# Chemical properties of upland forest soils in the Catskills region

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**Abstract**

The Catskills forest provides a valuable array of ecosystem services for local and regional populations, including the provision of forest products, wildlife habitats and high-quality water. These services depend on chemical and biological processes that occur in forest soils. In 2011 we sampled soils in 25 headwater catchments in the Catskills region to quantify the pools of soil nutrients and examine the variation in soil properties in the region. The average soil depth in the 50 excavated pits was 56.6 cm. Average soil mass was 205 kg m$^{-2}$. The pools of soil C and N averaged 58.5 and 3.95 Mg ha$^{-1}$, respectively. The thin organic horizons accounted for less than 1% of soil mass, but included 14% of the soil C and 11% of soil N. Catskills forest soils are highly acidic, with mean pH ranging between 3.9 and 4.75. Base saturation was high (>60%) in organic horizons and low (12-31%) in mineral soils. The pool of exchangeable Ca is approximately equivalent to 20 years of Ca export from headwater streams, raising concerns regarding the ability of these catchments to maintain current stream Ca concentrations. The data and samples collected in this study provide a baseline for future soil monitoring in the region.

**Introduction**

Soils provide a wide range of ecosystem services that benefit communities, individuals and the environment. In the Catskills region of New York, forest soils provide key provisioning services including timber production and the maintenance of excellent water quality. Indeed, the region is the principal watershed area for New York City and soil processes maintain the purity of a billion gallon per day water supply which at present does not require filtration prior to human consumption.[1] This high level of service persisted despite high inputs of acid deposition in the second half of the 20th century.[2] In recent years, inputs of nitric and especially sulfuric acid have declined throughout the northeastern United States as a result of provisions in the Clean Air Act Amendments of 1990.[3,4] The response of soils and surface waters to these decreased acid inputs has been complex, yet is crucial to the sustainability of water quality and forest production in the region.

A number of investigators have documented decreases in sulfate concentrations and increases in pH and acid neutralizing capacity (ANC) in Catskills streams in response to declining acid precipitation.[5,6] However, the magnitude of the pH and ANC increases has not matched the magnitude of the decline in acid inputs. This sluggish recovery of surface water acid-base status has been observed throughout the northeastern United States and has been attributed decreases in stream Ca concentrations.[5-7] Decreased stream Ca has, in turn, been attributed to decreased Ca deposition and declines in available Ca in soils.[8,9]

Recent decreases in soil exchangeable Ca have been observed in several studies in forest soils of the region. Bailey *et al.* reported a decrease of more than 75% in mean exchangeable Ca concentrations in Oa and A horizon soils between 1967 and 1997 on the Allegheny Plateau in Pennsylvania.[10] Warby *et al.* found significant decreases in exchangeable Ca in O horizon soils

between 1984 and 2001 across the northeastern U.S., from the Pocono Mountain region of Pennsylvania to northern Maine.[11] Johnson *et al.* observed significant decreases in extractable Ca between the 1930s and 1984 in sites across the Adirondack Mountain region, decreases which continued through 2004 in a follow-up study.[12,13] These studies also found significant increases in exchangeable acidity, Al in particular. Therefore, the observation of decreasing soil Ca between the mid-1980s and 2000s indicates that forest soils of the region have continued to acidify during a period of sharp decreases in acid inputs.[4,14]

If forest soils in the northeastern United States continue to acidify despite further reductions in acid deposition, there may be long-term impacts on forest health and/or water quality in the region. Furthermore, climate change may impact soil chemistry through changes in rates of organic matter decomposition, soil moisture and soil carbon storage. Considering the importance of the Catskills region to regional water supply, there is a clear need to study and monitor soil quality over time. The objective of this research was to create a baseline data set on forest soil chemistry in the Catskills for future researchers to document changes in soil chemistry. Soil samples from across the region were analyzed for a variety of chemical properties and are archived and available for future use. This paper includes sampling and analytical information, summary data, and discusses the nutrient content and acid-base chemistry of these soils.

**Methods**

*Site Selection and Sampling*

Soil samples were collected from fifty forested upland sites in the Catskills (Fig. 1). The region is an uplifted plateau of Devonian age. Erosion and glaciation have produced a series of

narrow valleys, with the surrounding "mountains" comprised of generally undeformed bedrock layers in stratigraphic sequence.[15] The sites chosen for soil sampling all lie in areas underlain by the three uppermost bedrock units – the Oneonta, Walton and Slide Mountain formations (Fig. 1). All of these units are comprised of mixed sandstones and conglomerates, with some mudstones and shales in the Oneonta and Walton formations. Soils in the region have developed in glacial till of largely local origin, with till depth ranging from zero on ridge-tops to tens of meters in the valleys.[16] Soil texture varies considerably, but most Catskill soils are rocky, sandy loams, with about 10% clay, 25% silt and 65% sand.[16] Most are classified as Inceptisols, with Lithic and Typic Dystrochrepts, and Typic and Aquic Fragiochrepts being the most dominant groups.

Twenty-five headwater catchments were selected from among those studied by Gary Lovett in his work on watershed nitrogen cycling.[17] The watersheds were selected to represent upland catchments with perennial streams and little or no residential or commercial development. In each catchment two sampling locations were selected – one within 250 m of the stream sampling site used by Lovett and another at an elevation approximately half-way between the elevation at the stream sampling site and the elevation at the watershed divide. All of the soil sampling sites were located on New York State land. Specific locations were selected to represent a diverse array of forest types,[18] and to take advantage of access by hiking trails where possible. Soil sampling was conducted in May-July, 2011. The sampling locations were adjusted by as much as 10 meters in the field if the chosen site was exposed bedrock or at the edge or base of a cliff face. The locations of the sites may be found in Appendix I.

