ash application to soils is widely recognized in literature (Vance 1996; Pitman 2006; Augusto 2008). For example, 7 years following ash addition to an acidic forest Podzol (0–30 cm), Saarsalmi et al. (2001) found Ca concentrations in fly ash ($3 \text{ Mg}\cdot\text{ha}^{-1}$) amended plots ($350 \text{ mg}\cdot\text{kg}^{-1}$) to be 2.3 times higher compared with control plots ($150 \text{ mg}\cdot\text{kg}^{-1}$), which is similar to this study (3600 and $8600 \text{ mg}\cdot\text{kg}^{-1}$ in 4 and $8 \text{ Mg}\cdot\text{ha}^{-1}$ fly ash plots, respectively, compared with $2800 \text{ mg}\cdot\text{kg}^{-1}$ in control plots). Decreases in Pb concentration following addition of soil amendments such as ash or calcium carbonate has been found in other studies (Arvidsson and Lundkvist 2003; Pugliese et al. 2014) and may be the result of increasingly basic conditions resulting in the precipitation of lead hydroxides and phosphates (Bradl 2004).

Although not significantly different, soil Na concentrations were slightly higher in fly ash ($4 \text{ Mg}\cdot\text{ha}^{-1}$) amended plots compared with controls, a result consistent with Domes et al. (2018) for ash applied to Luvisolic soils in northern British Columbia.

Sodium concentrations were only 2 times higher in the fly-ash-amended plots in our study 4 years after application compared with 43 times higher in fly-ash-amended plots compared with the control in a study by Pugliese et al. (2014) 8 weeks after application. Pugliese et al. (2014) conducted a sealed jar microcosm experiment using ash from the same boiler as our study (just 2 years earlier), and other larger changes in soil nutrient and metal levels reported in their study compared with our present study indicate that ash effects are more muted with field applications. The concentrations of Na in fly ash used in this study ($36.4 \text{ g}\cdot\text{kg}^{-1}$) and that used in Pugliese et al. (2014) ($34.0 \text{ g}\cdot\text{kg}^{-1}$) are high compared with those reported by Augusto et al. (2008) ($2\text{--}5 \text{ g}\cdot\text{kg}^{-1}$), which suggests that immediately following application, increased Na concentrations are a result of direct transfer from the ash to the soil. Over time, Na concentrations most likely dissolve in soil water and exit the forest ecosystem, as Na interacts weakly with the system (Bailey et al. 2003).

Concentrations of acid extractable trace metals in the soil varied slightly by treatment, with fly ash showing the most

Fig. 5. Concentration (mean \pm SE) of Al, Cu, and Pb in soil water (0–20 cm) extracted from Haliburton Forest wood ash experimental plots ($n = 4$) and subject to two treatments: 30-day drought (black circle) and wet (open diamond). Statistical significance: *, $p < 0.1$; **, $p < 0.05$; ***, $p < 0.001$. BOT4T and BOT8T, bottom ash at 4 and 8 Mg·ha⁻¹, respectively; FLY4T and FLY8T, fly ash at 4 and 8 Mg·ha⁻¹, respectively.



significant differences. Four years after application of fly ash, Fe, Cd, As, Ni, Zn, and Sr concentrations were significantly higher (relative to control plots) in some wood ash treatment plots in the top 30 cm of the soil profile. These results are consistent with other studies that showed increases in Fe, Mn, Cd, Zn, Cu, Pb, Cr, and Ni (Nieminen et al. 2005; Singh and Agrawal 2010; Hansen et al. 2018) in the upper 10–20 cm of soil following ash application. However, mobility of these metals is likely to occur only under acidic conditions, and soils with higher organic matter concentrations and pH should be less vulnerable to trace metal toxicities than more acidic soils (McBride et al. 2004).

