

Base cations and micronutrients in forest soils along three clear-cut chronosequences in the northeastern United States

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Abstract Determining effects of clear-cutting on base cations and micronutrients is essential for ensuring the sustainability of forestry for biofuels and wood products. The objective of this study was to quantify long-term changes in forest floor and mineral soil base cations (Ca, Mg, and K) and micronutrient (Mn, Zn, and Cu) concentrations and pools following clear-cutting in forests aged 1–120 years. We studied forest soils along three clear-cut chronosequences located in the Adirondack Ecological Center in Newcomb, NY, Bartlett Experimental Forest in Bartlett, NH, and Harvard Forest in Petersham, MA. We utilized a strong-acid extraction to quantify base cations and micronutrient concentrations and pools, which may better assess nutrients over the chronosequences than the conventional exchangeable extraction.

Generalized linear mixed-effect models (GLMMs) show forest floor and mineral soil Ca, Mg, Mn, and Cu concentrations and pools decreased with increasing forest age across the three study areas. Potassium and Zn concentrations and pools were not significantly different with stand age and neither did soil C and N pools and pH using GLMMs. We calculated that 32–67% of the Ca pool decrease can be attributed to uptake by regenerating vegetation but only 0.02–9% of Mg, Mn, and Cu after harvest. Thus, leaching was likely to the dominant loss process for Mg, Mn, and Cu following clear-cutting. Our results suggest nutrient pools decreased for over a century following clear-cutting, but it is unclear if this will impact plant growth.

Keywords Trace metals · Macronutrients · Calcium · Magnesium · Potassium · Manganese · Zinc

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Introduction

Quantifying long-term effects of clear-cutting on forest nutrients is necessary to ensure the sustainable harvest of northern forests to meet the growing demand for biofuels (Janowiak and Webster 2010; USDA 2011) and wood products (USDA 2011). Clear-cutting is a common method of tree harvesting in the northeastern United States, because it allows for large machinery and promotes shade intolerant species

(USDA 1973; Hornbeck et al. 1986). Clear-cutting can affect physical, chemical, and biological processes occurring in forests and their soils (Bormann et al. 1968; Feller 2005; Phillips and Watmough 2012). Heavy machinery used during clear-cutting can cause soil compaction, alter soil hydrology, mix soil horizons and alters microbial metabolism of soil organic matter (SOM) (Bormann et al. 1968; Ballard 2000; Scott et al. 2001; Nave et al. 2010; Zummo and Friedland 2011; Wall 2012; Diochon et al. 2009; Petrenko and Friedland 2014; Eroğlu et al. 2016).

Many studies on forests in the northeastern US and southeastern Canada have shown that C pools in the organic and mineral soil horizons have decreased significantly for decades after clear-cutting (e.g. Covington 1981; Diochon et al. 2009; Vario et al. 2014; Petrenko and Friedland 2014; Dean et al. 2016). Other studies have found an increase or no effect on soil C (e.g. Yanai et al. 2003; Nave et al. 2010; Grand and Lavkulich 2012; Puhlick et al. 2016). Because base cations and micronutrients are complexed or sorbed to SOM (Essington 2003), changes in soil C storage could also have a long-term impact on them in forest soils. However, base cations (e.g. Ca, K, Mg) and micronutrients (e.g. Mn, Cu, Zn) may not be impacted by changes in soil C dynamics because of their dependence on other inorganic retention mechanisms, such as adsorption to clays, secondary oxides (e.g. Al, Fe, Mn), and precipitation reactions (Brümmer 1986; Essington 2003). Because of their complex behaviors, changes to base cations and micronutrients in forest soils following clear-cutting are described less frequently than C and N, often with similarly contradictory results (Table 1). Previous studies have found increases in soil concentrations of base cations and micronutrients with <20 years after clear-cutting (e.g. McLaughlin and Philips 2006; Brandtberg and Olsson 2012), while other studies have found depletion or losses 20–40 years after clear-cutting (e.g. Olsson et al. 1996; Fuller et al. 1988; Vanguelova et al. 2010; Zetterberg et al. 2016) or no significant changes (e.g. Wilhelm et al. 2013; Grand et al. 2014).

Understanding changes to soil base cations and micronutrients in forest soils is essential to quantifying effects on fertility from clear-cutting. Depletion of K, Ca, and Mg has been hypothesized to be a primary limitation for the growth of many northern hardwoods tree species across the northeastern US (Federer et al. 1989; St. Clair et al. 2008; Vadeboncoeur et al. 2014).

The loss of Ca and Mg can negatively affect the mineral nutrition of trees soil acidity and soil base saturation (Johnson et al. 1991; Zetterberg et al. 2016). In addition to Ca and Mg, the micronutrients (Mn, Cu, and Zn) may also reduce or limit the growth of vegetation. As an example, excessive or limiting Mn can reduce the regeneration of commercially important species such as *Acer saccharum* Marsh (St. Clair et al. 2008; Bal et al. 2015). Moreover, Cu and Zn are essential as enzyme catalysts and cofactors in trees (Boardman and McGuire 1990; Jones 2012).

The primary sources of base cations and micronutrients in forest soils are from decomposition of plant matter, atmospheric deposition, and weathering of minerals (Olsson et al. 1996; Likens et al. 1998; Wilhelm et al. 2013). In the northeastern United States, base cations and micronutrients are primarily derived from the weathering of silicates and other primary minerals (e.g. feldspar, hornblende, biotite, and minor constituents such as garnets, apatite, sulfides) (Binkley and Richter 1987; Bailey et al. 1996; Likens et al. 1998; Schide and Munroe 2015). Clear-cutting may enhance weathering of rates and increase uptake by regenerating forest vegetation (Bailey et al. 1996; Vadeboncoeur et al. 2014; Starr et al. 2014). Base cations and micronutrients undergo several processes by trees because of their nutritional role: uptake, internal transport in vascular tissue, and recycling to soil in senesced leaves and woody debris (Hamburg et al. 2003; Schroth et al. 2007; Wilhelm et al. 2013) and clear-cutting can alter these biogeochemical cycles by disturbing the plant-soil interface. Moreover, base cations and micronutrients export could be increased by changes in soil chemistry (Fuller et al. 1988; Dahlgren and Driscoll 1994). Base cations and micronutrients losses from forest soils are primarily driven by downward leaching (Binkley and Richter 1987; Likens et al. 1998; Hamburg et al. 2003; Schroth et al. 2007), which is dependent on acidity, redox conditions, atomic charge density, and sorption capacity of the soil (Brümmer 1986; Likens et al. 1998; Essington 2003; Vanguelova et al. 2010). Increased soil acidity, increased SOM mobilization, soil compaction, and decreased cation exchange capacity have also been linked to greater losses of base cations and micronutrients following clear-cutting (Johnson et al. 1991; Olsson et al. 1996; McLaughlin and Philips 2006; Wilhelm et al. 2013; Zetterberg et al. 2016; Eroğlu et al. 2016).

Table 1 Review of studies on clear-cutting effects on base cations and micronutrients in forest soils