At each sampling location one soil pit was excavated using the quantitative approach described in Vadeboncoeur *et al.*[19] A square 0.61 x 0.61 m frame was placed on the ground and

secured using rebar. Soil was removed from within the frame in the following layers: Oi+Oe horizons together as a single sample; Oa and/or A horizon, if present; 0-10 cm mineral soil layer; 10-20 cm layer; and 20 cm to bedrock or C horizon. The distance from the plane of the frame to the soil surface was measured in the center of 16 grid cells before excavation and after every layer. Average layer thicknesses were computed using these values. The Oi+Oe and Oa/A samples were bagged in their entirety and returned to the lab. The mineral soil layers were screened in the field using a 12-mm screen. All excavated materials – passing and not passing the screen – were weighed in the field using a portable dairy scale. A subsample of the screened material was bagged and returned to the lab. In the lab, the samples were air-dried to constant weight and sieved using a 5-mm (Oi+Oe and Oa/A samples) or 2-mm (mineral soil samples) stainless-steel screen. A subsample of the material passing the final screen was oven-dried at 85 ºC. The various weights and moisture conversions were then used to compute the mass of oven-dry soil per square meter of land surface area in each layer. The volume occupied by stones in each layer was computed by dividing the mass of material that was greater than 2-mm by an average rock density of 2.4 g cm$^{-3}$. Bulk density was then computed by dividing the mass of soil by the excavated volume less the rock volume.

The dried and sieved soil samples are stored in glass jars for long-term preservation. The jars are currently stored at Syracuse University, with the goal of entering them into the collection at the New York State Museum, where they would be accessible to all researchers.

*Sample Analysis*

Organic matter content of each sample was estimated by loss-on-ignition, which was measured at 500 ºC overnight in a muffle furnace. Soil carbon and nitrogen were measured by combustion-gas chromatography using a Costech ECS 4010 elemental analyzer. Results were

deemed acceptable if verification samples (atropine, included every 10-15 samples) were within 10% of their known concentrations.

Soil pH was measured in deionized water ($pH_w$) and 0.01 M $CaCl_2$ ($pH_s$). The soil:solution ratio was 1 g soil to 1 g solution for mineral soils and 1 g soil to 5 g solution for Oi+Oe and Oa/A samples. The $CaCl_2$ suspensions were allowed to equilibrate for 30 minutes prior to analysis, with occasional stirring. The $pH_s$ in acid soils is generally lower than $pH_w$ because $Ca^{2+}$ displaces acidic cations (primarily $H^+$ and $Al^{3+}$) from exchange sites. Although this paper focuses on the $pH_w$, $pH_s$ data are given as well for researchers who prefer that measure. Exchangeable Ca, Mg, K and Na were determined on 1M $NH_4Cl$ extracts. The extractions were performed overnight (12 hr) on a mechanical vacuum extractor using a target soil:solution ratio of 1:20. The concentrations of the basic cations ($C_B$: Ca, Mg, K and Na) in the extract solutions were measured using inductively coupled plasma emission spectroscopy (ICP-OES). Exchangeable acidity was determined by titration of 1M KCl extracts to the phenolphthalein end-point using NaOH. The soil:solution ratio for these extractions was also 1:20. Exchangeable Al was calculated from the concentrations of Al in the KCl extracts, measured by ICP-OES. Exchangeable H was estimated as the difference between exchangeable acidity and exchangeable Al and assumed to be zero in the few cases where exchangeable Al was greater than exchangeable acidity. Effective cation exchange capacity ($CEC_e$) was computed by summing exchangeable acidity and exchangeable $C_B$, expressed in equivalent units ($cmol_c$ $kg^{-1}$). Effective base saturation was calculated as the percentage of $CEC_e$ that was satisfied by exchangeable $C_B$.

Total acidity was measured using the $BaCl_2$-TEA method.[20] This method extracts acidic cations using a 0.5 M $BaCl_2$ solution buffered at pH 8.2 by 0.2 M triethanolamine. Copper

chloride (0.5M; soil:solution = 1 g : 10 ml) was used to extract exchangeable + organically bound Al.[21] The Al concentrations in the extracts were measured by ICP-OES.

From this suite of measurements, the following derived quantities were calculated:

Total CEC = $CEC_T$ = Total Acidity + Exchangeable $C_B$            [1]

Organically Bound Al = $Al_{org}$ = $Al_{CuCl_2}$ - $Al_{KCl}$            [2]

Organically Bound H = $H_{org}$ = Total Acidity – Exchangeable Acidity – $Al_{org}$      [3]

## Results

*Soil Mass and Thickness*

The mean soil depth to bedrock or C horizon at the 50 sites ranged from 21.7 to 100.9 cm, and averaged 56.6 cm (Table 1), while the mass of soil ranged from 41 to 660 kg m$^{-2}$, with an average of 205 kg m$^{-2}$. Soil depth was approximately normally distributed, whereas soil mass was less so (Fig. 2). Soils in the region are very stony, with stones occupying an average of 25-27% of the soil volume in mineral horizons (Table 1). Stone content was fairly uniform throughout the profile. Mineral soils had low bulk density, ranging from 0.44 Mg m$^{-3}$ in the 0-10 cm layer to 0.65 Mg m$^{-3}$ in the 10-20 cm layer (Table 1), suggestive of high water permeability.

Organic horizons accounted for a small fraction of soil depth and mass. All 50 sites had an Oi+Oe layer, which averaged 1.37 kg m$^{-2}$ (Table 1). However, only 22 of the 50 sites had an identifiable Oa or A horizon, and only 10 of those sites had Oa/A horizons with a mass of 1.0 kg m$^{-2}$ or more. On average, the O horizons accounted for 3.0 cm of the total soil depth of 56.6 cm, and less than 1% of the total soil mass (Table 1).

*Soil Organic Matter*

Upland forest soils in the Catskills contain large amounts of organic matter (OM), even in lower mineral-soil horizons. The concentration of organic matter declined steadily from 891 g kg$^{-1}$ (89% by mass) in the Oi+Oe layer to 64.3 g kg$^{-1}$ (6.4%) in mineral soils below 20 cm (Table 2). Carbon and nitrogen followed the same depth pattern. The average C:N ratio declined from 19.8 in the Oi+Oe layer to 13.4 in the lower mineral soil, while the mean C:OM ratio declined from 0.53 to 0.37.

Although O and A horizons accounted for less than 1% of the total soil mass (Table 1), they contained 10% of the total OM, 14% of the total C, and 11% of the total N in the soil (Table 2). Nevertheless, most of the OM, C and N in these soils lies in mineral horizons. Indeed, 43% of the OM, 38% of the C, and 40% of the N was in mineral soils below 20 cm depth.

