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High elevation watersheds in the southern Appalachians: Indicators of sensitivity to acidic deposition and the potential for restoration through liming

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ABSTRACT

Southern Appalachian high elevation watersheds have deep rocky soils with high organic matter content, different vegetation communities, and receive greater inputs of acidic deposition compared to low elevation sites within the region. Since the implementation of the Clean Air Act Amendment in the 1990s, concentrations of acidic anions in rainfall have declined. However, some high elevation streams continue to show signs of chronic to episodic acidity, where acid neutralizing capacity (ANC) ranges from 0 to $20 \, \mu eq \, L^{-1}$. We studied three 3rd order watersheds (North River in Cherokee National Forest, Santeetlah Creek in Nantahala National Forest, and North Fork of the French Broad in Pisgah National Forest) and selected four to six 1st order catchments within each watershed to represent a gradient in elevation (849–1526 m) and a range in acidic stream ANC values ($11–50 \, \mu eq \, L^{-1}$). Our objectives were to (1) identify biotic, physical and chemical catchment parameters that could be used as indices of stream ANC, pH and Ca:Al molar ratios and (2) estimate the lime required to restore catchments from the effects of excess acidity and increase base cation availability. We quantified each catchment's biotic, physical, and chemical characteristics and collected stream, O-horizon, and mineral soil samples for chemical analysis seasonally for one year. Using repeated measures analysis, we examined variability in stream chemistry and catchment characteristics; we used a nested split-plot design to identify catchment characteristics that were correlated with stream chemistry. Watersheds differed significantly and the catchments sampled provided a wide range of stream chemical, biotic, physical and chemical characteristics. Variability in stream ANC, pH, and Ca:Al molar ratio were significantly correlated with catchment vegetation characteristics (basal area, tree height, and tree diameter) as well as O-horizon nitrogen and aluminum concentrations. Total soil carbon and calcium (an indicator of parent material), were significant covariates for stream ANC, pH and Ca:Al molar ratios. Lime requirement estimates did not differ among watersheds but this data will help select catchments for future restoration and lime application studies. Not surprisingly, this work found many vegetation and chemical characteristics that were useful indicators of stream acidity. However, some expected relationships such as concentrations of mineral soil extractable Ca and SO_4 were not significant. This suggests that an extensive test of these indicators across the southern Appalachians will be required to identify high elevation forested catchments that would benefit from restoration activities.

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1. Introduction

Ecosystem responses to acidic deposition were a significant concern and a focus of research in the later part of the 20th century in the eastern United States (Johnson et al., 1982, 1992). The Clean Air Act of 1970 and the Clean Air Act Amendments of 1990 (CAAA), along with other emission reduction regulatory programs, have resulted in declining concentrations of sulfate (SO_4) and hydrogen (H^+) in wet deposition, consistent with the declines in sulfur dioxide (SO_2) emissions across the eastern US (Driscoll et al., 2003). For example, the U.S. Environmental Protection Agency (2015) reported that the three-year average for 1989–1991 and

2009–2011 sulfur (S) and total nitrogen (N) deposition (dry plus wet) decreased by 55% in the eastern US. Similarly, NADP reported a decline in SO_4 deposition in most southern Appalachian monitoring sites beginning in 1990 (NADP, 2007). This decline was also evident in data from Great Smoky Mountains National Park (Pardo and Duarte, 2007) and the Coweeta Hydrologic Laboratory in southwestern North Carolina, US (Knoepp, unpublished data). Despite reductions in emissions, many areas of the US still exhibit evidence of the negative impacts of acidic atmospheric deposition (Greaver et al., 2012). For example, some high elevation streams in the eastern U.S. continue to show signs of chronic to episodic acidity (Sullivan et al., 2007). Modeled patterns of SO_4 + nitrate (NO_3) deposition and ecosystem critical loads, exceeded the capacity of forest soils in approximately 17% of forested sites across the conterminous United States (McNulty et al., 2007) and numerous aquatic ecosystems in the southern Appalachians (McDonnell et al., 2014).

