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Acid-base characteristics of the Grass Pond watershed in the Adirondack Mountains of New York State, USA: interactions between soil, vegetation and surface waters

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Abstract

Grass Pond watershed is located within the Southwestern Adirondack Mountain region of New York State, USA. This region receives some of the highest rates of acidic deposition in North America and is particularly sensitive to acidic inputs due to many of its soils having shallow depths and being generally base-poor. Differences in soil chemistry and tree species between seven subwatersheds were examined in relation to acid-base characteristics of the seven major streams that drain into Grass Pond. Mineral soil pH, stream water BCS and pH exhibited a positive correlation with sugar maple basal area ($p = 0.055$; 0.48 and 0.39, respectively). Black cherry basal area was inversely correlated with stream water BCS, ANC_c and NO_3^- ($p = 0.23$; 0.24 and 0.20, respectively). Sugar maple basal areas were positively correlated with watershed characteristics associated with the neutralization of atmospheric acidic inputs while in contrast, black cherry basal areas showed opposite relationships to these same watershed characteristics. Canonical Correspondence Analysis indicated that black cherry had a distinctive relationship with forest floor chemistry apart from the other tree species, specifically a strong positive association with forest floor NH_4 while sugar maple had a distinctive relationship with stream chemistry variables, specifically a strong positive association with stream water ANC_c, BCS and pH. Our results provide evidence that sugar maple is acid-intolerant or calciphilic tree species and also demonstrate that black cherry is likely an acid-tolerant tree species.

1 Introduction

The Adirondack Mountain region of New York State is characterized by high elevations, granitic bedrock and is particularly sensitive to acidic atmospheric inputs due to many of the soils in this region having shallow depths and generally being base-poor (Ito et al., 2002). Acidic deposition alters soils through the depletion of calcium (Ca^{2+}) and other plant nutrient cations (Mg^{2+}, K^+) and the mobilization of inorganic monomeric

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aluminum (Al) (Lawrence et al., 1997). Both of these factors may stress forest vegetation and deleteriously affect water quality (Cronan and Grigal, 1995; Horsley et al., 2000; MacAvoy and Bulger, 1995). Countering forces that may reduce the deleterious effects of acidic deposition include nutrient recycling, mineral weathering, and the release of exchangeable base cations (McFee et al., 1977).

Within the northern hardwood forests, sugar maple (*Acer saccharum*) and other species such as American basswood (*Tilia americana*), eastern hophornbeam (*Ostrya virginiana*) and white ash (*Fraxinus americana*) require base-rich soils and are acid-intolerant, while American beech (*Fagus grandifolia*), and red spruce (*Picea rubens*) are acid-tolerant species (Christopher et al., 2006; Duchesne et al., 2005; Fujinuma et al., 2005; Mitchell et al., 2003). Sugar maple often does poorly in soils that are low in Ca and Mg, high in Al and have a low pH (Burns and Honkala, 1990; Van Breemen et al., 1997). Previous studies indicate black cherry (*Prunus serotina*) might be an acid-tolerant species although research on this tree species in relation to site acid-base characteristics is very limited (Aguilar and Arnold, 1985; Godefroid et al., 2005; Lorenz et al., 2004).

In addition to species-specific nutrient requirements, various tree species will differ in their cycling of base cations and may result in differences in soil base cation concentrations in forest stands. Differences in the base cation content of the soil will also have an important influence on the base cation concentrations in soil, ground and surface waters. Watersheds containing greater basal areas of acid-intolerant tree species are expected to contain soils and streams with greater base cation concentrations. Specifically, positive correlations are expected between sugar maple basal areas and soil Ca concentrations, stream water Ca concentrations and surface water acid neutralizing capacities. These relationships may be due to greater nutrient base cation requirements and greater nutrient base cation release from the mineralization of sugar maple leaf litter compared to other tree species including American beech and eastern hemlock.

Despite receiving similar rates of acidic deposition, subwatersheds within Grass Pond watershed differentially neutralize acidic surface waters (Ito et al., 2007).

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Understanding the relationships between watershed characteristics and acid neutralizing capacity provides insight into the sensitivity or resilience of watersheds and the relative importance of different tree species with respect to the deleterious impacts of acidic deposition and the potential for different forest management scenarios and strategies. The objective of our study was to evaluate the relationships between stream and soil acid-base chemistry as a function of the presence and abundance of acid tolerant and acid intolerant tree species within Grass Pond subwatersheds.

2 Methods

2.1 Site description

Grass Pond watershed is located within the Ha-De-Ron-Dah Wilderness Area at 43°41′25″ N, 75°3′54″ W in the Southwestern Adirondack Mountains of New York State. The watershed is divided into seven adjacent subwatersheds that exhibit substantial differences in stream water acid-base chemistry (Ito et al., 2007) (Fig. 1). The entire Grass Pond watershed has an area of 237 ha with elevation ranges from 552 to 684 m. The parent material has variable thickness and is derived from glacial till. Soils are predominantly Spodosols. Vegetation is typical of a northern hardwood mixed forest containing red maple, yellow birch (*Betula alleghaniensis*), American beech, and sugar maple, with some black cherry, red spruce and eastern hemlock. A more detailed description of the seven Grass Pond subwatersheds is available in Ito et al. (2007).

2.2 Site history

In the 1800's to the early 1900's, large portions of the Southwestern Adirondacks were cleared for timber harvest and for agriculture (Schneider, 1998). It is likely that during this time landowners logged Grass Pond watershed. In 1903, a 25 000-acre fire burned the Ha-De-Ron-Dah area (Gray, 1995). From 1909 to 1981, New York State acquired

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parcels of land including the Grass Pond watershed and in 1986 the State designated this area as the 26 600-acre Ha-De-Ron-Dah Wilderness Area (Gray, 1995).

2.3 Sampling

2.3.1 Stream water

In October 2008, a period for which discharge was reflecting base flow conditions, 37 stream water samples were collected along an elevational gradient along the seven streams located within the Grass Pond watershed. Stream samples were collected starting at each stream inlet to Grass Pond and taken at ~150 m longitudinal increments going upstream. Streams 2 and 5 had two main tributaries that joined and drained into the inlet to Grass Pond. For streams 2 and 5, samples were collected at the inlet downstream from where the two tributaries joined as well as upstream both tributaries. Stream water samples were collected and stored in 250 ml polyethylene bottles at 4 °C until chemical analysis. Stream samples were filtered through 0.45 µm HV membrane filters to remove particulate matter prior to analysis.