Author, year published	Clear-cutting harvesting method	Forest age (years)	Study area	Material analyzed	Base cations and micronutrients	Effects observed
Bélanger et al. (2003)	Whole-tree, stem-only	3	Grouin, Quebec, Canada	Forest floor, Mineral soil	Exchangeable Ca, Mg, K	No significant difference
Brandtberg and Olsson (2012)	Whole-tree	10–15	Tönnersjöheden and Kosta, Sweden	Forest floor, Mineral soil	Exchangeable Ca, Mg, K, Mn, Zn	Decreasing Ca, Mg, K, Mn, Zn with stand age after clear-cutting
Dahlgren and Driscoll (1994)	Whole-tree	5	Hubard Brook, NH, USA	Soil solution, Stream water	Dissolved Ca, Mg, Na	Increased Ca, Mg, K in soil and stream waters after clear-cutting
Eroğlu et al. (2016)	Conventional and skidded	<1	Taşlıca, Turkey	Mineral soil	Ca, Mg, Zn, Mn, Cu	Decreased Ca, Mg, Zn, and Mn after harvesting
Fuller et al. (1988)	Whole-tree	1–2	Hubard Brook, NH, USA	Stream water	Mn, Zn	Increased Mn and Zn in stream water after clear-cutting
Grand et al. (2014)	Stem-only	1–5, 8–15	Roberts Creek, BC, Canada	Forest floor, Mineral soil	Exchangeable Ca, Mg, K	No significant difference
Hamburg et al. (2003)	Whole-tree	2–80	Hubard Brook, NH, USA	Forest floor, Mineral soil	Exchangeable Ca, strong acid Ca	Decreased forest floor Ca with age after clear-cutting
Hendrickson et al. (1989)	Whole-tree	3	Petawawa, Ontario, Canada	Forest floor, Mineral soil, Soil solution.	Strong acid Ca, K, Mg	Higher Ca and Mg in soil solution and soil samples after clear-cutting
Jang et al. (2015)	Stem only, burned	38	Coram, Montana, USA	Forest floor, Mineral soil	Exchangeable Ca, Mg, K	Higher forest floor Ca and mineral soil K in clearcut than control
Johnson et al. (1991)	Whole-tree	3	Hubard Brook, NH, USA	Forest floor, Mineral soil	Exchangeable Ca, Mg, K	Decreased Ca, Mg, K organic, mineral soils
McLaughlin and Phillips (2006)	Whole-tree	17	Central Maine, USA	Forest floor, Mineral soil	Exchangeable Ca, Mg, K	Higher Ca, Mg, K in mineral soil, soil solution and stream water than reference
Olsson et al. (1996)	Whole-tree	15–16	Tönnersjöheden and Kosta, Sweden	Forest floor, mineral soil	Exchangeable Ca, Mg, K, Mn, Zn	Decreased Ca, Mg, K, Mn, and Zn in clear cut stand
Roberts and Gilliam (1995)	Conventional	8–70	northern Michigan, USA	Mineral soil	Dilute acid extratable Ca, K, Mg	Lower Ca, K, and Mg in older stands
Snyder and Harter (1985)	Stem-only	3–30	White Mountains, NH, USA	Mineral soil	Exchangeable Ca, Mg, K	Increased mineral soil Ca, Mg, and K
Vangelova et al. (2010)	Whole-tree, stem-only	28	Kielder, Northumberland, UK	Forest floor, Mineral soil	Exchangeable Ca, Mg, K, Na	Decreased Ca, Mg, K organic, mineral soils in older stands
Walmesley et al. (2009)	Whole-tree, stem-only	23	Beddgelert, Wales, UK	Forest floor, Mineral soil	Exchangeable Ca, K, Na	Decreased Ca and K with whole-tree harvesting

Table 1 continued

Author, year published	Clear-cutting harvesting method	Forest age (years)	Study area	Material analyzed	Base cations and micronutrients	Effects observed
Wilhelm et al. (2013)	Whole-tree	1–2	northwestern Wisconsin, USA	Forest floor, Mineral soil	Exchangeable Ca, Mg, K	No significant difference in Ca and Mg. Higher K in unharvested stands
Zetterberg et al. (2016)	Whole-tree	32–35	Tönnersjöheden and Kosta, Sweden	Forest floor, Mineral soil Soil solution	Exchangeable Ca	Lower Ca in soil solution and mineral soil in whole-tree harvested stands
Zetterberg et al. (2016)	Whole-tree, stem-only	20–40	Tönnersjöheden, Kosta, and Lövliden, Sweden	Forest floor, Mineral soil Soil solution	Exchangeable Ca, Mg, K, Na	Decreases in soil Ca due to tree uptake

Base cations and micronutrients exist in soils as different chemical phases and the biologically-relevant fractions are commonly assessed using exchangeable and strong-acid extractions. The exchangeable fraction of base cations and micronutrients is predominantly used and is typically measured using a 1 M NH_4Cl or KCl extraction procedure to quantify nutrients that are most easily taken up by plants (Page et al. 1982; e.g. Grand and Lavkulich 2012; McLaughlin and Philips 2006). Exchangeable cations are frequently studied because of easier methodological demands than strong-acid extractions, which uses concentrated nitric and hydrochloric acids, and the close relationship between exchangeable nutrients and cation exchange capacity. However, exchangeable concentrations do not necessarily reflect total plant availability of base cations and micronutrients. Exchangeable Ca, K, and Mg concentrations in soils are often not correlated to uptake by vegetation (e.g. Schaberg et al. 2006; Brandtberg and Olsson 2012). This has been attributed to microbial and root exudates capable of accessing base cations and micronutrients from non-exchangeable sources such as secondary minerals and organic compounds (see Landeweert et al. 2001). Furthermore, exchangeable nutrient concentrations may be less relevant over long-time scales, such as multiple decades to centuries (e.g. Bailey et al. 2003; Hamburg et al. 2003). By using a strong-acid extraction, which extracts all base cations and micronutrients not in crystalline silicate minerals, it is possible to better quantify nutrients that may be accessed by plants than just the exchangeable fraction (Bailey et al. 2003). For example, Hamburg et al. (2003) showed that non-exchangeable Ca was 1–2 orders of magnitude greater than exchangeable phases and were likely the dominant source for trees over many decades. In addition, Zetterberg et al. (2016) found that changes in exchangeable Ca in forest soil chronosequences in Sweden may not reflect actual depletion of Ca because plants may uptake and mobilize Ca from other sources, i.e. the non-exchangeable fraction. In spite of these caveats, most studies have focused on exchangeable nutrient concentrations (e.g. Olsson et al. 1996; McLaughlin and Philips 2006; Vanguelova et al. 2010; Brandtberg and Olsson 2012; Grand and Lavkulich 2012; Vadeboncoeur et al. 2014) but strong acid extractable base cations and micronutrients may better assess the larger

nutrient fraction that is more important on longer term scales.

Few studies have examined changes occurring in soils >50 years after clear-cutting (Table 1; Grigal 2000). Studies have primarily focused on the first five years postharvest (e.g. Fuller et al. 1988; Hendrickson et al. 1989; Johnson et al. 1991; Belleau et al. 2006; Grand et al. 2014) or within 10–20 years postharvest (e.g. Rosén et al. 1996; McLaughlin and Philips 2006; Walmsley et al. 2009; Vanguelova et al. 2010; Brandtberg and Olsson 2012). Additional studies focusing on changes occurring over periods >50 years are needed to understand long-term sustainability (e.g. Vadeboncoeur et al. 2014; Zetterberg et al. 2016). Few long-term research sites exist that have continuous records examining the effect of clear-cutting or traditional forestry practices on forest base cations and micronutrients (e.g. >30 years at Hubbard Brook Experimental Forest). Thus, it is essential to rely on other methods to examine changes on the multi-decadal to century time scale. The chronosequence approach, where soils in forest stands varying different ages are sampled, can be used to reconstruct changes in nutrient cycling during forest regrowth on the decadal to century time scale (e.g. Zetterberg et al. 2016). Covington (1981) used the chronosequence approach show changes in C in the forest floor and more recently has shown decreases in mineral soil C (e.g. Diochon et al. 2009; Petrenko and Friedland 2014) and base cations (e.g. Ca by Hamburg et al. 2003).

Here, we utilize the chronosequence approach for different age forest stands to substitute space for time and examine strong-acid extractable base cations (Ca, Mg, K) and micronutrients (Mn, Cu and Zn) in a subset of forest soils from Petrenko and Friedland (2014). We tested the hypothesis that forest floor and mineral soil nutrient pools have decreased following clear-cutting for an unknown duration (e.g. Covington 1981; McLaughlin and Philips 2006; Zetterberg et al. 2016). This hypothesis was based upon previous studies that found increased exchangeable cation exports for years following clear-cutting (e.g. Olsson et al. 1996; Scott et al. 2001; Zetterberg et al. 2016) following harvesting but stabilization after decades (Brandtberg and Olsson 2012). Our null hypothesis was no significant difference in nutrient concentrations or pools with stand age across study areas. Additionally, we tested the hypothesis that decreases

in base cations and micronutrient pools would correspond with changes in soil C, N, and pH. Similarly, our null hypothesis was significant differences in C, N, and pH with stand age across study areas. The information from this study may help managers of temperate forests and terrestrial biogeochemists assess long-term changes in soil nutrients from forest management.