Patterns of atmospheric S and N deposition in mountainous terrain varies across landscapes and is related to rainfall amount, the presence of clouds and fog, elevation, forest edges, aspect, and vegetation composition (Weathers et al., 2000; Sullivan et al., 2007) with an estimated a 4–6-fold range in spatial variability (Weathers et al., 2006). Within the southern Appalachian Mountains high elevation sites receive higher rainfall (Swift et al., 1988) and greater inputs of nutrient and pollutant deposition (Swank, 1988; Swank and Vose, 1997; Sullivan et al., 2007) than low elevation sites. High elevation watersheds also have deep rocky soils with high organic matter content (Knoepp and Swank, 1998; Knoepp et al., 2000) and vegetation communities similar to forests in the northeastern U.S. (Elliott et al., 1999; Elliott and Swank, 2008). The deposition of SO_4 and NO_3 anions and their movement through the forest floor (soil O-horizon) and mineral soil profile results in the removal of base cations (calcium (Ca), magnesium (Mg), and potassium (K)) from soils. When base cations are removed from soils without adequate buffering capacity, soil pH decreases and aluminum (Al) is solubilized resulting in increased Al concentrations in soil solution and streams. As a result, stream acid neutralizing capacity (ANC) and stream pH decline. Examination of the effects of regional changes in acidic deposition, using biogeochemical models such as NuCM (Elliott et al., 2008) and MAGIC (Sullivan et al., 2007, 2011) found sensitivity to SO_4 deposition was related to soils and parent material; soils and parent material with low base cations concentrations were particularly sensitive to SO_4 deposition.

Base cation depletion in southern Appalachian high elevation watersheds is indicated by stream ANC values below 50 µeq L^{-1}, a value that has been defined as acidic (Bulger et al., 2000; Sullivan et al., 2007). Sullivan et al. (2008) examined the possibility of ANC recovery in Shenandoah National Park, Virginia US and found that watersheds located on siliciclastic bedrock would require a 77% decrease in atmospheric SO_4 deposition, compared to 1990 levels, to reach an ANC level of 50 µeq L^{-1} due to low concentrations of base cations in the soil. Sullivan et al. (2011) used the biogeochemical cycling model MAGIC and data from 65 acid sensitive watersheds in eastern Tennessee and western Carolina to back cast historical ANC values; they estimated that in 1860, ANC was as low as 30 µeq L^{-1} with a median of 65 µeq L^{-1}. Likens et al. (1996) estimated that pre-industrial revolution stream ANC in the Northeastern US averaged 20 µeq L^{-1}. While stream chemistry at Hubbard Brook Experimental Forest has shown consistent improvement (declining SO_4, increasing pH and ANC) since the implementation of the Clean Air Act in 1970, stream ANC values remain low. Likens and Buso (2012) concluded that soil weathering processes have not been rapid enough to replenish stream Ca concentrations, leaving diluted streams with altered cation ratios. Soils in the southern Appalachians have high SO_4 retention

capacity, which may delay the recovery of stream base cations. Rice et al. (2014) predicted that soils at three locations in western North Carolina will crossover from retaining to releasing SO_4 between 2023 and 2025.