2.3.2 Vegetation

Tree vegetation surveys were conducted during August, September and October 2008. Each subwatershed was sampled using 9 m radius plots selected from a grid of transects, accounting for ~1 % of the area of each subwatershed with a total of 80 plots. All tree species ≥ 5 cm in diameter at 1.4 m above the ground (dbh) within each selected sample plot were identified and dbh measured to determine total and relative (percent) basal area for each species within plots and subwatersheds.

2.3.3 Soil

Soil samples were collected at Grass Pond watershed in October 2008 within the selected vegetation plots. In each plot, the forest floor (Oe/Oa horizon) and upper mineral

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soil (0–10 cm) were sampled from three locations, homogenized in a bucket and a subsample was sealed in a polyethylene bag. The forest floor was sampled by removing litter (Oi horizon) and by cutting a small square, approximately 20 × 20 cm, into the Oe/Oa horizon with a knife. The upper mineral soil was sampled using a "bulb planter corer" under the location of the forest floor sample. All collected samples were kept refrigerated at 4 °C until further sample preparation and chemical analysis. A total of 59 mineral soil and 63 forest floor samples were collected. At locations where insufficient soil development occurred, samples were not collected and at locations with forest floor soil layers deeper than approximately a meter, mineral soil samples were not collected.

2.4 Sample analysis

2.4.1 Stream water

Stream water samples were analyzed for pH potentiometrically, using a MI-410 combination pH electrode (Microelectrodes, Inc.) in conjunction with an Accumet®, AR50, Dual Channel pH/Ion/Conductivity meter. Stream water samples were analyzed for dissolved organic carbon (DOC) using persulfate oxidation using a Tekmar Phoenix 8000 Carbon Analyzer. Ammonium (NH_4) and total N were determined using the Autoanalyzer3. Stream water samples were analyzed for cation (Al, Ca, K, Mg, Na and Si) concentrations using a Perkin-Elmer Optima DIV 3300®, Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) and for anion (Cl^-, NO_3^- and SO_4^{2-}) concentrations using a Dionex ICS-2000® Ion Chromatograph (IC).

Stream water acid neutralizing capacity (ANC_c) was calculated using the equation $ANC_c = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] - [Cl^-] - [NO_3^-] - [SO_4^{2-}]$, in which concentrations are expressed in $\mu eq\,l^{-1}$.

The base-cation surplus (BCS) was calculated using the equation $BCS = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] - [Cl^-] - [NO_3^-] - [SO_4^{2-}] - [RCOO_s^-]$, in which concentrations are expressed in $\mu eq\,l^{-1}$ (Lawrence et al., 2007). In the equation for BCS, $[RCOO_s^-]$ equals the concentration of strong organic anions. Estimates of the contribution of organic anions to a solution charge were calculated using the equation $[RCOO_s^-] = 0.071[DOC] - 2.1$ (Lawrence et al., 2007). Where $[RCOO_s^-]$ is the ($\mu eq\,l^{-1}$) organic anion concentration, [DOC] is the ($\mu eq\,l^{-1}$) dissolved organic carbon concentration.

2.4.2 Soil

Fresh forest floor and mineral soil samples were homogenized and sieved to 6.4 mm to remove coarse fragments. Percent organic matter was determined as loss-on-ignition at 470 °C for 16 h (Wilde et al., 1972). Soil pH was determined potentiometrically in 2 : 1 slurry of 0.01 molar $CaCl_2$: fresh soil sample (Sparks et al., 1996).

Total N and NH_4^+ were determined by combining soil samples (approximately 10 g for forest floor and 20 g for mineral soil) with 70 ml of 2 molar KCl. The solution was then shaken for 1 h, filtered through Whatman 42® ashless filter paper (pore size 2.5 µm), rinsed three times and then raised to 100 ml volume with 2 molar KCl (modified from Blume et al., 1990; Page and Mitchell, 2008). A 20 ml sub-sample of the filtrate was decanted and analyzed using continuous flow colorimetry on a Bran-Luebbe AutoAnalyzer3® for NH_4^+ and total N.

Forest floor soil samples were ground in a Wiley® Mill using a #20 (0.85 mm) screen and were analyzed for percent C and N on a Thermo Electron Flash EA 1112® elemental analyzer to determine C : N mass ratio. Forest floor soil samples were analyzed for total elemental Al, Ca, K, Mg, Na, and P by ashing a 1 g homogenized sample at 470 °C for 16 h. The ash was then dissolved in 10 ml of 6 molar HCl, evaporated to dryness on a hot plate, re-dissolved in 10 ml of 6 molar HCl, filtered through a Whatman 42® ashless filter paper, rinsed three times with deionized, distilled water (DDW) and raised to 100 ml with DDW (Page and Mitchell, 2008; modified from Sparks et al., 1996). Total elemental concentrations (Al, Ca, K, Mg, Na, and P) were then determined using ICP-AES.

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Mineral soils were analyzed for exchangeable elements (Al, Ca, K, Mg, Na, and Si) by extracting approximately 10 g dry soil in 50 ml of 1 M NH_4Cl. The solution was then filtered through a Whatman 42® ashless filter paper, rinsed three times with 10 ml of 1 molar NH_4Cl, and then raised to a volume of 100 ml with 1 molar NH_4Cl (Blume et al., 1990). Samples were then frozen until analyzed for exchangeable cation concentrations using ICP-AES.

2.5 Statistical analyses

Pearson correlations were used to determine the significance of relationships between soil chemical measurements and tree species basal areas, as well as between stream chemistry and tree species basal areas. Analyses were based on samples sizes of 60 and 55 for the forest floor and mineral soil, respectively, after removal of 7 outliers (< 6 % of all samples) to help facilitate multivariate analysis assumptions. We also did the statistical determinations with the outliers and found there was no substantive effect on the overall results. The plot data and stream chemistry were averaged by the 7 subwatersheds for analysis (sample size of 7). Variables used in the analysis include the chemical constituents of the forest floor, mineral soil, and stream (pH, Ca^{2+} etc.) and the total basal areas of specific tree species. Within our study, all statistical analysis were assessed at a significance level of $\alpha = 0.05$.