Methods

Study area and stand descriptions

We collected data along chronosequences at three study areas: Adirondack Ecological Center (AEC) in Newcomb, NY, Bartlett Experimental Forest (BEF) in Bartlett, NH, and Harvard Forest (HF) in Petersham, MA (Table 2). Four forest stands of varying ages at each study area (AEC, HF, and BEF) were selected with assistance from local land managers and using harvest records for the area (Table 2) (Leak and Smith 1996; Zummo and Friedland 2011; Vario et al. 2014; Petrenko and Friedland 2014). HF and BEF have been studied in tandem in prior studies due to their similarity in tree species composition, soil parent material, proximity, and climatic setting (e.g. Dharmala and Mitchell 1996). Details of the study areas can be found in Petrenko and Friedland (2014). Forests were mixed hardwoods, *Acer* spp., *Betula* spp., *Fagus grandifolia* Ehrh., *Populus* spp., *Quercus* spp., with interspersed eastern hemlock (*Tsuga Canadensis* (L.) Carrière). Practices of harvesting have been generally similar across the study areas with the exception of mechanized equipment replacing manual animal labor during the 1960s (Yanai et al. 2003). However, specific date implementation across study areas was unknown. Soils at AEC and BEF were predominantly Spodosol-Inceptisol complexes, while soils at HF were only Inceptisols (see Petrenko and Friedland 2014). Although Spodosols and Inceptisols have been shown to have different vertical distributions of elements (e.g. Richardson et al. 2013), soils shared similar physical and chemical properties, comparable morphological horizons (Oi, Oe, Oa, A and E, B horizons) and comparisons were focused on variations among forest stands at each chronosequence and not across study areas. All soils were moderately- to well-drained and commonly with large rock fragments,

Table 2 Study area descriptions

Study area	Code	Latitude (d.d.)	Longitude (d.d.)	Elevation (m)	Soil parent material	Stand ages [†] (years)
Adirondack Ecological Center	AEC	43.9694	-74.1647	550	Phyllitic to gneissic glacial-till	1, 19, 55, 120 [^]
Bartlett Experimental Forest	BEF	44.0778	-71.2828	304	Phyllitic to gneissic glacial-till	5, 25, 55, 120
Harvard Experimental Forest	HF	42.4875	-72.1875	360	Granitic and gneissic glacial-till	5, 20, 64, 84

[†] Stand ages are based upon their age in 2011

[^] The 120 year old stand at AEC has not been clear-cut in the past 120 years and may be much older

physical root restrictions, and fragipans in the 30–45 cm depths.

Soil sampling methods

Sampling took place during the summers of 2011 through 2013. Details of the soil sampling can be found in Vario et al. (2014) and Petrenko and Friedland (2014). In brief, the forest floor was sampled using a 15 × 15 cm template. At each forest stand, nine soil cores were collected using a gas-powered auger (EarthquakeTM 9800B) with a 9.5 cm diameter drill bit. The mineral soil was sampled incrementally: 0–10, 10–20, 20–30 and 30–45 cm (Zummo and Friedland 2011). Locations with obvious disturbances (e.g. wheel-ruts) and downed woody debris were not sampled. After collection, the nine soil cores were combined into three samples based on proximity for each depth increment in order to achieve a larger, more representative soil sample, similar to that of a quantitative soil pit. The addition of metals from the diamond-tipped stainless steel drill bit or from the grinding of rock was considered and would likely increase metal concentrations commonly found in steel alloys (Fe, Mn, Cr, Ni, Mo) for soils with higher rock content (Levine et al. 2012). Coring methods were not found to significantly increase Mg or Ca concentrations when sampling glacial-till soils in NH and NY (Levine et al. 2012) and based upon comparisons with soils excavated using hand tools at BEF and other sites not included in this study, we would do not expect Mn, Cu, and Zn to be added during coring. Additional information about sample collection and processing are available in Vario et al. (2014) and Petrenko and Friedland (2014).

Soil physicochemical analyses

Soils samples were air-dried in closed paper bags to a constant weight. Roots and twigs >5 mm in diameter were removed from forest floor samples. The remaining forest floor was subsequently ground to <2 mm. Forest floor and soil samples were sieved to <2 mm and sub-samples were ground to <0.05 mm using a ball mill. For C and N analyses in soil, 5-mg subsamples were combusted in a Carlo-Erba NA 1500 Series 2 gas analyzer (CE Instruments, Milan, Italy). For every 12 samples, we included a duplicate, a quartz blank, and the standard reference materials (SRMs) atropine and acetanilide. Soil pH was determined using a 1:2 soil–water slurry for mineral soil samples and 1:4 soil–water slurry for forest floor samples. The pH of the slurries was measured with a VWR 8015 electroprobe pH meter (VWR, Radnor, PA). Percent clay (% clay) (g/g) was measured using a modified Bouyoucos method with hydrometer readings taken at 30, 60, 1.5 and 24 h after mixing in columns (Gee and Bauder 1986; Richardson et al. 2013). Soil C and N concentrations, pH and, % clay content for each study area are given in Table 3.

A strong acid digestion following USEPA method 3051A was used to quantify Ca, Mg, K, Mn, Cu, and Zn concentrations through open vessel digestion. Strong acid digestion was used instead of other operationally-defined methods to measure all non-primary silicate mineral lattice metals that may become dissolved or biologically-relevant over the time scale of interest (Chen and Ma 1998; Melo et al. 2016). This method is able to dissolve metals within organic matter, apatite, secondary oxides, and poorly crystalline secondary minerals that undergo

Table 3 Typical soil morphology and average soil properties and chemistry at each of the three study areas

Study area	Depth (cm)	Typical horizons	Carbon concentrations (mg/g)	Nitrogen concentrations (mg/g)	pH (log units)	%clay (g/g)
AEC	Organic horizons	Oi, Oe, Oa	355 ± 31	18.7 ± 2.3	4.5 ± 0.2	–
	0–10	A, E	104 ± 10	7.9 ± 1.7	4.6 ± 0.3	11.0 ± 1.5
	10–20	Bs1	36 ± 5	4.0 ± 0.7	4.6 ± 0.3	13.0 ± 1.9
	20–30	Bs1, Bs2	66 ± 7	2.8 ± 0.3	4.7 ± 0.2	10.1 ± 1.2
	30–45	Bs2	42 ± 6	2.1 ± 0.4	4.5 ± 0.3	9.8 ± 9.8
BEF	Organic horizons	Oi, Oe, Oa	298 ± 27	11.9 ± 0.5	4.5 ± 0.3	–
	0–10	A, E	56 ± 3	2.4 ± 0.4	4.3 ± 0.3	6.4 ± 0.9
	10–20	E, Bs1	44 ± 6	1.9 ± 0.4	4.4 ± 0.2	10.0 ± 0.8
	20–30	Bs1	26 ± 4	1.2 ± 0.2	4.5 ± 0.3	4.5 ± 0.8
	30–45	Bs1, Bs2	14 ± 2	0.8 ± 0.1	4.6 ± 0.3	4.2 ± 0.6
HF	Organic horizons	Oi, Oe, Oa	333 ± 22	13.6 ± 0.8	4.6 ± 0.3	–
	0–10	A, E	55 ± 9	2.7 ± 0.3	4.8 ± 0.3	2.1 ± 0.9
	10–20	Bw1	27 ± 1	1.4 ± 0.1	4.9 ± 0.3	8.7 ± 0.9
	20–30	Bw1, Bw2	18 ± 1	0.8 ± 0.1	4.8 ± 0.2	7.5 ± 0.9
	30–45	Bw2	15 ± 2	0.7 ± 0.1	4.9 ± 0.2	8.0 ± 1.0

dissolution below pH 0. Minerals such as quartz and feldspars are not completely dissolved, but edges on mineral surfaces can be corroded (Chen and Ma 1998; Melo et al. 2016). The digestion process used 250 mg (± 1 mg) sub-samples, digested with 5 mL of 9:1 ratio of trace metal grade nitric acid to hydrochloric acid (15 M HNO₃ + 10 M HCl, Fisher Scientific). The solution was degassed for 24 h and microwave digested at 90 °C for 45 min using a CEM MARS (CEM, Matthews, NC). Digests were analyzed with an Agilent 7500 series inductively coupled plasma – mass spectrometer (Agilent Technologies, Santa Clara, CA). For every 20 samples we included a replicate, a preparation blank, and a SRM. Peach leaves SRM 1547 and Montana soil SRM 2711a (National Institute of Standards and Technology Gaithersburg, MD) were used as SRMs for forest floor and mineral soil samples, respectively. All Ca, Mg, K, Mn, Cu and Zn concentrations for SRM materials were within 10% of their certified values. Preparation blanks had concentrations below detection limits for all metals.