Liming is a potential management option to restore streams and forest soils by decreasing acidity and increasing base cation availability. Lime is routinely used in agricultural systems, increasing soil pH, as well as Ca and Mg availability while also reducing Al solubility. Lime contains Ca and Mg, the two major divalent base cations; the ratio of these cations is dependent on the lime sources. Huettl (1993) and more recently Reid and Watmough (2014) review benefits and problems of lime applications in forest liming studies. The meta-analysis conducted by Reid and Watmough (2014) found that 67% of lime treatment trials showed increased soil pH and foliar Ca concentration. Soil pH response was greater in organic compared to mineral soils and Ca foliar response was positively correlated with treatment dose. Huettl (1993) focused on historic liming studies in Germany with reported benefits including increased soil Ca and Mg in O-horizons and surface mineral soils, which was accompanied by increased soil cation exchange capacity (CEC) and percent base saturation (%BS). Conversely, there was also evidence of increased soil NO_3 production following liming that resulted in cation leaching from subsoils. Increased rates of nitrification following liming were also found in forested sites in Finland (Priha and Smolander, 1995) and was stated as a concern because of the potential for accelerated cation leaching losses. Elliott et al. (2013) measured the response of soil and soil solution to liming following a wildfire in the Linville Gorge Wilderness Area in western North Carolina, a site previously shown to have low soil cation availability and acidic streams (Elliott et al., 2008). They found significant increases in surface mineral soil ECEC, pH, and Ca and a decline in Al as well as increases in soil solution NO_3. However, the lime response was short-lived, which they attributed to the small amount of lime added to the site (1.1 Mg ha^{-1}). In other forest liming studies, the effects of liming in the O-horizon and surface mineral soils were long-term, up to 21 years (Long et al., 2015), and in some cases resulted in the accumulation of organic material in the O-horizon (Johnson et al., 1995).

The continued sensitivity of southern Appalachian streams to atmospheric deposition emphasizes the need to identify watershed characteristics that influence stream chemistry responses to acidic deposition. For example, McDonnell et al. (2014) developed a screening tool that used a mass balance model to estimate critical loads for watersheds at risk of acidification based on S deposition. Although coarsely modeled at the regional scale, their work suggested that catchment characteristics could be used to identify catchments at risk and help managers prioritize stream monitoring and restoration efforts through liming. Hence, our first objective was to identify catchment biotic, physical and chemical characteristics, that are potential indices of stream acidity measured as ANC, pH, or Ca:Al molar ratio. A better understanding of these catchment scale characteristics and their relationship with stream chemistry could be used to evaluate restoration options such as liming. Our second objective was to estimate catchment lime requirements and consider how liming may improve stream chemistry.

To address these objectives we studied three large watersheds in the southern Appalachian Mountains along a gradient of acidic deposition with differing geology. Within each watershed we selected first order catchments that represented a range of elevations (849–1526 m) and stream ANC values based on previous studies (W. A. Jackson, unpublished data). We characterized all catchments in terms of overstory tree species composition and stand characteristics, site and soil morphology and chemistry, and soil lime requirement. Stream, O-horizon, and mineral soils, were intensively sampled four times over one year to capture sea-

sonal variability in stream chemistry and soil/stream connectivity (Swank and Vose, 1997; McHale et al., 2002).

2. Materials and methods

2.1. Site selection

Study watersheds were selected based on the following criteria: (a) they exceeded critical loads of acidic deposition (McNulty et al., 2007; McDonnell et al., 2014) and (b) they were included in a USDA Forest Service, regional synoptic sampling effort to identify streams in 1st order catchments with low ANC (W. A. Jackson, unpublished). The three watersheds are from west to east, North

River (NR, 35° latitude, 84° longitude; Cherokee National Forest, Tennessee), Santeetlah Creek (SC, 35° latitude, 84° longitude; Nantahala National Forest, North Carolina), and the North Fork of the French Broad (FB, 35° latitude, 82° longitude; Pisgah National Forest, North Carolina) (Fig. 1). Watershed size ranged from 4800 ha at NR to 9800 ha at FB; between 17% (NR) and 53% (SC) of the watershed area was above 1000 m in elevation. All watersheds contained numerous 1st order catchments with a range of median ANC values classified as, not acidic (ANC > 50 μeq L^{-1}), intermediate (ANC = 20–50 μeq L^{-1}), episodically acidic (ANC = 0–20 μeq L^{-1}), and chronically acidic (ANC < 0 μeq L^{-1}) (Bulger et al., 2000).