Canonical Correspondence Analysis (CCA) is a well-established multivariate technique to analyze species-environment relationships (Khattree and Naik, 2000; Ter Braak, 1986). It is a two-step gradient analysis, in which ordination axes are extracted from species abundance data, followed by identifying gradient from environment variables. Thus, the dominant pattern of variation in species community can be directly related to variation in environmental variables. The results of CCA is commonly displayed by a biplot, which is a graphical presentation of the data matrix by two sets of plots overlaid on the same coordinate system, one plot representing species and the other plot representing environment variables (Hodge and Naik, 1999). In addition, the percentage variations accounted for by the two ordination axes are computed as the proportion of the first two eigen values to the sum of all eigen values of species-environment correlations (Ter Braak, 1986).

In our study, CCA was used to relate tree species basal areas to forest floor, mineral soil, and stream chemistry, respectively. In the resultant biplots, species are shown as points, while chemical variables are represented by arrows from the origin of the biplot. Important chemical variables tend to be represented by longer arrows than less important chemical variables, and the relative locations of species points to the direction of arrows (chemical variables) indicate the association and correlation of each species with respect to each chemical variable (Ter Braak, 1986; Khattree and Naik, 2000).

3 Results

3.1 Watershed characteristics

The major tree species within Grass Pond watershed included American beech, black cherry, eastern hemlock, red maple, red spruce, striped maple (*Acer pensylvanicum*), sugar maple and yellow birch (Fig. 2). Red maple and American beech were the most abundant species within the watershed with 28 % and 34 % relative basal area, respectively. Black cherry, with 4 % relative basal area, occurred in nine plots, primarily in the upper elevations of subwatersheds 4 and 5. Sugar maple, with 9 % relative basal area occurred primarily in subwatershed 3.

Forest floor and mineral soils within Grass Pond watershed were generally acidic with mean pH values less than 4.0 (Fig. 3b). Forest floor mean C : N mass ratios were below 20 indicating elevated nitrogen levels (Driscoll et al., 2003). Within Grass Pond watershed, both forest floor and mineral soil samples had relatively high Al concentrations and relatively low Ca concentrations (Tables 1 and 2).

Within Grass Pond watershed, streams 4, 5, 6 and 7 were acidic with ANC $< 0\,\mu\text{eq}\,\text{l}^{-1}$ (Table 3 and Fig. 3a). All stream sample sites had moderate to low nitrate levels ($< 40\,\mu\text{eq}\,\text{l}^{-1}$) and only two stream sample sites exhibited high DOC levels

(> 600 µmol Cl^{-1}), which were located in the headwater sample sites of Stream 5 (Table 3).

3.2 Sugar maple site characteristics

Mineral soil pH and sugar maple basal area exhibited a positive correlation ($r = 0.26$, $p = 0.055$) (Table 4). Stream water BCS and pH were positively correlated with sugar maple basal area ($r = 0.32$, $p = 0.48$ and 0.39, 0.39, respectively) (Fig. 4a and Table 5). Stream water DOC concentrations were significantly inversely correlated with sugar maple basal area ($r = -0.89$, $p = 0.0077$) (Table 5).

3.3 Black cherry site characteristics

Forest floor NH_4 and black cherry basal area exhibited a significant positive correlation ($r = 0.32$, $p = 0.013$) (Table 4). Black cherry basal area was inversely correlated with stream water BCS, pH, NO_3^- and ANC_c ($r = -0.52$, $p = 0.23$; −0.36, 0.43; −0.55, 0.20 and −0.51, 0.24, respectively) (Fig. 4b and Table 5). Stream water DOC concentrations were positively correlated with black cherry basal area ($r = 0.26$, $p = 0.58$) (Table 5).

3.4 Canonical correspondence analysis (CCA)

The most important environmental variables associated with tree species basal area in the forest floor CCA biplot, as indicated by the longer arrows, were forest floor Ca and NH_4 (Fig. 5a). The most important environmental variables associated with tree species basal area in the mineral soil CCA biplot were mineral soil Ca, NH_4 and pH (Fig. 5b). Forest floor Al and mineral soil Al are the least important environmental variables as indicated by the shortest arrows in the biplots (Fig. 5a, b). Stream water DOC was the most important environmental variable associated with tree species basal area in the stream water CCA biplot (Fig. 5c).

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The relative location of black cherry in the CCA biplot indicated a strong positive association with forest floor NH_4 (Table 4 and Fig. 5a). Both the forest floor and mineral soil CCA biplots indicated a strong positive association between yellow birch and Ca levels, a strong positive association between sugar maple and pH and a strong negative association between black cherry and pH (Table 4, Fig. 5a, b). The relative location of sugar maple in the CCA biplot indicated a strong positive association between sugar maple and stream water ANC_c, BCS and pH and a strong positive association between American beech and stream water NO_3 (Table 5 and Fig. 5c).

4 Discussion and conclusion

Northern hardwood forests are comprised of a mix of acid-intolerant and acid-tolerant species, primarily American beech, basswood, black cherry, eastern hemlock, red maple, red spruce, sugar maple, white ash, white pine and yellow birch (Braun, 1950). Acidic deposition has accelerated the loss of exchangable Ca and the mobilization of monomeric Al in forest stands resulting in the decline of sugar maple stands in the Northeastern United States (Lawrence et al., 1999). Sugar maple decline has most predominantly occurred on ridge tops and on upper slopes, where soil base availability is much lower than at mid and low slopes on the landscapes (Bailey et al., 2004). In forest stands with substantial tree mortality between 1989 and 1994, within the Alleghany National Forest, Pennsylvania, the dominant tree species has shifted from sugar maple to black cherry and red maple (McWilliams et al., 1996). Such a shift in three species composition would be consistent with a shift to more acid tolerant tree species.

In Grass Pond watershed, forest composition is dominated by red maple and American beech with black cherry and sugar maple only comprising 4 % and 9 % relative basal area, respectively. At Grass Pond watershed, sugar maple basal area was correlated with watershed attributes associated with the neutralization of atmospheric acidic inputs, including high stream water ANC_c, BCS, pH and Ca : Al, low stream water DOC and high soil pH (Fig. 6). Other research has suggested that sugar maple tree

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characteristics, such as high Ca concentrations and low C : N ratio leaf litter, will result in high mineralization and nitrification rates within the soil, contributing to increased nutrient cycling and nitrate leaching (Christ et al., 2002; Lovett and Rueth, 1999; Page and Mitchell, 2008). The correlations between sugar maple basal area and high stream water Ca : Al, high ANC and low stream water DOC indicates deep sub-surface hydrological flow paths through thick mineral soil layers and parent material (Fig. 6). In general, sites with thick soil layers with relatively high soil pH and Ca concentrations are more likely to be colonized by sugar maple trees than other less suitable more acidic sites because of the relatively high nutrient demands of this tree species.

