Published March 28, 2019

North American Forest Soils Conference - International Symposium on Forest Soils

Decadal Change in Soil Chemistry of Northern Hardwood Forests on the White Mountain National Forest, New Hampshire, USA

Olivia L. Fraser*
Dep. of Natural Resour. and Environ.
Univ. of New Hampshire
Durham, NH 03824

Scott W. Bailey
Northern Research Station
USDA Forest Service
North Woodstock, NH 03262

Mark J. Ducey
Dep. of Natural Resour. and Environ.
Univ. of New Hampshire
Durham, NH 03824

Soils are subject to a variety of stressors including human land use, air pollution and climate change. A challenge for detecting temporal change is disentangling heterogeneity at multiple spatial scales. Forty permanent plots were sampled across the US White Mountain National Forest (WMNF) in 2001 or 2002 and resampled in 2014. Paired *t* tests detected significant increases in carbon and base cations concentrations and a decrease in Al in the Oa horizon while base cations decreased and Al increased in some mineral horizons. A subset of six plots were intensively resampled in 2015. Pooled variances were calculated using all the six intensively sampled plots from 2014 to 2015. Within-site variability was comparable to overall variability across the WMNF. When study sites were stratified into hydrologic groups, we found a strong signal in the Oa horizon of increasing carbon and base cation concentrations from 2001–2002 to 2014, suggesting that soils influenced by shallow groundwater contributions from upslope may be more responsive to acidification recovery than soils influenced only by vertical percolation. The initial study design did not consider the role of hydrologic pathways in susceptibility of soils to temporal change and did not include enough plots in each hydrologic group to maximize the power of this stratification approach. However, these results illustrate the potential for hydrologic stratification to improve change detection and interpretation in forest soil monitoring programs. The combined approach to hydrologic stratification and estimating variance components simultaneously at the landscape and within-plot scales is crucial for calculating sample size needed to detect temporal change.

Core Ideas

- **Soils in the northeastern United States show signs of recovery from acidification between 2001-2002 and 2014.**
- **Variation in soil chemistry at the landscape and plot-scales was similar, informing study design.**
- **Soils influenced by shallow groundwater were more dynamic than well-drained soils.**

Soils are the foundation of healthy, productive forests and their associated terrestrial and aquatic ecosystems. Long-term productivity of forests depends on amounts of available nutrients and quantifying change over time is an important component to assessing the overall health of forest ecosystems (Federer et al., 1989). Soil monitoring was developed as a means of evaluating soil condition, assessing susceptibility to environmental stressors, and informing land management practices (Mangold, 2000; Neary et al., 2010; Lawrence et al., 2013). Chemical properties of soils are monitored as indicators of essential forest functions to evaluate overall soil productivity (Cronan and Grigal, 1995; Schoenholtz et al., 2000; Richter and Markewitz, 2001). However, temporal-change detection is challenging since soil chemistry is highly variable spatially and typically requires a large number of samples to achieve statistical significance (Johnson et al., 1990; Conant et al., 2003).

Soil monitoring efforts in the northeastern United States were primarily initiated due to suspected impacts of acid deposition (Driscoll et al., 2001; Likens, 2013). Studies monitoring soil chemistry change spanning ~1967 to 2000, a period straddling peak atmospheric acid deposition, typically found significant decreases in Ca and significant increases in Al in the organic horizon and upper mineral horizons (Bailey et al., 2005; Warby et al., 2009; Bedison and Johnson, 2010).

Soil Sci. Soc. Am. J. 83:S96–S104
doi:10.2136/sssaj2018.08.0301
Received 17 Aug. 2018.
Accepted 11 Dec. 2018.
*Corresponding author (olbartlett@wildcats.unh.edu).

However, during approximately the same time frame, Yanai et al. (1999) reported no significant change in the forest floor due to high spatial variance of Ca and Mg and a loss of 1.4% per year would have been detectable. A more recent regional compilation of resampling efforts at 27 sites across the Northeast, comparing samples collected in the 1980s and 1990s with samples collected in the late 2000s, a period of strongly declining atmospheric acid deposition, reported signs of recovery, with modest decreases of exchangeable Al in the O and upper B horizon (Lawrence et al., 2015). However, base saturation continued to decrease in the B horizon of some sites suggesting ongoing acidification. Overall soil resampling studies have varied drastically in design and few studies have investigated sampling size and study design needed to detect change across a landscape scale; nor have there been many attempts to stratify sites by properties that could reduce spatial soil variation.

A primary challenge for soil monitoring is to disentangle heterogeneity at multiple spatial scales so variation occurring over space is not confounded with change across time. It is crucial for a monitoring protocol to account for the high variance of soil chemistry at multiple spatial scales when calculating sample size (Muukkonen et al., 2009). Often, the number of samples are determined from a site-specific perspective, which is then used as a reference for future monitoring. Previous studies have suggested sample design considerations for site-specific change detection of forest floor horizons as well as watershed-scale forest floor and mineral horizon sample size (Johnson et al., 1990; Mäkipää et al., 2008). There are no long-term studies at a landscape-scale that monitored soil by leveraging a stratified sampling design based on hillslope position or other local factors driving soil formation processes to reduce the influence of horizontal and vertical variability of soil chemistry for the purposes of change detection.

Identifying site characteristics that may influence susceptibility of soil chemistry change due to acid rain or other perturbations may increase the sensitivity of monitoring programs. In the northeastern United States where Spodosols are a dominant soil order, podzolization contributes to the high-variance of soil chemistry, with eluvial and illuvial processes having greatly different expression at both the profile and hillslope scale (Bailey et al., 2014). At the profile scale, podzolization promotes translocation of soluble organic compounds, complexed with aluminum and iron, from shallow to deeper portions of soil profiles (De Coninck, 1980). In addition, the dominant hydrologic pathway through a soil profile can either vertically drive leaching processes via unsaturated flow at the pedon scale, or laterally influence the leaching process, particularly in areas where shallow groundwater is flowing within the solum, connecting pedons at the hillslope scale (Lundström et al., 2000; Sommer et al., 2000; Gannon et al., 2014). Sites that are developed by vertical hydrologic flow may be more susceptible to leaching processes as buffering from atmospheric deposition and mineral weathering is limited to inputs at the pedon scale. On the other hand, sites that are developed laterally under the influence of shallow groundwater, have pedons influenced by solute inputs from upslope, with potential buffering from chemical cycling processes from a larger area than the pedon itself (Clarholm and Skyllberg, 2013). Thus, these sites are potentially less susceptible to depletion processes and more responsive to recovery processes. Incorporating site characteristics to estimate the variance components simultaneously at the landscape scale, and at the profile-scale is crucial for calculating sample size and quantifying temporal rates of change when designing monitoring systems.

