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Long-term monitoring of Vermont's forest soils: early trends and efforts to address innate variability

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Abstract Long-term monitoring of forest soils is necessary to understand the effects of continued environmental change, including climate change, atmospheric deposition of metals, and, in many regions, recovery from acidic precipitation. A monitoring program was initiated in 2002 at five protected forest sites, primarily Spodosol soils, in Vermont, northeastern USA. Every 5 years, ten soil pits were sampled from random subplots in a 50 × 50-m plot at each site. Samples were taken by genetic horizon and, to reduce variability and improve comparability, from four specific layers: the combined Oi/Oe layer, the combined Oa/A layer, the top 10 cm of the B horizon, and 60–70 cm below the soil surface (usually the C horizon). The samples were archived and a subset analyzed for carbon, nitrogen, and exchangeable cations. After four sampling campaigns, the average coefficients of variation (CVs) at each site had a broad range, 10.7% for carbon in the Oa/A horizon to 84.3% for exchangeable Ca^{2+} in the B horizon. An investigation of variability within the upper 10 cm of the B horizon across a 90-cm soil pit face showed similar CVs to the entire site, emphasizing the need for consistent and careful sampling. After 15 years, temporal trends were significant in the Oa/A and B horizons at two of the five sites, with one site showing an increase in carbon concentration in both layers along with increases in both exchangeable Ca^{2+} and Al^{3+} in the B horizon, perhaps linked to recovery

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from acidification. The monitoring program plans to continue at 5-year intervals for the next century.

Keywords Forest soil · Soil monitoring · Acid deposition · Climate change · Soil carbon · Calcium · Aluminum

Introduction

Long-term monitoring of forest soils is critical for detecting the effects of environmental change on this valuable resource (Lawrence et al., 2013). Potential drivers include climate change, atmospheric deposition of contaminants, changes in forest management, and recovery from acidic precipitation. This need became evident during the latter part of the last century when the effects of acidic deposition were difficult to statistically document because of a lack of baseline data. Only a few ongoing monitoring programs, e.g., the Calhoun Long-Term Soil Experiment (Richter et al., 1994), and resampling studies (e.g., Bailey et al., 2005) were able to unequivocally demonstrate change attributable to past deposition of sulfate and nitrate. After dramatic reductions in both these pollutants, although more so with sulfate, a number of monitoring programs and resampling studies were begun in Europe and North America (e.g., Lawrence et al., 2015; Morvan et al., 2008). Long-term monitoring is also essential for determining the effects of ongoing climate change, especially through tracking the rates of carbon sequestration or loss. It is also needed for tracking the fate of air-borne metal deposition, such as lead and mercury. Long-term monitoring programs that maintain a sample archive will also enable the analysis and temporal tracing of the effects of pollutants not currently recognized as threats.

A diverse range of challenges are faced by soil monitoring programs (Desaules, 2012; Lawrence et al., 2013), including the difficulty of maintaining funding and the necessity for consistency in laboratory methods with changes in both instrumentation and personnel (Ross et al., 2015). Another challenge, perhaps more prominent with forest soils than with other environmental monitoring, is the innate spatial variability in both physical and especially chemical soil properties (Conant et al., 2003; Johnson et al., 1990; Kirwan et al., 2005; Li et al., 2010; Mobley et al., 2019). In early work on this topic, Blyth and MacLeod (1978) found that an average of 29 samples was needed from an 0.01-ha plot in order to have a confidence interval of ± 10% around the mean for extractable nutrient concentrations in soils of Sitka spruce (*Picea sitchensis*) stands in Scotland. Within-plot variation was sometimes higher than the variation among plots within a forest stand. In even earlier work in Sweden, Troedsson and Tamm (1969) showed high variability in soil properties among 1-m^2 subplots within 10 × 10-m plots on two different soil types with either Norway spruce (*Picea abies*) or Scots pine (*Pinus sylvestris*) stands. Their analyses showed that 10–15 subsamples were needed to provide a coefficient of variation below 10% for total nitrogen and extractable nutrients. They also demonstrated that fewer samples were needed if the results were expressed on a weight basis rather than an areal basis because of the high spatial variability in the thickness and bulk density of different soil horizons. Ike and Clutter (1968) showed similar high variability in chemical properties of forest soil in the Blue Ridge Mountains of Georgia. High vertical spatial variation in forest soil profiles is also well established (Lawrence et al., 2013). Numerous thin, but physically and chemically distinct, horizons can be found near the surface in soils that have never been tilled. This may be most dramatic in Spodosols, where a dark, high-carbon Oa horizon can be separated from a series of thin Fe- and Al-rich spodic B horizons by a thin ash-colored chemically depleted E horizon. High horizontal variability in the number and thickness of these various horizons makes it difficult to design a sampling scheme that allows valid comparisons to determine possible changes in the soil over time. Efforts to address spatial variability in soil monitoring programs include attempts to choose plots that are as uniform as possible, which may not result in a “representative” soil (Desaules, 2012), and the inclusion of sufficient replication to increase statistical power (Lawrence et al., 2016).

We initiated a long-term forest soil monitoring program in Vermont with a goal of enabling the detection of future change by establishing baseline chemical properties and maintaining a sample archive for future use. The sampling began in 2002 and is scheduled to continue every five years for the next century. We deliberately chose to monitor changes in the concentrations of elements (carbon, nitrogen, exchangeable cations) in different soil horizons or layers instead of attempting to measure entire pools of these elements. This is based on both experience and some evidence (e.g., Troedsson & Tamm, 1969) that variation will be lower in this type of analysis, making detecting change more likely. Our initial approach and deliberate changes to our sampling protocols designed to minimize variability are described in the following sections. We also present significant trends in element concentrations found at some of the sites after four sampling campaigns and relate those to findings from other repeated sampling studies.

Materials and methods

Initial site selection

Site location targeted two protected areas: Mount Mansfield State Forest in northcentral Vermont and the Lye Brook Wilderness Area, part of the Green Mountain National Forest in southwestern Vermont (Fig. 1). These areas have had active monitoring and research programs under the auspices of the Vermont Monitoring Cooperative, now the Forest Ecosystem Monitoring Cooperative (FEMC). Much of the

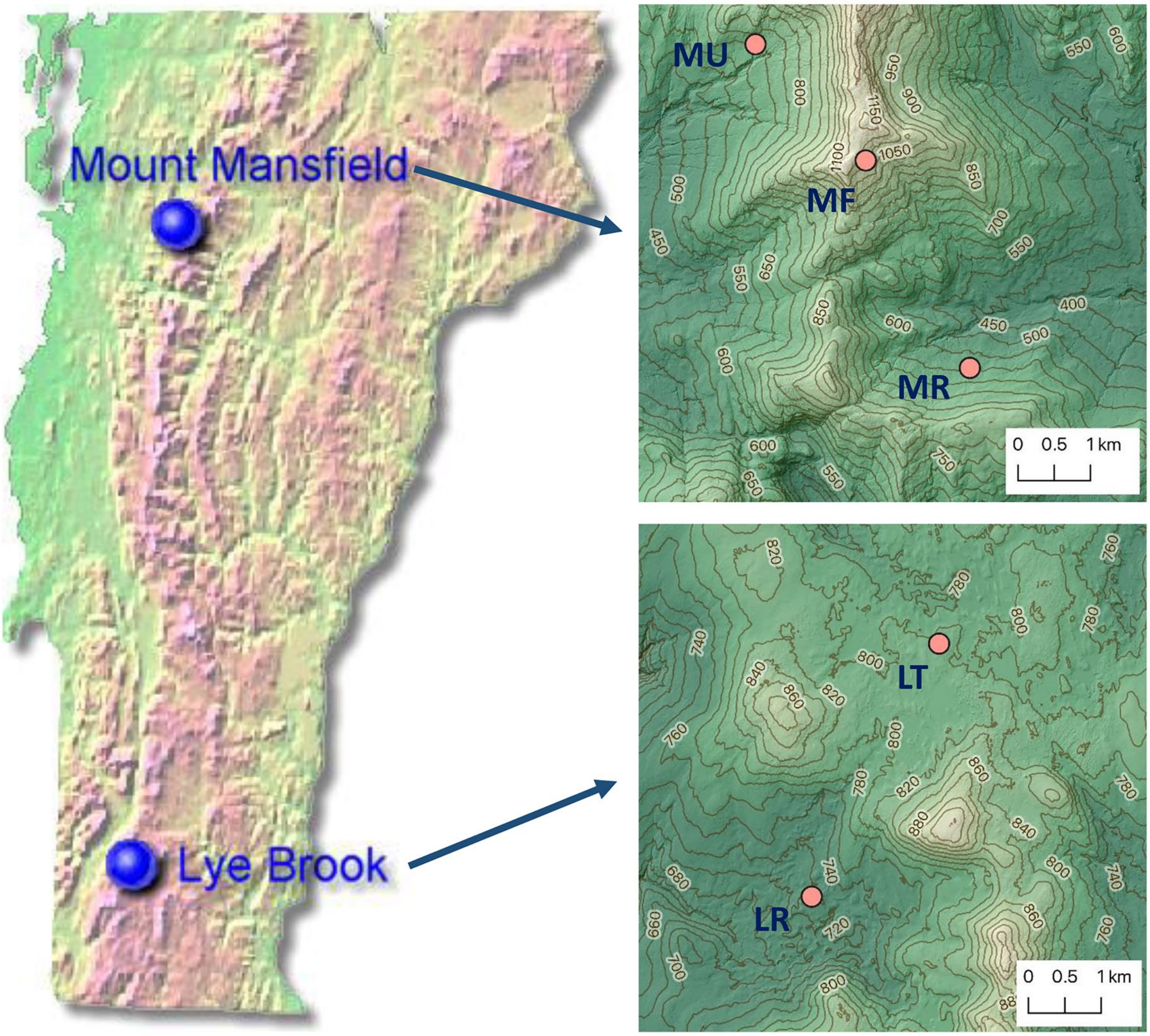


Fig. 1 Location of monitoring sites in Vermont. See Table 1 for explanation of site abbreviations. Contour lines in small maps have elevation in meters. Inset provides location of Vermont (red) in the northeastern USA

ongoing work focuses on forest health, forest regeneration, and indicators of climate change (https://www.uvm.edu/femc/cooperative). Our sites were selected following extensive field reconnaissance that closely examined a number of potential sites initially identified through soil mapping. At each candidate site, physiographic position, slope and aspect, species composition, and representative measurements of tree species were noted. Test holes were hand-dug, chosen to represent the variety of conditions present within a 50 × 50-m area. Five sites were chosen to represent a range of forest cover types, elevations, and soil conditions (Fig. 1 and Table 1), and were not intended to be replicates of each other. Each 50 × 50-m plot was selected with the goal of internal soil uniformity to minimize potential spatial variability in soil characteristics. As part of the Green Mountain Biophysical Region, the soils and vegetation at these sites are representative of large forested areas in Vermont (Thompson & Sorensen, 2005).