*Exchangeable Cations and Soil Acidity*

The forest soils at the 50 sites in this study were acidic, with mean pH$_w$ values ranging from 4.75 in the Oi+Oe layer to 3.89 in the top 10 cm of the mineral soil (Fig. 3a). Soils were uniformly acidic – the highest pH$_w$ recorded in any sample was 5.79 and the standard errors were small for all layers. Even the C horizon, which represents the parent material in which the mineral horizons were formed, had an average pH$_w$ of only 4.52.

The effective cation exchange capacity (CEC$_e$) was greatest in the O horizons and decreased sharply with depth in the mineral soil (Fig. 3e). This pattern mimicked the pattern for soil C and OM concentration (Table 2), resulting in significant ($P < 0.05$) correlations between CEC$_e$ and soil C in both mineral and organic soil layers (Fig. 4). Calcium was the dominant exchangeable cation in organic layers (Oi+Oe and Oa/A horizons), whereas Al was the dominant exchangeable cation in mineral soils (Fig. 3b,c). In all horizons, Ca was the dominant base

cation, typically accounting for about ¾ of the total base cation charge. Consequently, base saturation followed a depth pattern similar to the one exhibited by exchangeable Ca (Fig. 3f). Base saturation exceeded 60% in 48 of the 50 Oi+Oe layers and 17 of the 22 Oa/A layers, while mean base saturation levels in mineral soils were 30% or less (Fig. 3f).

Exchangeable acidity is predominantly in the form of exchangeable H in O and A horizons. Exchangeable H concentrations in the Oi+Oe and Oa/A horizons averaged 4.81 and 3.43 $cmol_c$ $kg^{-1}$, respectively, exceeding exchangeable Al, which averaged 0.37 and 1.85 $cmol_c$ $kg^{-1}$ in the same horizons (Fig. 3c,d). In the mineral soil, however, exchangeable Al was the dominant form of soil acidity. For example, in the layer below 20 cm, the mean exchangeable Al concentration was 5.37 $cmol_c$ $kg^{-1}$, more than five times the exchangeable H mean of 0.99 $cmol_c$ $kg^{-1}$ (Fig. 3c,d).

The pools of exchangeable cations in the soil were computed by multiplying the concentrations by the corresponding soil masses (Table 3). Of particular interest are the pools of exchangeable base cations, due to concerns about long-term depletion of Ca resulting from chronic acidification.[10,11,22] Upland forest soils in the Catskills contain an average of 403 kg $ha^{-1}$ of exchangeable Ca (Table 3). Exchangeable Ca in the Oi+Oe and Oa/A horizons accounted 19% of this pool despite very small soil mass. Similarly, organic layers contained 17% and 19% of the exchangeable Mg and K pools, respectively (Table 3). In contrast, more than 99% of the exchangeable Al was found in the mineral soil.

In all layers, $H_{org}$ accounted for the largest fraction of $CEC_t$ (Figure 5). Typically, $H_{org}$ was 50-70% of $CEC_t$, while $Al_{org}$ only comprised 2-10% of $CEC_t$. Because of the large amount of bound H the $CEC_e$ only represented 20-35% of the $CEC_t$ (Fig. 5). Despite very high effective base saturations in the organic layers (Table 3), base cations only represented 30% of $CEC_t$ in the

Oi+Oe layer and 17% of $CEC_t$ in the Oa/A horizons (Fig. 5). These percentages declined further in the mineral-soil layers, where $CEC_t$ was dominated by exchangeable acidity, $H_{org}$ and $Al_{org}$.

**Discussion**

*Soil Mass, Organic Matter and Carbon Pools*

Soils in the Catskills region are largely derived from residuum from the withdrawal of the Laurentide ice sheet in the Wisconsinan period, approximately 10,000-14,000 years ago. Where the till is shallow (less than 1m), soil profiles often lie directly on bedrock. Where the till is deep, the biologically active soil zone ends at a C horizon. On average, depth to bedrock or C horizon in the 50 pits in this study was 56.6 cm (Table 1). This average soil depth is similar to other glaciated sites in the northeastern USA. For example, mean depth to C horizon or bedrock in 119 pits excavated at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire was 59 cm,[23] while mean soil depth ranged from 40.5 cm to 92.9 cm at sites across the White Mountains.[19] The soil mass reported here (205 g m$^{-2}$; Table 1) is on the lower end of the range reported for glaciated sites in New England and Pennsylvania.[19] This low soil mass was related to the high stone content (25-27% by volume) and low bulk density (0.4-0.7 Mg m$^{-3}$) of the Catskills soils. The low bulk densities we measured for Catskills mineral soils are partly the result of frequent voids in the soil profile, especially in the most rocky sites. Also, we may have underestimated rock volumes slightly by using a stone density of 2.4 g cm$^{-3}$.

The average mass of organic horizons (Oi+Oe and Oa/A) was 1.81 kg m$^{-2}$, about 1% of the total soil mass (Table 1). These values are lower than other reported masses for the Catskills and the Pocono region of Pennsylvania. The average O-horizon mass ranged from 12 to 20 kg m$^{-2}$ at four sites sampled in the early 1990s in the Pocono Barrens.[24] A study conducted in the

Catskills in 2000-2003 reported average O-horizon masses of 6 to 10 kg m$^{-2}$.[25] The most likely explanation for the differences in our results is a difference in sampling. The boundary between the O horizon and mineral horizons is difficult to detect in the field, especially in soils that have a surface A horizon,[26] as nearly all of the sites in this study did. The mean C concentration in the 0-10 cm layer (63.7 g kg$^{-1}$; Table 2) was greater than the mean C concentration in surface mineral horizons from the same 2000-2003 Catskills study (54.4 g kg$^{-1}$; G. Lovett, personal communication), suggesting that our 0-10 cm layers may have contained some material that was included in the Oa/A horizons collected by Lovett et al.[25]