National forests, covering approximately 190 million acres in the United States, are mandated to protect the longterm soil productivity by the National Forest Management Act (NFMA, 1976). The White Mountain National Forest (WMNF) in New Hampshire and Maine established a decadal monitoring program to measure forest soil productivity (US Forest Service, 2005) to fulfill the NFMA mandate. However, it is not known how sensitive the sampling design is to detect change. The first objective of this study was to investigate overall change in soil chemistry of mid-elevation, northern hardwood Spodosols across the White Mountain National Forest (WMNF) by resampling plots that were originally sampled in 2001–2002. This included further investigating temporal-change detection by simultaneously calculating the variance components within-plot using a subset of plots with more intensive sampling. The second objective was to stratify sampling sites by dominant hydrologic pathways to determine if groundwater influenced soils were more responsive to acidification recovery processes compared to soils developed vertically via unsaturated flow.

METHODS

Study Site

The White Mountain National Forest (WMNF) covers approximately 800,000 acres located in north-central New Hampshire and adjacent western Maine. Dominant vegetation types include northern hardwood, spruce-fir, and mixed-species forests. Annual precipitation averages 90 to 180 cm and total annual snowfall ranges from 250 to 400 cm (McNab and Avers, 1994). The WMNF is a glacially scoured, irregular highland characterized by clusters of low, rounded and scattered mountains where the soils are typically less than 3 m deep, strongly acid, and consist of Haplorthods, Haplaquepts, and Dystrochrepts (McNab and Avers, 1994). Figure 1 depicts the forty permanent plot locations across the White Mountain National Forest (WMNF) established in 2001–2002 to monitor soil productivity (US Forest Service, 2005). Plot locations were selected to be representative of mid-elevation mature northern hardwoods (between 60 and 120 yr of age), Spodosols developed in deep glacial till, and varying hillslope position (Supplemental Table S1). Topographic maps, aerial imagery, and Ecological Land Types (US Forest Service, 2005) were used to initially to identify locations and ensure plots were spatially distributed across the WMNF. The focus was on mid-elevation, mature northern hardwoods since this is the portion of the WMNF most actively managed for timber products where maintenance of site productivity directly informs the achievement of goals set out in the WMNF Forest Management Plan.

Sample Collection and Analysis

Once the plots were established, aspect was measured with a handheld compass in degrees relative to true north. Slope was measured in percent with a clinometer in both up and downslope directions 5 m from plot center. Soil pits were hand dug, approximately 0.75 m by 0.5 m wide and 1.2 m deep to sample the entire solum and the upper portion of the C horizon. In 2001–2002, soil pits were hand dug at plot center; in 2014 plots were relocated and 37 plots were resampled. Of the 40 original plots, two plots could not be relocated in 2014 due to incorrect coordinates and one plot was resampled but classified as an Inceptisol rather than a Spodosol which was the focus of the study; these plots were excluded from the analysis presented here. In 2014 new pits were installed and sampled along the topographic contour from the plot center of the 2001–2002 pit (Fig. 1). A subset of six plots were selected for additional intensive sampling by stratifying all the plots based on exchangeable Al concentration. In each of the Oa, spodic (Bhs, Bh, Bs), and transitional (BC, CB) horizons, exchangeable Al concentration was classified as low, medium or high based on the entire range measured in that horizon. Two plots from each of the three categories were randomly selected for further sampling in 2015; additional pits were 2 m on topographic contour in both directions from the plot center of the 2001–2002 pit and from the 2014 pit, as well as 2 m upslope and downslope of the 2014 soil pit (Fig. 1, magnified plot inset).

Genetic horizons were described and sampled by Munsell color, texture, structure, moist consistence, presence of redoximorphic features, rooting density, and coarse fragment content (Schoeneberger, 2012). Soil samples, consisting of approximately 2 to 3 L of each horizon, were collected by the full height of the horizon and width of the pit. Volumetric coarse fragment (2 to 75 mm) content was estimated visually on the pit face. Rooting density was described semi-quantitatively as few (<1), common (1 to 5) or many (≥5) fine and very fine roots (≤2 mm diameter) per square centimeter. B horizon subdivisions were designated based on Munsell color based on criteria shown to distinguish spodic horizons influenced by shallow groundwater at the nearby Hubbard Brook Experimental Forest (Bailey et al., 2014). Bhs horizons had a Munsell hue of 7.5YR or redder and value and chroma ≤3. Bs horizons were a 7.5YR or redder hue and a value or chroma >3 and Bh horizons had a hue of 10YR and a value and chroma both <3 (Bourgault et al., 2015).

All samples were air-dried, sieved to remove particles >2 mm, homogenized and split to generate a subsample for chemical analysis. Samples from 2001–2002, 2014, and 2015 were measured for pH in 0.01 mol L^{-1} $CaCl_2$ (Robarge and Fernandez, 1987). All archived 2001 or 2002 samples, and new 2014 or 2015 samples were analyzed in 2016 for carbon and nitrogen on a CN elemental analyzer (CE-Elantech Thermo FlashEA 1112 Series NC Soil Analyzer) using pulverized subsamples. Soil standards obtained from the North American Proficiency Testing program were used to standardize the instrument. Exchangeable cations were also measured in 2016 on all samples from both time periods in an extract obtained from a mechanical vacuum extractor

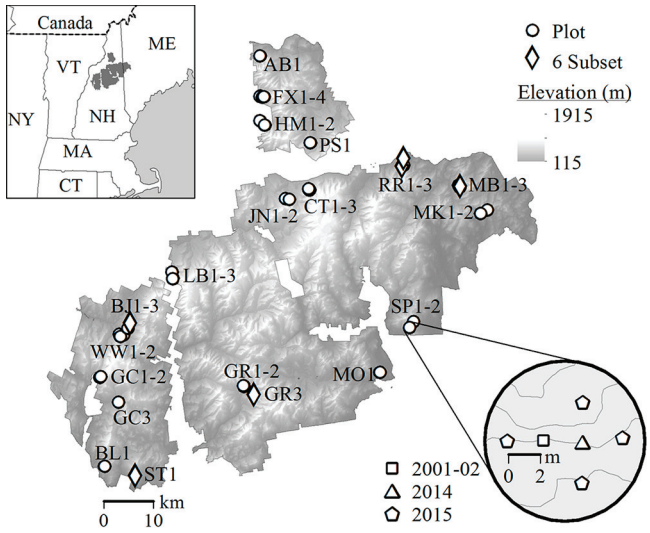

Fig. 1. White Mountain National Forest (WMNF) location within the northeastern United States and the 40 permanent plot locations established in 2001 to 2002 across the WMNF. Each general study area is indicated by a two letter abbreviation; numbers indicate the number of plots in each general area, which ranged from one to four. In 2014, plots were sampled at 2-m intervals along topographic contour (depicted with a triangle in the magnified plot inset). Six plots, depicted with diamonds on the WMNF map, were randomly selected for additional intensive sampling in 2015. The additional pits were sampled 2 m on contour on each side of the 2014 pit and 2 m upslope and downslope (depicted with pentagons in the plot inset) for a total of four pits sampled in the intensive plots in 2015.

using 1 M NH_4OAc buffered at pH 4.8. Cation concentrations were measured with an Agilent inductively coupled plasma spectrometer (Agilent Technologies 700 Series ICP–OES) at the US Forest Service laboratory in Durham, NH. Reference samples of Oa and Bs horizons from Vermont were included in all analytical streams and yielded values of C, N, pH, and exchangeable cations comparable to the median values reported in an interlaboratory study (Ross et al., 2015). All profile descriptions and chemistry data will be published on the US Forest Natural Resource Manager (US Forest Service, 2018).