For initial characterization after plot establishment, approximately 5 m outside of one corner of each plot, in 2000, a large pit was excavated and soils were described and sampled using United States Department of Agriculture (USDA) Natural Resource Conservation Service (NRCS) procedures and personnel. Soil horizons were described to a depth of > 1.5 m, except for the Mansfield Forehead site where bedrock was encountered at 47 cm, and classified using USDA Taxonomy, 8th edition (Table 2; Soil Survey Staff, 1998). Samples of each horizon were chemically characterized at the NRCS Kellogg Soil Survey Laboratory and these reports, along with complete profile descriptions, can be obtained using the pedon ID from Table 2 as "User pedon ID" at this NRCS website: https://ncsslabdatamart.sc.egov.usda.gov/querypage.aspx. To provide supplementary climate data, two NRCS Soil Climate Analysis Network (SCAN) sites were established—one near the Lye Road site and one near Mansfield Underhill. These continually monitor soil temperature and moisture at five depths, along with standard meteorological measurements (https://www.nrcs.usda.gov/wps/portal/wcc/home/snowClimateMonitoring/soilClimateConditions/).

Sampling plan

The 50 × 50-m plots were oriented approximately north–south, with some adjustment for local topography, and subdivided into 100 5 × 5 m subplots (Fig. 2). Prior to initiating the monitoring in 2002, 10 subplots were randomly selected for each future

Table 1 Site elevation and stand description. Tree data are from the 2017 measurements of each entire site

Site	Abbrev	Elevation (m)	Basal area (m^2/ha)	Median dbh[a] for stems > 5 cm	Stems/ha 2.5–5.0 cm (n)	Major tree species % of stems > 5 cm dbh % of basal area
Lye Kelly Stand Road	LR	739	30.4	12.3	448	*Acer saccharum 26%, 55%* *Fagus grandifolia 65%, 32%* *Betula alleghaniensis 3%, 7%* *Acer rubrum 3%, 4%*
Lye Branch Pond Trail	LT	808	36.4	17	56	*Acer rubrum 28%, 55%* *Betulla cordifolia 16%, 22%* *Picea rubens 26%, 8%* *Abies balsamea 18%, 12%*
Mansfield Ranch Brook	MR	590	35.5	20.2	328	*Acer saccharum 63%, 77%* *Fagus grandifolia 32%, 13%* *Fraxinus Americana 1%, 6%*
Mansfield Forehead	MF	1140	33.6	8.1	2416	*Abies balsamea 97%, 96%* *Betula cordifolia 2%, 35*
Mansfield Underhill State Park	MU	695	36.1	13.5	236	*Betula alleghaniensis 45%, 78%* *Fagus grandifolia 13%, 7%* *Abies balsamea 13%, 5%* *Picea rubens 15%, 3%* *Betula cordifolia 5%, 5%*

[a] Diameter at breast height (1.37 m)

Table 2 Classification and brief description of soil pits from just outside each of the five plots

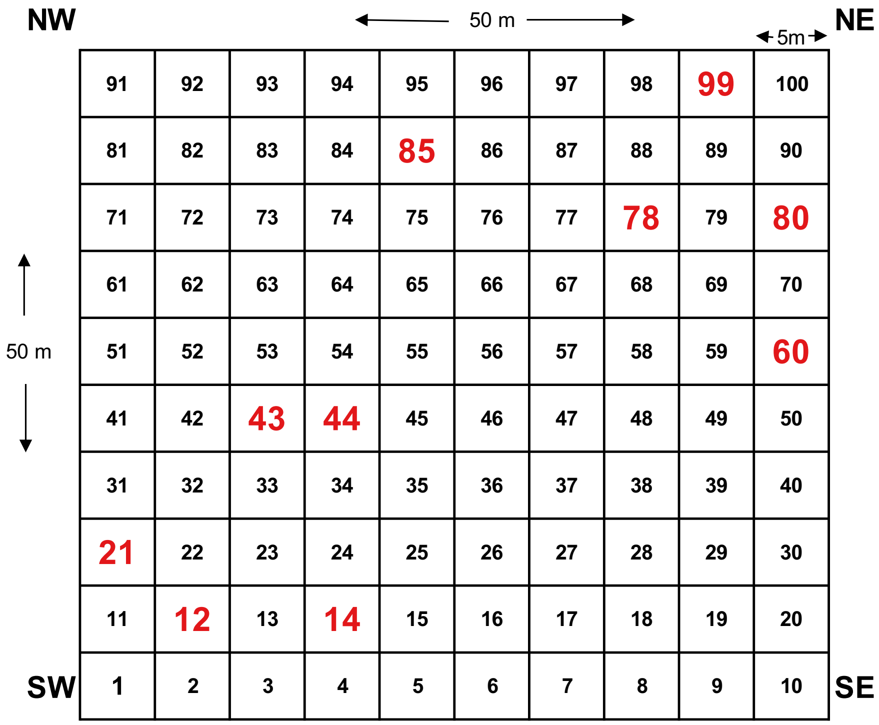
Site	Soil series[a]	Taxonomy	Depth of O/A horizons (cm)	Depth of E horizons (cm)	Depth of B horizons (cm)	Depth of C horizons (cm)	Texture of B horizons	NRCS Pedon ID
Lye Road	Mundal	Coarse-loamy, isotic, frigid Oxyaquic Haplorthod	Oa 5–9	9–18	18–74	74–177	Fine sandy loam	00VT003002
Lye Trail	Mundal	Coarse-loamy, isotic frigid Oxyaquic Haplorthod	Oe 3–9	9–24	24–58	58–152	Fine sandy loam	00VT003001
Mansfield Ranch	Peru Taxadjunct	Coarse-loamy, isotic, frigid Aquic Dystrudent	A 5–10	–	10–76	76–174	Very fine sandy loam	00VT015002
Mansfield Forehead	Londonberry	Loamy, mixed, active, acid Lithic Cryorthent	Oe 0–16	16–47	bedrock at 47	–	E2: fine sandy loam	00VT015001
Mansfield Underhill	Peru	Coarse-loamy, isotic, frigid Aquic Haplorthod	A 3–8	8–13	13–51	51–165	Fine sandy loam	00VT007001

[a] Soil series and taxonomy based on initial field and lab data. Subsequent Natural Resource Conversation Service (NRCS) recorrelation has changed the Lye Trail and Mansfield Underhill sites to Typic Endoaquods

sampling time. This provided 10 possible sampling dates and the initial experimental design called for increasingly longer intervals between sampling, with an overall 200-year timeframe. It was subsequently decided that continuing the initial five-year sampling interval would provide a more robust method to examine temporal trends (see Desaules, 2012). Therefore, prior to the fourth sampling date in 2017, the remaining 70 subplots were further subdivided into four 2.5 × 2.5-m quadrants and one quadrant was randomly selected for sampling with the others randomly ranked as alternates in case a quadrant could not be sampled due to large boulders or trees. After all 100 subplots have had a quadrant sampled, ten of the remaining subplots with sampleable quadrants will be randomly assigned to the next sampling date. In 2017, there were a total of eight unsampleable quadrants found, occurring in three of the five plots. If 30% of the quadrants are not useable, as was the case at two sites, then this design allows for 18 more sampling dates. With the continued five-year interval, sampling would proceed through the year 2207; longer would be possible at the sites where fewer quadrants are unsampleable.

To establish the corners of the subplots for the first three sampling times (2002, 2007, and 2012), the south and north sides of each site were flagged every 5 m and baling twine was stretched perpendicular to the sides as a guide. The four corners of each subplot to be sampled were then flagged. In order to more precisely delineate the quadrants established in 2017, professional land surveyors used a total station to flag the boundaries of each subplot to be sampled and its four quadrants. Positions for all the vertices were calculated so that plots could be laid out in subsequent samplings to within 2.5 cm. All flagging and twine were removed from the site after sampling was completed.