As a shade intolerant, early successional species, black cherry is associated with shallow soils on steep slopes where blowdowns and other disturbances create gaps that allow adequate sunlight for black cherry regeneartion and growth (Aguilar and Arnold, 1985). At Grass Pond watershed, black cherry basal area was correlated with those watershed attributes associated with the inability to neutralize atmospheric acidic inputs, including low stream water ANC_c, BCS, pH and Ca : Al, high stream water DOC and total Al, low soil Ca concentrations, and high C : N ratios (Fig. 6). The negative correlation between black cherry basal area and stream water ANC_c and BCS and the positive correlation with stream water DOC is likely due to black cherry stands occurring on relatively steep slopes with thin soils and due to the predominance of shallow flow paths through forest floor soil layers (Fig. 6). The significantly positive correlation between black cherry basal area and forest floor NH_4^+ concentrations, indicates slow decomposition of black cherry litter that is relatively low in nutrient base cations (Fig. 6). Other research has also found that the basal area of acid-tolerant tree species is inversely correlated with nitrification rates due to leaf litter nutrient concentrations and C : N ratios (Christ et al., 2002; Finzi et al., 1998; Mitchell et al., 2003; Ross et al., 2009). Within the upper elevations of Grass Pond Subwatershed 5 where black cherry groves were identified, fresh black bear scat loaded with black cherry seeds was observed during early October field sampling, indicating a bear den in the area. The high frequency and distribution of black cherry trees within this portion of the subwatershed

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may be related to locations of disturbances that would allow light necessary for black cherry growth and also related to seed dispersal by black bear movements. It is also possible that the bear scat located at these sites may have contributed to high forest floor NH_4^+ (Fig. 6).

The limited significant statistical relationships between tree species basal area, stream and soil chemistry was most likely due to the limited presence of sugar maple and black cherry within Grass Pond watershed, generally low soil Ca concentrations, low variations in soil Ca concentrations between plots and the lack of mineral and forest floor soil development in the high elevation and steep sloped plots. These soil conditions combined with influences of the vegetation components are the major drivers affecting the spatial variation in the surface water chemistry of the Grass Pond watershed. Although correlations have been identified between tree species basal area, soil chemistry and stream chemistry, it is unclear whether the presence of sugar maple (conversely, black cherry) in base-rich soils is due to sugar maple contributing base-rich nutrients to the forest floor or if it is due to base-rich soils promoting sugar maple growth.

Documented disturbance history indicates that trees within Grass Pond watershed were likely logged and burned over 100 yr ago, potentially influencing soil, vegetation and stream characteristics of the watershed. Other studies have found that in the short term following a disturbance, northern hardwood watersheds in New Hampshire exhibited an increase in stream water NO_3^-, Al and base cations, and a decrease in stream water SO_4 and pH (Lawrence et al., 1987). Additionally, other studies have found that forests in the Adirondack Mountains of New York, with varying disturbance histories have similar soil C : N ratios, net N mineralization rates and net nitrification rates (Latty et al., 2004).

Our results are also supported by previous results that have shown that sugar maple is acid-intolerant or calciphilic tree species and we provide new information that demonstrates that black cherry is an acid-tolerant tree species and hence may be associated with those areas with low surface water ANC and pH values. Similarly, sugar maple

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presence is a good indicator of basic soil and stream conditions compared to stands containing black cherry. These soil and site characteristics are not only important in determining which tree species colonize an area but also ultimately affect how these tree species will concomitantly influence soil and forest patterns including variations in litter nutrient concentrations and mineralization rates and hence surface water characteristics (Christ et al., 2002; Lovett and Rueth, 1999; Page and Mitchell, 2008).

Our results show that black cherry has a distinctive relationship with forest floor variables, while sugar maple has a distinctive relationship with stream chemistry variables. Understanding the interactions among tree species and watershed acid-base status provides insight into the sensitivity or resilience of the watershed to inputs of acidic deposition. The continual depletion of base cations from northern hardwood forest soil, primarily due to the effects of acidic deposition, will reduce the area favorable for growing sugar maple and increase area available for black cherry and other acid-tolerant tree species. Shifts in the tree species from those that require relatively high soil base concentrations such as sugar maple to those acid tolerant species such as black cherry could have major impacts on these forest ecosystems and their associated surface waters. Future shifts in tree species composition and soil nutrient dynamics will presumably be accompanied by concomitant shifts in stream chemistry throughout the watershed. These evaluations of the spatial and temporal patterns soil and surface water chemistry in northern hardwood forests provide new insights into the continued and long-term effects of acidic deposition on forested watersheds.

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References

Aguilar, R. and Arnold, R. W.: Soil-landscape relationships of a climax forest in the Alleghany high plateau, Pennsylvania, Soil Sci. Soc. Am. J., 49, 695–701, 1985.

Bailey, S. W., Horsley, S. B., Long, R. P., and Hallett, R. A.: Influence of edaphic factors on sugar maple nutrition and health on the Allegheny Plateau, Soil Sci. Soc. Am. J., 68, 243–252, 2004.

Blume, L. J., Schumacher, B. A., Schaffer, P. W., Cappo, K. A., Papp, M. L., Van Remortal, R. D., Coffey, D. S., Johnson, M. G., and Chaloud, D. J.: Handbook of methods for acid deposition studies: laboratory analysis for soil chemistry, United States Environmental Protection Agency EPA/600/4-90/023, Washington, DC, 1990.

Braun, E. L.: Deciduous forests of Eastern North America, The Blakiston Co., Philadelphia, PA, 1950.

Burns, R. M. and Honkala, B. H. (tech. Coords.): Silvics of North America: 1. Conifers; 2. Hardwoods Agriculture Handbook 654, vol. 2, US Dept. of Agriculture, Forest Service, Washington, DC, 1990.

Christ, M. J., Peterjohn, W. T., Cumming, J. R., and Adams, M. B.: Nitrification potentials and landscape, soil and vegetation characteristics in two Central Appalachian watersheds differing in NO_3^- export, Forest Ecol. Manag., 159, 145–158, 2002.

Christopher, S. F., Page, B. D., Campbell, J. L., and Mitchell, M. J.: Contrasting stream water NO_3^- and Ca^{2+} in two nearly adjacent catchments: the role of soil Ca and forest vegetation, Global Change Biol., 12, 362–381, 2006.