The 2001–2002 exchangeable cation determinations (Al, Ca, Mg, Mn, Na, and K) were originally measured in 1 M NH_4Cl extracts obtained by mechanical vacuum extraction (Blume, 1990). Then 30 archived samples from 2001–2002 were randomly selected and re-analyzed in 2017 using 1 M NH_4Cl to determine if changes had occurred due to archiving or method differences. The re-analysis was completed by the same laboratory that made the original measurements. Regression showed new analyses of the 2001–2002 archived samples were highly correlated with original analyses. The Al, Ca, Mg, Mn, and K concentrations were less than 5% lower in recent measurements, though there was a high correlation (r^2 = 0.86 for Al; 0.95 for Ca; 0.87 for Mg; 0.97 for Mn, 0.94 for K). Na, however, had an intercept of 7.18 and a slope of 1.05 (r^2 = 0.10). The high correlation of Al, Ca, Mg, Mn, and K suggests change was not detectable and change is smaller than the detection limit in archived samples. The consistently higher concentrations of Na may have resulted from the differences in the extracts and analytical noise on the ICP.

Statistical Analyses

Differences among observers may have led to sampling more than one subhorizon in the first sampling year compared to one horizon in another sampling year. Therefore, genetic horizons were combined into general categories for comparison of results between sample years. The Oa, spodic, transition, and C horizon categories were created to include all samples separated into subhorizons (e.g., Oa1 and Oa2). A general spodic horizon category combined all illuvial B horizons, including Bhs, Bh, and Bs and the transition horizon category included BC and CB horizons. Temporal change in E horizons was not explored because E horizons were typically thin and discontinuous, and their low organic matter content makes them uniformly low in C and N content and extractable cations.

Analytical results for individual genetic horizons were aggregated into a general horizon category by using a weighted average to determine overall exchangeable cations, pH, C and N concentration. The weighted average was calculated by multiplying the thickness, bulk density, and one minus the proportional coarse fragments to determine a unit area mass for every individual horizon within a general horizon. The individual horizon mass was then divided by the sum of all horizon masses in the general horizon, multiplied by a soil chemistry variable measured, and the sum of products used for the general horizon value. Bulk density was estimated by the relationship with organic matter reported by (Federer et al., 1993) and assuming organic matter is 50% carbon. Across all plots, average top and bottom depths (cm) and color were calculated by general horizon category for both sampling years. Munsell colors were averaged by converting colors to RGB color coordinates, averaged by general horizon category for the purposes of comparison, and then converted back to Munsell color to report averages by general horizon category using the 'aqp' package in R (Beaudette et al., 2013).

Pairwise *t* tests of mean top and bottom depths, color, pH, C, N, and log-transformed cation concentrations were used to compare years on a plot by plot basis for the first objective of this study when the horizon was present during both sample times. For example, Oa horizons were present in 25 plots during both sampling years, whereas spodic horizons were present in both sampling years in all 37 plots. In addition, a Wilcoxon signed-rank test was also used to compare years on a plot by plot basis on non-transformed cation concentrations.

Pooled variance was calculated to determine within-plot spatial variability (Eq. [1]). The pooled approach for calculating variance accounts for the lack of variance present from the first sampling time since variance cannot be calculated using one sample; at the second sampling time, the number of samples (5) is very small for obtaining a reliable estimate of the variance. A pooled variance loses site-specific information about the variability, but provides a more reliable estimate of the variability that would be encountered under typical conditions. The pooled variance is calculated as:

$$s^2 = \frac{1}{\left(\sum n_j\right) - n_i} \sum \left(x_{ij} - \overline{x_j}\right)^2 \qquad [1]$$

where x_{ij} is the ith pit of the jth site and $\overline{x_j}$ is the sample mean of the site. The total number of pits sampled from both samplings is n_j, and n_i represents the total number of subsampled sites. The magnitude of change that could be accounted for based on sampling variability alone is then determined as the standard error of the difference between two sets of measurements, one based on a single pit and one based on multiple pits, with the sampling variance for a single pit estimated as the pooled variance:

$$s_\Delta = \sqrt{s^2 + \frac{s^2}{n_{t2}}} \qquad [2]$$

where s_Δ is the standard error of the estimated change, n_{t2} is the number of pits sampled from the second sampling time at the jth site. To evaluate the influence of variability on the sample size needed to detect plot-specific change, we used a power analysis approach. Required sample sizes were calculated based on the pooled variances of the subset of six intensively sampled plots, with a power (i.e., probability of a statistically significant change detection) of 0.8 and significance of 0.05 to detect plot-specific change and the observed magnitude of change found across all 37 plots.

For the second objective, plots were partitioned into three groups, vertical, lateral, or bimodal, representing the dominant hydrologic pathway influencing soil formation. Vertical hydrologic development was defined as profiles with morphology indicating a lack of watertable incursion in the solum (Gannon et al., 2014). Lateral sites had morphology indicating regular water saturation throughout the solum (Sommer, 2006) while bimodal sites were intermediate with some evidence of watertable influence primarily in the lower portion of the solum (Bailey et al., 2014). Figure 2 depicts representative soil profiles (plots GC2, GR3, and GC3) of vertical, lateral, and bimodal hydrologic regimes that influence soil horizon sequence.

Topography, horizon sequences, and soil profile characteristics were all used to assign each plot to a hydrologic group (Bailey et al., 2014). A multivariate analysis of variance (MANOVA) was used to evaluate temporal change between 2001–2002 and 2014 in C, N, pH, and exchangeable cation concentrations between hydrologic groups. To assess the influence of this stratification on change detection, an ANOVA power analysis was also completed to determine how many sites of each hydrologic group were necessary for detecting a significant difference (α = 0.05) with a power of 0.8. All analyses were completed using base packages in R (R Development Core Team, 2018).