Soil pits, ~ 0.7–0.9 m per side, were dug at the center point of each subplot or quadrant, with some adjustment for trees or stones. All excavated material from each soil pit was placed on tarps to avoid contamination of surrounding surface soil, with the organic layer stockpiled separately from the excavated mineral soil to facilitate replacement following sampling. Pits were dug to 75 cm where possible. Bedrock was frequently encountered at more shallow depths at the Mansfield Forehead site but not elsewhere. One face of the pit, along with the surface ~ 0.5 m immediately beyond, was kept undisturbed and used for profile description and sampling. Profile description followed NRCS guidelines (Schoeneberger et al., 1998,



91	92	93	94	95	96	97	98	**99**	100
81	82	83	84	**85**	86	87	88	89	90
71	72	73	74	75	76	77	**78**	79	**80**
61	62	63	64	65	66	67	68	69	70
51	52	53	54	55	56	57	58	59	**60**
41	42	**43**	**44**	45	46	47	48	49	50
31	32	33	34	35	36	37	38	39	40
21	22	23	24	25	26	27	28	29	30
11	**12**	13	**14**	15	16	17	18	19	20
1	2	3	4	5	6	7	8	9	10

Fig. 2 Site (50 × 50 m) and subplot (5 × 5 m) plan for all locations. This example shows the subplots sampled in 2002 (in bold red) at the Lye Road site

2002, 2012) with additional guidelines instituted to provide greater consistency among soil describers (methods manual: https://www.doi.org/10.18125/j2oftg). Features described included horizon designation, depth, color, texture, coarse fragments, structure, consistence, redoximorphic features, and roots. After the first sampling year, a decision was made to no longer describe transitional horizons, such as BC, that could be difficult to interpret in the future but instead, to assign each horizon a single designation. While USDA soil taxonomy has a rule that a cambic horizon cannot occur below a spodic horizon, a Bw horizon is not consistently synonymous with cambic. We chose the field designation of Bw based on soil color in order to maintain consistency among different describers and avoid ambiguity. Photographs of a typical profile from each site are provided in Supplemental Fig. S1.

In the first sampling year, 2002, soil samples were collected only by genetic horizon and no Oi, Oe, or C horizons were sampled. This resulted in 204 total samples that included 49 Oa, 22 A, 30 E, 91 B, and 12 BC horizons. In subsequent sampling years, all genetic horizons thicker than ~ 1 cm, including Oi, Oe, and C, were sampled resulting in totals for the five sites of 340, 371, and 357 individual horizon samples for 2007, 2012, and 2017 respectively. Additionally, four larger "bulk" samples were taken from each pit of the following horizon combinations or depths (where present): (1) combined Oi/Oe, (2) combined Oa/A, (3) top 10 cm of the uppermost B, and (4) 60–70 cm below the soil surface (defined as the top of Oi). These larger samples were intended to provide both a more representative sample from each pit and a more comparable soil "unit" to compare across each plot and across sampling years. Consistent with other recent studies (Bailey et al., 2021; Ross et al., 2021), the Oa and A horizons were combined for two reasons: (i) samples from different plots at our sites spanned the USDA taxonomy prescribed cutoff of 200 g/kg carbon between A and Oa horizons, and (ii) distinguishing the boundary in the field between an Oa and a high-carbon A horizon has proven difficult. Because the Mansfield Forehead site had few B and C horizons, the E horizon was sampled where the B horizon was absent. Overall there were 192, 197, and 194 bulk samples taken in 2007, 2012, and 2017 respectively. Organic horizons were sampled from the undisturbed surface, working downwards from the top, i.e., Oi, Oe followed by Oa. Mineral soil was sampled from across the pit face beginning with the lowest depths and horizons.

Sampling to examine variability within the B horizon

In 2017, additional samples were taken from the top 10 cm of the B horizons at two of the sites, Lye Road and Mansfield Ranch, to investigate spatial variability in chemical properties across the pit face within the zone included in one of the bulk samples. Nine samples were taken from the ~0.9-m-wide pit face, with three each near the left, center, and right of the face, evenly spaced vertically from the top, middle, and bottom thirds of the top 10 cm of the B horizons (Fig. 3). One large, composite sample was also collected as part of the routine sample, resulting in 100 B horizon samples from each of the two sites. Chemical analysis of these samples is described below.

Sample processing and analysis

All samples were placed in polyethylene bags and kept out of direct sunlight at ambient temperatures until returning to the laboratory, usually the same day. Subsequently, samples were air-dried in the dark on clean black polyethylene sheets, put through a 2-mm polyethylene sieve, and separated into four or more 125–500-mL polyethylene containers using a stainless-steel riffle sample splitter to ensure homogeneity. These splits are saved for archival storage and will be available for future analysis.

Chemical analyses have been conducted at three laboratories: UVM Agricultural and Environmental Testing Laboratory, USDA-FS Northern Research Station Laboratory in Durham, NH, and the USDA-NRCS KSSL. The UVM and FS labs determined exchangeable cations in the B horizons using a mechanical vacuum extractor (MVE) and 60 mL of 1 M NH_4Cl to 2.5 g of soil (Blume et al., 1990). This procedure performs a slow (~12 h), continual leaching and extracts more Al than shorter batch extractions but usually produces similar results in exchangeable Ca, Mg, and K (Ross et al., 2015). A reference Bs horizon sample, taken from near the Mansfield Underhill site and analyzed by 13 soil testing laboratories (Ross et al., 2015), was used for quality control. The KSSL determined carbon, nitrogen, and acid ammonium oxalate extractable metals on the Oa, A, and B horizon samples from 2002 and on the four bulk samples from subsequent years. The pH 3 0.2 M NH_4-oxalate procedure (KSSL method 4G2a, Soil Survey Staff, 2014) is intended to remove both organically complexed and noncrystalline Fe and Al and is used to classify spodic B horizons. An elemental analyzer (dry combustion) was used for carbon and nitrogen analysis (KSSL method 4H2a, Soil Survey Staff, 2014). Additional analyses (including Na-pyrophosphate extraction, total elemental analysis, and particle size) were performed on selected layers and are available, along with all the above analyses and relevant metadata, at the FEMC data archive (https://www.doi.org/10.18125/58h5df). For the B horizon variability study, cations were extracted by MVE at the FS lab with the same procedure as described above except using pH 4.8 NH_4-acetate (1.25 M with respect to the acetate) as the extractant.

Vegetation metrics

At each soil sampling time, trees on the site with a diameter at breast height (dbh, 1.37 m) ≥ 5 cm were

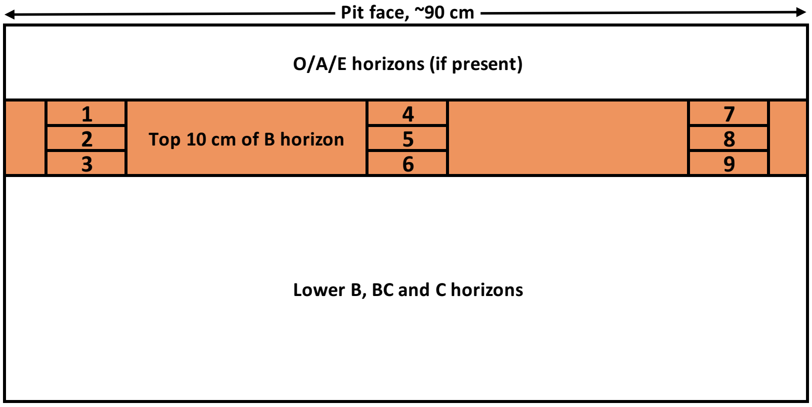


Fig. 3 Schematic of the sampling scheme for examining variability in the top 10 cm of the B horizon across the soil pit face. In 2012 at the Lye Road and Mansfield Ranch sites, nine subsamples were taken from the locations shown, along with one composite sample from the entire 10-cm-deep section of the pit face

tallied by species, regeneration measured, and a list was made of all herbaceous species present on the site. In the first three sampling times, some sites only had a quarter of their area measured for tree species. In 2017, all sites had the entire area tallied down to a dbh of 2.5 cm to better assess regeneration. These 2017 data are summarized in Table 1 and all vegetation data are available on the Forest Ecosystem Monitoring Website: https://www.doi.org/10.18125/58h5df.

Calculations and statistical analysis

Because the sampling procedure was different for the first year of this study, conversion of the results was necessary to make them comparable with the subsequent three samplings. The average thickness of the uppermost B horizon was 11.1 cm (median 9.0 cm). If the thickness was ≥ 10 cm, then the results of the chemical tests were not changed. If the thickness was < 10 cm, as in 21 of the 42 plots that had multiple B horizons in 2002, the chemical result was prorated to a depth of 10 cm by using data from the B horizon(s) immediately below; e.g., if there was a 7-cm-thick Bhs1 with an 8-cm-thick Bhs2 below it, the adjusted concentration was $0.7 \times$ the Bhs1 concentration $+ 0.3 \times$ the Bhs2 concentration. For the Oa/A horizon (combined in latter sampling years), 2002 multiple Oa ($n = 12$), A ($n = 3$), or Oa-over-A ($n = 6$) horizons were simply averaged by their prorated depths. This could arguably lead to some artifact introduced by differences in bulk density but was likely only a factor in the six instances of averaging an Oa and an A horizon.

Statistical analyses were performed either using JMP Pro 14.2 (SAS Institute, 2018) or SAS 9.4 software (SAS Institute, 2012). Before analysis, normal distribution was checked graphically and with the Shapiro–Wilk *W* test. If needed, data were transformed by various approaches to achieve a normal distribution, including deriving the log, square root, square, or using a Box Cox formula. The minimum detectable change (MDC) based on standard deviations at individual sites and years was calculated using a power value of 0.95 in the Sample Size and Power function in Design Diagnostics of JMP 14.2. The MDC based on the full set of temporal data, i.e., 10 replicates in each of four sampling years, was determined via a repeated-measures model that accounts for any temporal autocorrelation, which is often found in monitoring data. This “full data” MDC was calculated using the formulas and code provided in Mobley et al. (2019), with autocorrelation measured by the AR(1) lag and residual error from a SAS proc mixed with an autoregressive covariance structure. Significant temporal changes were determined with SAS Proc Mixed using a growth curve random coefficients model (example code provided in Supplementary Information). Because of the clear differences among sites, and the fact that Mansfield Forehead only had 18 (instead of the usual 40) B horizon samples collected over the four sampling periods, the analyses were done separately by site. To examine possible vegetation changes, tree data with dbh ≥ 5 cm were analyzed with JMP 14.0.0 (SAS Institute, 2018). Regression analysis was used to test for differences in species composition and tree mortality by plot over time. Changes in basal area per species were similarly tested by plot over time.