The organic matter (OM) concentration declined downward in the soil profile, from an average of 891 g kg$^{-1}$ in the Oi+Oe horizon to 64.3 g kg$^{-1}$ in the mineral soil below 20 cm (Table 2). Carbon and nitrogen concentrations followed the same pattern, though there were significant changes in C:OM and C:N ratios with depth. The mean C:OM ratio declined from 0.53 in the Oi+Oe horizon to 0.37 in the mineral soil below 20 cm (Table 2). Carbon and oxygen together account for most of the mass of natural organic matter.[27] Therefore, the decline in the C:OM ratio with depth suggests that the oxygen concentration in organic matter in Catskills forest soils increases substantially with depth. Humification during decomposition results in the relative accumulation of oxygen-bearing functional groups, especially carboxyl (COOH) groups, causing a decrease in the C:OM ratio.[28, 29] Others have also observed a decrease in C:OM with depth in forest soils in the northeastern USA, hypothesizing that deeper soils contain older OM which has been subjected to a greater degree of humification.[28]

The C:N ratio also decreased sharply with soil depth in the forest soils in this study (Table 2). The average C:N ratios in Oi+Oe (19.8) and Oa/A (17.0) horizons are consistent with C:N ratios reported in other studies in the region. A study at six sites in the region reported C:N

ratios in the combined Oe+Oa horizon ranging from 16 in maple-dominated stands to 23 in hemlock-dominated stands.[25] At the Dry Creek watershed near Frost Valley, the average C:N ratio was reported to be 18.6 in Oi horizon samples and 16.4 in Oa/A horizons.[30]

The C:N ratio in mineral soils declined to an average of 13.4 below 20 cm depth. This is similar to the 11.8 value reported for B horizon soils at the Dry Creek watershed.[30] The C:N ratio generally declines with depth in forest soils because forest litter is rich in carbohydrates, which are a good substrate for soil microbes. Selective decomposition and the production of nitrogen-rich soil microbial biomass and microbial exudates, results in lower C:N ratios in deeper soils. It is also possible that there are mineral sources of N in the parent material that contribute to low C:N ratios at depth. Black shales and mudrocks in Catskills bedrock units contain organic matter trapped during sedimentation, which may be a source of N during weathering.[15] We observed C:N ratios as low as 7.4 in soils below 20 cm, and values below 5 in a few C horizons, where one expects little or no biological activity, suggesting a possible bedrock contribution. However, the frequency of these OM-bearing rocks decreases in the upper bedrock strata, where our sites were located.[15]

Most of the OM and C in the soil profiles in this study was found in the mineral soil (Table 2). This was the product of relatively high concentrations of OM and C in mineral horizons and high mineral soil masses. Other forest soils in glaciated regions of the northeastern USA exhibit this pattern. For example, more than 80% of the C in soils at the HBEF in New Hampshire was reported to be in the mineral soil.[31] Nevertheless, the organic horizons (Oi+Oe and Oa/A) in this study together contained an average of 10% of the OM and 14% of the C in the entire soil profile (Table 2), despite representing less than 1% of the soil mass. The likely fate of soil C in a changing climate remains unclear. Temperate forest soils are a significant terrestrial C

pool.[32] With 10-20% of the total soil C in relatively thin surficial O horizons, increased decomposition rates, should they be stimulated by higher temperatures and higher precipitation, could cause a globally meaningful loss of terrestrial C.

*Controls on Soil Acidity*

Upland forest soils in the Catskills are moderately to highly acidic, with mean $pH_w$ values ranging from 3.8 to 4.8 (Fig. 3a). Organic horizons have high exchangeable Ca concentrations and high base saturations due to the release of Ca, Mg and K from plant tissues during OM decomposition and low mineral contents, which limit the availability of Al. Exchangeable acidity in O horizons is largely exchangeable H, probably associated with weakly acidic carboxylic functional groups (—COOH) in the OM.[29] In mineral horizons, mean exchangeable Ca and H drop below 2 $cmol_c$ $kg^{-1}$ and exchangeable Al becomes the most abundant exchangeable cation (Fig. 3). This pattern, which is seen in acid forest soils across the northeastern USA,[30,33,34] results in mean base saturation values below 20% in mineral soils (Fig, 3f).

Both effective ($CEC_e$) and total ($CEC_t$) cation exchange capacity were positively correlated with soil C (Fig. 4). Although there is considerable variability among the sites, especially in organic horizons, these correlations illustrate the important role that soil organic matter plays in providing exchange sites for cation retention. Indeed, as the mineral soil C values approach zero in Fig. 4, both $CEC_e$ and $CEC_t$ approach zero. Thus, most of the exchange capacity in the soils in this study can be attributed to functional groups, especially carboxyl groups, in soil organic matter.

Carboxyl groups in natural organic matter are weakly acidic, with acid dissociation constants (pKa) in the 2-6 range.[29,35] One would therefore expect the negative charge, and hence CEC, to increase with increasing pH. The organic soils in this study showed a significant

positive relationship between $CEC_e$ and $pH_w$, but there was a significant negative relationship in mineral soils (Fig. 6a). Several investigators have observed negative relationships between $CEC_e$ and pH in acid forest soils.[21,36,37] This is partly a consequence of the dominant role that OM plays in providing exchange sites – higher OM content increases $CEC_e$ and $CEC_t$ (Fig. 4), but also decreases the soil pH due to the abundance of weak-acid functional groups, which release $H^+$ to solution when they deprotonate. Also, the solubility of Al decreases with increasing pH, so Al held on exchange sites is less likely to be released to solution as pH increases. The $CEC_e$ will therefore be somewhat lower since it is the sum of all exchangeable cations.

Exchangeable cations occupied about 20-35% of the negatively charged sites in these soils (Fig. 5). Most of the negative charge was satisfied by organically bound H and Al, which are too strongly held to be displaced by the neutral salt solutions used to measure exchangeable cations. The bound H ($H_{org}$) is probably associated with protonated functional groups whose pKa values are greater than the soil pH (e.g., phenolic groups[29]). The bound Al ($Al_{org}$) is Al that has formed strong complexes with organic functional groups in OM. If soil pH increases in the long term as soils recover from chronic acidic deposition, additional organic functional groups will deprotonate, resulting in the release of $H^+$ from $H_{org}$ to solution, an increase in $CEC_e$, and an increased ability for the soil to retain nutrient cations such as $Ca^{2+}$, $Mg^{2+}$ and $K^+$. On the other hand, increased soil pH would have little or no effect on $Al_{org}$, since Al solubility decreases with increasing pH, limiting the release of Al to solution. The fact that $Al_{org}$ is a small component of $CEC_t$ compared to $H_{org}$ indicates that these soils have a high potential for additional storage of basic cations (and increased base saturation) if soil pH increases in the future.