In late 2011, we selected 4–6 first order catchments within each watershed that represented the range in elevation and stream ANC described above. The stream collection location for all catchments
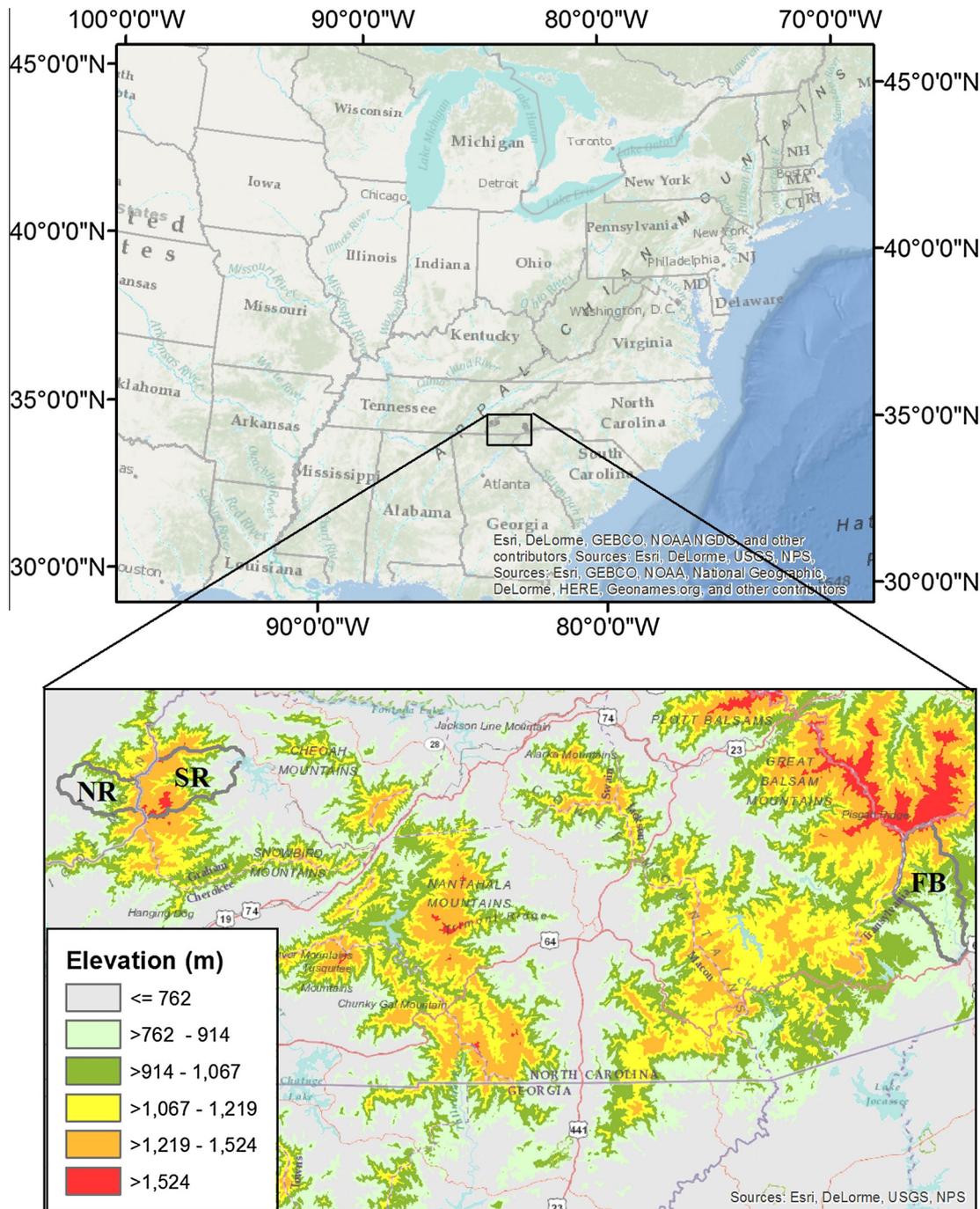

Fig. 1. Location of three watersheds sampled in this study.

was >850 m in elevation; 5 catchments in NR, 4 catchments in SC, and 6 catchments in FB (N = 15 catchments). Within each catchment we established 2–10 m diameter circular sample plots, one in the riparian zone and one on the hillslope. The center of the riparian plot was 6 m from the stream and the hillslope plot was ca. 40 m upslope from the riparian plot, where soil morphology and vegetative composition was different than the riparian zone. The total number of plots per watershed were, NR, n = 10; SC n = 8; FB, n = 12; a total of 30 plots. Seasonal stream, O-horizon and mineral soil sample collection began in May 2012. Table 1 contains a list of all measurements divided into catchment, catchment geochemical, soil O-horizon, mineral soil and stream chemistry variables.