Soil and sugar maple seedling tissue chemistry

Trace metals in ash could have the potential to accumulate in sugar maple seedling tissues, leading to restricted growth or lower survival rates. In this study, there was no significant increase in foliar concentrations of any metal analyzed 4 year after ash addition, except for Fe, which increased from about 40 mg·kg⁻¹ in control plots to 70–100 mg·kg⁻¹ in treatment plots. These elevated foliar Fe concentrations are still within the range of 59–130 mg·kg⁻¹ for healthy sugar maples (Kolb and McCormick 1993). The initial increase in soil pH brought about by soil amendments such as wood ash generally show a decreased availability of Cd, Zn, Cu, Pb, Ni, and other metals (Sommers 1980), through either the precipitation of insoluble phases (such as metal hydroxides) or promoting metal sorption via surface complexation processes (Querol et al. 2006). Several metals (Al, Fe, Zn, Pb, Ni, and Sr) were significantly higher in the roots of seedlings from treatment plots compared with control plots. Increased metal levels in roots could possibly be due to uptake and restricted translocation or surface contamination by ash residues or may simply be a result of surface adsorption as roots can be difficult to clean. Elements of interest should be considered when determining methods for washing roots free of soil particles (Park and Yanai 2009). Cadmium, Zn, and Pb have shown translocations from roots to other plant parts following

ash addition in field studies (Rumpf et al. 2001; Ludwig et al. 2002; Arvidsson and Lundkvist 2003; Deighton and Watmough 2020).

Simulated drought

The potential for enhanced metal mobility following drought was tested under experimental conditions. While minimal mobility and uptake was observed over the 4-year period, repeated applications of wood ash as a forest soil amendment may lead to metal retention if the rate of trace metal input exceeds the rate of loss (Lindberg and Turner 1988). The organic horizons of forest soils have been shown to naturally accumulate metals (Friedland et al. 1984), and metal concentrations in soil water could be higher following severe drought (Dillon et al. 1997), and possibly elevated even further at sites with organic soils that act as sinks for metals from atmospheric deposition (Juckers and Watmough 2014).

The experimental drought data for Haliburton show that drought conditions can cause acidification of soil water in the surface horizons of upland forest soils. Simulated drought resulted in the release of SO₄ and NO₃ in soil water of the control treatment because of the oxidization of reduced S and N, which is consistent with other studies (Dillon et al. 1997; Clark et al. 2006; Juckers and Watmough 2014). These studies also show a decrease in pH following drought due to oxidation of reduced S and N compounds creating SO₄ and NO₃, which increase H⁺ ions in soil water upon rewetting. In this study, S and N content was similar in all ash-treated plots, and all soils behaved similarly for SO₄ in response to drought, although the response of NO₃ in soil water to ash treatment was more variable but differences were not significantly different.

Concentrations of base cations (Ca, Mg, K, Na) and some metals (Mn, Fe, As, Cd, and Zn) increased in soil water following drought, regardless of wood ash treatment. The increased solution concentration of base cations and weakly binding metals, such as Cd and Zn, corresponds with drought-induced acidification of soil and incoming H⁺ ions competing for exchange sites that mobilizes base cations and metals in the soil solution (Brown et al.

2000). Drought has also been shown to increase salinity by concentrating salts in soil water (McKee et al. 2004), which is why increases in K and Na were most likely seen. Arsenic and Fe concentrations in soil water also increased following drought. Other studies have also shown that As and Fe are immobilized following oxidation during dry periods on ferric iron hydroxides in surface peat and then can be rapidly mobilized by iron reduction upon rewetting (Appleyard et al. 2006; Blodau et al. 2008).

Dissolved organic carbon concentrations in soil water declined following drought. Following drying events, DOC concentrations in soil water are thought to decrease mainly due to SO₄-induced acidification of soil water but could also be due to abiotic factors such as increased microbial consumption of DOC and subsequent respiration of carbon dioxide (Clark et al. 2012). Aluminum, Cu, and Pb soil water concentrations declined in response to the simulated drought in a pattern similar to that of DOC. Strongly binding metals such as Al, Cu and Pb can displace H⁺ ions from soil exchange sites following acidification, resulting in the immobilization of these metals in an organic form (Tipping et al. 2003; Clark et al. 2012). If drought events persist, however, release of these metals has been shown after 60 days due to increasing amounts of H⁺ ions outcompeting metals, particularly Al and Cu, for binding sites (Juckers and Watmough 2014).