*Implications for Forest Sustainability*

Forest soils in the Catskills provide crucial ecosystem services, including the provision of high-quality drinking water for New York City and nutrition for the maintenance of a healthy forest. The soil is the principal source of the nutrients N, Ca, Mg, and K for trees, so maintaining the pool of these nutrients in the rooting zone is key to forest sustainability. The average pool of N in the 50 sites sampled in this study was 3.95 Mg ha$^{-1}$ (Table 2). The average pools of exchangeable Ca, Mg and K were 403, 63 and 80 kg ha$^{-1}$, respectively (Table 3). Using the same sampling method, Vadeboncoeur *et al.* measured mean soil N pools ranging from 3.68 to 7.77 Mg ha$^{-1}$ at 14 forested sites in New Hampshire[19] and Huntington *et al.* measured a mean N pool of 7.2 Mg ha$^{-1}$ at the HBEF.[31] Pools of exchangeable Ca, Mg, and K in the northern hardwood forest at the HBEF were reported to be 320, 38 and 160 kg ha$^{-1}$ respectively.[33] The differences in the N and K pools between the Catskills sites and the HBEF can largely be explained by the differences in soil mass, which was 59% higher at the HBEF.[23] The Ca and Mg pools at the Catskills sites were greater than the pools at the HBEF, despite the lower average soil masses. Unlike N and K, which are rapidly cycled in various nutrient cycling processes, Ca and Mg fluxes are more dependent on mineral weathering.[38] The higher pools of Ca and Mg at the Catskills sites therefore suggests that the weathering of parent materials in the Catskills results in higher production of Ca and Mg than the weathering of the till at the HBEF, which is largely derived from granitic bedrock.[38] Chlorite is an important mineral in Catskills mudrocks and, to a lesser extent, sandstones.[15] Weathering of chlorite to vermiculite and/or smectite results in the release of large amounts of Mg. The possible weathering sources of Ca are less clear. There is scant evidence for carbonates in the upper bedrock units in which our soils were collected,[15]

leaving plagioclase feldspars and various Ca-bearing minerals in metamorphic rock fragments found in the region's sandstones as the most likely sources.[15]

Estimates of the nutrient content of trees in the Catskills watersheds in this study are not available. However, the nutrient pools in the forest at the HBEF can provide an approximate comparison. Like the Catskills, the experimental watersheds at the HBEF host a successional forest that experienced large-scale disturbance in the late 1800s and early 1900s. The pools of N, Ca, Mg and K in above-ground vegetation at the HBEF in 2007 are estimated to be 499, 543, 47 and 198 kg ha$^{-1}$, respectively (http://hubbardbrook.org/w6_tour/biomass-stop/biomassw6.htm; accessed 6/13/13). The soil N pool in the Catskills sites (3950 kg ha$^{-1}$) is approximately eight times the above-ground N content of the HBEF forest, suggesting that there is sufficient soil N to support several forest rotations. However, the Ca and K pools in Catskills soils are substantially lower than the content of Ca and K in above-ground biomass at the HBEF. Assuming that the values for HBEF vegetation are similar in magnitude to the Catskills watersheds in this study, there may be concern about the ability of Catskills soils to support multiple rotations of the current forest.[39,40] Additional data on the chemistry of forest vegetation in the region are required to answer this question satisfactorily.

Chronic acid deposition in the Catskills is believed to have resulted in declines in exchangeable Ca in soils and in Ca concentrations in drainage waters.[11,41,42] Maintaining adequate Ca concentrations in Catskills stream waters is important to minimize corrosion in the aqueducts serving New York City and for the maintenance of hardness levels for household and commercial use. Calcium export from the Biscuit Brook watershed in the Neversink drainage basin of the Catskills (and one of the sites in this study) was estimated to be 28.8 kg ha$^{-1}$ in the mid-1980s.[2] By the mid-2000s, Ca+Mg concentrations had declined by approximately 20-25%.[43]

Assuming a present-day export of around 20 kg ha$^{-1}$, the average soil exchangeable Ca pool represents about 20 years of Ca export. The sustainability of Ca export from Catskills streams ultimately depends on the steady-state release of Ca in weathering processes, about which little is known. With continuing declines in atmospheric Ca inputs,[3] however, continued declines in stream water Ca seem likely.

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**Figure Captions**

**Figure 1.** Map of soil sampling sites. Sites are superimposed on a bedrock geological map; see ref. 15 (in this volume) for detail.

**Figure 2**. Histograms showing the distributions of soil depth and soil mass at 50 upland forest sites in the Catskills region.

**Figure 3**. Depth patterns in (a) soil pH; (b) exchangeable calcium; (c) exchangeable aluminum; (d) exchangeable hydrogen; (e) effective cation exchange capacity; and (f) effective base saturation. Soil layers are arranged vertically in the order in which they appear in the field. Error bars represent one standard error.

**Figure 4**. Relationships between (a) effective, and (b) total, cation exchange capacity and the concentration of carbon in mineral and organic soils from 50 upland forest sites in the Catskills.

**Figure 5**. Cation binding in upland forest soils in the Catskills region. Left-to-right the stacked bars show exchangeable base cations (sum of Ca, Mg, K, Na); exchangeable acidity (sum of Al, H); organically bound H (equation [3]); and organically bound Al (equation [2]). The sum of the first two segments (exchangeable bases and acidity) equals the effective cation exchange capacity ($CEC_e$). The sum of all four segments equals the total cation exchange capacaity ($CEC_t$).

**Figure 6**. Relationships between soil pH in deionized water ($pH_w$) and: (a) effective cation exchange capacity ($CEC_e$); (b) effective base saturation in mineral and organic soils from 50 upland forest sites in the Catskills region.