2.2. Catchment characterization

We collected several types of data from all riparian and hillslope plots to characterize each catchment. Plot measurements included mineral soil morphology (A horizon depth, total profile depth to saprolite or bedrock), O-horizon morphology (Oi and Oe + Oa weight, Oe + Oa depth), plot morphology (elevation, slope, aspect), and vegetation characteristics. From the center point of each plot, overstory vegetation characteristics were obtained using a variable radius plot sampling method with a wedge prism (2.0 BAF, metric), and tree diameters within the variable plot were measured at breast height (DBH at 1.37 m aboveground) to calculate species-specific basal area and species composition. We measured tree height, using a clinometer, of the six dominant or co-dominant trees within the variable radius plot.

2.3. Stream sample collection and analysis

To capture seasonal variation, stream samples were collected from each catchment in early summer (May 2012), mid-summer (July/August 2012), fall (November 2012), and spring (April 2013)

a total of four collections; all sample collections were conducted while streams were at baseflow levels. For each date, we collected stream water grab samples in each catchment adjacent to riparian plots (n = 4, 5 or 6 catchment samples per watershed per date). Water samples were collected in three bottles, one sample bottle was filtered in the field (<0.70 μm pre-muffled glass fiber filter), and all were stored in a cooler, then placed in a refrigerator (4 °C) or a freezer until analyses were conducted using standard laboratory procedures (Miniat et al., 2014). Solution pH was determined on an unfrozen unfiltered sample within 24 h of collection using an Orion Research digital pH meter 611 with a Broadley James pH probe. Cation concentrations (Ca, Mg, Na, K, and Al) were determined on previously frozen unfiltered samples using an inductively coupled plasma spectrometer (ICP) (Thermo Fisher iCAP 6300, Thermo Fisher Scientific, Madison, WI). Stream Ca:Al molar ratios were calculated as mmol L^{-1}. Anion concentrations (NO$_3$, SO$_4$, and Cl), were determined on previously frozen unfiltered samples using a Dionex ICS 4000 Capillary Ion Chromatograph (Thermo Fisher Scientific, Madison, WI). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) analysis was determined on filtered previously frozen sample on a Shimadzu TOC-VCPH TNM-1 (Shimadzu Scientific Instruments, Columbia, MD). Cation and anion concentrations are reported as μeq L^{-1} and DOC and TDN are reported as mg L^{-1}. Stream acid neutralizing capacity (ANC) was calculated as:

$$\text{ANC} \ (\mu eq \ L^{-1}) = \sum \text{base cations} \ (Ca + Mg + Na + K) \\ - \sum \text{acid anions} \ (SO_4 + NO_3 + Cl)$$

2.4. Soil O-horizon sampling and analysis

Soil O-horizon samples were collected using a 30×30 cm (0.09 m^2) frame (3 sample frames per plot) at random distances and directions from the plot center for each collection date;

Table 1
Variables measured for catchment characterization, catchment geochemical characterization, soil O-horizon, mineral soil, and stream chemistry. Variables marked with '*' were identified as significant covariates in stream chemistry statistical models (Tables 3 and 4).