RESULTS

Overall Decadal Soil Change

There were no significant differences in sampling depths or color by general horizon between sampling years except for a slightly greater bottom depth of sampling of the C horizon in the original 2001 and 2002 sampling years (Table 1).

Mean carbon (C) and nitrogen (N) concentration (g kg^{-1}), pH, and exchangeable cation concentration ($cmol_c$ kg^{-1}) for each general horizon category (Oa, spodic, transition, and C) by sam-

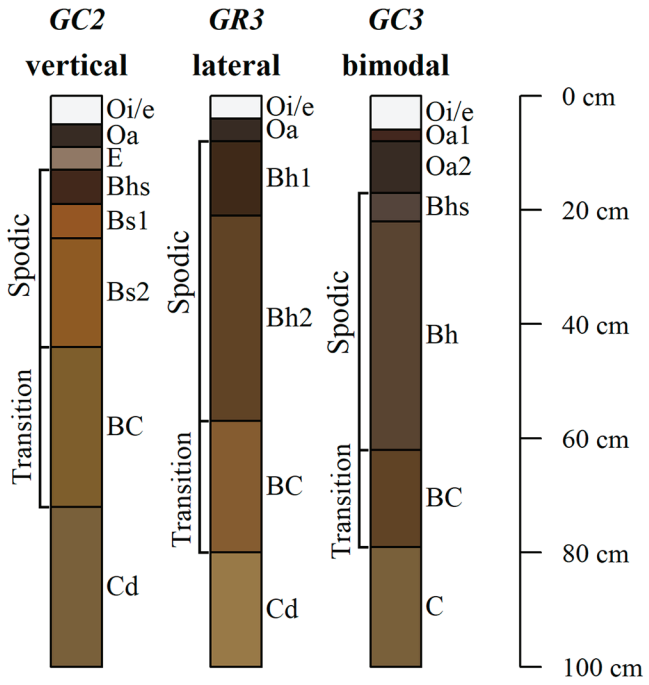

Fig. 2. Representative soil profiles (plots GC2, GR3, and GC3) from 2001–2002 depicting the common horizon sequence associated with the dominant hydrologic pathway influencing a soil developed vertically, laterally, or bimodally. Plots were partitioned into three hydrologic groups based on topography, horizon sequences, and soil profile characteristics (Bailey et al., 2014). Laterally influenced profiles generally lacked an E horizon and a Bh horizon was the dominant illuvial horizon type. Bimodal profiles may have a thin E horizon and had a Bh horizon underneath a lighter colored Bhs and or Bs horizon. Brackets parallel to each soil profile indicate the subhorizons aggregated within spodic and transition categories for comparison.

pling year are listed in Table 2. Significant differences between sample years are in indicated in bold. The results from the paired *t* tests found significant increases in C and N of the Oa horizons with approximately 30% higher C concentrations in 2014 than in 2001–2002. A smaller but significant decrease in C concentration also occurred in the transition horizons. There were no significant differences in pH at any depth, although the 37 soil profiles were consistent with chemical indicators of Spodosols by exhibiting increasing pH by depth (Table 2; Supplemental Fig. S1).

Table 1. Average top and bottom depths and color by sample year listed for each general horizon category (Oa, spodic, transition, and C). The bottom depth of the C horizon is the depth observed, not necessarily the bottom of the horizon. Average colors were calculated by converting Munsell colors to RGB color coordinates, calculating the mean, and converting back to Munsell color.

General horizon	*n*†	Year	Top	Bottom	Average color
			cm	cm	
Oa	25	2001–2002	3.9	9.9	10YR 2/1
		2014	3.6	9.2	7.5YR 2/1
Spodic	37	2001–2002	13.4	48.2	7.5YR 3/3
		2014	14.9	54.6	7.5YR 3/3
Transition	32	2001–2002	47.8	84.0	10YR 4/5
		2014	51.5	87.1	10YR 4/4
C	37	2001–2002	80.2	115.7	2.5Y 5/3
		2014	82.7	102.1	2.5Y 4/3

† *n*, number of plots with each general horizon category present in both sampling years.

Paired *t* tests on log-transformed cation concentrations found significant decreases in Al in Oa horizons and mean exchangeable Al was 1.5-fold higher in 2001–2002 than in 2014 within Oa horizons. Conversely, significant increases of Ca, K, and Mg occurred in the Oa horizon. Significant increases in Al occurred in spodic horizons and mean exchangeable Al was approximately 35% lower in 2001–2002 than in 2014 within spodic horizons. Significant increases in Al below the Oa horizons were not coupled with any detectable change in pH (Supplemental Fig. S2). Significant decreases in Ca, Mg, and Na concentrations were also detected in the spodic horizons. A significant increase of 27% in Al concentration was found in the transition horizons. Mean exchangeable Ca was approximately 1.6-fold higher in 2001–2002 than 2014 in the transition horizons. Finally, a significant increase in Al concentrations occurred in the C horizons. The non-parametric analyses yielded similar results and no difference in interpretation as the paired *t* tests.

Table 2. Average carbon (C) and nitrogen (N) concentration (g kg $^{-1}$), pH, and exchangeable cation concentration (cmol$_c$ kg^{-1}) for each general horizon category (Oa, spodic, transition, and C) by sampling year. Paired *t* tests were performed to determine differences between sample years. Significance testing was conducted on log-transformed cation concentrations when residuals did not meet normality.

General horizon	*n*	Year	C	N	pH	Al	Ca	K	Mg	Mn	Na
			g kg^{-1}			cmol$_c$ kg^{-1}					
Oa	25	2001–2002	**33.4a†**	**1.6a**	3.12	**5.00a**	**9.69a**	**0.75a**	**1.77a**	0.47	0.09
		2014	**42.6b*****	**2.0b*****	3.21	**3.47b***	**13.61b***	**1.07b***	**2.27b***	0.46	0.08
Spodic	37	2001–2002	5.4	270	3.67	**13.21a**	**0.45a**	0.08	**0.09a**	0.03	**0.03a**
		2014	5.3	290	3.77	**17.89b*****	**0.40b****	0.07	**0.08b****	0.02	**0.02b*****
Transition	32	2001–2002	**1.2a**	70	4.14	**6.92a**	**0.20a**	0.04	0.03	0.01	0.02
		2014	**1.0b****	60	4.22	**8.79b****	**0.12b****	0.03	0.02	0.00	0.02
C	37	2001–2002	0.6	30	4.30	**3.22a**	0.14	0.03	0.03	0.01	0.02
		2014	0.6	30	4.34	**6.67b*****	0.21	0.03	0.07	0.01	0.02

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.01 probability level.

† Significant differences between sample years are indicated in bold and different lowercase letters.