Conclusion

Over the 4-year study period there were few significant increases in soil water metal concentrations collected at 30, 50, and 100 cm soil depth compared with the control plots after fly and bottom ash additions in an upland northern hardwood forest soil. Treatment plots receiving fly ash had higher concentrations of some metals (Al, Cd, Zn, and Sr) in the top 0–30 cm of soil 4 years after application, although soil pH tended to be higher, which likely limits metal mobility and availability. Wood ash had no effect on sugar maple foliar metal concentrations, with the exception of Fe, which were still within the healthy range for sugar maple seedlings 4 years after application. Significant differences in root metal chemistry were seen, which could be due to restricted metal translocation or uptake or to surface absorption from improper cleaning. Simulated drought led to an increase in some metal concentrations in soil water, but this occurred in all treatments including the control. Our results suggest that applying wood ash with low trace metal concentrations in low to moderate doses to an acidic Brunisol leads to only moderate increases in soil concentrations of some metals 4 years after ash application.

Acknowledgements

We thank Natural Resources Canada and the University of Toronto for funding this study. Funding for the lysimeters, plot setup, and soil water analyses came from a NSERC Collaborative Research and Development Grant to Honghi Tran (University of Toronto, Department of Chemical Engineering and Applied Chemistry), Nathan Basiliko, and others. Additional funding came from an NSERC Discovery Grant awarded to Shaun Watmough. The authors would also like to thank Kevin Adkinson, Kristi Broad, Sharon Gibbs, Laura Hawdon, Emma Horriggan, Edward Kellaway, and Linda Vogel for their technical assistance with this project.

References

Alberta Environment. 2002. Standards and guidelines for the use of wood ash as a liming material for agricultural soils [online]. Available from <https://archive.org/details/standardsguideli00albe>.

Appleyard, S.J., Angeloni, J., and Watkins, R. 2006. Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia. *Appl. Geochem.* **21**(1): 83–97. doi:10.1016/j.apgeochem.2005.09.008.

Arvidsson, H., and Lundkvist, H. 2003. Effects of crushed wood ash on soil chemistry in young Norway spruce stands. *For. Ecol. Manage.* **176**: 121–132. doi:10.1016/S0378-1127(02)00278-5.

Augusto, L., Bakker, M.R., and Meredieu, C. 2008. Wood ash applications to temperate forest ecosystems — potential benefits and drawbacks. *Plant Soil*, **306**: 181–198. doi:10.1007/s11104-008-9570-z.

Bailey, S.W., Buso, D.C., and Likens, G.E. 2003. Implications of sodium mass balance for interpreting the calcium cycle of a forest ecosystem. *Ecology*, **84**(2): 471–2484. doi:10.1890/0012-9658(2003)084[0471:IOSMBF]2.0.CO;2.

Bieser, J., and Thomas, S. 2019. Biochar and high-carbon wood ash effects on soil and vegetation in a boreal clearcut. *Can. J. For. Res.* **49**(9): 1124–1134. doi:10.1139/cjfr-2019-0039.

Blodau, C., Fulda, B., Bauer, M., and Knorr, K.-H. 2008. Arsenic speciation and turnover in intact organic soil mesocosms during experimental drought and rewetting. *Geochim. Cosmo. Acta*, **72**(16): 3991–4007. doi:10.1016/j.gca.2008.04.040.

Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soils constituents. *J. Colloid. Interface Sci.* **277**: 1–18. doi:10.1016/j.jcis.2004.04.005. PMID:15276031.

Bramryd, T., and Fransman, B. 1995. Silviculture use of wood ashes — effects on the nutrient and heavy metal balance in a pine (*Pinus sylvestris*, L.) forest soil. *Water Air Soil Pollut.* **85**: 1039–1044. doi:10.1007/BF00476967.