**Table 1.** Physical properties of soils excavated at 50 upland forest sites in the Catskills. Uncertainties (±) are standard errors. For thickness and soil mass, zeroes were included when a layer was not present at a site. For bulk density and stone content, N=50 for the 0-10 cm and 10-20 cm layers, while N=49 for the 20 cm – C layer.

| Layer | Thickness | Soil Mass[a] | Bulk Density | Stone Content |
|---|---|---|---|---|
| | (cm) | (kg m$^{-2}$) | (Mg m$^{-3}$) | Volume % |
| Oi + Oe | —[b] | 1.37 ± 0.12 | ND[c] | 0[d] |
| Oa/A | —[b] | 0.44 ± 0.09 | ND[c] | ND[c] |
| 0 – 10 cm | 10.6 ± 0.13 | 32.3 ± 2.2 | 0.44 ± 0.02 | 25.8 ± 1.8 |
| 10 – 20 cm | 10.4 ± 0.16 | 43.1 ± 2.8 | 0.65 ± 0.03 | 27.3 ± 1.5 |
| 20 cm – C | 32.7 ± 2.5 | 127 ± 15 | 0.61 ± 0.03 | 25.4 ± 1.1 |
| Total: O Horizons | 2.96 ± 0.21 | 1.81 ± 0.16 | | |
| Total: Mineral Horizons | 53.6 ± 2.5 | 203 ± 18 | | |
| Soil Total | 56.6 ± 2.5 | 205 ± 18 | | |

[a] Mass of soil passing a 5-mm (O horizons) or 2-mm (mineral horizons) sieve.

[b] Thickness was not measured separately for Oi+Oe and Oa/A horizons. Total thickness is reported below (Total: O Horizons)

[c] ND – not determined.

[d] None of the Oi+Oe samples contained stones.

**Table 2.** Organic matter, carbon and nitrogen concentrations and pools in soils excavated at 50 upland forest sites in the Catskills. The C:N and C:OM ratios are mass ratios. Uncertainties (±) are standard errors.

| Layer | Concentrations | | | C:N | C:OM | Pools | | |
|---|---|---|---|---|---|---|---|---|
| | Organic Matter | Carbon | Nitrogen | | | Organic Matter | Carbon | Nitrogen |
| | (g kg$^{-1}$) | (g kg$^{-1}$) | (g kg$^{-1}$) | | | (Mg ha$^{-1}$) | (Mg ha$^{-1}$) | (Mg ha$^{-1}$) |
| Oi + Oe | 891 ± 11 | 468 ± 9 | 24.1 ± 0.6 | 19.8 ± 0.4 | 0.53 ± 0.01 | 12.5 ± 1.2 | 6.6 ± 0.6 | 0.34 ± 0.03 |
| Oa/A | 639 ± 39 | 319 ± 25 | 18.6 ± 1.2 | 17.0 ± 0.4 | 0.49 ± 0.01 | 2.9 ± 0.7 | 1.5 ± 0.4 | 0.08 ± 0.02 |
| 0 – 10 cm | 142 ± 8 | 63.7 ± 3.6 | 4.0 ± 0.2 | 16.1 ± 0.5 | 0.45 ± 0.01 | 40.3 ± 2.1 | 17.9 ± 0.9 | 1.16 ± 0.07 |
| 10 – 20 cm | 74.9 ± 5.0 | 29.7 ± 1.8 | 2.1 ± 0.1 | 13.9 ± 0.4 | 0.39 ± 0.01 | 28.0 ± 1.6 | 11.1 ± 0.6 | 0.80 ± 0.04 |
| 20 cm – C | 64.3 ± 5.4 | 20.7 ± 1.7 | 1.5 ± 0.1 | 13.4 ± 0.5 | 0.37 ± 0.04 | 63.1 ± 6.0 | 21.9 ± 2.2 | 1.59 ± 0.14 |
| Total: O Horizons | | | | | | 15.3 ± 1.4 | 8.0 ± 0.8 | 0.43 ± 0.04 |
| Total: Mineral Horizons | | | | | | 131 ± 8 | 50.5 ± 2.9 | 3.53 ± 0.20 |
| Soil Total | | | | | | 147 ± 8 | 58.5 ± 2.9 | 3.95 ± 0.20 |

**Table 3.** Pools of exchangeable cations in upland forest soils of the Catskills region. Effective cation exchange capacity ($CEC_e$) is the sum of exchangeable base cations (Ca, Mg, K, Na) and exchangeable acidity (see Methods), expressed in equivalent units. Effective base saturation ($BS_e$) is the percentage of $CEC_e$ satisfied by base cations. Uncertainties (±) are standard errors.

| Layer | Exchangeable | | | | | | $CEC_e$ | $BS_e$ |
|---|---|---|---|---|---|---|---|---|
| | Al | H | Ca | Mg | K | Na | | |
| | (kg ha$^{-1}$) | (kg ha$^{-1}$) | (kg ha$^{-1}$) | (kg ha$^{-1}$) | (kg ha$^{-1}$) | (kg ha$^{-1}$) | (kmol$_c$ ha$^{-1}$) | (%) |
| Oi + Oe | 0.6 ± 0.2 | 0.7 ± 0.1 | 64 ± 6 | 9 ± 1 | 13 ± 1 | 0.3 ± 0.04 | 5.1 ± 0.4 | 84 ± 1.2 |
| Oa/A | 0.9 ± 0.5 | 0.2 ± 0.03 | 12 ± 4 | 2 ± 0.4 | 2 ± 0.5 | 0.3 ± 0.06 | 1.1 ± 0.3 | 69 ± 4.6 |
| 0 – 10 cm | 141 ± 15 | 6.8 ± 0.7 | 131 ± 22 | 21 ± 2 | 23 ± 2 | 2.3 ± 0.4 | 31.2 ± 2.3 | 28 ± 2.9 |
| 10 – 20 cm | 219 ± 14 | 5.6 ± 0.8 | 71 ± 16 | 12 ± 2 | 15 ± 1 | 2.2 ± 0.4 | 34.5 ± 2.0 | 15 ± 2.3 |
| 20 cm – C | 541 ± 53 | 12.3 ± 2.4 | 128 ± 28 | 20 ± 3 | 28 ± 3 | 5.3 ± 1.1 | 81.3 ± 7.5 | 11 ± 3.2 |
| Total: O Horizons | 1.6 ± 0.7 | 0.9 ± 0.1 | 76 ± 10 | 11 ± 1 | 15 ± 2 | 0.5 ± 0.08 | 6.1 ± 0.6 | |
| Total: Mineral Horizons | 890 ± 69 | 24.4 ± 3.2 | 327 ± 59 | 52 ± 7 | 65 ± 4 | 9.7 ± 1.6 | 145 ± 10 | |
| Soil Total | 892 ± 69 | 25.2 ± 3.2 | 403 ± 66 | 63 ± 7 | 80 ± 4 | 10.3 ± 1.6 | 151 ± 10 | |