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

Driscoll, C. T., Whitall, D., Aber, J., Boyer, E., Castro, M., Cronan, C., Goodale, C., Groffman, P., Hopkinson, C., Lambert, K., Lawrence, G., and Ollinger, S.: Nitrogen pollution in the Northeastern US: sources, effects, and management options, Bioscience, 53, 357–373, 2003.

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9, 10775–10803, 2012

Duchesne, L., Ouimet, R., Moore, J. D., and Paquin, R.: Changes in structure and composition of maple-beech stands following sugar maple decline in Quebec, Canada, Forest Ecol. Manag., 208, 223–236, 2005.
Finzi, A. C., Van Breemen, N., and Canham, C. D.: Canopy tree-soil interactions within temperate forests: species effects on soil carbon and nitrogen, Ecol. Appl., 8, 440–446, 1998.
Fujinuma, R., Bockheim, J., and Balster, N.: Base-cation cycling by individual tree species in old-growth forests of Upper Michigan, USA, Biogeochemistry, 74, 357–376, 2005.
Godefroid, S., Phartyal, S. S., Weyembergh, G., and Koedam, N.: Ecological factors controlling the abundance of non-native invasive black cherry (*Prunus serotina*) in deciduous forest understory in Belgium, Forest Ecol. Manag., 210, 91–105, 2005.
Gray, D. V.: First 5-year revision to Ha-De-Ron-Dah Wilderness unit management plan, New York State Department of Environmental Conservation, Albany, New York, 1995.
Hodge, L. M. and Naik, D. N.: Canonical correspondence analysis in SAS software, in: Proceedings of the 24th Annual SAS Users Group International Conference, 11–14 April 1999, Miami Beach, Florida, 1607–1613, 1999.
Horsley, S. B., Long, R. P., Bailey, S. W., and Hall, T. J.: Factors associated with the decline of sugar maple on the Allegheny Plateau, Can. J. Forest Res., 30, 1365–1378, 2000.
Ito, M., Mitchell, M. J., and Driscoll, C. T.: Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York, Atmos. Environ., 36, 1051–1062, 2002.
Ito, M., Mitchell, M. J., Driscoll, C. T., Newton, R. M., Johnson, C. E., and Roy, K. M.: Controls on surface water chemistry in two lake-watersheds in the Adirondack region of New York: differences in nitrogen solute sources and sinks, Hydrol. Process., 21, 1249–1264, 2007.
Khattree, R. and Naik, D. N.: Multivariate data reduction and discrimination with SAS software, SAS Institute Inc., Carry, NC, 558 pp., 2000.
Latty, E. F., Canham, C. D., and Marks, P. L.: The effects of land-use history on soil properties and nutrient dynamics in northern hardwood forests of the Adirondack Mountains, Ecosystems, 7, 193–207, 2004.
Lawrence, G. B., Fuller, R. D., and Driscoll, C. T.: Release of aluminum following whole-tree harvesting at the Hubbard Brook Experimental Forest, New Hampshire, J. Environ. Qual., 16, 383–390, 1987.
Lawrence, G. B., David, M. B., Bailey, S. W., and Shortle, W. C.: Assessment of calcium status in soils of red spruce forests in the Northeastern US, Biogeochemistry, 38, 19–39, 1997.

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Lawrence, G. B., David, M. B., Lovett, G. M., Murdoch, P. S., Burns, D. A., Stoddard, J. L., Baldigo, B. P., Porter, J. H., and Thompson, A. W.: Soil calcium status and the response of stream chemistry to changing acidic deposition rates, Ecol. Appl., 9, 1059–1072, 1999.
Lawrence, G. B., Sutherland, J. W., Boylen, C. W., Nierzwicki-Bauer, S. W., Momen, B., Baldigo, B. P., and Simonin, H. A.: Acid rain effects on aluminum mobilization clarified by inclusion of strong organic acids, Environ. Sci. Technol., 41, 93–98, 2007.
Lorenz, K., Preston, C. M., Krumrei, S., and Feger, K.: Decomposition of needle/leaf litter from Scots pine, black cherry, common oak and European beech at a conurbation forest site, Eur. J. Forest Res., 123, 177–178, 2004.
Lovett, G. M. and Rueth, H.: Soil nitrogen transformations in beech and maple stands along a nitrogen deposition gradient, Ecol. Appl., 9, 1330–1344, 1999.
MacAvoy, S. E. and Bulger, A. J.: Survival of brook trout (*Salvelinus fontinalis*) embryos and fry in streams of different acid sensitivity in Shenandoah National Park, USA, Water Air Soil Poll., 85, 445–450, 1995.
McFee, W. W., Kelly, J. M., and Beck, R. H.: Acid precipitation effects on soil pH and base saturation of exchange sites, Water Air Soil Poll., 7, 401–408, 1977.
McWilliams, W. H., White, R., Arner, S. L., Nowak, C. A., and Stout, S. L.: Characteristics of declining forest stands on the Allegheny National Forest, US Department of Agriculture Forest Service, Warren, PA, 1996.
Mitchell, M. J., Driscoll, C. T., Inamdar, S., McGee, G. G., Mbila, M. O., and Raynal, D. J.: Nitrogen biogeochemistry in the Adirondack Mountains of New York: hardwood ecosystems and associated surface waters, Environ. Pollut., 123, 355–364, 2003.
Page, B. D. and Mitchell, M. J.: The influence of basswood (*Tilia americana*) and soil chemistry on soil nitrate concentrations in a northern hardwood forest, Can. J. Forest Res., 38, 667–676, 2008.
Ross, D. S., Wemple, B. C., Jamison, A. E., Fredriksen, G., Stanley, J. B., Lawrence, G. B., Bailey, S. W., and Campbell, J. L.: A cross-site comparison of factors influencing soil nitrification rates in Northeastern USA forested watersheds, Ecosystems, 12, 158–178, 2009.
Schneider, P.: The Adirondacks: A History of America's First Wilderness, Henry Holt and Company, LLC, New York, NY, 1998.
Sparks, D. L., Page, A. L., Helmke, P. A., Loeppert, R. H., Soltanpour, P. N., Tabatabai, M. A., Johnston, C. T., and Sumner, M. E. (Eds.): Methods of Soil Analysis: Part 3 Chemical Methods, Soil Science of America, Inc., Madison, Wisconsin, 1996.