Brown, P.A., Gill, S.A., and Allen, S.J. 2000. Review paper: metal removal from wastewater using peat. *Water Res.* **34**(16): 3907–3916. doi:10.1016/S0043-1354(00)00152-4.

Campbell, A.G. 1990. Recycling and disposing of wood ash. *Tappi J.* **73**(9): 141–146.

CCME (Canadian Council of Ministers of the Environment). 1987. Guidelines for the protection of aquatic life [online]. Available from <http://st-ts.ccme.ca/en/index.html>.

Chapman, L.J., and Putnam, D.F. 1984. The physiography of southern Ontario. 3rd ed. Ontario Geological Survey, Government of Ontario, Canada. Special Volume 2, p. 270.

Chirenje, T. 2000. Chemical and physical changes in a wood ash-amended forest soil. Doctoral Dissertation, University of Florida, Gainesville, Fla., USA.

Clark, J.M., Pippa, J., Chapman, A., Heathwaite, L., and Adamson, J.K. 2006. Suppression of dissolved organic carbon by sulfate induced acidification during simulated droughts. *Environ. Sci. Technol.* **40**(6): 1776–1783. doi:10.1021/es051488c. PMID:16570597.

Clark, J.M., Heinemeyer, A., Martin, P., and Bottrell, S.H. 2012. Processes controlling DOC in pore water during simulated drought cycles in six different UK peats. *Biogeochemistry*, **109**: 253–270. doi:10.1007/s10533-011-9624-9.

Deighton, H.D., and 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. doi:10.3390/f11060693.

Demeyer, A., Nkana, J.C.V., and Verloo, M.G. 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresour. Technol.* **77**(3): 287–295. doi:10.1016/S0960-8524(00)00043-2. PMID:11272014.

Dillon, P.J., Molot, L.A., and Futter, M. 1997. The effect of El Niño-related drought on the recovery of acidified lakes. *Environ. Monit. Assess.* **46**: 105–111. doi:10.1023/A:1005740002952.

Domes, K.A., de Zeeuw, T., Massicotte, H.B., Elkin, C., McGill, W.B., Jull, M.J., et al. 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. *Can. J. Soil Sci.* **98**(2): 246–263. doi:10.1139/cjss-2017-0115.

Emilsson, C.E., Bélanger, N., Brais, S., Chisholm, C.E., Diochon, A., Ruth, J., et al. 2020. Short-term growth response of jack pine and spruce spp. to wood ash amendment across Canada. *Glob. Chang. Biol. Bioenergy*, **12**: 158–167. doi:10.1111/gcbb.12661.

Environment Canada. 2019. Canadian climate normals 1981–2010 station data [online]. Available from https://climate.weather.gc.ca/climate_normals/results_1981_2010_e.html?stnID=5170&autofwd=1.

Environment Canada. 2020. Daily data report for Haliburton 3 Ontario [online]. Available from https://climate.weather.gc.ca/climate_data/daily_data_e.html?hlyRange=%7C&dlyRange=1987-09-01%7C2020-06-22&mlyRange=1987-01-01%7C2006-12-01&StationID=5170&Prov=ON&urlExtension=_e.html&searchType=stnName&optLimit=yearRange&StartYear=1840&EndYear=2020&selRowPerPage=100&Line=1&searchMethod=contains&txtStationName=haliburton&timeframe=2&Day=1&Year=2013&Month=1#.

Eriksson, H.M., Nilsson, T., and Nordin, A. 1998. Early effects of lime and hardened and non-hardened ashes on pH and electrical conductivity of the forest floor, and relations to some ash and lime qualities. *Scand. J. For. Res. Suppl.* **2**: 56–66.

Friedland, A.J., Johnson, A.H., and Siccama, T.G. 1984. Trace metal content of the forest floor in the green mountains of Vermont: spatial and temporal patterns. *Water Air Soil Pollut.* **21**(1–4): 161–170. doi:10.1007/BF00163621.