## Bedrock

**Upper Devonian**
- Dwh — Honesdale Formation
- Dws — Slide Mountain Formation
- Dww — Upper Walton Formation
- Dsw — Lower Walton Formation
- Dgo — Oneonta Formation

**Middle Devonian**
- Dgu — Gilboa Formation
- Dhmo — Manorkill/Moscow Formation
- Dhpm — Panther Mountain Formation
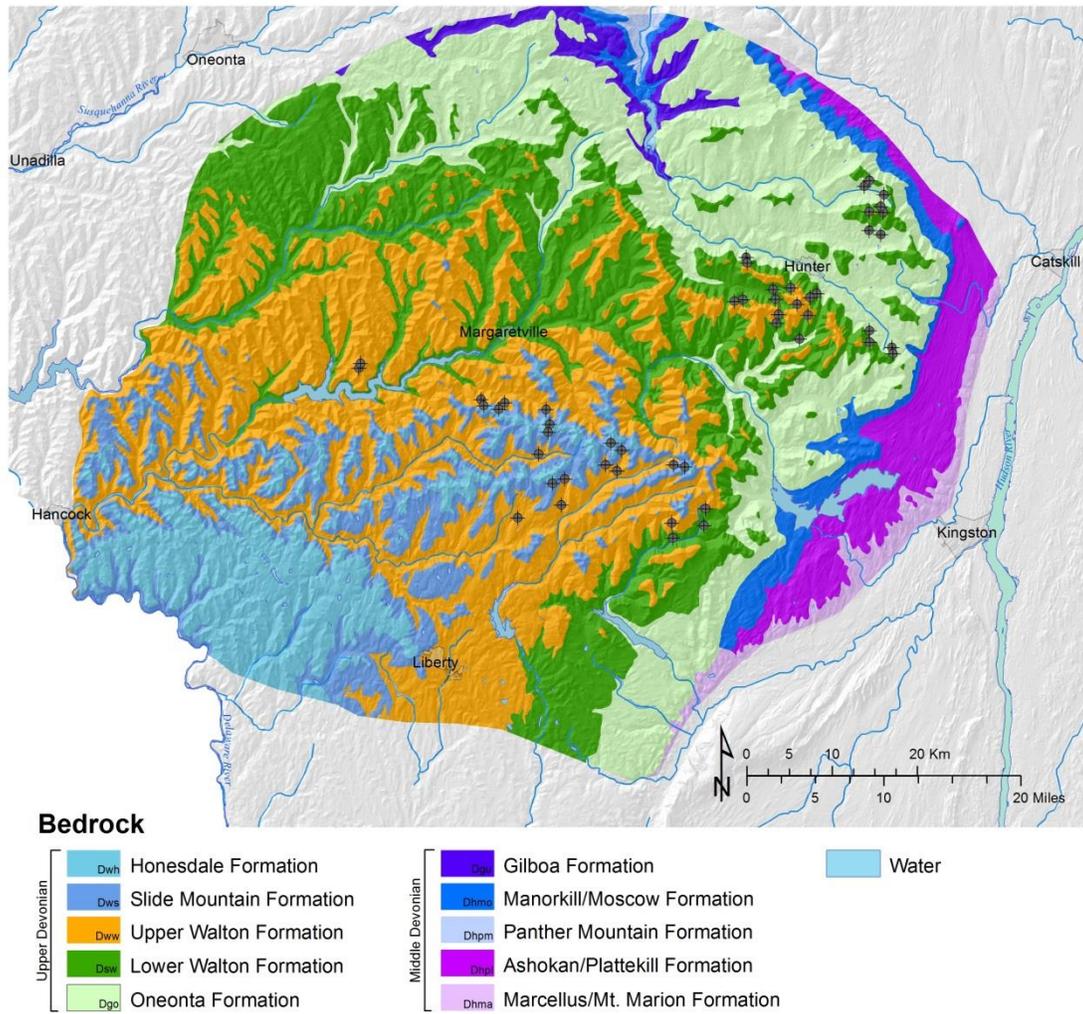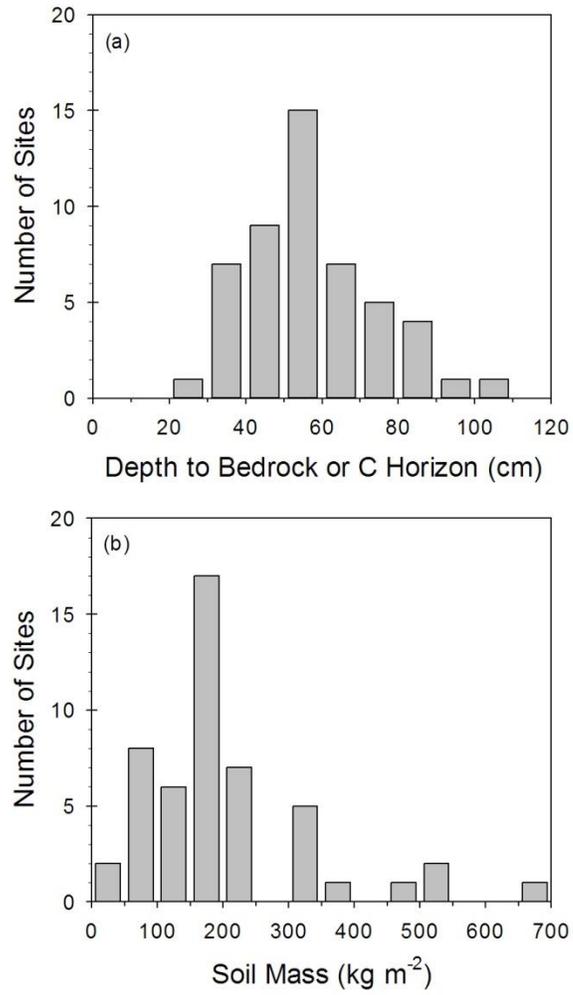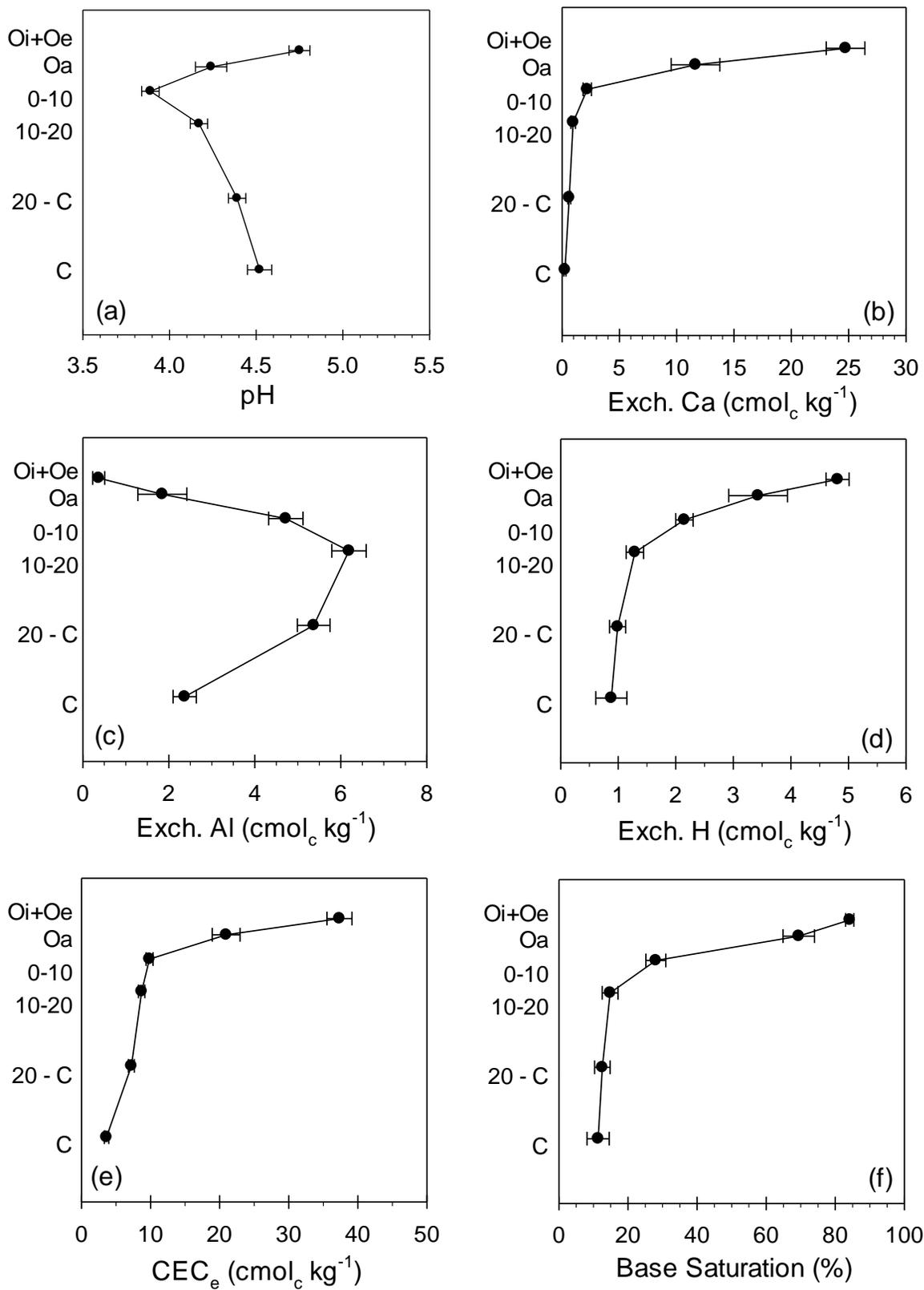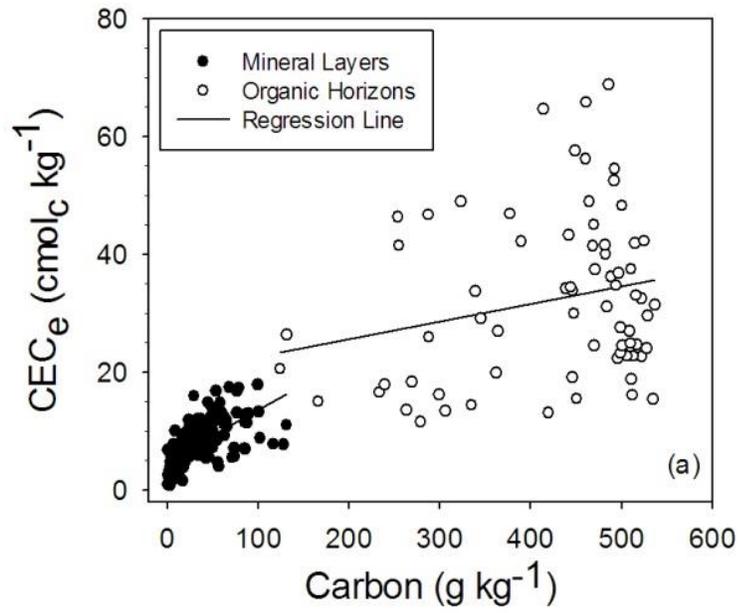- Dhpl — Ashokan/Plattekill Formation
- Dhma — Marcellus/Mt. Marion Formation

- Water

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6