Ter Braak, C. J. F.: Canonical correspondence analysis: a new eigenvector technique for multivariate direct gradient analysis, Ecology, 67, 1167–1179, 1986.
Van Breemen, N., Finzi, A. C., and Canham, C. D.: Canopy tree-soil interactions within temperate forests: effects of soil elemental composition and texture on species distributions, Can. J. Forest Res., 27, 1110–1116, 1997.
Wilde, S. A., Voight, G. K., and Iyer, J. C.: Soil and plant analysis for tree culture, Oxford and IBH Publishing Co., New Delhi, India, 1972.

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Table 1. Forest floor (total) chemistry means (standard deviation) for sample plots within Grass Pond subwatersheds.

Subwatershed	Forest Floor					
	n	pH (units)	Al ($mg\,g^{-1}$)	Ca ($mg\,g^{-1}$)	NH_4 ($\mu mol\,N\,g^{-1}$)	C : N (Mass Ratio)
1	4	3.0 (0.4)	2.28 (0.45)	1.95 (1.09)	0.58 (0.39)	19.3 (1.8)
2	3	3.6 (0.3)	11.0 (13.9)	0.78 (0.21)	0.36 (0.84)	18.1 (2.1)
3	16	3.3 (0.5)	3.97 (2.37)	1.21 (0.81)	0.53 (0.34)	18.9 (1.4)
4	11	3.0 (0.5)	4.59 (6.91)	1.18 (0.64)	0.50 (0.50)	18.7 (1.6)
5	7	3.0 (0.3)	4.54 (3.03)	1.27 (0.60)	0.62 (0.64)	19.6 (1.1)
6	11	3.3 (0.5)	11.1 (10.8)	1.03 (0.76)	0.54 (0.51)	19.1 (2.0)
7	8	3.2 (0.4)	3.86 (4.18)	1.53 (0.88)	0.53 (0.55)	19.8 (1.3)

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Table 2. Mineral soil (exchangeable) chemistry means (standard deviation) for sample plots within Grass Pond subwatersheds.

Subwatershed	Mineral Soil				
	n	pH (units)	Al ($mg\,g^{-1}$)	Ca ($mg\,g^{-1}$)	NH_4 ($\mu mol\,N\,g^{-1}$)
1	2	3.4 (0.7)	0.23 (0.06)	0.27 (0.30)	0.72 (0.37)
2	4	3.8 (0.3)	0.36 (0.19)	0.09 (0.05)	0.39 (0.15)
3	13	3.6 (0.4)	0.39 (0.23)	0.13 (0.18)	0.45 (0.19)
4	9	3.3 (0.2)	0.31 (0.17)	0.15 (0.14)	0.46 (0.14)
5	8	3.6 (0.4)	0.32 (0.15)	0.10 (0.05)	0.44 (0.23)
6	11	3.7 (0.4)	0.39 (0.22)	0.09 (0.08)	0.37 (0.15)
7	8	3.5 (0.6)	0.27 (0.14)	0.12 (0.09)	0.51 (0.21)

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Table 3. Grass Pond stream chemistry means (standard deviation) analyzed from stream samples collected in October 2008.

Stream	*n*	ANC_c ($\mu eq\,l^{-1}$)	BCS ($\mu eq\,l^{-1}$)	pH (units)	DOC ($\mu mol\,C\,l^{-1}$)	NO_3^- ($\mu eq\,l^{-1}$)
1	2	35 (15)	11 (18)	6.4 (0.06)	367 (45)	7 (3)
2	3	55 (47)	40 (47)	6.2 (0.14)	244 (40)	7 (4)
3	6	152 (19)	122 (18)	6.8 (0.09)	459 (37)	22 (2)
4	7	−6 (52)	−31 (53)	5.4 (0.86)	374 (26)	12 (4)
5	7	−33 (13)	−65 (21)	4.9 (0.19)	485 (139)	4 (3)
6	6	−38 (8)	−68 (11)	4.9 (0.10)	449 (74)	10 (2)
7	6	−42 (8)	−72 (8)	4.7 (0.04)	457 (43)	1 (1)

Table 4. Factor analysis. Forest floor data and tree species basal area Pearson correlation coefficients ($n = 60$) and Mineral soil data and tree species basal area Pearson correlation coefficients ($n = 55$) with p-values.

	Forest Floor Chemistry					Mineral Soil Chemistry			
	pH (units)	NH_4 (µmol N g^{-1})	Ca (mg g^{-1})	Al (mg g^{-1})	C : N (molar ratio)	pH (units)	NH_4 (µmol N g^{-1})	Ca (mg g^{-1})	Al (mg g^{-1})
American Beech ($m^2 ha^{-1}$)	−0.091 (0.49)	−0.010 (0.45)	−0.21 (0.10)	−0.11 (0.40)	0.026 (0.84)	−0.059 (0.67)	−0.045 (0.74)	−0.16 (0.25)	0.19 (0.16)
Black Cherry ($m^2 ha^{-1}$)	−0.079 (0.55)	0.32 (0.013)	0.035 (0.79)	0.12 (0.36)	0.048 (0.77)	−0.18 (0.20)	0.13 (0.34)	0.25 (0.071)	0.036 (0.79)
Red Maple ($m^2 ha^{-1}$)	−0.16 (0.21)	0.21 (0.11)	0.024 (0.86)	−0.18 (0.17)	0.0082 (0.95)	−0.16 (0.24)	0.38 (0.0038)	0.0039 (0.98)	−0.13 (0.36)
Sugar Maple ($m^2 ha^{-1}$)	0.13 (0.32)	−0.12 (0.38)	−0.11 (0.40)	0.14 (0.30)	−0.23 (0.08)	0.26 (0.055)	−0.080 (0.56)	−0.083 (0.55)	0.14 (0.31)
Yellow Birch ($m^2 ha^{-1}$)	0.014 (0.92)	−0.0014 (0.99)	0.22 (0.091)	0.016 (0.90)	0.10 (0.44)	0.0002 (0.99)	0.061 (0.66)	0.39 (0.0035)	−0.077 (0.57)

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Table 5. Factor analysis. Watershed average stream chemistry data and tree species basal area Pearson correlation coefficients ($n = 7$) with p-values.