Table 3. Standard deviation of the concentrations of carbon (C), and exchangeable cations (Ca, K, Mg, Mn, and Na) from a single soil pit at each of the 37 plots sampled in 2014 ("All 2014"). Standard deviation calculated from the pooled variances of C, Ca, K, Mg, Mn, and Na from five soils pits at each of the six intensively sampled plots sampled in 2014 to 2015 ("Subset 2014–2015").

General horizon	Top†	Bottom†	C	Al	Ca	K	Mg	Mn	Na
	cm		g kg^{-1}	cmol$_c$ kg^{-1}					
Oa (All 2014)	3.6	9.2	0.06	1.54	0.90	0.59	0.59	1.26	0.30
Oa (Subset 2014–2015)	4.1	9.8	0.06	1.48	0.99	0.48	0.65	1.12	0.42
Spodic (All 2014)	14.9	54.6	0.03	0.39	1.20	0.67	0.93	0.97	0.45
Spodic (Subset 2014–2015)	15.8	53.1	0.03	0.45	1.05	0.76	0.97	1.17	0.53
Transition (All 2014)	51.5	87.1	0.01	0.40	1.14	0.77	1.14	0.75	0.60
Transition (Subset 2014–2015)	50.6	81.2	0.01	0.41	1.05	1.13	1.31	1.19	0.64

† Average top and bottom depths.

Within-Site Pooled Variance

We found that within-site variability was comparable to overall regional variability across the WMNF. Table 3 provides the standard deviation of concentrations of carbon (C), and exchangeable cations (Al, Ca, K, Mg, Mn, and Na) from 1 soil pit at each of the thirty-seven plots sampled in 2014 ("All 2014") as well as standard deviation calculated from the pooled variances from 5 soils pits at each of the 6 intensively sampled plots sampled in 2014 and 2015 ("Subset 2014–2015").

Overall, exchangeable Al concentrations exhibited the highest variance both at the within-plot scale and landscape-scale across general horizons compared to the other analytes. Figure 3 depicts the exchangeable Al concentrations in each general horizon category from all 2001–2002 and 2014 pits as well as from the six subset intensively sampled plots with one soil pit from 2001–2002 compared to five soil pits sampled in 2014 to 2015. Higher variance in Al was found across all 2014 plots in the Oa horizon then in the pooled variance from the subset of six intensively sampled plots. Conversely, higher variance in Ca was found in the six-subset plots intensively sampled in 2014–2015 then all 2014 plots in the Oa horizon. Lower variance in Al was found across all 2014 plots in the spodic and transition horizons then in the pooled variance from the six-subset plots intensively sampled in 2014–2015. However, higher variance in Ca was found across all 2014 plots in the spodic and transition horizons then in the pooled variance from the six-subset plots intensively sampled in 2014–2015.

The number of plots needed to detect significant change ($\alpha = 0.05$) and equal magnitude of observed change for overall significant differences was calculated using a power analysis. For example, 7 within-plot soil pits were required from both sampling periods to detect the same magnitude of significant change in C of the Oa horizons as was found across all 37 plots. The power analysis also showed 20 within-plot soil pits were required from both sampling years to detect both significant change and the observed magnitude of overall change found from all plots of Al in the spodic horizons. The results from this pooled variance approach showed that at least 27 plot-specific samples from both sampling years across all horizons are necessary to detect significant change of the same magnitude as the overall change in Al observed at the WMNF scale. Similarly, at least 28 soil pits at one plot are needed from both sampling years across all horizons to detect significant temporal change in Ca. However, for analytes with higher variances, including K, Mg, and Mn, more pits at both a site-specific and landscape scale would be required in subsequent sampling years to detect change.

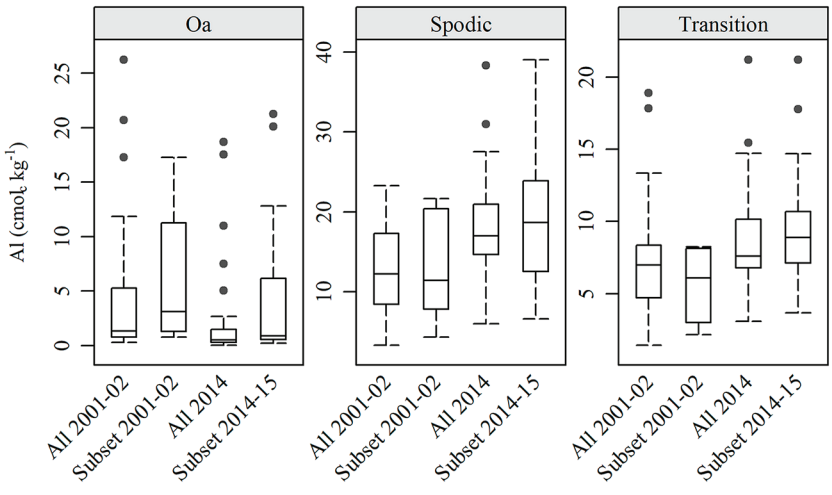

Fig. 3. Extractable Al concentrations (cmol$_c$ kg^{-1}) in each general horizon category from all 2001 to 2002 ("All 2001–02) and from 2014 ("All 2014") plots. In addition, Al from the six subset plots with one soil pit from 2001 to 2002 ("Subset 2001–02") at each location and five soil pits sampled in 2014 to 2015 at each location ("Subset 2014–15"). The Subset 2001–2002 values represents one soil pit at each of the six sites and Subset 2014–2015 values represent five total soil pits from each of the six sites. The box represents the 25th and 75th quantiles, the whiskers represent the 5th and 95th quantiles, the median is marked by a straight line, and outliers are indicated by a solid dot.

Stratification by Hydrologic Groups

The 2001–2002 and 2014 element concentration differences between sampling years for the 3 dominant hydrologic groups influencing soil development, including vertical, lateral, or bimodal were calculated using MANOVA. There were 22 plots designated as developed vertically, 9 developed laterally, and 6 developed bimodally. The MANOVA results within the Oa horizon were significantly different ($p < 0.002$) between groups with an F-value of 3.290 (Pillai-Bartlett test statistic). Only 25 sites had an Oa present from both sampling years in 2001 to 2002 and 2014; within those sites that had an Oa present, 18 of those sites were developed vertically,

4 sites were developed laterally, and 3 sites were identified as bimodal. Significant differences between groups in the Oa horizon were found in C (g kg^{-1}), Ca ($cmol_c$ kg^{-1}), and Na with F-values of 4.15, 2.70, and 15.6 respectively (Fig. 4). There were no significant differences in the Oa horizon of N, pH, Al, K, Mg, and Mn (F-value < 2.00).