Results and discussion

The soil profiles were typical of those found in upland areas of northern New England developed on glacial drift (e.g., Fraser et al., 2019; Ross et al., 2021). The texture of the mineral soil horizons at all the sites was almost always a fine sandy loam. The Spodosols found at Lye Trail and Mansfield Underhill consistently had Oa, rather than A horizons, above E horizons (Fig. 4). The Lye Road soils, also Spodosols, usually had A horizons, sometimes below a thin Oa, with E horizons found in about half of the pits sampled. All three sites had well-developed spodic B horizons (Bhs and Bs), sometimes underlain by transitional BC horizons (considered here Bw horizons; Fig. 4). The soils at Mansfield Ranch exhibited weak or no signs of podzolization with typically an A horizon, no E horizon, and one or more Bw horizons. The C horizons at all four of these sites were usually dense Cd horizons, assumed to be inherited from the glacial drift parent material. The soils at the high-elevation Mansfield Forehead site were typically shallow to bedrock and only had B horizons in 18 of the 40 pits sampled. All profiles had Oa horizons and almost always an E horizon. In a quirk of USDA soil taxonomy, the relative thickness of the organic layer and the mineral soil layers, along with the absence or presence of E or B horizons,

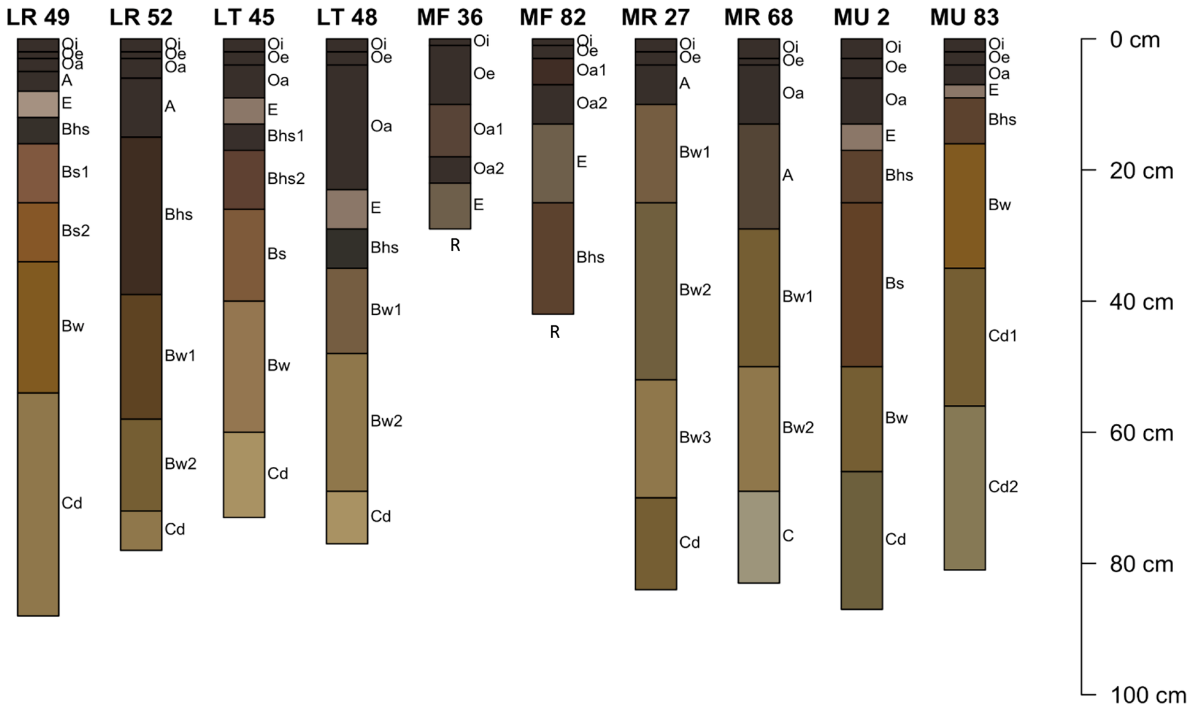


Fig. 4 Two representative soil profiles from each site for the 2012 sampling. Bedrock (R) was reached only at the Mansfield Forehead (MF) site

resulted in four different USDA soil orders found at this one site: Entisols, Inceptisols, Histosols and Spodosols (Villars et al., 2015). However, podsolization was the dominant soil-forming process and the physical and chemical properties of the Oa horizons did not differ among the different soil orders. At all sites, there was considerable variability in the thickness and number of the various genetic soil horizons (Fig. 4), which presented challenges if attempting to compare their chemistry among the different sampling years.

The carbon concentration in the bulk Oa/A horizon sample ranged from ~ 100 g/kg at Mansfield Ranch, dominated by A horizons, to > 400 g/kg at Lye Trail (Fig. 5, Table S1) where only Oa horizons were usually found. These two sites also had the lowest and highest average C/N ratios, 14.9 for Mansfield Ranch and 23.3 for Lye Trail (Fig. 5, Table S1). In the upper 10 cm of the B horizons, carbon concentration was also low at Mansfield Ranch (overall mean of 27.3 g/kg) and ranged from ~ 50–60 g/kg at the other three sites with deep soils (Fig. 5, Table S2). The limited number of B horizons sampled at Mansfield Forehead had numerically the lowest carbon of all site B horizons (mean of 22.7 g/kg). With the exception of Mansfield Ranch, exchangeable Al^{+3} concentration was relatively high and exchangeable Ca^{2+} concentration was low (Fig. 5), typical of upland forest soils in this region (e.g., Fraser et al., 2019; Ross et al., 2021). The overall means for additional exchangeable cations and acid-NH_4-oxalate Al, Fe, and Mn are given in Supplementary Table S2.

Variability at the site level

The relative variability for the different chemical tests was assessed by their coefficients of variation (CVs) for each site, averaged from each year's CV (Table 3 for the Oa/A horizons and Table 4 for the top 10 cm of the B horizons). The average CVs for each site, across the four sampling years, ranged widely from a low of 10.7% for carbon in the Oa/A horizons at Lye Trail (Table 3) to a high of 84.3% for exchangeable Ca^{2+} in the B horizons at Mansfield Ranch (Table 4).

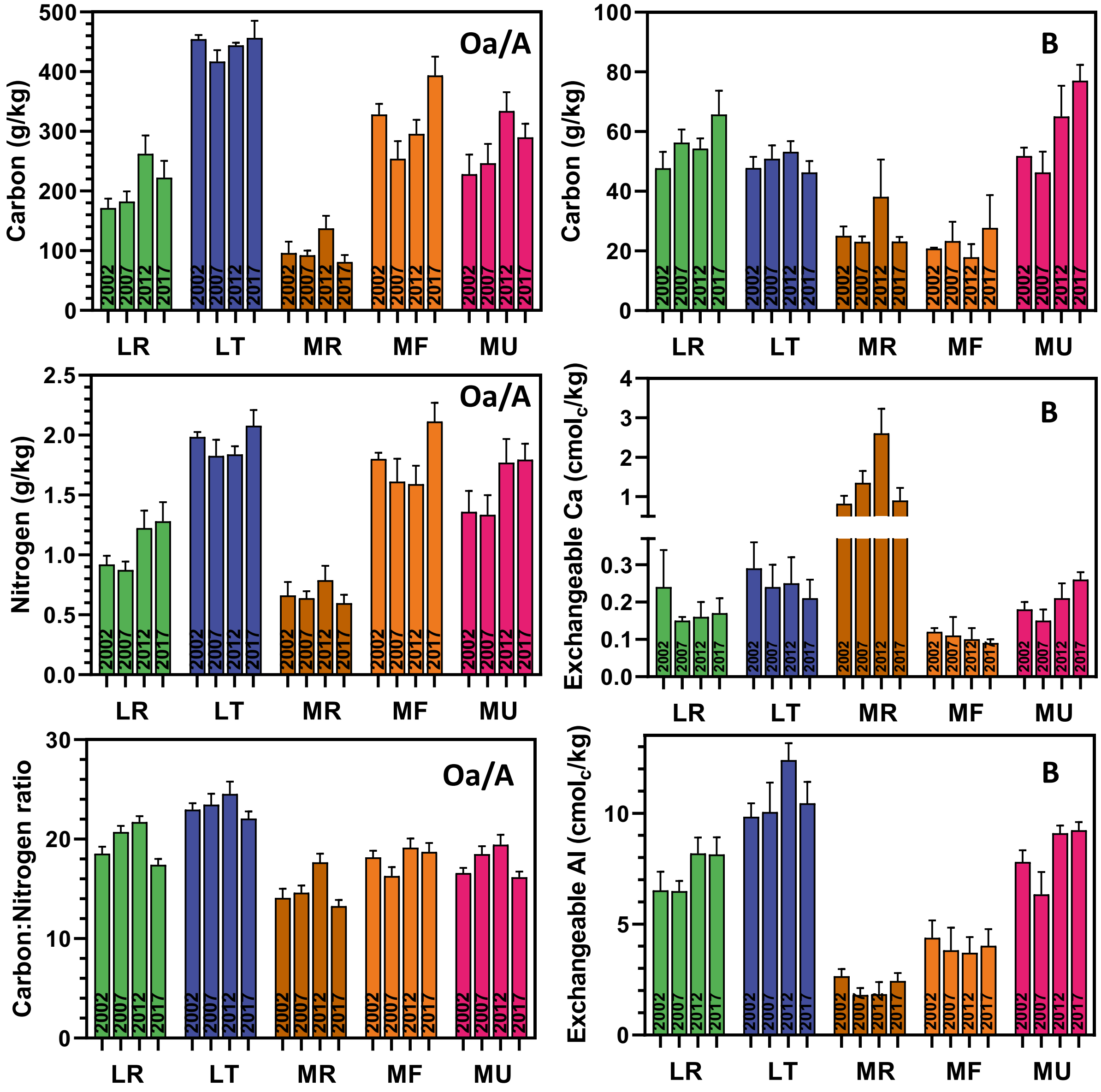


Fig. 5 Means of selected chemical tests for the combined Oa/A horizons (left column) and the top 10 cm of the B horizons (right column) for soil pit-face samples collected from five sites sampled in 2002, 2007, 2012, 2017. Error bars represent the standard error of the mean