Soil mineralogy was determined for each bulked 0–10 and 30–45-cm depth cored sample for each forest stand at each study area to investigate the least and

most weathered minerals of the soil profile. First, 1 g of sample ≤ 2 -mm was ground to < 0.1 -mm treated with 30% (w/w) H₂O₂ to remove organic matter. Samples were dispersed with sodium-hexametaphosphate (50 g L⁻¹), washed to remove salts with multiple sets of wrist-action shaking with DI water, centrifuging, and decanting. Samples were then Mg-saturated and an internal standard zinc oxide (certified ACS; Fisher Scientific Inc.) was added to the sample. The resulting pastes were smear mounted onto glass slides. The process was repeated in triplicate (n = 3) with internal standards at 10 and 25% of the total sample mass.

Samples were scanned with CuK α radiation (40 mA, 40 kV) using a Bruker-AXS D8 ADVANCED X-ray diffractometer (Bruker Corp., Billerica, MA) equipped with a Ge crystal monochromator using a step size of 0.02° 2 θ from 10° to 90°. Counting time was 4 s per increment. Mineral masses were quantified using the ZnO internal standards and calculated following Eq. (1), from Feldman et al. (1991). Mass of mineral (M_m) was determined using the ratio of the integrated count peak at (001) for a mineral (I_m) to the known mass of the internal standard (M_{ZnO}) and the integrated peak for

ZnO at (001) (I_{ZnO}). The constant C is an empirical constant determined from the slope of a linear regression of I_m/I_{ZnO} with M_m/M_{ZnO} . Findings are given in Supplemental Table 1.

$$\frac{I_m}{I_{ZnO}} = C \frac{M_m}{M_{ZnO}} \quad (1)$$

Data analyses

Base cation and micronutrient pools for each forest stand were calculated using their concentration and the soil bulk density estimated with bulked soil core samples (Petrenko and Friedland 2014). Forest floor nutrient pools were calculated as the entire forest floor mass multiplied by the average metal concentration. Mineral soil nutrient pools were calculated as the summation of the 0–10-, 10–20-, 20–30-, and 30–45-cm depth intervals pools, which was the measured metal concentration multiplied by the soil bulk density and recorded depth.

We utilized a Generalized Linear Mixed-effect Models (GLMM) to determine if nutrient concentrations and pools significantly varied with forest stand age and among study areas. We tested several models with Gamma, Poisson and binomial distributions with -1 , log, and logit link functions, respectively. The final model was: response nutrient = 1 + Study area (AEC, BEF, or HF) + Forest stand age (continuous age) + error. Study area was considered a random effect. The Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) were used to choose the optimal GLMM model configuration across all data. We found Poisson distributions with log link functions gave the lowest absolute AIC and BIC values, thus, all GLMM results refer to this model only. A GLMM was also used to investigate soil C, C:N ratio, pH, bulk density, and mineralogical composition (%quartz, %plagioclase, %orthoclase, %illite) using the model 1 + Study area (AEC, BEF, or HF) + Forest stand age (continuous age) + error and utilized GLMMs using both Poisson distribution and log link function for each variable.

Base cation and micronutrient pools from all study areas were combined to evaluate an integrated measure of change among pools with stand age across all study areas simultaneously. This assumes that forest floor and mineral soil pools at each study area can be combined as representative samples of northern

forests, which was the case for most base cations and micronutrients. Although the nutrient pools may have been different among study areas, the combination of all study areas allows for a broad examination of changes pool dynamics with forest regrowth. An exponential regressions were used to capture the non-linear changes in base cations and micronutrient pools through time and because clear-cut events are non-continuous, pulse events (e.g. Buchmann 2000; Richardson et al. 2014). Statistical analyses were performed in Matlab (Mathworks, Boston MA, version 2011B). Mean values in the text and figures are given ± 1 standard error.

Results

Changes in nutrient concentrations along chronosequences

We compared base cation and micronutrient concentrations with stand age and study areas using GLMMs for each depth interval at each study area (Table 4). Calcium concentrations for the forest floor, 0–10-, 10–20-cm and 30–45-cm depth intervals were negatively correlated with stand age and varied significantly among study areas for the forest floor and 0–10-cm depths (Table 4). Magnesium concentrations in the forest floor, 0–10-, and 30–45-cm depth intervals decreased significantly with stand age and 0–10-cm depth interval was different among study areas (Table 4). Potassium concentrations did not vary with stand age but was significantly different among study areas for the forest floor, 0–10-, and 10–20-cm, and 30–45-cm depth intervals (Table 4). Manganese concentrations varied with stand age for the 0–10-, 10–20-, and 30–45-cm depth intervals and among study areas for the 10–20-cm depth interval (Table 4). Copper concentrations significantly varied with stand age in the 0–10-cm depth interval and among study areas in the 10–20-cm depth interval (Table 4). Zinc concentrations did not vary with stand age or study area for any depth interval (Table 4).

Changes in nutrient pools along chronosequences

Forest floor and mineral soil pools of base cations and micronutrients were compared with stand age

Table 4 Generalized linear mixed-effect model results for inorganic nutrient concentrations for the five depth intervals

	Stand age <i>p</i> value	Study area <i>p</i> value	AIC	BIC	Deviation
<i>Calcium</i>					
Forest floor	(−) <0.01	<0.01	11.8	14.1	3.8
0–10 cm	(−) <0.01	<0.01	24.1	26.3	16.1
10–20 cm	(−) <0.01	n.s.	15.8	18.1	7.8
20–30 cm	n.s.	n.s.	23.9	26.2	15.9
30–45 cm	(−) <0.01	n.s.	16.4	18.3	8.1
<i>Magnesium</i>					
Forest floor	(−) <0.01	n.s.	31.3	33.6	23.3
0–10 cm	(−) <0.01	<0.01	56.7	58.9	48.7
10–20 cm	n.s.	n.s.	44.7	46.9	36.7
20–30 cm	n.s.	n.s.	35.7	38.1	27.9
30–45 cm	(−) <0.01	n.s.	36.5	38.7	28.5
<i>Potassium</i>					
Forest floor	n.s.	<0.01	9.5	11.7	4.7
0–10 cm	n.s.	<0.05	23.6	25.8	15.6
10–20 cm	n.s.	n.s.	21.4	26.4	13.4
20–30 cm	n.s.	<0.05	11.4	14.1	4.9
30–45 cm	n.s.	<0.05	2.9	5.1	5.1
<i>Manganese</i>					
Forest floor	n.s.	n.s.	35.8	37.9	27.7
0–10 cm	(−) <0.01	n.s.	46.5	48.7	38.5
10–20 cm	(−) <0.01	<0.01	49.7	51.9	41.6
20–30 cm	n.s.	n.s.	33.1	35.3	25.1
30–45 cm	(−) <0.01	n.s.	20.2	22.4	18.2
<i>Copper</i>					
Forest floor	n.s.	n.s.	28.9	31.2	20.9
0–10 cm	(−) <0.05	n.s.	55.5	57.8	47.5
10–20 cm	(−) <0.01	<0.01	20.4	23.6	12.1
20–30 cm	n.s.	n.s.	31.3	33.6	23.3
30–45 cm	(−) <0.05	n.s.	40.5	42.7	42.4
<i>Zinc</i>					
Forest floor	n.s.	n.s.	25.8	28.1	17.8
0–10 cm	n.s.	n.s.	35.2	37.5	27.2
10–20 cm	n.s.	n.s.	31.1	33.4	23.2
20–30 cm	n.s.	n.s.	25.6	27.8	18.6
30–45 cm	n.s.	n.s.	23.2	25.5	15.2

The model equation was: response nutrient = 1 + Study area (AEC, BEF, or HF) + Forest stand age (continuous age) + error and a Poisson distribution with log link function were used. N = 12 for each model
(−) Indicate a negative trend with stand age

and among study areas using GLMMs. Forest floor and mineral soil Ca, Mn, and Cu pools were decreased with increasing stand age significantly (Table 5). Magnesium mineral soil pools also decreased with stand age significantly (Table 5). Potassium forest floor pools and Cu mineral soil pools were significantly different among study areas

(Table 5). Zinc forest floor and mineral soil pools did not vary significantly with stand age or study area (Table 5).