Oa horizons at sites that developed laterally showed significant increases in exchangeable Ca by 3.5-fold from 2001–2002 to 2014. Oa horizons at sites that developed vertically or bimodally showed a mean increase of approximately 1.3-fold higher in 2014 than in 2001–2002 or stayed approximately the same, respectively. There were no significant differences of element concentrations in the other horizons (spodic, transition, and C) between hydrologic groups. Insignificant changes included increasing in Al and decreases in Ca in the spodic horizons at sites developed vertically, whereas Al in the spodic horizons decreased at sites developed laterally and Ca increased.

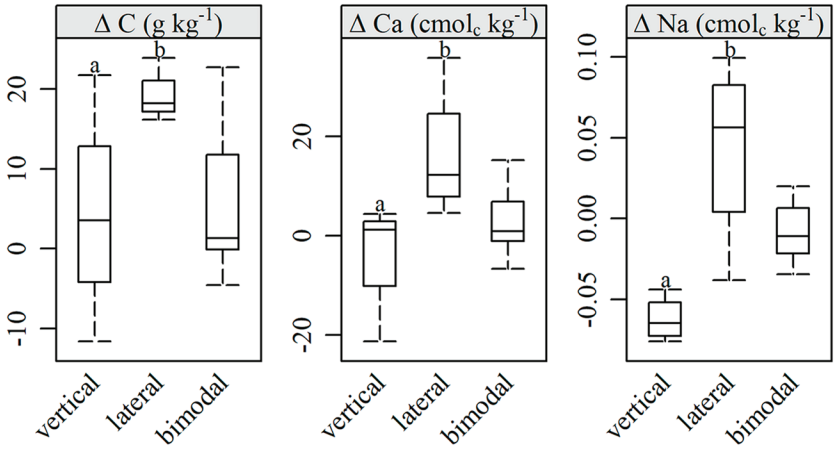

Fig. 4. Significant differences between 2001–2002 and 2014 for the Oa horizon in C (g kg^{-1}) and Ca, and Na concentrations ($cmol_c$ kg^{-1}) by hydrologic group. Groups represent the dominant hydrologic flowpaths influencing soil development, including vertical, lateral, or bimodal.

An ANOVA power analysis was completed to determine how many sites per hydrologic group were necessary for significant ($\alpha = 0.05$) difference detection. For example, 14 was the smallest sample size per hydrologic group at the landscape-scale needed to detect significant change of C, Al, Ca, and Na in the Oa horizon. However, 20 was the smallest sample size per hydrologic group at the landscape-scale needed to detect a significant change of C, Al, Ca, and Na in the spodic and transition horizons. Sample sizes per dominant hydrologic group in the Oa horizon ranged from 14 to 36, with the fewest for Al, Ca, and Mg, and the most pH, Mn, and Na. Selecting the element with the largest sample size will enable detection of differences for the other elements.

DISCUSSION

Study Design Options for Maximizing Temporal-Change Detection

Differences between observers resampling a site as well as spatial variation in soils are common obstacles in detecting temporal change in soil chemistry (Lawrence et al., 2013). For example, sampling the Oa horizon deeper into the mineral horizon one sampling year than another sampling period can result in lower concentrations of C, as observed in 2001–2002 from this study. In addition, differences in the presence and thickness of genetic horizons, caused by small scale spatial variation, can inhibit detection of soil change over time. Therefore, ensuring sampling consistency, particularly depth, as well as methods for comparing differing horizon sequences are essential for comparing measurements between time periods. Previous soil resampling studies have implemented various protocols to ensure consistency. For example, Bailey et al. (2005) used a combined Oa/A and the horizon sample straddling-specific depths, for example, the 50- and 100-cm depths for comparing two sampling periods. Bedison and Johnson (2010) pooled previous sampling measures into appropriate depth intervals based on the most recent sampling intervals. Our study also leveraged a pooled horizon approach by aggregating subhorizons into a general genetic horizon category. Any differences in horizon depths or colors that might have occurred between sampling years were not great enough to be detected with the study methods. Spatial variability in these measures can be much greater than expected from temporal changes over a decade, results suggested that sampling was done consistently to minimize those effects and that spatial variability was well addressed with these methods.

Another challenge in this study arose from the paired resampling design, which could not account for within-plot variability from one soil pit per site over two sampling time periods. It is often anticipated that magnitude of soil variability increases with the size of the study area. However, we found that within-site variability was comparable to overall regional variability across the WMNF. The pooled variance approach to estimate the magnitude of change necessary to detect plot-specific change equal to overall significant change loses site-specific information about within site variability, but provides a more reliable estimate of the change over time at the WMNF scale. Therefore, our study suggests the magnitude of change across the WMNF was greater than potential differences between observers, sampling depth, and within-plot spatial variability. Confining the boundaries of this study based on physiographic characteristics was important for limiting spatial variability and likely more difficult to address beyond the White Mountain region.

Temporal Change on the WMNF Compared with Other Studies

Declines in acidic deposition across Europe and North America (Lehmann et al., 2005; Greaver et al., 2012) have led to signs of chemical recovery of soils from acidification (Lawrence et al., 2015; Berger et al., 2016). Lawrence et al. (2012) also reported significant Al decreases in the Oa horizon at two sites on the WMNF where red spruce was a major species in the canopy, and a significant Ca decrease in upper B horizon at one of the two sites. In addition, Lawrence et al. (2015) reported overall

decreases of exchangeable Al in the O horizon as early indications of recovery while decreases in base saturation of mineral horizons continued at some sites. Changes in Al and Ca within the deeper parts of the profile (transition and C horizon) have not been previously reported since past research commonly focused on O and upper B horizons. The overall decrease in Al and increase in Ca within the Oa horizons across the WMNF are consistent with indications of recovery, but were coupled with continued acidification in the spodic and transition horizons as indicated by increases in exchangeable Al concentrations in deeper portions of the soil profile.

The results from this study indicate vertical mobilization of exchangeable Al from the upper forest floor into the rooting zone of trees which has long-term implications on forest health. Recovery from acid deposition in soil chemistry would be expected to result in decreases in Al and increases in Ca of the mineral horizons. Subsequent sampling periods, as this study continues at an approximately decadal resampling scale into the future, may reveal a longer term temporal trajectory of increased Al and mobilization deeper into the soil profile and perhaps an eventual decrease as excess Al accumulated over the acid deposition period is flushed from the soil system. It is unlikely the observed decadal change is caused by natural soil development since podzolization occurs over a much larger time-scale. The significant results in the Oa horizon from soil resampling are more consistent with reports suggesting indications of recovery.