For all sites averaged, exchangeable Ca^{2+} in the B horizons (not run on the Oa/A samples) had the highest CV and the C/N ratio, along with carbon, had the lowest CVs for both layers (Tables 3 and 4). When using a power analysis for Oa/A carbon in an individual site and year, the variability at Lye Trail in 2012 (CV 3.4%) resulted in a minimum detectable change (MDC) of 19 g/kg or 4.3% of the mean whereas the higher variability in Oa/A carbon at Mansfield Underhill in 2012 (CV 30.2%) could only show a MDC of 130 g/kg or 39% of the mean. Assuming a sampling interval of five years, as in our study, this would be an annual MDC of 4 g/kg for Lye Trail and 26 g/kg for Mansfield Underhill. For exchangeable

Table 3 Oa/A bulk horizon range and mean of sampling year coefficients of variation (%) for selected chemical tests at each of the five study sites

	LR		LT		MR		MF		MU		All sites
	CV Range	CV Mean	CV Range	CV Mean	CV Range	CV Mean	CV Range	CV Mean	CV Range	CV Mean	CV Mean
	%	%	%	%	%	%	%	%	%	%	%
Carbon	29.5–40.3	34.3	4.6–19.9	10.7	27.6–63.2	46.1	17.2–36.7	26.2	25.4–45.5	35.7	30.6
Nitrogen	25.2–40.6	32.4	5.7–23.6	23.9	28.4–54.5	42.3	9.2–37.8	25.2	23.6–40.5	34.6	31.7
C/N ratio	9.4–12.1	10.3	8.1–16.0	12.2	14.7–20.9	16.8	11.8–17.7	15.0	10.2–16.2	12.7	13.4
Overall	9.4–40.6	25.7	4.6–23.6	15.6	14.7–63.2	35.1	9.2–37.8	22.1	10.2–45.5	27.7	25.2

Ca^{2+} in the B horizon, Mansfield Underhill in 2017 had the lowest CV (25.3%), which produces an MDC of 0.084 $cmol_c$/kg (0.017 $cmol_c$/kg per year) or 32% of the mean. Four of the sites were quite low in exchangeable Ca^{2+} (Fig. 5) and a change over time of this magnitude is not out of the question. These individual site/year MDC examples are less robust than the MDCs calculated from the full temporal data set of repeated measures over time, discussed below, but simply serve to illustrate the potential effect of the range in variability on the ability to monitor change.

Further illustration of within-site variability is provided with two examples: low variability in Oa/A carbon at Lye Trail (Fig. 6) and high variability in B horizon exchangeable Ca^{2+} at Mansfield Ranch (Fig. 7). The Lye Trail site had the most clearly developed podzolized profiles, usually with thick E horizons overlain by thick high-carbon Oa horizons (e.g., LT48 profile in Fig. 4). This was consistent across the site and may help to explain the low variability, i.e., most of the Oa horizons could be asymptotically approaching their maximum carbon concentration. Temporal variation was low, although the five subplots with carbon > 1 standard deviation above the overall mean were all from the most recent sampling year of 2017. Two of the four subplots with carbon > 1 standard deviation below the mean were also from 2017 (Fig. 6), resulting in more variability in this year (CV 19.9%) than any other and limiting the ability to determine any temporal trend. That said, the overall relatively low variation in carbon concentration in this layer at Lye Trail should enhance our ability to detect future change. Conversely, Mansfield Ranch showed the highest variability for most of the chemical tests (Tables 3 and 4), with especially high variability in exchangeable Ca^{2+} (Fig. 7). There was a clear spatial pattern, with higher Ca^{2+} concentrations in the eastern subplots. Simply dividing the site in half, east and west, the average eastern concentration was 2.63 $cmol_c$/kg while the western half had a much lower mean of 0.52 $cmol_c$/kg. The B horizon exchangeable Al^{3+} was 50% lower in the east vs. the west and acid NH_4-oxalate Mn was overall quite high (Table S2) but close to double eastern vs. western half. Combined, these are clues that shallow hydrology has affected soil development, with inputs of relatively higher-pH and Ca-rich waters into the eastern portion of the plots that also decreased exchangeable Al^{3+}. The high Mn concentration is further evidence of a groundwater source of reduced Mn that is retained in soils surrounding its upwelling (Bourgault, 2014). While not obvious during site selection, subsequent closer inspection of the eastern half of the Mansfield Ranch site has revealed some dry, assumed ephemeral, surface flow paths. Using technology not available at the time of site selection, a 1-m interval contour map from a LiDAR-derived digital elevation model shows likely shallow-to-bedrock areas outside of the plot that could be the source of shallow groundwater inputs (Fig. S2). The other four sites do not show any evidence of this type of topography or structured spatial variability in soil chemistry. Detecting temporal change at Mansfield Ranch will be difficult, using the current statistical approach. The random assignment of subplots to each sampling year resulted in only two from the higher-Ca east subplots in 2017 and only three in 2002, and the lower Ca and lower variability is clearly evident in the boxplots in Fig. 7. However, it may be possible to develop a model of the site that incorporates the known spatial variability that can then be used to detect temporal differences. Fraser et al. (2019) found that soils experiencing inputs from upslope of shallow groundwater were more responsive to recovery from acidic deposition. This may be the case with Mansfield Ranch and a revised statistical approach may be needed.

Table 4 B horizon (top 10 cm) average of yearly coefficients of variation (%) for selected chemical tests at each of the five study sites

	LR		LT		MR		MF		MU		All sites
	CV Range	CV Mean	CV Range	CV Mean	CV Range	CV Mean	CV Range	CV Mean	CV Range	CV Mean	CV Mean
	%	%	%	%	%	%	%	%	%	%	%
Carbon	19.9–38.6	29.8	21.5–27.8	24.9	22.6–103.7	48.2	2.0–97.6	54.0	17.3–50.7	34.5	38.3
Nitrogen	32.1–42.7	36.3	27.4–41.4	34.1	23.5–87.1	45.2	28.3–69.5	47.2	14.6–62.2	37.0	40.0
C/N ratio	8.9–60.3	24.9	9.9–76.0	34.0	14.6–28.8	20.5	6.8–39.0	24.4	7.8–14.6	11.7	23.1
Oxalate-Fe	33.1–48.6	40.6	30.1–51.2	37.0	23.9–43.3	36.6	26.3–99.2	61.9	19.2–40.8	26.1	40.4
Oxalate-Al	25.6–112.9	55.4	18.3–54.3	31.4	25.5–42.4	35.6	28.3–126.5	64.1	24.2–52.2	38.6	45.0
Oxalate-Mn	24.2–57.0	39.7	17.2–109.0	63.6	24.7–59.8	43.2	45.8–141.4	75.1	32.2–61.4	49.7	54.3
Exch-Al	23.1–40.5	30.4	197–41.9	27.5	37.6–94.6	58.6	25.4–53.4	42.7	12.1–50.5	24.1	36.7
Exch-Ca	23.1–128.7	77.7	74.1–86.9	78.5	71.2–114.1	84.3	11.8–83.1	47.3	25.3–66.9	45.0	66.5
Exch-Mg	35.0–69.3	50.0	26.4–66.0	49.8	60.7–80.3	70.1	38.6–67.8	56.5	21.2–59.9	36.6	52.6
Exch-K	32.4–63.3	50.3	19.1–47.1	35.5	21.1–46.4	30.6	28.3–66.7	49.7	21.0–57.6	38.8	41.0
Mean of first three[a]	8.9–60.3	30.3	9.9–76.0	31.0	14.6–103.7	38.0	6.8–97.6	41.8	7.8–62.2	27.7	33.8
Overall range and mean	9.9–128.7	43.5	9.9–109.0	41.6	14.6–114.7	47.3	6.8–141.1	52.3	7.8–66.9	34.2	43.8

[a] Range and mean of first three rows for comparison with results from the Oa/A horizons (Table 3)