Galloway, J.N., Schofield, C.L., Peters, N.E., Hendrey, G.R., and Altwicker, E.R. 1983. Effect of atmospheric sulfur on the composition of three Adirondack lakes. *Can. J. Fish. Aquat. Sci.* **40**(6): 799–806. doi:10.1139/f83-103.

Gorgolewski, A., Caspersen, J., Hazlett, P., Jones, T., Tran, H., and Basiliko, N. 2016. Responses of eastern red-backed salamander (*Plethodon cinereus*) abundance 1 year after application of wood ash in a northern hardwood forest. *Can. J. For. Res.* **46**(3): 402–409. doi:10.1139/cjfr-2015-0230.

Government of Ontario. 2002. Nutrient and Management Act. O Reg. 267/03: GENERAL [online]. Queen's Printer for Ontario. Available from <https://www.ontario.ca/laws/regulation/030267>.

- Hannam, K.D., Deschamps, C., Kwiaton, M., Venier, L., and Hazlett, P.W. 2016. Regulations and guidelines for the use of wood ash as a soil amendment in Canadian forests. Information Report No. GLC-X-17. Natural Resources Canada, Canadian Forestry Service, Sault Ste. Marie, Ontario [online]. Available from <http://cfs.nrcan.gc.ca/pubwarehouse/pdfs/37781.pdf>.
- Hannam, K.D., Venier, L., Hope, E., McKenney, D., Allen, D., and Hazlett, P.W. 2017. AshNet: Facilitating the use of wood ash as a forest soil amendment in Canada. *For. Chron.* **93**(1): 17–20. doi:10.5558/tfc2017-006.
- Hannam, K.D., Venier, L., Allen, D., Deschamps, C., Hope, E., Jull, M., et al. 2018. Wood ash as a soil amendment in Canadian forests: What are the barriers to utilization? *Can. J. For. Res.* **48**(4): 442–450. doi:10.1139/cjfr-2017-0351.
- Hansen, M., Kepfer-Rojasm, S., Bjerager, P.E.R., Holm, P.E., Skov, S., and Ingerslev, M. 2018. Effects of wood ash application on nutrient and heavy metal fluxes in the soil and soil solution in a Norway spruce plantation in Denmark. *For. Ecol. Manage.* **424**: 226–240. doi:10.1016/j.foreco.2018.05.005.
- Hart, S.C., Massicotte, H.B., Rutherford, P.M., Elkin, C.M., and Rogers, B.J. 2019. Early response of understory vegetation to wood ash fertilization in the sub boreal climatic zone of British Columbia. *For. Chron.* **95**(2): 135–142. doi:10.5558/tfc2019-020.
- Health Canada. 2016. Guidelines for Canadian drinking water quality: guideline technical document – manganese. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Healthy Canada, Ottawa, Ontario [online]. Available from <https://www.canada.ca/en/health-canada/services/publications/healthy-living/guidelines-canadian-drinking-water-quality-guideline-technical-document-manganese.html>.
- Health Canada. 2019. Guidelines for Canadian drinking water quality: guideline technical document – strontium. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Healthy Canada, Ottawa, Ontario. Catalogue No – H144-13/14-2019E-PDF [online]. Available from <https://www.canada.ca/en/health-canada/programs/consultation-strontium-drinking-water-document.html>.
- Huang, Y., Jin, B., Zhong, Z., Xiao, R., Tang, Z., and Ren, H. 2004. Trace elements (Mn, Cr, b, Se, Zn, Cd and Hg) in emissions from a pulverized coal boiler. *Fuel Process. Technol.* **86**(1): 23–32. doi:10.1016/j.fuproc.2003.10.022.
- Huotari, N., Tillman-Sutela, E., Moilanen, M., and Laiho, R. 2015. Recycling of ash — For the good of the environment? *For. Ecol. Manage.* **348**(1): 226–240. doi:10.1016/j.foreco.2015.03.008.
- Jacobson, S. 2003. Addition of stabilized wood ashes to Swedish coniferous stands on mineral soils — effects on stem growth and needle nutrient concentrations. *Silva Fenn.* **37**(4): 437–450. doi:10.14214/sf.483.
- Johnson, D.W., Richter, D.D., Van Miegroet, H., and Cole, D.W. 1983. Contributions of acid deposition to cation leaching from forest soils: a review. *J. Air Pollut. Control Assoc.* **33**(11): 1036–1041. doi:10.1080/00022470.1983.10465688.
- Juckers, M., and Watmough, S.A. 2014. Impacts of simulated drought on pore water chemistry of peatlands. *Environ. Pollut.* **184**: 73–80. doi:10.1016/j.envpol.2013.08.011. PMID:24035912.