Dataset	Variables measured
Catchment characteristics	Elevation (m)*
	Slope and aspect (°)
	Soil morphology (A horizon, profile depth; cm)*
	O-horizon morphology (cm depth)
	Overstory basal area (m^2 ha^{-1})*
	Overstory species composition
	Height of 6 dominant trees (m)*
	DBH of all trees (cm)*
Catchment geochemical characteristics	Nutrient Uptake index; litterfall represented by November Oi-horizon collection*
	Soil total elemental analysis (g kg^{-1}) (Ca, Mg, K, Na, Al, P, calculated Felsic:Mafic, Fe:Al)*
	Total mineral soil elemental nutrient content (kg ha^{-1})*
	Total mineral soil extractable nutrient content (kg ha^{-1})
Soil O-horizon; sampled by date and horizon	Mass per unit area (g m^{-2})*
	Total base cations (g kg^{-1}) (Ca, Mg, K, Na)
	Total Al (g kg^{-1})*
	Total C and N (g kg^{-1})*
Mineral soil; sampled by date and soil depth	pH
	Extractable base cations (g kg^{-1}) (Ca, Mg, K, Na)
	Base saturation (%)*
	ECEC (cmol$_c$ kg^{-1})
	Extractable Al (g kg^{-1})*
	Lime Requirement (to pH 5.5)
	Total C and N (g kg^{-1})*
	Extractable SO$_4$-S (g kg^{-1})
Stream chemistry; sampled by date	Calculated ANC
	pH
	Molar Ca:Al
	Other: DOC and TN, NO$_3$-N, SO$_4$-S, Cl, NH$_4$-N, Base cations, and Al

collection dates coincided with stream sampling dates (i.e., early summer (May 2012), mid-summer (July/August 2012), fall (November 2012), and spring (April 2013)). The O-horizon was separated into Oi and Oe + Oa horizons in the field, and each horizon from each location was placed in a paper bag (3 frames × 30 plots × 4 dates × 2 horizons; a total of 720 O-horizon samples). The November 2012 sample collection was conducted soon after leaf-fall from all watersheds and we used the Oi horizon chemistry data as a proxy for litterfall and an index of soil nutrient availability, a geochemical characteristic. Depth of the Oa + Oe horizon was measured along the edge of each sample frame and recorded. Upon returning to the laboratory, all samples were oven dried at 60 °C until reaching a constant weight; samples were weighed to the nearest 0.01 g. Dried samples were thoroughly mixed, composited by plot and horizon, ground to <1 mm using a Retsch grinding mill (Retsch, Inc., Newtown, PA), mixed again, and a subsample was placed in a glass vial for storage prior to analysis. Samples were analyzed for total C and N by combustion on a Flash EA 1112 series (CE Elantech, Lakewood, NJ). Total phosphorus (P) and cation (Ca, Mg, Na, K, and Al) concentrations were determined by dry-ashing a 0.5 g sample at 500 °C for 4 h. followed by digestion in 2.2 M nitric acid (Miniat et al., 2014), the resulting solution was analyzed using ICP as described above. Ash-free dry weight of all O-horizon samples was measured during the dry-ashing/digestion process to allow sample weight correction for mineral soil contamination. All weight and nutrient concentration data presented for Oe + Oa horizon samples are presented on an ash-free basis. Oi horizon samples contained <5% mineral material, data are presented on an oven-dry weight basis.