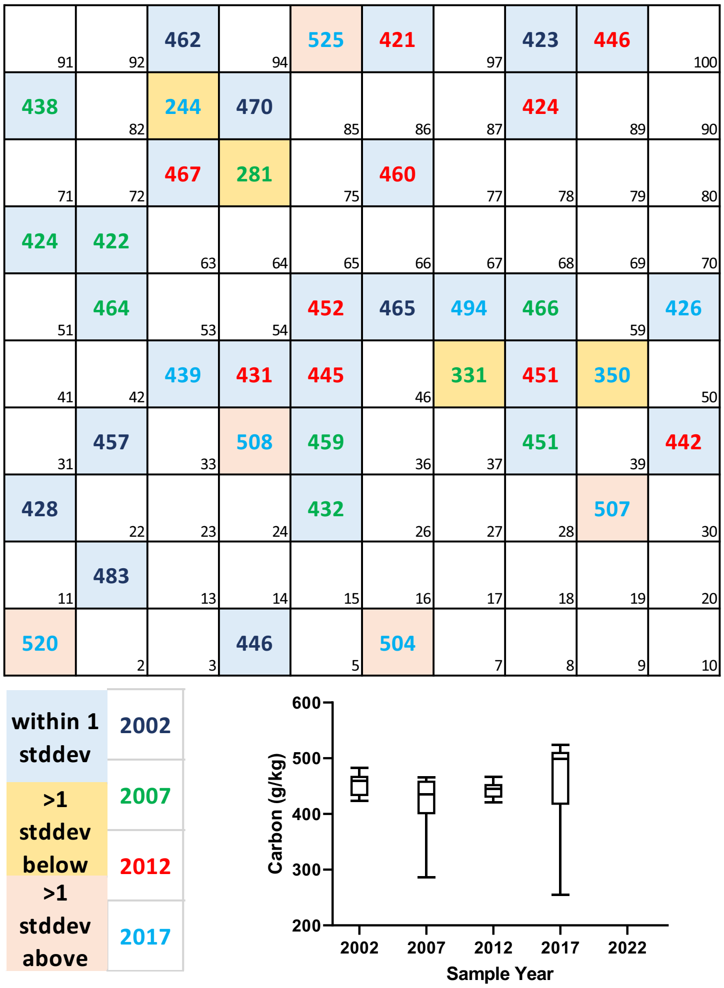
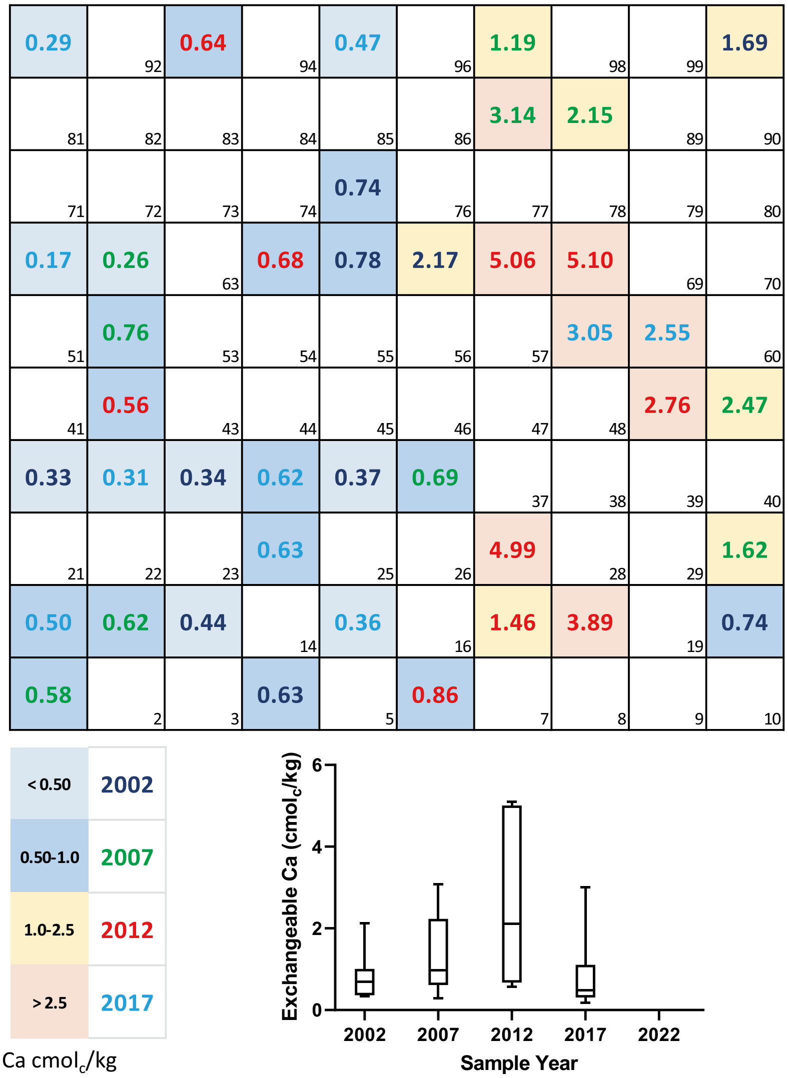


Fig. 6 Carbon concentrations (g/kg) in the Oa/A layer collected from subplots over four years at the Lye Trail site. Subplots are shaded by deviation from the overall mean of 442 g/kg (std. dev. 58 g/kg) with text colored by collection year. Boxplots whiskers show the 10–90 percentiles, boxes give the 25–75 percentiles, and horizontal lines provide the median

Variability within a pit

The 2012 experiment at Lye Road and Mansfield Ranch to measure the variability within a soil pit revealed a considerable range in extractable elements across a 90 × 10-cm soil pit face (Figs. 8, S3, and Table 5). The overall variability that can be introduced by a small sample size is clearly shown when comparing a box plot of the 10 subplot bulk samples with that of the 90 small (10 × 3.3 cm) samples collected in this experiment (first two boxplots from the left in Figs. 8 and S3). The Ca^{2+} in the top 10 cm of the B horizon showed more variability in the 10 pits sampled across the two sites (CV 77.8% and 75.1% for Lye Road and Mansfield Ranch, respectively) than within any individual pit (mean CV 36.2% and 31.7%, respectively) (Table 5). However, there was a wide divergence in the results found within some pits; Lye Road pit 100 had an overall range of 0.08–0.44 $cmol_c$/kg Ca^{2+}, and these extremes occurred in two samples taken from the same depth about 40 cm apart horizontally (Fig. 9). There was also a high variation with depth within the 10-cm-thick sampling zone in the upper B horizon. For example, Mansfield Ranch pit 17 had a Ca^{2+} concentration of 0.57 $cmol_c$/kg in a 10 × 3.3-cm-thick subsample that was taken immediately above another 10 × 3.3-cm-thick swath with 2.00 $cmol_c$/kg (Fig. 9). Overall at both sites, the concentration of extractable Ca^{2+} (and Mg^{2+} and K^{+}) was significantly lower in the 6.7–10-cm depth of the B horizon vs. the 0–3.3-cm depth (Fig. S4). This is consistent with an assumed decrease in carbon and, therefore, CEC with depth. The extractable Al^{3+} concentration trended higher with depth at Lye Road but



0.29	92	0.64	94	0.47	96	1.19	98	99	1.69
81	82	83	84	85	86	3.14	2.15	89	90
71	72	73	74	0.74	76	77	78	79	80
0.17	0.26	63	0.68	0.78	2.17	5.06	5.10	69	70
51	0.76	53	54	55	56	57	3.05	2.55	60
41	0.56	43	44	45	46	47	48	2.76	2.47
0.33	0.31	0.34	0.62	0.37	0.69	37	38	39	40
21	22	23	0.63	25	26	4.99	28	29	1.62
0.50	0.62	0.44	14	0.36	16	1.46	3.89	19	0.74
0.58	2	3	0.63	5	0.86	7	8	9	10

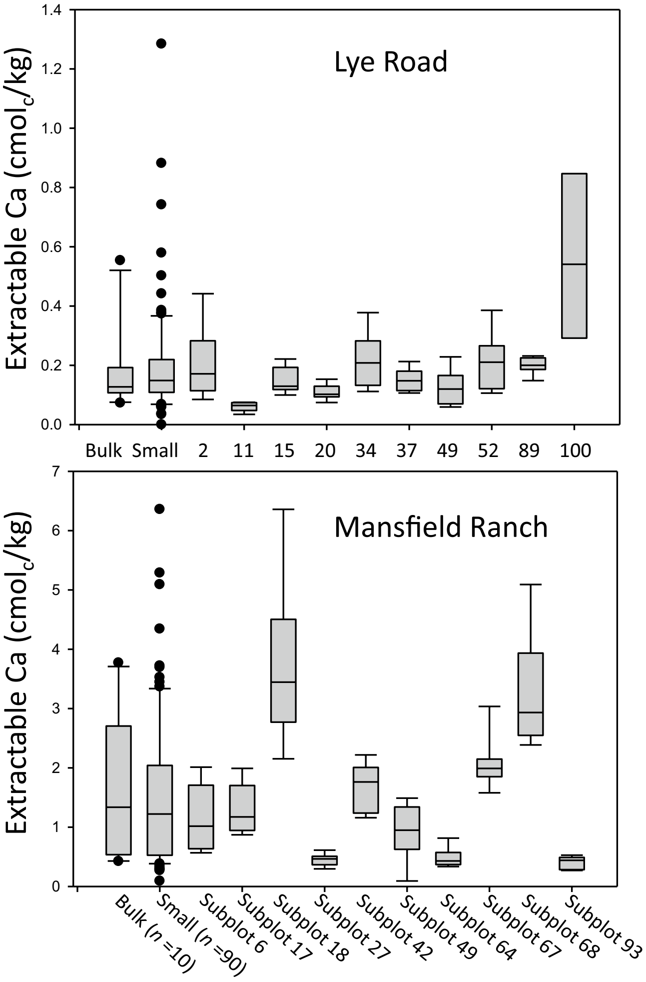
Fig. 7 Exchangeable calcium concentrations (cmol$_c$/kg) in the top 10 cm of the B horizon subplots at the Mansfield Ranch site shaded by concentration ranges with text colored by collection year. Boxplots whiskers show the 10–90 percentiles, boxes give the 25–75 percentiles, and horizontal lines provide the median

not at Mansfield Ranch (Fig. S4). These trends with depth were expected but the across-pit variation was not, and should be a caution for anyone designing a soil sampling approach. In the more variable pits (LR 100 and MR 17 in Fig. 9) there were four- to five-fold differences in extractable Ca^{2+} across the pit face. It is interesting to note that Mansfield Ranch, which had high across-site spatial variability as discussed above, had lower average within-pit variability than Lye Road for all extractable cations reported (Table 5). For extractable K^+ and Mg^{2+} at Lye Road, the means of the within-pit CVs (32.5 and 39.3, respectively) trended higher than the overall site mean (28.2 and 37.6, respectively) (Table 5). This, alone, should be a cause for concern. It is clear from these results that care needs to be taken to evenly sample the pit face in order to obtain a sample that is representative.