Hydrologic Gradients for Stratifying Soil Monitoring

Partitioning sample sites by the dominant hydrologic pathway influencing soil formation may help reduce landscape-scale soil chemistry heterogeneity and potentially increase sensitivity of change detection associated with specific horizons. Sites developed by vertical hydrologic flow were more susceptible to leaching processes as buffering from atmospheric deposition and mineral weathering is more limited. Sites developed by lateral hydrologic regimes were less susceptible to depletion processes and potentially more responsive to recovery processes from the influence of shallow groundwater and solute inputs from upslope. Significant differences by dominant hydrologic pathways in the Oa horizons suggests high turnover may contribute to faster rates of detectable change whereas the rates of detectable change in deeper portions of soil profiles may be slower. Hazlett et al. (2011) also discussed the effect of topographic position on detectable soil chemical changes and found increases in base cation concentrations in upper mineral soil horizons for plots in poorly drained convergent topographic locations.

In addition, our ability to identify the areal extent and topographic features commonly associated with different hydrologic influences on soil formation has greatly improved and was not considered when the sites in this study were originally established. However, the uneven number of sites for this study within each hydrologic group could influence detection between groups in the spodic, transition, or C horizons. Most of the plots in this study were developed vertically which could contribute to the overall regional detection of significant Al change in the Oa horizons. Whereas the 9 plots developed laterally are contributing to the overall Al distribution within the spodic and transition horizons. An even number of sites within each hydrologic group could be selected in future studies by delineating the areal extent of the dominant hydrologic patterns influencing soil formation for initial design stratification. In regions where hydrologic gradients occur across the landscape, we recommend this method of stratification to help identify sites more susceptible to change. For example, in this study, the WMNF could continue resampling the 37 permanent plots, intensively sample the 6 subset plots, and consider intensively sampling more plots that were developed laterally or bimodally.

CONCLUSION

A rapidly changing environment has highlighted the need for more effective and site-specific soil monitoring over short time scales. This regional soil monitoring approach investigated a paired-resampling design by general genetic horizon groups to detect significant decadal change in soil chemistry within the same general soil and forest type. The monitoring design was created for the WMNF to establish a long-term understanding of how soil chemistry is changing at a landscape scale and to inform soil quality standards. The results from this study highlight how within-site variability is equal to the landscape-scale of Spodosols in northern hardwood forests. Finally, it is important to incorporate landscape–soil–water dynamics when characterizing change by the dominant processes of soil formation and horizonation because groundwater influenced soils were more responsive to recovery processes in the Oa horizons compared to soils developed vertically via unsaturated flow.

From a forest management perspective, an ecosystem's response to changes in soil properties provides the context to determine how potential soil property changes may affect ecosystem composition, processes and function. This serves as the basis for national forests and other forest land managers to determine whether a response to a management activity is moving the ecosystem toward or away from a desired condition. This approach to estimate the variance components simultaneously at the landscape scale, and at the within-plot or micro-scale is crucial for calculating sample size and increases our technical understanding of how management or external forcings such as air pollution or climate change may alter soil over time.

SUPPLEMENTAL MATERIAL

Supplemental material is available with the online version of this article. The supplement contains Table S1, Plot location names, ID, elevation, aspect, plan curvature, slope, dominant hydrological pathway influencing soil formation, slope position, and landform element; Fig. S1, pH vertical distributions by depth for 39 sites; and Fig. S2, Exchangeable Al vertical distributions by depth for 39 sites.

ACKNOWLEDGMENTS

We thank the White Mountain National Forest (WMNF) and Robert A. Colter, WMNF Soil Scientist, for sponsoring this project. We also thank Stephen Fay, WMNF Soil Scientist, for co-establishing the

permanent plots, Jeff Merriam, USFS, Durham, NH for soil analysis, and Emily Piché for assisting with fieldwork.

REFERENCES

Bailey, S.W., P.A. Brousseau, K.J. McGuire, and D.S. Ross. 2014. Influence of landscape position and transient water table on soil development and carbon distribution in a steep, headwater catchment. Geoderma 226-227:279–289. doi:10.1016/j.geoderma.2014.02.017

Bailey, S.W., S.B. Horsley, and R.P. Long. 2005. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. Soil Sci. Soc. Am. J. 69:681–690. doi:10.2136/sssaj2004.0057

Beaudette, D.E., P. Roudier, and A.T. O'Geen. 2013. Algorithms for quantitative pedology: A toolkit for soil scientists. Comput. Geosci. 52:258–268. doi:10.1016/j.cageo.2012.10.020

Bedison, J.E., and A.H. Johnson. 2010. Seventy-four years of calcium loss from forest soils of the Adirondack Mountains, New York. Soil Sci. Soc. Am. J. 74:2187–2195. doi:10.2136/sssaj2009.0367

Berger, T.W., S. Türtscher, P. Berger, and L. Lindebner. 2016. A slight recovery of soils from Acid Rain over the last three decades is not reflected in the macro nutrition of beech (*Fagus sylvatica*) at 97 forest stands of the Vienna Woods. Environ. Pollut. 216:624–635. doi:10.1016/j.envpol.2016.06.024

Blume, L.J. 1990. Handbook of methods for acid deposition studies: Laboratory analyses for soil chemistry. USEPA, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Bourgault, R.R., D.S. Ross, and S.W. Bailey. 2015. Chemical and morphological distinctions between vertical and lateral podzolization at Hubbard Brook. Soil Sci. Soc. Am. J. 79:428–439. doi:10.2136/sssaj2014.05.0190

Clarholm, M., and U. Skyllberg. 2013. Translocation of metals by trees and fungi regulates pH, soil organic matter turnover and nitrogen availability in acidic forest soils. Soil Biol. Biochem. 63:142–153. doi:10.1016/j.soilbio.2013.03.019

Conant, R.T., G.R. Smith, and K. Paustian. 2003. Spatial variability of soil carbon in forested and cultivated sites. J. Environ. Qual. 32:278–286. doi:10.2134/jeq2003.2780

Cronan, C.S., and D.F. Grigal. 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. J. Environ. Qual. 24:209–226. doi:10.2134/jeq1995.00472425002400020002x

De Coninck, F. 1980. Major mechanisms in formation of spodic horizons. Geoderma 24:101–128. doi:10.1016/0016-7061(80)90038-5

Driscoll, C.T., G.B. Lawrence, A.J. Bulger, T.J. Butler, C.S. Cronan, et al. 2001. Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. The effects of acidic deposition in the northeastern United States include the acidification of soil and water, which stresses terrestrial and aquatic biota. Bioscience 51:180–198. doi:10.1641/0006-3568(2001)051[0180:ADITNU]2.0.CO;2

Federer, C.A., J.W. Hornbeck, L.M. Tritton, C.W. Martin, R.S. Pierce, et al. 1989. Long-term depletion of calcium and other nutrients in eastern US forests. Environ. Manage. 13:593–601. doi:10.1007/BF01874965

Federer, C.A., D.E. Turcotte, and C.T. Smith. 1993. The organic fraction–bulk density relationship and the expression of nutrient content in forest soils. Can. J. For. Res. 23:1026–1032. doi:10.1139/x93-131