2.5. Mineral soil sampling and analysis

Composite mineral soil samples were collected using a 2.5 cm diameter soil probe from each plot by depth (surface soil, 0–10 cm; subsoil, 10–30 cm; and deep soil, 30+ cm), for each date as described above (i.e., early summer (May 2012), mid-summer (July/August 2012), fall (November 2012), and spring (April 2013)). Composite samples consisted of 12–20 individual soil cores from random locations within each 10-m circular plot. Total profile depth to saprolite reached at each location sampled was recorded; a total of 360 soil samples were collected (30 plots × 3 soil depths × 4 dates). Mineral soil samples were placed in re-sealable plastic bags, returned to the lab, air dried to a constant weight, sieved to <2 mm and stored in a 120 ml glass jar for storage prior to chemical analysis. Soil pH was determined in a 1:1 soil to 0.01 M CaCl$_2$ slurry with a Thermoscientific Orion 3 star pH benchtop meter with a Thermo Scientific Orion pH probe. We determined exchangeable cation concentrations (Ca, Mg, Na, K, and Al) as well as effective cation exchange capacity (ECEC) by extracting cations from 5.0 g of soil with 50 ml 1.0 M NH$_4$Cl on a mechanical vacuum extractor (SampleTek, Science Hill, KY), followed by rinsing the soil with 95% EtOH and extraction of remaining NH$_4$ with 1 M KCl to determine ECEC. Cation concentrations in NH$_4$Cl solution were determined using ICP as described above; NH$_4$ concentration in KCl extraction solution was determined colorimetrically using the alkaline phenol method (USEPA, 1983), and used to calculate ECEC (cmol kg^{-1}). Percent base saturation (%BS) was calculated: %BS = ((Ca + Mg + Na + K)/ECEC) ∗ 100. Ca to Al ratio was calculated using molar concentrations (Ca:Al mmol kg^{-1}). Extractable phosphate (PO$_4$) was determined by extracting 5.0 g of soil in 20 ml dilute double acid (0.05 M HCl + 0.0125 M H$_2$SO$_4$) followed by centrifugation and determination of PO$_4$ in solution by ICP as described above (Kuo, 1996; Miniat et al., 2014). Sub-samples (∼5 g) of each soil sample were ground to a fine powder prior to total C and N analysis by combustion as described above.

We conducted total elemental analysis of soils from each watershed, catchment, plot, and depth collected in April 2012 using the closed vessel aqua regia and hydrofluoric acid dissolution method (Hossner, 1996) followed by analysis with ICP as described above on soils as a proxy for total mineral availability and soil parent material as geochemical characteristics. We calculated an indicator of the ratio of felsic to mafic parent material (Felsic:Mafic) as K + Na: Ca + Mg. Felsic parent materials are dominated by K and Na (monovalent ions) and Mafic parent materials by Ca and Mg (divalent ions). We also calculated the Fe:Al ratio as an indicator of the mineralogy of the soils clay component, which regulates the soil cation exchange capacity. We used recent soil surveys for catchment within watershed descriptions including soil bulk density and percent coarse fragment of each soil type by depth (Soil_Survey_Staff, 2014); these values were used with laboratory determined soil chemistry (extractable and total elemental cations) to calculate total available and total mineral nutrient content of the soil profile (kg ha^{-1}) for each plot within each catchment.

2.6. Catchment lime requirement

To estimate the lime requirement for each catchment, we analyzed mineral soils collected at all four dates, from all plots, catchments, and watersheds (3 depths × 4 dates × 2 plots × 15 catchments = 360 samples). We used the Mehlich Single Buffer method (Sims, 1996), to estimate lime addition required to adjust the mineral soil to pH to 5.5. This method yields lime application estimates in Mg ha^{-1} of CaCO$_3$ assuming a 20 cm soil depth. We estimated the lime required to adjust the surface mineral soil (0–10 cm), dividing the estimated lime requirement by 2 (Lime Required 0–10 cm = Lime Mg ha^{-1}/2). We calculated the sum of the surface and subsoil mineral soil depths by summing the lime requirement for each depth (Lime Required 0–30 cm = Lime Required 0–10 cm + Lime Required 10–30 cm).