Base cation and micronutrient pools in the forest floor and mineral soil from all study areas were combined to evaluate an integrated measure of change among nutrient pools with stand age across

Table 5 Generalized linear mixed-effect model results for inorganic nutrient concentrations for the five depth intervals

	Stand age	Study area	AIC	BIC	Deviation
<i>Calcium</i>					
Forest floor	(-) <0.01	n.s.	8.5	10.5	5.5
Mineral soil	(-) <0.001	n.s.	10.2	12.4	2.8
<i>Magnesium</i>					
Forest floor	n.s.	n.s.	38.8	40.7	30.8
Mineral soil	(-) <0.01	n.s.	22.3	24.6	14.3
<i>Potassium</i>					
Forest floor	n.s.	<0.01	17.9	19.9	9.9
Mineral soil	n.s.	n.s.	13.9	16.1	5.9
<i>Manganese</i>					
Forest floor	(-) <0.05	n.s.	23.9	25.0	22.1
Mineral soil	(-) <0.001	n.s.	20.9	23.1	12.9
<i>Copper</i>					
Forest floor	(-) <0.01	n.s.	14.2	16.1	6.2
Mineral soil	(-) <0.01	<0.001	39.6	41.9	31.6
<i>Zinc</i>					
Forest floor	n.s.	n.s.	20.8	22.7	12.8
Mineral soil	n.s.	n.s.	28.4	30.6	20.4

The model equation was: response nutrient = 1 + study area (AEC, BEF, or HF) + Forest stand age (continuous age) + error and a Poisson distribution with log link function were used. N = 12 for each model
 (-) Indicate a negative trend with stand age

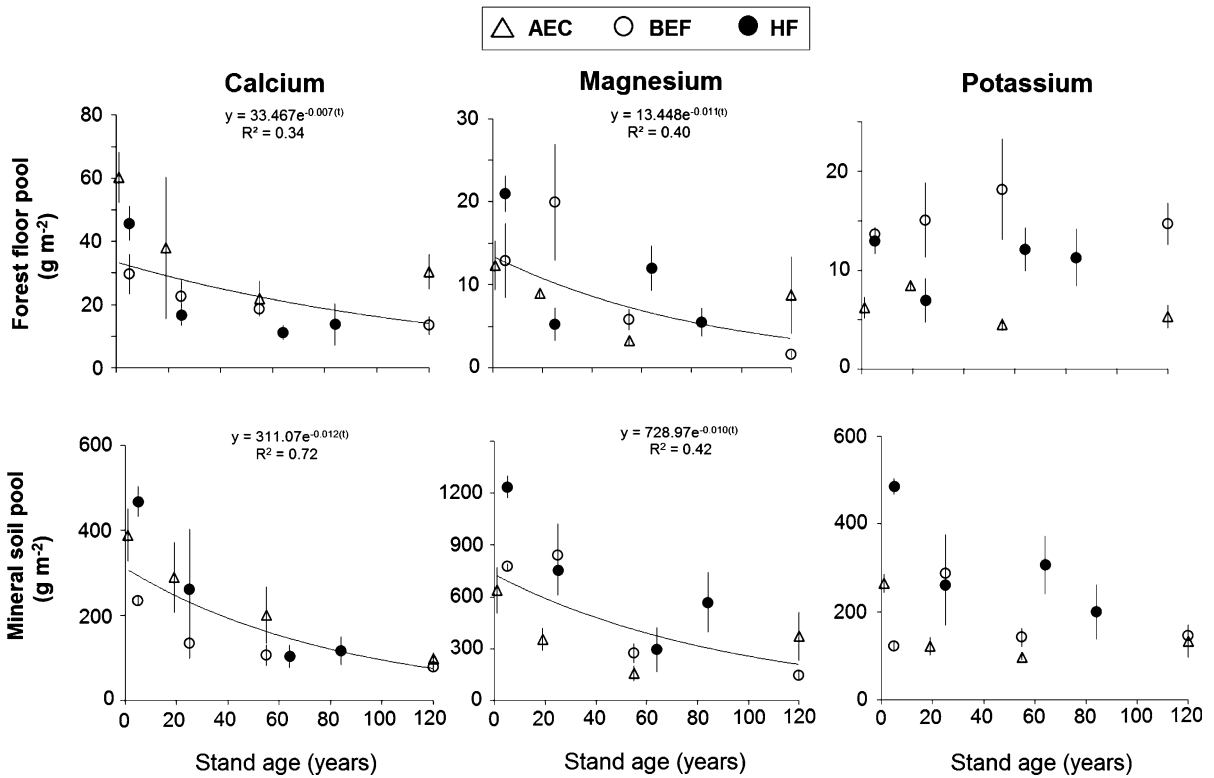


Fig. 1 Forest floor and mineral soil base cation pools across three chronosequences: AEC (Adirondack Ecological Center), BEF (Bartlett Experimental Forest), and HF (Harvard Forest).

Changes are modeled using an exponential regression model. Only significant models are shown

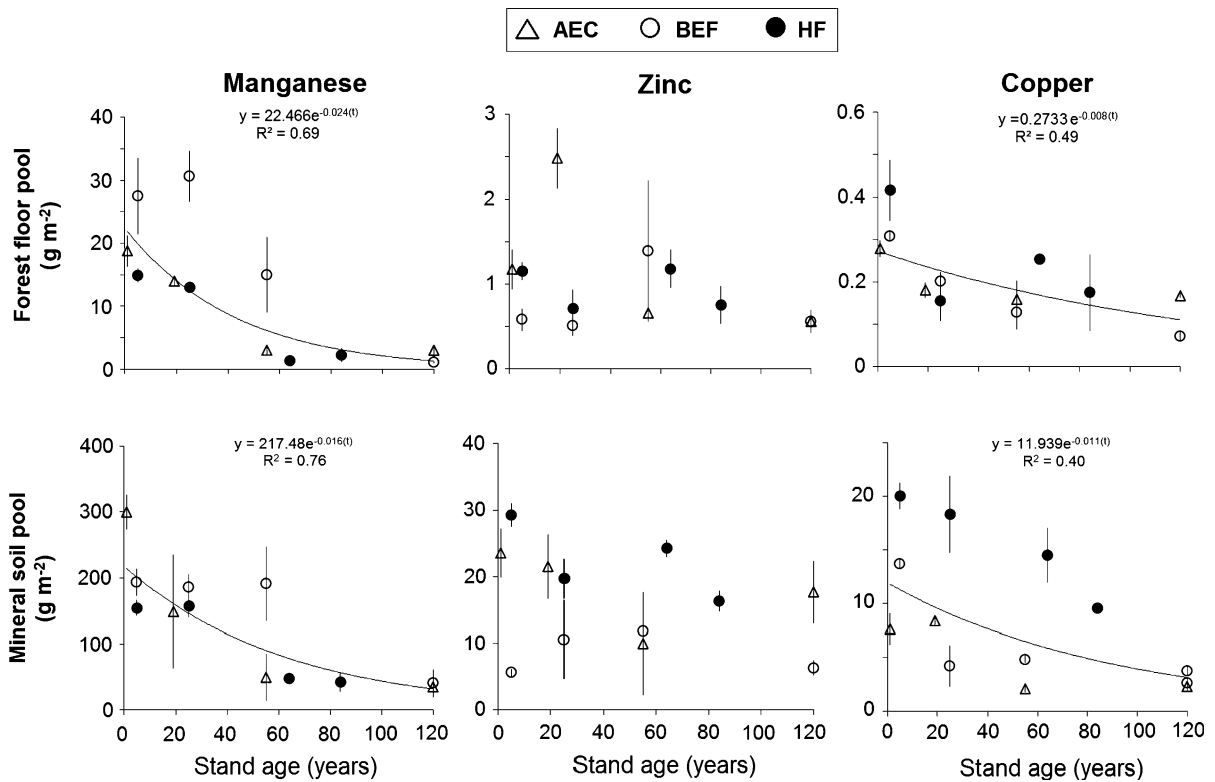


Fig. 2 Forest floor and mineral soil micronutrient pools across three chronosequences: AEC (Adirondack Ecological Center), BEF (Bartlett Experimental Forest), and HF (Harvard Forest).