- Juice, S.M., Fahey, T.J., Siccama, T.G., Driscoll, C.T., Denny, E.G., Eagar, C., et al. 2006. Response of sugar maple to calcium addition to northern hardwood forest. *Ecology*, **87**(5): 1267–1280. doi:10.1890/0012-9658(2006)87[1267:ROSMT]2.0.CO;2. PMID:16761605.
- Kahl, J., Fernandez, R., Rustad, L., and Peckenham, J. 1996. Threshold application rates of wood ash to an acidic forest soil. *J. Environ. Qual.* **25**: 220–227. doi:10.2134/jeq1996.00472425002500020003x. doi:10.2134/jeq1996.252220x.
- Kolb, T.E., and McCormick, L.H. 1993. Etiology of sugar maple decline in four Pennsylvania stands. *Can. J. For. Res.* **23**(11): 2395–2402. doi:10.1139/x93-296.
- Landre, L.A., Watmough, S.A., and Dillon, P.J. 2010. Metal pools, fluxes, and budgets in an acidified forested catchment on the Precambrian Shield, Central Ontario, Canada. *Water Air Soil Pollut.* **209**: 209–228. doi:10.1007/s11270-009-0193-7.
- Lawrence, G.B., David, M.B., Lovett, G.M., Murdoch, P.S., Burns, D.A., Stoddard, J.L., et al. 1999. Soil calcium status and the response of stream chemistry to changing acid deposition rates. *Ecol. Appl.* **9**(3): 1059–1072. doi:10.1890/1051-0761(1999)009[1059:SCSATR]2.0.CO;2.
- Likens, G.E., Driscoll, C.T., and Buso, D.C. 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science*, **272**(5259): 244–246. doi:10.1126/science.272.5259.244.
- Lindberg, S.E., and Turner, R.R. 1988. Factors influencing atmospheric deposition, stream export, and landscape accumulation of trace metals in forested watersheds. *Water Air Soil Pollut.* **39**: 123–156. doi:10.1007/BF00250954.
- Litaor, M.I. 1988. Review of soil solution samplers. *Water Resour. Res.* **24**(5): 727–733. doi:10.1029/WR024i005p00727.
- Long, R.P., Horsley, S.B., and Lilja, P.R. 1997. Impact of forest liming on growth and crown vigor of sugar maple and associated hardwoods. *Can. J. For. Res.* **27**(10): 1560–1573. doi:10.1139/x97-074.
- Ludwig, B., Rumpf, S., Mindrup, M., Meiwes, K.-J., and 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. *Scand. J. For. Res.* **17**: 225–227. doi:10.1080/02875802753742891.
- Lundström, U.S., Bain, D.C., Taylor, A.F.S., and van Hees, P.A.W. 2003. Effects of wood acidification and its mitigation with lime and wood ash on forest soil processes: a review. *Water Air Soil Pollut.* **3**: 5–28. doi:10.1023/A:1024115111377.
- McBride, M.B., Richards, B.K., and Steenhuis, T. 2004. Bioavailability and crop uptake of trace elements in soil columns amended with sewage sludge products. *Plant Soil*. **262**: 71–84. doi:10.1023/B:PLSO.0000037031.21561.34.
- McKee, K.L., Mendelssohn, I.A., and Materne, M.D. 2004. Acute salt marsh dieback in the Mississippi River deltaic plain: A drought-induced phenomenon? *Glob. Ecol. Biogeogr.* **13**(1): 65–73. doi:10.1111/j.1466-882X.2004.00075.x.
- Moilanen, M., Hytönen, J., and Leppälä, M. 2012. Application of wood ash accelerates soil respiration and tree growth on drained peatland. *Eur. J. Soil Sci.* **63**: 467–475. doi:10.1111/j.1365-2389.2012.01467.x.
- Moore, J.-D., Ouimet, R., and Duchesne, L. 2012. Soil and sugar maple responses 15 years after dolomitic lime application. *For. Ecol. Manage.* **281**: 130–139. doi:10.1016/j.foreco.2012.06.026.
- Neary, A.J., Mistry, E., and Vanderstar, L. 1987. Sulphate relationships in some central Ontario forest soils. *Can. J. Soil Sci.* **67**(2): 341–352. doi:10.4141/cjss87-030.
- Nieminen, M., Piirainen, S., and Moilanen, M. 2005. Release of mineral nutrients and heavy metals from wood and peat ash fertilizers: field studies in Finnish forest soils. *Scand. J. For. Res.* **20**(2): 146–153. doi:10.1080/02827580510008293.
- Norström, S.H., Bylund, D., Vestin, J.L.K., and Lundström, U.S. 2012. Initial effects of wood ash application to soil and soil solution chemistry in a small, boreal catchment. *Geoderma*, **187–188**: 85–93. doi:10.1016/j.geoderma.2012.04.011.