Gannon, J.P., S.W. Bailey, and K.J. McGuire. 2014. Organizing groundwater regimes and response thresholds by soils: A framework for understanding runoff generation in a headwater catchment. Water Resour. Res. 50:8403–8419. doi:10.1002/2014WR015498

Greaver, T.L., T.J. Sullivan, J.D. Herrick, M.C. Barber, J.S. Baron, et al. 2012. Ecological effects of nitrogen and sulfur air pollution in the US: What do we know? Front. Ecol. Environ. 10:365–372. doi:10.1890/110049

Hazlett, P.W., J.M. Curry, and T.P. Weldon. 2011. Assessing decadal change in mineral soil cation chemistry at the Turkey Lakes Watershed. Soil Sci. Soc. Am. J. 75:287–305. doi:10.2136/sssaj2010.0090

Johnson, C.E., A.H. Johnson, and T.G. Huntington. 1990. Sample size requirements for the determination of changes in soil nutrient pools. Soil Sci. 150:637. doi:10.1097/00010694-199009000-00010

Lawrence, G.B., I.J. Fernandez, D.D. Richter, D.S. Ross, P.W. Hazlett, et al. 2013. Measuring environmental change in forest ecosystems by repeated soil sampling: A North American perspective. J. Environ. Qual. 42:623–639. doi:10.2134/jeq2012.0378

Lawrence, G.B., P.W. Hazlett, I.J. Fernandez, R. Ouimet, S.W. Bailey, et al. 2015. Declining acidic deposition begins reversal of forest-soil acidification in the northeastern US and eastern Canada. Environ. Sci. Technol. 49:13103–13111. doi:10.1021/acs.est.5b02904

Lawrence, G.B., W.C. Shortle, M.B. David, K.T. Smith, R.A.F. Warby, et al. 2012. Early indications of soil recovery from acidic deposition in US red spruce forests. Soil Sci. Soc. Am. J. 76:1407–1417. doi:10.2136/sssaj2011.0415

Lehmann, C.M.B., V.C. Bowersox, and S.M. Larson. 2005. Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. Environ. Pollut. 135:347–361. doi:10.1016/j.envpol.2004.11.016

Likens, G.E. 2013. Biogeochemistry of a forested ecosystem. Springer Science & Business Media, Berlin. doi:10.1007/978-1-4614-7810-2

Lundström, U.S., N. van Breemen, and D. Bain. 2000. The podzolization process. A review. Geoderma 94:91–107. doi:10.1016/S0016-7061(99)00036-1

Mäkipää, R., M. Häkkinen, P. Muukkonen, and M. Peltoniemi. 2008. The costs of monitoring changes in forest soil carbon stocks. Boreal Environ. Res. 13:11.

Mangold, R. 2000. Overview of the forest health monitoring program. In: M. Hansen, and T. Burk, editors, Integrated tools for natural resources inventories of the 21st century. Rep. NC-212. USDA Forest Service, North Central Forest Experimental Station, St. Paul, MN. p. 129–140. https://www.fs.usda.gov/treesearch/pubs/15807 (accessed 5 Aug. 2018).

McNab, W.H., and P.E. Avers. 1994. Ecological subregions of the United States: Section descriptions. Admin Publ WO-WSA-5. US Forest Service, Washington, DC.

Muukkonen, P., M. Häkkinen, and R. Mäkipää. 2009. Spatial variation in soil carbon in the organic layer of managed boreal forest soil—implications for sampling design. Environ. Monit. Assess. 158:67–76. doi:10.1007/s10661-008-0565-2

National Forest Management Act (NFMA). 1976. National Forest Management Act of 1976. NFMA, Washington, DC. https://www.fs.fed.us/emc/nfma/includes/NFMA1976.pdf (accessed 20 May 2018).

Neary, D.G., C.C. Trettin, and D. Page-Dumroese. 2010. Soil quality monitoring: Examples of existing protocols. In: D. Page-Dumroese, D. Neary, and C. Trettin, editors, Science background soil monitoring- Natl. For. Rangel. Workshop Proc. 29-30 Apr. 2008. Denver, CO. USDA Forest Service, Rocky Mountain Research Station, Fort Collins, CO. p. 61–82.

R Development Core Team. 2018. R: A language and environment for statistical computing. Version 3.5.1. R Foundation for Statistical Computing, Vienna.

Richter, D.D., and D. Markewitz. 2001. Understanding soil change: Soil sustainability over millennia, centuries, and decades. Cambridge Univ. Press, Cambridge Univ., UK.

Robarge, W.P., and I.J. Fernandez. 1987. Quality assurance methods manual for laboratory analytical techniques. US Environmental Protection Agency, USDA Forest Service, Washington, DC.

Ross, D.S., S.W. Bailey, R.D. Briggs, J. Curry, I.J. Fernandez, et al. 2015. Inter-laboratory variation in the chemical analysis of acidic forest soil reference samples from eastern North America. Ecosphere 6:1–22. doi:10.1890/ES14-00209.1

Schoeneberger, P.J. 2012. Field book for describing and sampling soils. NRCS National Soil Survey Center, Lincoln, NE.

Schoenholtz, S.H., H.V. Miegroet, and J.A. Burger. 2000. A review of chemical and physical properties as indicators of forest soil quality: Challenges and opportunities. For. Ecol. Manage. 138:335–356. doi:10.1016/S0378-1127(00)00423-0

Sommer, M. 2006. Influence of soil pattern on matter transport in and from terrestrial biogeosystems—A new concept for landscape pedology. Geoderma 133:107–123. doi:10.1016/j.geoderma.2006.03.040

Sommer, M., D. Halm, U. Weller, M. Zarei, and K. Stahr. 2000. Lateral podzolization in a granite landscape. Soil Sci. Soc. Am. J. 64:1434–1442. doi:10.2136/sssaj2000.6441434x

US Forest Service. 2005. White Mountain National Forest: Land and resource management plan. US Forest Service, Washington, DC. http://www.fs.fed.us/r9/forests/white mountain/ (accessed 20 May 2018).

US Forest Service. 2018. Natural resource manager. US Forest Service, Washington, DC. https://www.fs.fed.us/nrm/ (accessed 20 May 2018).

Warby, R.A.F., C.E. Johnson, and C.T. Driscoll. 2009. Continuing acidification of organic soils across the northeastern USA: 1984–2001. Soil Sci. Soc. Am. J. 73:274–284. doi:10.2136/sssaj2007.0016

Yanai, R.D., T.G. Siccama, M.A. Arthur, C.A. Federer, and A.J. Friedland. 1999. Accumulation and depletion of base cations in forest floors in the northeastern United States. Ecology 80:2774–2787. doi:10.1890/0012-9658(1999)080[2774:AADOBC]2.0.CO;2