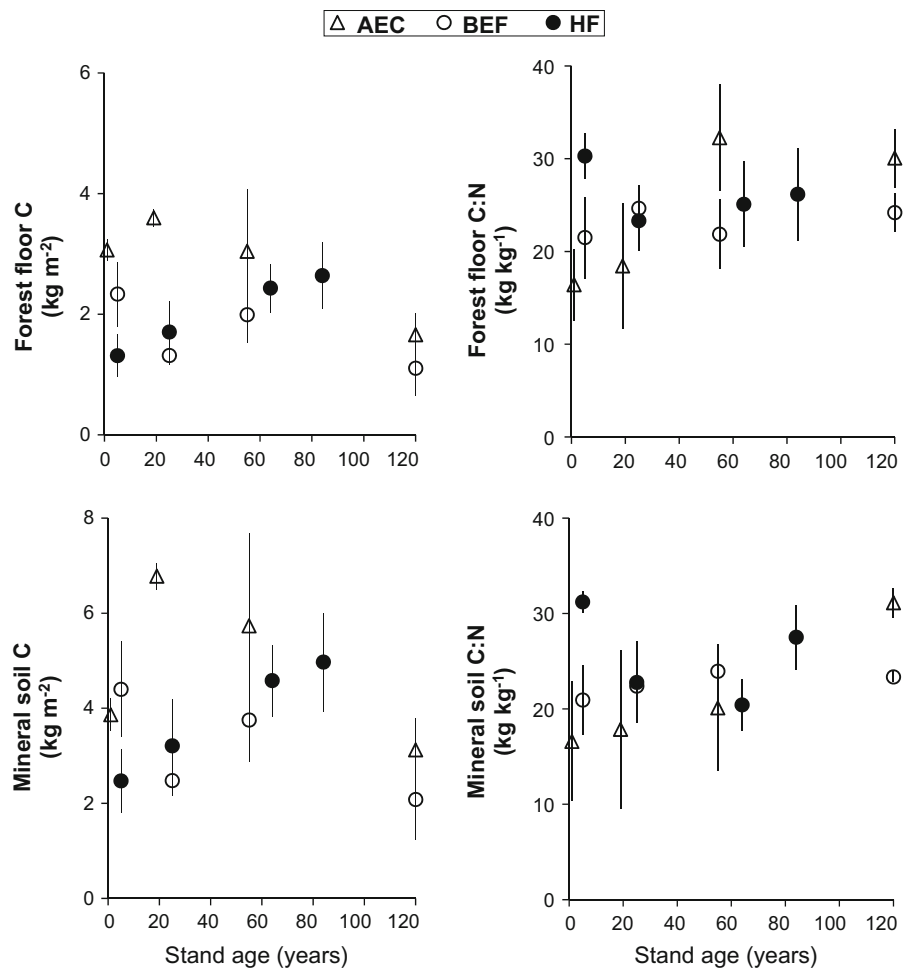
Changes are modeled using an exponential regression model. Only significant models are shown

all study areas simultaneously using an exponential regression. For the base cations, forest floor and mineral soil pools of Ca and Mg decreased significantly with increasing stand age (Table 5; Figs. 1, 2). Forest floor Ca pools decreased with increasing stand age, from an average of 36 g m⁻² for stands <10 years of age down to an average of 18 g m⁻² for stands >50 years of age (50% decrease) (Fig. 1). Mineral soil Ca pools decreased with increasing stand age, from an average of 296 g m⁻² for stands <10 years of age down to an average of 118 g m⁻² for stands >50 years of age (60% decrease). Forest floor Mg pools decreased with stand age, from 13 g m⁻² for stands <10 years of age down to 6 g m⁻² for stands >50 years of age (54% decrease) (Fig. 1). Mean mineral soil Mg pools decreased from 767 g m⁻² for stands <10 years of age down to 303 g m⁻² for stands >50 years of age (61% decrease) (Fig. 1). Forest floor and mineral soil K

pools did not exhibit a trend with stand age ($p > 0.10$; $R^2 < 0.20$) (Fig. 1).

For micronutrients, forest floor and mineral soil pools of Mn and Cu also decreased significantly with increasing stand age. Forest floor Mn pools exhibited the greatest decrease: from 20 g m⁻² for stands <10 years of age down to 4 g m⁻² for stands >50 years of age (79% decrease) (Fig. 2). Mineral soil Mn pools decreased from 190 g m⁻² for stands <10 years of age down to 68 g m⁻² for stands >50 years of age (64% decrease). Forest floor Cu pools decreased with stand age, from 0.26 g m⁻² for stands <10 years of age down to 0.16 g m⁻² for stands >50 years of age (38% decrease) (Fig. 2). Mineral soil Cu pools decreased with age, from 12 g m⁻² for stands <10 years of age down to 6 g m⁻² for stands >50 years of age (50% decrease) (Fig. 2). Forest floor and mineral soil Zn pools did not exhibit a trend with stand age ($p > 0.10$; $R^2 < 0.20$) (Fig. 2).

Fig. 3 Forest floor and mineral soil C pools and C:N ratio across the three chronosequences: AEC, BEF, and HF. Regression models were not significant for forest floor and mineral soil C and C:N ratio with stand age



Soil C, N, pH, and mineralogy along chronosequences

Forest floor and mineral soil C pools were not significantly different with stand age or among study areas using GLMMs ($p > 0.05$) (Fig. 3). We also compared the C:N ratio because it can be indicative of woody biomass inputs, decomposability, and microbial mineralization (Mattson et al. 1987; McGroddy et al. 2004; Nave et al. 2010; Grand and Lavkulich 2012). Forest floor and mineral soil C:N pools did not indicate a relationship with stand age using the GLMM ($p > 0.05$) (Fig. 3). Moreover, we did not find any relationships in soil pH with stand age for any depth interval using the GLMM (Supplemental Fig. 1).

We investigated soil bulk density and mineralogy among stands for each study area to determine potential influences on base cation and micronutrient pools along the chronosequences. Forest floor and mineral soil bulk density did not exhibit any trends with stand age for any depth interval at any study area ($p > 0.05$) (Supplemental Fig. 2). Mineralogy for 0–10 and 30–45 cm mineral soil samples did not vary significantly among forest stands along each chronosequence or among study areas using GLMMs. Quartz, plagioclase, orthoclase and illite fractions for the 0–10 cm depth ranged between 65–69, 11–22, 8–14 and 4–16%, respectively. For the 30–45 cm depth, quartz, plagioclase, orthoclase and illite fractions ranged between 51–60, 13–23, 14–30 and 2–12%, respectively.

Discussion

Using the chronosequence approach

Our experimental design utilized chronosequences at three study areas to quantify the effect of clear-cutting on base cations (K, Ca, and Mg) and micronutrients (Mn, Cu, and Zn) for more than a century after the event. The chronosequence approach relies on two primary assumptions (Johnson and Miyanishi 2008; Diochon et al. 2009; Grand and Lavkulich 2012; Petrenko and Friedland 2014). The first assumption was that climatic and environmental conditions were constant throughout the time span considered in this study. Changes in climate are expected to cause increases in mean annual temperatures and precipitation in the northeastern United States (Tang and Beckage 2010) and globally temperatures have increased ~ 0.8 °C since the first clear-cut in 1880s (NASA Goddard Institute for Space Studies). We assume changes in climate have had limited impacts on forest base cations and micronutrients during the time scale of interest. In addition to climate, the effects of acid rain may have impacted vegetation across the region by increasing Al and decreasing Ca and other base cations in forest soils (e.g. Driscoll et al. 2001). We hypothesize these environmental changes would be most impactful on stands regenerating after clear-cutting during peak acid rainfall in the 1970s. However, studies have observed that acid rain may not have substantially affected base cations and micronutrients in forest soils. For example, Johnson et al. (1994) did not observe a significant decrease from 1930 to 1984 in soil Ca storage at 48 soil profiles in the Adirondacks Mts, New York. In addition, Hamburg et al. (2003) found forest maturation had a greater effect on soil Ca pools than acid rain effects. For our study, we have assumed that changes in climate and environmental conditions have had limited effects on the base cation and micronutrient cycling during the regeneration of vegetation following clear-cutting. This simplifying assumption was likely untrue (e.g. Driscoll et al. 2001), thus, the inability to factor in potential impacts from environmental changes is a limitation to this study approach.