Temporal trends

After four sampling campaigns across a 15-year period, a number of temporal trends are evident and statistically significant (Table 6, Figs. 5 and 10). Carbon concentration increased in the Oa/A layer at Lye Road ($p = 0.024$) and Mansfield Underhill ($p = 0.047$), while an increase at Mansfield Forehead was marginally significant ($p = 0.076$). In the top 10 cm of the B horizon, an increase in carbon concentration was

Fig. 8 Variability in pH 4.8 NH_4-acetate extractable calcium concentration in the top 10 cm of the B horizon across all subplots and among nine samples taken within each subplot. The bulk samples were composite samples taken across the entire pit face. The “small” samples are subsamples at prescribed locations across the pit face as shown in Fig. 3. Each of the 10 subplots had 9 subsamples analyzed. Data are from two sites, Lye Road and Mansfield Ranch, sampled in 2012. Boxplot whiskers show the 10–90 percentiles, boxes give the 25–75 percentiles, horizontal lines provide the median, and individual points denote outliers



again found at Mansfield Underhill ($p = 0.006$) and was marginally significant at Lye Road ($p = 0.078$). The slopes translate to an annual increase of ~ 5 g/kg for the Oa/A layer and ~ 2 g/kg for the B horizon at Mansfield Underhill (Table 6). Because of the relatively few sampling times, the 95% confidence intervals for the slopes are rather wide and the maximum possible rate of change averaged ~ 100% higher for the trends with $p < 0.05$. There were also significant positive slopes for Oa/A layer nitrogen in both Lye Road ($p = 0.011$) and Mansfield Underhill ($p = 0.019$), more or less tracking the increases in carbon and maintaining a similar C/N ratio in year-15 as in year-0 (Fig. 5).

In addition to an increase in carbon in both layers, Mansfield Underhill also had an increase in exchangeable Ca^{2+} and Al^{3+} in the B horizon (Fig. 10). Exchangeable cations have not yet been measured in the Oa/A layer. The annual increase in B horizon Al^{3+} of 0.12 cmol$_c$/kg was 20 times that of Ca^{2+} (Table 6). These were the only significant changes in either exchangeable Ca^{2+} or Al^{3+} at any site, although Lye Road, which showed a marginally significant increase in B horizon carbon had a similar marginally significant increase in exchangeable Al^{3+} (Table 6). Exchangeable K^+ showed small, but significant, annual increases of 0.001–0.004 cmol$_c$/kg at Lye Road and Mansfield Underhill and a marginally significant ($p = 0.55$) 0.001 cmol$_c$/kg increase at Lye Trail (Table 6). No significant changes were found in exchangeable Mg^{2+}. Both positive and negative changes have been found in exchangeable cation concentrations in a number of resampling studies, discussed below.

The significant temporal changes were sometimes lower than the MDC simply calculated from one

Table 5 Means and coefficients of variation for the small 2012 study on variability of extractable elements from within a soil pit face in the top 10 cm of the B horizon for two sites, Lye Road and Mansfield Ranch. Cations were extracted with pH 4.8 NH4-acetate

	n	Ca^{2+} mean cmol$_c$/kg	Ca^{2+} CV %	Al^{3+} mean cmol$_c$/kg	Al^{3+} CV %	K^{+} mean cmol$_c$/kg	K^{+} CV %	Mg^{2+} mean cmol$_c$/kg	Mg^{2+} CV %
Lye road site mean[a]	10	0.18	77.83	23.23	35.85	0.12	28.19	0.09	37.60
Lye Road mean of within pits[a]	10	0.20	36.23	25.65	31.27	0.11	32.52	0.11	39.32
LR-2	9	0.22	41.41	16.50	18.96	0.10	20.93	0.11	37.69
LR-11	9	0.06	26.09	28.77	31.85	0.07	42.54	0.05	40.37
LR-15	9	0.15	28.06	41.62	37.51	0.15	31.45	0.10	35.55
LR-20	9	0.15	23.80	47.17	18.07	0.12	29.17	0.08	24.86
LR-34	9	0.12	44.76	21.87	29.02	0.10	31.07	0.10	38.53
LR-37	9	0.21	42.51	16.91	42.33	0.07	21.72	0.10	50.91
LR-49	9	0.20	12.99	28.35	52.93	0.13	21.07	0.11	29.34
LR-52	8	0.61	58.12	15.78	33.46	0.19	39.62	0.19	33.36
LR-89	9	0.20	62.32	18.25	33.01	0.10	41.83	0.13	58.00
LR-100	9	0.11	22.27	21.30	15.52	0.12	45.76	0.10	44.63
Mans. Ranch site mean	10	1.59	75.13	6.23	41.53	0.08	27.56	0.15	58.66
Mans. Ranch mean of within pits	10	1.54	31.69	5.97	25.06	0.07	23.32	0.15	30.73
MR-6	9	1.67	23.53	3.32	19.33	0.04	13.64	0.12	23.47
MR-17	9	0.93	47.22	7.50	43.07	0.08	31.35	0.11	39.55
MR-18	9	1.14	49.60	7.05	32.43	0.08	26.55	0.14	46.93
MR-27	9	1.31	32.61	2.68	20.87	0.03	21.21	0.10	30.41
MR-42	9	3.68	36.42	5.66	36.42	0.08	18.42	0.30	37.95
MR-49	9	0.45	21.95	7.51	16.13	0.09	32.88	0.08	30.48
MR-64	9	0.48	32.10	7.80	28.04	0.09	29.86	0.09	40.80
MR-67	9	2.07	19.86	5.80	23.97	0.07	17.91	0.20	18.71
MR-68	9	3.26	28.43	3.20	14.49	0.09	23.49	0.26	23.32
MR-93	9	0.41	25.12	9.20	15.84	0.07	17.85	0.06	15.73

[a] Mean and CV of composite samples from each of 10 pits

[b] Average of 10 means and CVs from 9 subsamples within each pit

site-year ($n = 10$) but consistent with MDCs calculated from the repeated measures using the method of Mobley et al. (2019). For example, based on the variability only from the 2012 sampling, the Oa/A carbon MDC at Mansfield Underhill was 26 g/kg/year, but the temporal data set showed a significant change of 5.4 g/kg/year (Table 6). This change is consistent with the MDC calculated from repeated measurements (Mobley et al., 2019), which ranged from 3.6–6.0 g/kg/year in the Oa/A layer. In the B horizon, we found a significant increase of 1.9 g/kg/year at one site, where the Mobley et al. (2019) formula predicted MDCs between 0.7–1.2 g/kg/year. For exchangeable Ca^{2+}, the change detected at Mansfield Underhill of + 0.006 cmol$_c$/kg/year or 3.3% was close to the calculated repeated-measures MDC. For the two Lye sites, where overall variability was higher (but not as extreme as Mansfield Ranch), the repeated-measures MDCs calculated with the Mobley et al. (2019) formula were 0.034 cmol$_c$/kg/year for Lye Road and 0.022 cmol$_c$/kg/year for Lye Trail, which equate to annual changes of 14.0% and 7.6% respectively. Overall, the low variability at Mansfield Underhill allowed us to detect relatively small changes in many of the chemical measurements.

No significant changes were found over the 15-year sampling period in tree species composition, individual species basal area, or mortality. There were nonsignificant trends for species composition at Mansfield Underhill, with decreasing *A. balsamea* and increasing *P. rubens*, and at Lye Trail, with decreasing *B. cordifolia*. Although not significant, these trends are

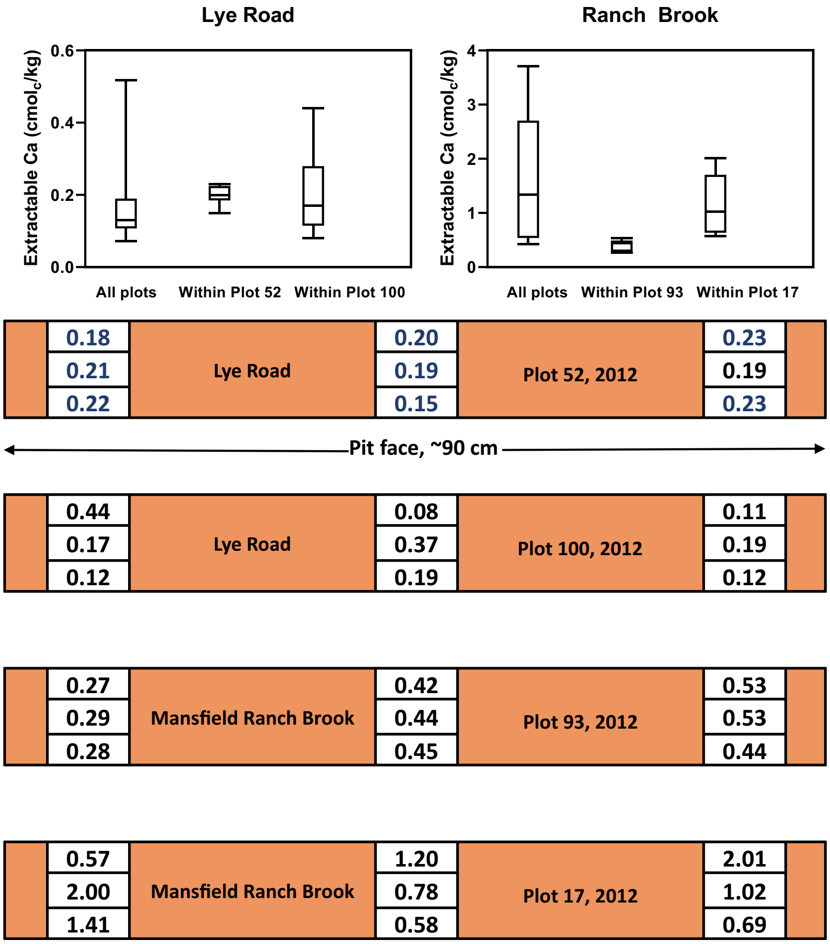


Fig. 9 Examples of high and low variability across the soil pit face for pH 4.8 NH_4-acetate extractable calcium concentration (cmol$_c$/kg) in the top 10 cm of the B horizon for two sites. Boxplot whiskers show the 10–90 percentiles, boxes give the 25–75 percentiles, and horizontal lines provide the median. The horizontal boxes below show the concentrations at each soil pit face, where the upper 10 cm of the B horizon was sampled at three equal intervals at three different points

consistent with recent work that has shown a resurgence of *P. rubens* associated with reduced acid deposition (Kosiba et al., 2018), as well as work that has shown impaired health of *B. cordifolia* in soils with low levels of exchangeable Ca (Halman et al., 2011).