- Olsson, B.A., Akerblom, S., Bishop, K., Eklöf, K., and Ring, E. 2017. Does the harvesting of logging residues and wood ash application affect the mobilization and bioavailability of trace metals? *For. Ecol. Manage.* **383**: 61–72. doi:10.1016/j.foreco.2016.09.017.
- Ozolincius, R., and Varnagiryte, I. 2005. Effects of wood ash application on heavy metal concentrations in soil, soil solution and vegetation in a Lithuanian Scots pine stand. *For. Stud.* **42**: 66–73.
- Park, B.B., and Yanai, R.D. 2009. Nutrient concentrations in roots, leaves and wood of seedling and mature sugar maple and American beech at two contrasting sites. *For. Ecol. Manage.* **257**(7): 1153–1160. doi:10.1016/j.foreco.2009.06.003.
- Phillips, T., and Watmough, S.A. 2012. A nutrient budget for a selection harvest: impacts for long-term sustainability. *Can. J. For. Res.* **42**(12): 2064–2077. doi:10.1139/cjfr-2012-0224.
- Pitman, R.M. 2006. Wood ash use in forestry — a review of environmental impacts. *J. For.* **79**(5): 563–588. doi:10.1093/forestry/cpl041.
- Pugliese, S., Jones, T., Preston, M.D., Hazlett, P., Tran, H., and Basiliko, N. 2014. Wood ash as a forest soil amendment: the role of boiler and soil type on soil property response. *Can. J. Soil Sci.* **94**(5): 621–634. doi:10.4141/cjss-2014-037.
- Querol, X., Alastuey, A., Moreno, N., Alvarez-Ayuso, E., García-Sánchez, A., Cama, J., et al. 2006. Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash. *Chemosphere*, **62**(2): 171–180. doi:10.1016/j.chemosphere.2005.05.029. PMID:16039695.
- Reid, C., and Watmough, S.A. 2014. Evaluating the effects of liming and wood-ash treatment on forest ecosystems through systematic meta-analysis. *Can. J. For. Res.* **44**(8): 867–885. doi:10.1139/cjfr-2013-0488.
- Reid, C., and 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. *Can. J. Fish. Aquat. Sci.* **73**(2): 382–393. doi:10.1139/cjfas-2015-0231.
- RStudio Team. 2016. RStudio: Integrated Development for R. RStudio, Inc., Boston, MA [online]. Available from <http://www.rstudio.com/>.
- Rumpf, S., Ludwig, B., and Mindrup, M. 2001. Effect of wood ash on soil chemistry of a pine stand in Northern Germany. *J. Plant Nutr. Soil Sci.* **164**(5): 569–575. doi:10.1002/1522-2624(200110)164:5<569::AID-JPLN569>3.0.CO;2-E.
- Saarsalmi, A., Mäliköinen, E., and Piirainen, S. 2001. Effects of wood ash fertilization on forest soil chemical properties. *Silva Fenn.* **35**(3): 355–368. doi:10.14214/sf.590.
- Saarsalmi, A., Derome, J., and Levula, T. 2005. Effect of wood ash fertilization on stand growth, soil, water and needle chemistry, and berry yields of lingonberry (*Vaccinium vitis-idaea* L.) in a Scots pine stand in Finland. *Metsäandusklikud For. Stud.* **42**: 13–33.
- Saarsalmi, A., Smolander, A., Moilanen, M., and Kukkola, M. 2014. Wood ash in boreal, low-productive pine stands on upland and peatland sites: long-term effects on stand growth and soil properties. *For. Ecol. Manage.* **327**: 86–95. doi:10.1016/j.foreco.2014.04.031.
- Siddique, R. 2008. Wood ash. In *Waste materials and by-products in concrete*. Springer-Verlag, Berlin, Germany. pp. 303–320.
- Singh, A., and Agrawal, S.B. 2010. Response of mung bean cultivars to fly ash: growth and yield. *Ecotoxicol. Environ. Saf.* **73**(8): 1950–1958. doi:10.1016/j.ecoenv.2010.07.023. PMID:20696477.
- Soil Classification Working Group. 1998. The Canadian System of Soil Classification. 3rd ed. Agriculture and Agri-Food Canada Publication 1646. NRC Research Press, Ottawa, Ont., Canada. p. 187.
- Sommers, L.E. 1980. Toxic metals in agricultural crops. In *Sludge — health risks of land application*. Edited by G. Bittan. Ann Arbor Science Publisher, Ann Arbor, MI, pp. 105–140.
- Tippling, E., Smith, E.J., Lawlor, A.J., Hughes, S., and Stevens, P.A. 2003. Predicting the release of metals from ombrotrophic peat due to drought-induced