The second assumption for the chronosequence approach was that soil properties were originally similar enough among forest stands at each study area

to detect impacts from clear-cutting. We argue that geologic and soil physicochemical properties along each chronosequence were similar enough to meet this assumption. Topography was similar among forest stands at each study area: upland, roughly planar features, with low to moderate slopes $< 8^\circ$. In addition, we avoided sampling soils in drainage pathways and in or near signs of natural tree fall or skidding areas disturbances. The principal parent material at all three study areas was glacial-till, composed of granitic and metamorphosed rocks. Despite the wide range in source rocks of the glacial-till, the mineralogy of the fine fraction (< 2 mm) of soil in the surface and deeper horizons were very similar. The composition remained similar among forest stands at each study areas: 50–70% quartz, 10–25% plagioclase, 8–30% orthoclase, 3–9% illite/mica (Supplemental Table 1). In addition, the physical particle size distribution of the soil was generally similar among forest stands at each study areas, all soils were sandy loams. Moreover, all soils were well to excessively-well drained (Petrenko and Friedland 2014).

Soil physical (e.g. bulk density) and chemical (e.g. pH, C) properties were generally similar among forest stands and even across study areas. Soil pH, C and %clay was determined to be similar among forest stands for each study area using GLMMs ($p > 0.05$; data shown in Supplemental Fig. 1). We also investigated the variation soil bulk density among study areas. We compared the forest floor and mineral soil bulk densities using GLMMs and determined bulk densities were similar for each soil depth interval among forest stands for each study areas (Supplemental Fig. 2). This shows that greater inclusion of mineral soil material in the forest floor did not occur, which can significantly impact estimates of soil nutrients in the forest floor (e.g. Brandtberg and Olsson 2012). In addition, differences in nutrient pools along the chronosequences were not artifacts of compaction. Given this evidence, we conclude that second assumption has been met. However, as noted by Grand et al. (2014), the variation in physical and chemical properties among forest stands increases the probability for a type II error of not detecting a significant effect. Grand et al. (2014) estimated that minimum differences of 35–150% would be required to observe an effect of clear-cutting in their forest soils and we hypothesize differences in our study would need to be of similar magnitude.

Base cations and micronutrient concentrations and pools along clear-cut chronosequences

The primary objective of this study was to identify and quantify long-term changes in forest floor and mineral soil base cations and micronutrients following clear-cutting. Our GLMM analyses show Ca, Mg, Mn, and Cu concentrations and pools were substantially affected by clear-cutting for greater than a century following the event. We initially hypothesized that forest floor and mineral soil nutrient pools would decrease due to disruption of aboveground cycling (see Covington 1981). Our results show that younger stands have significantly greater nutrient concentrations and pools than older stands (Figs. 1, 2) and thus we can reject the null hypothesis of no change in base cation and micronutrient pools with stand age. Our findings are in agreement with previous studies that observed increased export of base cations from forest soils immediately after clear-cutting (Fuller et al. 1988; Dahlgren and Driscoll 1994; McLaughlin and Philips 2006) and net nutrient losses many years after the event (Snyder and Harter 1985; Fuller et al. 1988; Hendrickson et al. 1989; Bélanger et al. 2003; Walmsley et al. 2009; Brandtberg and Olsson 2012; Grand et al. 2014; Dean et al. 2016). Our study also agrees with a limited number of others that observed decreases in micronutrients after tree harvesting (e.g. Fuller et al. 1988; Brandtberg and Olsson 2012). These observations were made on much shorter time scales, within 30 years following clear-cutting but our findings suggest base cation and micronutrient exports persisted beyond the first 50 years following clear-cutting.

Our results show that clear-cutting affected base cations and micronutrients in the forest floor and throughout the soil profile down to the 30–45-cm depth interval (Tables 4, 5). Our GLMMs revealed that study area played a significant role in the variation in forest floor and mineral soil Ca and K, and to lesser extent for Mg, Mn, and Cu (Tables 4, 5). AEC and BEF generally had higher Ca and K concentrations and pools than HF (Figs. 1, 2; Supplemental Table 2). However, the variation in base cation and micronutrient concentrations and pools among study areas did not appear to impact the detection of the effect of stand age. At forest stands with significantly different Ca among study areas, we still observed significantly different concentrations and pools with stand age. Our

use of three chronosequences at three different study areas to evaluate the effect clear-cutting was generally broader than previous studies and confirms that the effects of clear-cutting are beyond a single study area. However, we are limited in determining the ecosystem or soil properties responsible for susceptibility or resilience to effects from clear-cutting among our three study areas.

To ensure proper interpretation of the chronosequence data and changes in base cations and micronutrient pools through time, it was important to consider the two potential situations: (1) we assume the oldest stands (≥ 120 years in age) are representative of pools prior to clear-cutting and (2) in which we assume the youngest stands are still representative of pools at forest stands prior to clear-cutting. In situation (1), we presume that clear-cutting has caused a large pulse (i.e. rapid release) of Ca, Mg, Mn, and Cu to account for the much larger forest floor and mineral soil pools at study areas immediately after clear-cutting (≤ 5 years in age) compared to older stands (≥ 120 years in age). However, decomposition could not have occurred rapidly enough to cause an increase of 100–400% in the forest floor and mineral soil pools (e.g. Helmisaari et al. 2011). Thus, oldest stands (≥ 120 years in age) are unlikely to be representative of pools prior to clear-cutting. We reason that situation (2) was more likely, where the youngest stands (≤ 5 years) are assumed to be most representative of soil nutrient pools prior to clear-cutting and decreases in nutrient pools along the chronosequences are a net deficit. This framework agrees with previous studies that found mature forest stands have lower base cation concentrations and pools than younger stands (see Table 1).

Decreases in Ca, Mg, Mn, and Cu concentrations and pools following clear-cutting may have occurred due to uptake by vegetation and export from the soil profile via leaching. Studies from Hubbard Brook have observed increased soil solution and streamwater concentrations of base cations and micronutrients (e.g. Fuller et al. 1988; Dahlgren and Driscoll 1994). We used measurements for aboveground biomass in the northeastern United States from Keeton et al. (Keeton et al. 2011) and specifically at HF and BEF by Yao et al. (2011) (which ranged from 180 to 280 Mg ha⁻¹) and mean woody tissue nutrient concentrations from Richardson and Friedland (2016) from six major hardwood tree species to estimate

aboveground nutrient uptake of Ca, Mg, Mn, and Cu (Ca: $3700 \pm 520 \text{ mg kg}^{-1}$, Mg: $360 \pm 50 \text{ mg kg}^{-1}$, Mn: $280 \pm 70 \text{ mg kg}^{-1}$, Cu: $6.5 \pm 1.3 \text{ mg kg}^{-1}$). Aboveground uptake of Ca ($57\text{--}129 \text{ g m}^2$) represented approximately 32–67% of the observed change in forest floor and mineral soil nutrient pools over the 120 year chronosequence. This result suggests that changes in forest soil Ca pools may have been equally driven by leaching and uptake by vegetation. Aboveground uptake of Mg, Mn, and Cu only accounted for roughly 0.02–9% of the change in forest floor + mineral soil nutrient pools over the 120-year chronosequence. Our estimation implies leaching was the dominant loss pathway for Mg, Mn, and Cu (>95%). This agrees with many previous studies focusing on soil solution and streamwater at Hubbard Brook, Sweden, and elsewhere (Table 1) disruption of the plant-soil cycle likely accelerated the loss nutrients by removing the biological uplift effect by plants (see Jobbágy and Jackson 2001). In addition, there may have been potential effects from stimulation of microbial communities causing destabilization of SOM and organo-metal complexes and shifts in hydrology causing greater leaching of base cations and micronutrients from the clear-cut forest soils (e.g. Hornbeck et al. 1986; Rosén et al. 1996; Swank et al. 2001; Vanguelova et al. 2010; Wilhelm et al. 2013). The loss of base cations and micronutrients to surface waters has been generally confirmed by measuring outputs of base cations and micronutrients in stream waters, soil solution and changes in exchangeable pools by many previous studies (See Table 1).