	Stream Chemistry				
	pH (units)	NO_3 ($\mu eq\,l^{-1}$)	DOC ($\mu mol\,C\,l^{-1}$)	ANC_c ($\mu eq\,l^{-1}$)	BCS ($\mu eq\,l^{-1}$)
American Beech ($m^2\,ha^{-1}$)	−0.037 (0.94)	0.74 (0.056)	0.43 (0.34)	0.19 (0.69)	0.15 (0.75)
Black Cherry ($m^2\,ha^{-1}$)	−0.36 (0.43)	−0.55 (0.20)	0.26 (0.58)	−0.51 (0.24)	−0.52 (0.23)
Red Maple ($m^2\,ha^{-1}$)	0.023 (0.96)	−0.22 (0.64)	0.037 (0.94)	−0.19 (0.69)	−0.19 (0.69)
Sugar Maple ($m^2\,ha^{-1}$)	0.39 (0.39)	−0.17 (0.72)	−0.89 (0.0077)	0.25 (0.59)	0.32 (0.48)
Yellow Birch ($m^2\,ha^{-1}$)	0.44 (0.32)	0.11 (0.82)	0.15 (0.75)	0.25 (0.59)	0.23 (0.62)

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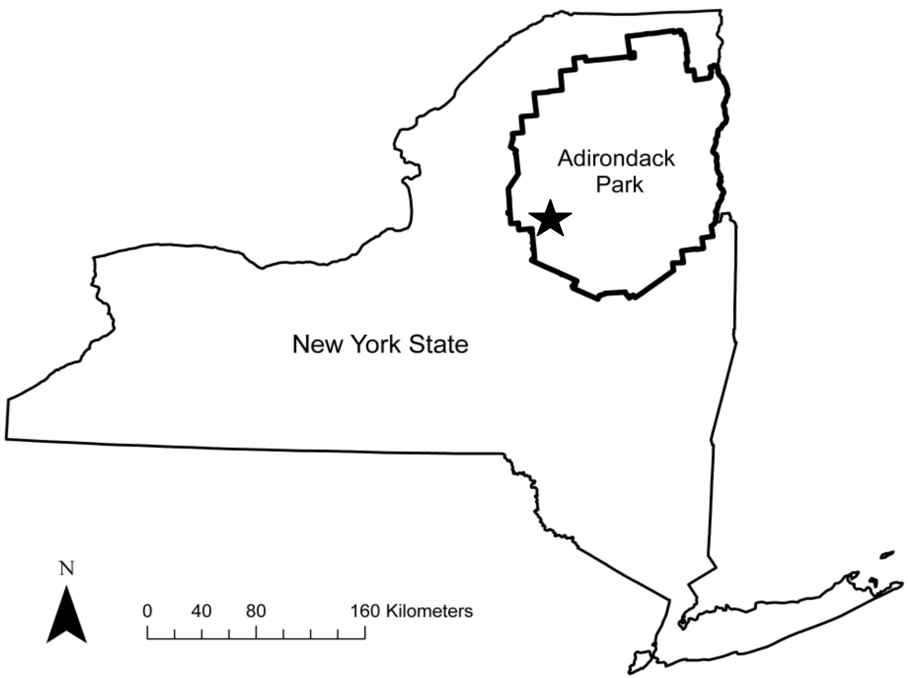

Fig. 1. The Adirondack Park located within New York State. The star indicates the location of Grass Pond watershed in the southwestern region of the Adirondacks.

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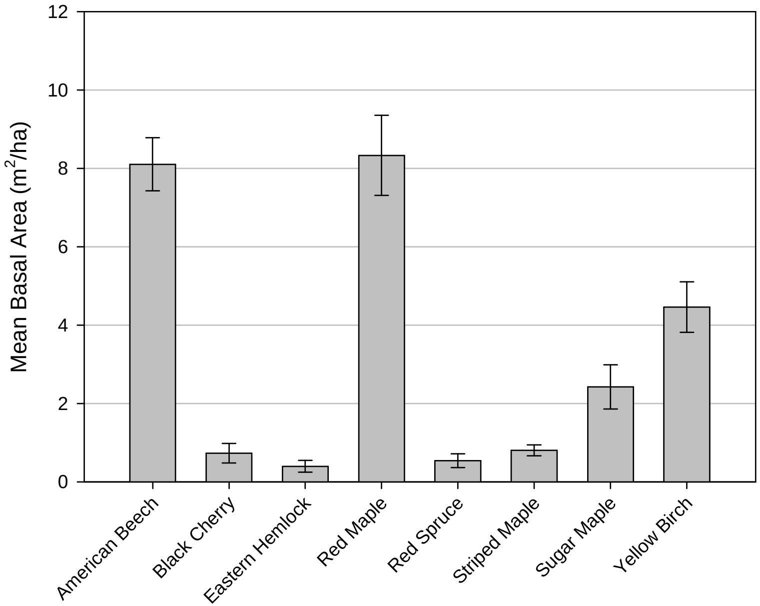

Fig. 2. Grass Pond watershed mean tree species total basal area ($m^2\,ha^{-1}$) calculated from plot data collected August–October 2008. Bars indicate one standard error.

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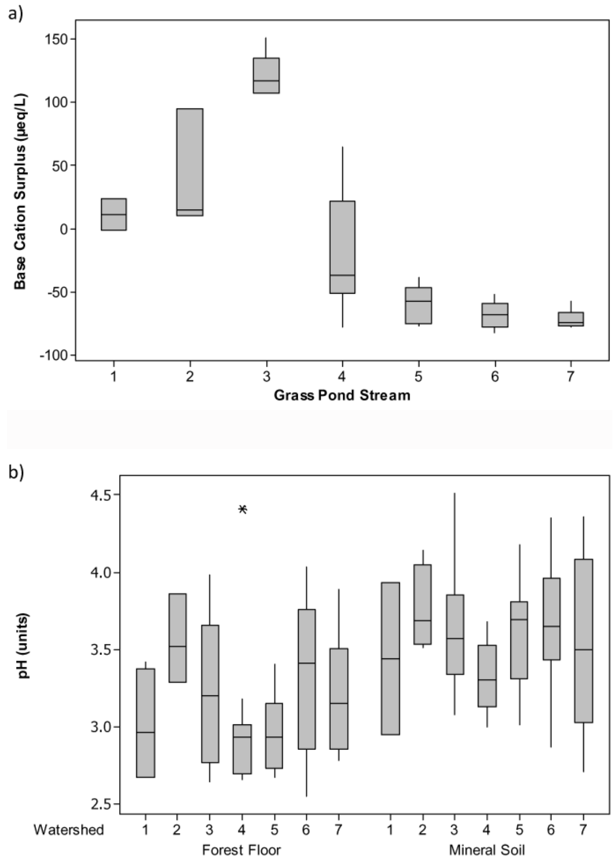

Fig. 3. (a) Base-cation surplus means ($\mu eq\,l^{-1}$) for each Grass Pond stream with bars indicating one standard deviation. Values $\leq 0\,\mu eq\,l^{-1}$ indicate a low capacity to neutralize acidic inputs. **(b)** Forest floor and mineral soil sample pH (units) for each Grass Pond subwatershed.