Relationship to other studies

As opposed to the soil carbon increases that we found, some recent studies in Europe have documented decreases in soil carbon during the decades following the decline in acidic deposition. Berger et al. (2016), working in Austria in a European beech (*Fagus sylvatica*) stand, found lower carbon concentration in the 0–5-cm depth in the area receiving stem flow, and Oulehle et al. (2011), who sampled a Czech Republic Norway spruce stand, found a 47% decrease in the carbon pool in the Oa horizon. Prietzel et al. (2020), in a 40-year monitoring study of two Scots pine stands in Germany, found a recent decrease at one site in the carbon pool in the top 30 cm of the mineral soil. In contrast, two recent studies in the northeastern USA have found increases in carbon over the last 1–2 decades. Fraser et al. (2019) found increases in Oa horizon carbon concentration in plots in the White Mountain National Forest of New Hampshire that were initially sampled in 2001–2002 and resampled in 2014 (close to our sampling interval of 2002–2017). Bailey et al. (2021), resampling sites in the Allegheny Plateau of Pennsylvania, found increases in both the thickness and carbon concentration of the Oa/A horizon between 1997 to 2017. In our study, we measured the depth of each horizon during the profile description process and found no temporal changes in thickness (Fig. S5). While our approach did not directly measure the carbon pools, the lack of any change in horizon thickness suggests that the pool size may have followed trends in carbon

Table 6 Linear temporal trends for four sampling campaigns (2002, 2007, 2012, 2017) for carbon in the Oa/A layers and carbon and exchangeable cations in the top 10 cm of the B horizons for five study sites

Layer/site	Transformation	*p* of slope[a]	Change per year	% change per year	Confidence interval for change per year	
Oa/A carbon (g/kg)						
LR	log	**0.024**	4.57	2.7%	0.05	10.75
LT	Box Cox, $\lambda = 4.4$	0.302	–	–	–	–
MR	log	0.899	–	–	–	–
MF	–	*0.076*	4.75	1.4%	−0.53	10.03
MU	–	**0.047**	5.44	2.4%	0.08	10.79
B horz. carbon (g/kg)						
LR	log	*0.078*	1.13	2.4%	−0.10	3.18
LT	–	0.895	–	–	–	–
MR	–	0.808	–	–	–	–
MU	–	**0.006**	1.89	3.7%	0.60	3.18
B horz. Ca^{2+} (cmol$_c$/kg)						
LR	log	0.926	–	–	–	–
LT	log	0.420	–	–	–	–
MR	Box Cox, $\lambda = -0.4$	0.817	–	–	–	–
MU	sqrt	**0.033**	0.006	3.3%	0.000	0.014
B horz. Al^{3+} (cmol$_c$/kg)						
LR	log	*0.083*	0.154	2.4%	−0.016	0.442
LT	–	0.321	–	–	–	–
MR	–	0.784	–	–	–	–
MU	square	**0.017**	0.115	1.5%	0.026	0.186
B horz. K^{+} (cmol$_c$/kg)						
LR	sqrt	**0.041**	0.001	1.6%	0.000	0.002
LT	–	*0.055*	0.001	2.6%	0.000	0.002
MR	log	0.592	–	–	–	–
MU	–	**0.001**	0.004	6.1%	0.002	0.006

[a] Bold denotes significant at the 0.05 level and italics denotes significant at the 0.10 level

concentration, i.e., increased at some of the sites. An explanation for the opposite trends in the European and North American studies could be due to differences in the intensity of acidification, which was much higher in Europe. Recovery from acidification was presumed to create more favorable conditions for mineralization of soil carbon (Oulehle et al., 2011; Prietzel et al., 2020). Looking at changes in 23 resampled sites in eastern Canada and the USA, Hazlett et al. (2020) concluded that the extent of recovery was a factor of both the intensity of acidification and the length of the recovery period. It may be that these Vermont sites, and those in the studies of Fraser et al. (2019) and Bailey et al. (2021), reflect a different dynamic than the European sites. Perhaps the recent large decrease in nitrogen deposition (Likens et al., 2021) has made conditions less favorable for soil carbon mineralization, resulting in the increases observed. A recent change in forest composition in the Allegheny Plateau, i.e., a decline in the abundance of black cherry (*Prunus serotina*), has been attributed to the decline in nitrogen deposition (Royo et al., 2021). Complex interactions among changes in climate, deposition of nutrients, vegetation, and soil biological activity affect soil carbon retention and loss. Continued monitoring and research should help clarify these processes. Vermont's climate has become warmer and wetter, with an 0.7 °C increase in average temperature and a 15-cm increase in annual precipitation since 1960 (Galford et al., 2014), trends that are projected to continue (Guilbert et al., 2014). SCAN data from installations adjacent to the Lye Trail and Mansfield Underhill sites did not show a significant increase in air or soil temperature over

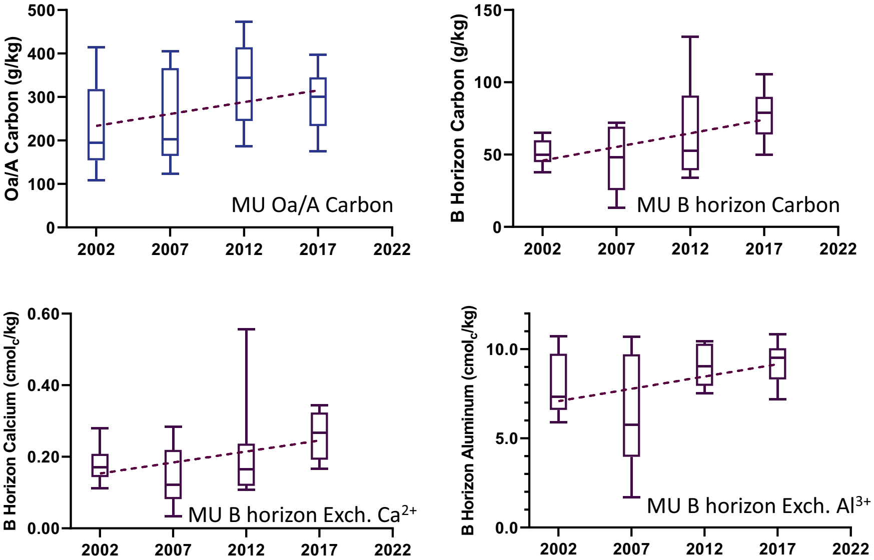


Fig. 10 Boxplots of Mansfield Underhill soil data with significant temporal trends. Boxplot whiskers show the 10–90 percentiles, boxes give the 25–75 percentiles, and horizontal lines provide the median. Dashed lines are the least-squares fit (see Table 6 for more details)

the 15-year sampling period but did show increases in both wet precipitation and soil moisture (Fig. S6). This increased moisture could play a role in the increasing concentrations of soil carbon.

A variety of trends have been documented for exchangeable cations in a number of other studies that have resampled sites over recent decades. Recovery from acidic deposition should lead to decreases in exchangeable Al^{3+} and increases in exchangeable Ca^{2+}, reversing trends resulting from acidification. In a resampling study of 27 sites in eastern Canada and the USA, Lawrence et al. (2015) found decreases in exchangeable Al^{3+} in the O layer but not in the B horizons. Fraser et al. (2019), in New Hampshire, found a decrease in exchangeable Al^{3+} and an increase in exchangeable Ca^{2+} in Oa horizons but the opposite in B horizons. Similar trends were found by Bailey et al. (2021) in Pennsylvania for Oa and A horizons with decreasing exchangeable Ca^{2+} in some B horizons. Lawrence et al. (2021) resampled soils in a number of watersheds in the Adirondack Mountains of New York and found a 23% increase in exchangeable Ca^{2+} in the Oe horizon, and an overall significant upward trend in Ca^{2+} in B horizons (although not significant in any single watershed). These sometimes conflicting results may be partially explained by changes in carbon and cation exchange capacity (CEC). In acidic forest soils of the northeastern USA, soil organic matter is the primary source of CEC with carbon and CEC linearly related (Ross & Bartlett, 1995). Any increase in soil carbon would result in an increase in CEC and the most readily available cation to balance the increase in charge would be Al^{3+} already present in non-exchangeable organically complexed form (Ross et al., 2008). The small, but significant, increases found in exchangeable Ca^{2+} and K^{+} at the Mansfield Underhill site could also be due to greater CEC. While the weathering release of these cations from B horizons is not known, greater retention of nutrients cycled through litter would be expected as the result of less leaching (from lower deposition acidity and ionic strength) relative to the peak of acidic deposition. The calcium status of our study soils prior to 2002 is unknown but can be assumed to have been decreased by acidic deposition, consistent with numerous studies throughout our region (Driscoll et al., 2001).

Conclusions

The design of this long-term soil monitoring program appears to be robust enough to detect relatively minor temporal changes in the concentration of soil chemical constituents, e.g., 1.5% increase per year in exchangeable Al^{3+} at one site (Mansfield Underhill). This standard has been achieved by taking a high number of replicate samples ($n = 10$) on a consistent

5-year interval from 50×50-m plots that, with one exception, were successfully selected to be relatively uniform. Modifications were made to the sampling protocol after the first year in order to obtain more representative and comparable horizon depths, i.e., combining the Oa and A horizons if both are present and sampling the top 10-cm of the B horizon. We have also demonstrated the need to carefully sample across the face of our individual sampling unit, the soil pit, in order to reduce short-range spatial variability. Continued sampling with consistent methods, along with further chemical analyses of archived samples, should provide additional evidence for temporal changes in soil chemistry.

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Data availability Soil chemical data, vegetation data, and related metadata are available on the Forest Ecosystem Monitoring Website: https://www.doi.org/10.18125/58h5df.

Declarations

Conflict of interest The authors declare no competing interests.

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