Our results show that K and Zn did not exhibit a significant trend with forest stand age following clear-cutting (Tables 4, 5; Figs. 1, 2), despite previous observations by others of increased K concentrations in soil, soil solution, and stream water following clear-cutting (e.g. Snyder and Harter 1985; Grand and Lavkulich 2012). Potassium and Zn concentrations and pools may not have been impacted by clear-cutting because of their specific biogeochemical properties. Vanguelova et al. (2010) noted that monovalent base cations (Na, K) are affected differently than divalent base cations (Ca, Mg) due to different mobility, i.e. sorption, precipitation, and speciation. However, Vanguelova et al. (2010) suggested K should be more susceptible to leaching than Ca since K should be less strongly adsorbed than Ca due to its lower atomic charge density. Mineral supply of K

from feldspars and other silicates may out pace depletion since soils and bedrock in the northeastern US typically have 2–20 times higher K than Ca and Mg concentrations (e.g. Munroe et al. 2007). Similarly, soils and bedrock have 3–10 times higher concentrations of Zn than Cu concentrations (Schide and Munroe 2015). The loss of Ca, Mg, Mn and Cu has important ramifications for plants that are sensitive to Ca and Mg depletion such as *Acer saccharum* (Bal et al. 2015). The loss of Ca and Mg from soil could decrease soil fertility for regenerating plants. Moreover, the loss of Ca from soils could cause excess Mn uptake by trees, particularly saplings (Richardson 2017; Dobson et al. 2017). The loss of Cu from forest soils could have potential impacts on photosynthesis, respiration, hormone synthesis and metabolism in regenerating plants (Burkhead et al. 2009). It is essential to note that our results do not explicitly indicate that clear-cutting has decreased soil fertility, as strong-acid extractable nutrient pools may not reliably assess if concentrations are limiting for vegetation.

The uptake of base cations and micronutrients from the forest floor and mineral soil pools by regenerating vegetation depends on many site-specific and species-specific attributes (see Cronan and Grigal 1995; Hamburg et al. 2003; Fahey et al. 2006). Because we utilized strong-acid extractions to estimate pseudo-total concentrations and pools, we are unable to differentiate the concentrations and pools that are considered to be more readily accessible as exchangeable nutrients or more strongly adsorbed or precipitated. However, our results show that other potentially biologically important reservoirs of base cations and micronutrients, generally not assessed using exchangeable extraction techniques, can be affected by clear-cutting. In spite of evidence of clear-cutting and other forestry practices affecting base cations and micronutrients in soils, mass balance approaches have suggested base cations may be utilized at sustainable rates (e.g. Phillips and Watmough 2012). For example, Wilhelm et al. (2013) estimated that under whole tree harvest management of a northern hardwood forest in Wisconsin, base cations and micronutrients were unlikely to be depleted due to mineral weathering and atmospheric inputs. Moreover, calculations by Vadeboncoeur et al. (2014) suggest that there was a net deficit in nutrient exports by harvesting practices but enhanced mineral weathering by vegetation may

make up the difference needed to avoid nutrient depletion. As noted by Hamburg et al. (2003), Zetterberg et al. (2016), and Phillips and Watmough (2012), base cations, and potentially micronutrients, can be supplied to vegetation by uptake from mineral dissolution. Additional work is needed to investigate if the decreased nutrient pools are affecting the bioavailable pools for re-establishing vegetation and if subsequent clear-cuts result in cumulative losses to forest soil base cations and micronutrients.

Base cation and micronutrient relationships with soil C and N

In our second hypothesis, we expected decreases in the base cation and micronutrient pools to correspond to decreases in soil properties that promote metal sorption and retention, specifically C, N, and pH because of their roles in organo-metallic complexations (Brümmer 1986; Essington 2003; Grand and Lavkulich 2012). However, our results suggest that forest floor and mineral soil C pools exhibited a different pattern than the base cations and micronutrients (Fig. 3). Following clear-cutting, previous studies have observed both net increases in mineral soil C pools (e.g. Nave et al. 2010) and net decreases in mineral soil C pools (e.g. Diochon et al. 2009; Petrenko and Friedland 2014 who investigated the study areas used in this study). We can identify two primary reasons why we were not able to duplicate their findings for soil C pools: (1) the current study utilized only 12 of the 20 study areas from Petrenko and Friedland (2014); (2) compared only the top 0–45 cm of mineral soil instead of the 0–60 cm (Petrenko and Friedland 2014). Decreases in base cations and micronutrients may not have been linked to changes in SOM because their dominant sources are inorganic phases such as weatherable primary minerals, precipitated secondary minerals, colloids, clays, adsorbed phases, and other inorganic phases (Brümmer 1986; Essington 2003). Moreover, C and N in SOM have different biogeochemical pathways. Decreases in base cations and micronutrients may be dominated by longer decadal processes while C and N can be rapidly decomposed and re-accumulated with regrowth of the forest stand (Covington 1981; Vario et al. 2014).

As described by previous studies, we hypothesized decreases in base cations, and potentially

micronutrient, concentrations and pools would be linked to decreases in pH. Changes in soil pH have been hypothesized to accelerate the weathering of primary minerals. McLaughlin and Philips (2006) observed a decrease in soil pH after whole-tree harvesting, but the difference between the 17-year harvested and 77–85-year regenerating stand was only 0.27 pH units. A similar level of acidification was observed by Johnson et al. (1991) and Wall (2012). In our study, soil pH did not vary significantly for any soil depth interval among forest stands at each study area (Supplemental Fig. 1).

Conclusions

Our study has demonstrated that some forest floor and mineral soil base cations (Ca and Mg) and micronutrients (Mn and Cu) decreased with increasing stand age following clear-cutting, and we propose that the decrease in nutrient pools occurred from uptake by regenerating vegetation and leaching from the soil profile. We estimated that 32–67% of Ca but only 0.02–9% of Mg, Mn, and Cu may have undergone uptake by the regenerating vegetation. We hypothesized Mg, Mn, and Cu were primarily lost from the soil by leaching. Under the assumption that the youngest forest stands best represent conditions prior to clear-cutting, forest floor and mineral soil nutrient pools dramatically decreased following clear-cutting. Thus, our results suggest clear-cutting negatively impacted base cations and micronutrient pools for over a century following the clear-cutting event. This provides a greater context and may explain the contradictory results from previous studies on forests of varying ages in Table 1. Higher concentrations and increased exports of base cations and micronutrients occur 0–15 years after clear-cutting but mature forest stands >40 years in age have lower base cation and nutrient pools due to decreased forest floor and mineral soil nutrient pools. Implications for effects on site fertility and uptake of nutrients by trees remain uncertain, because strong-acid extractable pools cannot assess the fraction of base cations and micronutrients that will be used by regenerating vegetation.

We hypothesized that changes to nutrients would correspond to changes in soil properties, specifically C, N, or pH. Although we did not observe any trends in C, N, or pH corresponding with changes in

nutrient pools in this study, more in depth C studies have identified decreasing trends using an expanded network of study areas including those from this study. We suspect that using only three study areas with four forest stands and the fact that SOM cycles differently than inorganic nutrients are responsible for the discrepancy. More work is needed to determine if nutrient pools will return to the original nutrient pool size or if fertilization of base cations are required. In addition, field plot studies are required determine if decreased base cations and micronutrients in the forest floor and mineral soil will impact plant uptake. In addition, continued monitoring of existing projects (e.g. Hubbard Brook LTER, see Dahlgren and Driscoll 1994) are required to validate proxy methods, such as the chronosequence approach.

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