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Fig. 4. (a) Stream base-cation surplus (BCS) and sugar maple basal area upstream from the sample location exhibited a positive correlation ($p = 0.04$). **(b)** Stream base-cation surplus (BCS) and black cherry basal area upstream from the stream sample location exhibited an inverse correlation ($p = 0.02$).

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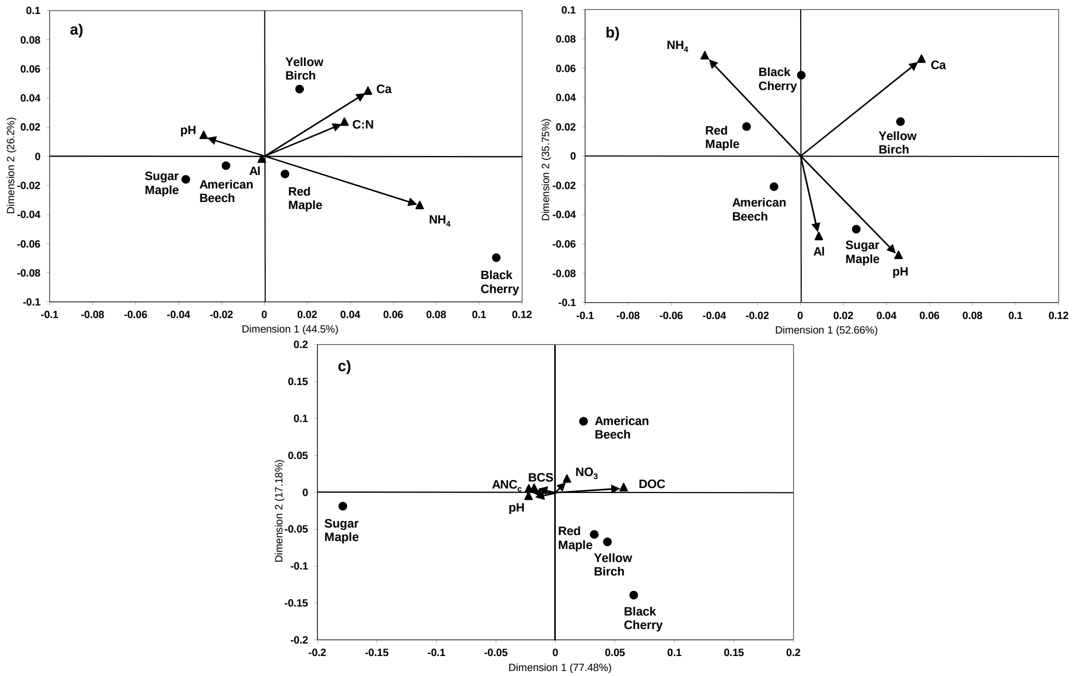

Fig. 5. CCA biplots with tree species basal area ($m^2\,ha^{-1}$) represented by circles and environmental variables. The environmental variables (arrows) are **(a)** forest floor pH (units), NH_4 ($\mu mol\,N\,g^{-1}$), Ca ($mg\,g^{-1}$), Al ($mg\,g^{-1}$) and C : N (molar ratio); **(b)** mineral soil pH (units), NH_4 ($\mu mol\,N\,g^{-1}$), Ca ($mg\,g^{-1}$) and Al ($mg\,g^{-1}$); and **(c)** stream sample pH (units), NO_3 ($\mu eq\,l^{-1}$), DOC ($\mu mol\,C\,l^{-1}$), ANC_c ($\mu eq\,l^{-1}$) and BCS ($\mu eq\,l^{-1}$).

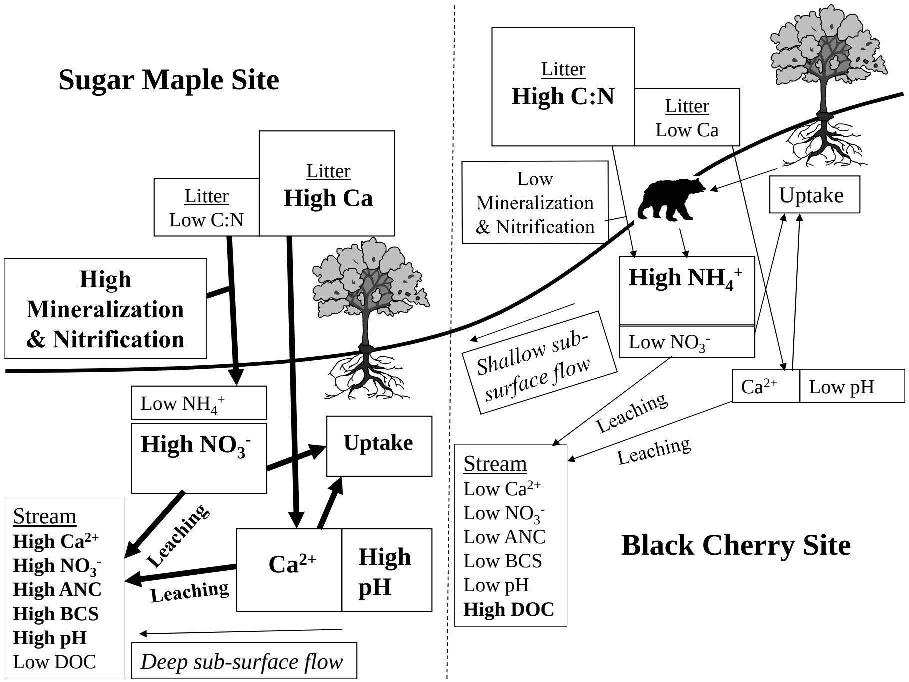

Fig. 6. Conceptual model indicating the dominant factors controlling the variation in stream water chemistry between sites with similar atmospheric deposition and land use but varying hydrology, tree species and soil processes in a northern hardwood dominated ecosystem. Thicker arrows indicate relatively greater fluxes and larger boxes indicate relatively larger pools between sites.

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