- acidification. *Environ. Pollut.* **123**(2): 239–253. doi:[10.1016/S0269-7491\(02\)00375-5](https://doi.org/10.1016/S0269-7491(02)00375-5). PMID:[12628203](https://pubmed.ncbi.nlm.nih.gov/12628203/).
- Titus, B.D., and Mahendrappa, M.K. 1996. Lysimeter system designs used in soil research: a review. Information Report N-X-301. Natural Resources Canada, Canadian Forest Service, Newfoundland and Labrador Region, St. John's, Newfoundland.
- Vance, E.D. 1996. Land application of wood-fired and combination boiler ashes: an overview. *J. Environ. Qual.* **25**(5): 937–944. doi:[10.2134/jeq1996.00472425002500050002x](https://doi.org/10.2134/jeq1996.00472425002500050002x).
- Watmough, S.A., and Dillon, P.J. 2004. Major element fluxes from a coniferous catchment in central Ontario, 1983-1999. *Biogeochemistry*, **67**(3): 369–398. doi:[10.1023/B:BIOG.0000015792.42624.57](https://doi.org/10.1023/B:BIOG.0000015792.42624.57).
- Williams, T.M., Hollis, C.A., and Smith, B.R. 1996. Forest soil and water chemistry following bark and boiler bottom ash application. *J. Environ. Qual.* **25**(5): 955–961. doi:[10.2134/jeq1996.00472425002500050005x](https://doi.org/10.2134/jeq1996.00472425002500050005x).
- Zhan, G., Erich, S., and Ohno, T. 1996. Release of trace elements from wood ash by nitric acid. *Water Air Soil Pollut.* **88**: 297–311. doi:[10.1007/BF00294107](https://doi.org/10.1007/BF00294107).