2.7. Statistical analysis

Our statistical analysis varied depending on whether we were testing for spatial vs. temporal differences in variables. For variables sampled by date (i.e., stream chemistry, mineral soil chemistry and O-horizon chemistry) sample date was included as a discrete qualitative repeated measures factor because we did not expect a trend over time that could be modeled with a mathematical function (Littell, 2007). We tested several covariance structures for each dataset as suggested by Littell et al. (1998) and Littell (2007), including compound symmetry (CS), Huynh-Feldt (HF), spatial power structure (SP(POW)), variance components (VC) and others, selecting the covariance structure that resulted in the minimum corrected Akaike's Information Criterion (AICC) value (Hurvich and Tsai, 1991). We examined watershed, sample collection date, and watershed by date interaction effects on stream chemistry variables using a nested plot experimental design with watershed and date (fixed effects) and catchment nested within watersheds (random effect) using Proc Mixed (SAS v9.3 (SAS, 2013)). We included sample date in a repeated measures statement, using compound symmetry (CS) as the covariance structure. A nested split-plot experimental design was used to examine watershed and date effects on O-horizon and mineral soil chemistry data with watershed (fixed effect), date (fixed effect), catchment nested within watershed (random effect), and slope position as a split plot within watersheds (fixed effect) using Proc Mixed (SAS, 2013). We included sample date in a repeated measures statement using Huynh-Feldt (HF) covariance structure for O-horizon chemistry and a spatial power structure (SP(POW)) for mineral soil chemistry. O-horizon and soil depths were analyzed

separately. For testing spatial differences in variables (i.e., among and within watersheds and catchments), we used a nested split-plot experimental design, examining watershed effects (fixed effect), catchment within watershed effect (random) and the split-plot of slope position (i.e., midslope vs. riparian) within catchment (fixed) using Proc Mixed (SAS, 2013); we used variance components (VC) covariance structure.

We used Proc Mixed (SAS, 2013) to select catchment characteristics, O-horizon chemistry, mineral soil chemistry and catchment chemical characteristic variables that were significant in informing the best statistical model of stream chemistry variables (ANC, pH, and Ca:Al molar ratio). For these analyses, we used mean catchment values (i.e., average of the hillslope and riparian plots) for catchment characteristics, O-horizon chemistry, mineral soil chemistry and catchment chemistry as the independent variables. We also examined the influence of the riparian zone by examining riparian plot data separately. First, we conducted linear regression analysis (Proc Reg (SAS, 2013)) for each data set (catchment characteristics, O-horizon, soil chemistry, and catchment chemical characteristics), to reduce the number of variables included in the analysis. Regression analyses included comparison of the same measurements made in different O-horizons and mineral soil depths. Variables that did not exhibit significant collinearity (r^2-value < 0.70) were used in the first step of model analysis. We also included variables (i.e., extractable Ca:Al molar ratio, ratio of cation concentrations in surface mineral soil relative to deep soil) that utilized several measurements and were potentially useful as explanatory variables. Next, variables from each data set were included as covariates in the mixed model analysis; variables were eliminated if the probability (P) of an F-value was >0.25; the result yielded 2–8 variables for final testing. We included all of these variables (those with $P < 0.25$) to select the final model which included only variables with $P \leqslant 0.05$. By examining datasets separately we were able to identify the best statistical model and significant covariates for stream chemistry. We used the nested experimental design with repeated measures to identify O-horizon and mineral soil chemistry variables that were significant covariates of stream chemistry. We used the mean stream chemistry data (four sample collection dates), in the nested split-plot experimental design to develop the best statistical model for catchment characteristic data, both non-chemical and chemical. The results presented are primarily the variables that were identified as significant covariates in the statistical models examining variation in stream chemistry (Section 3.6).

3. Results

3.1. Watershed and catchment characterization

The catchments and plots within watersheds represented a broad range of morphological and vegetative characteristics. Soil A-horizon depth ranged from 5 to 33 cm and total soil profile depth ranged from 43 cm to 92 cm (Fig. 2). Overstory basal area ranged from 14 m^2 ha^{-1} to 56 m^2 ha^{-1} and mean plot tree height ranged from 18.5 m to 54.1 m (Fig. 2). Basal area of *Quercus* spp. ranged from 0 to 22 m^2 ha^{-1}, and *Acer* spp. ranged from 0 to 14 m^2 ha^{-1} (Fig. 2). Basal area of *Quercus* spp. varied with slope position ($F = 12.58$; $P < 0.01$) with greater *Quercus* spp. present in the hillslope position.

3.2. Variation in O-horizon mass and chemistry

Watershed did not have a significant effect on Oi horizon mass, total C or total N concentrations however, date effect and date by
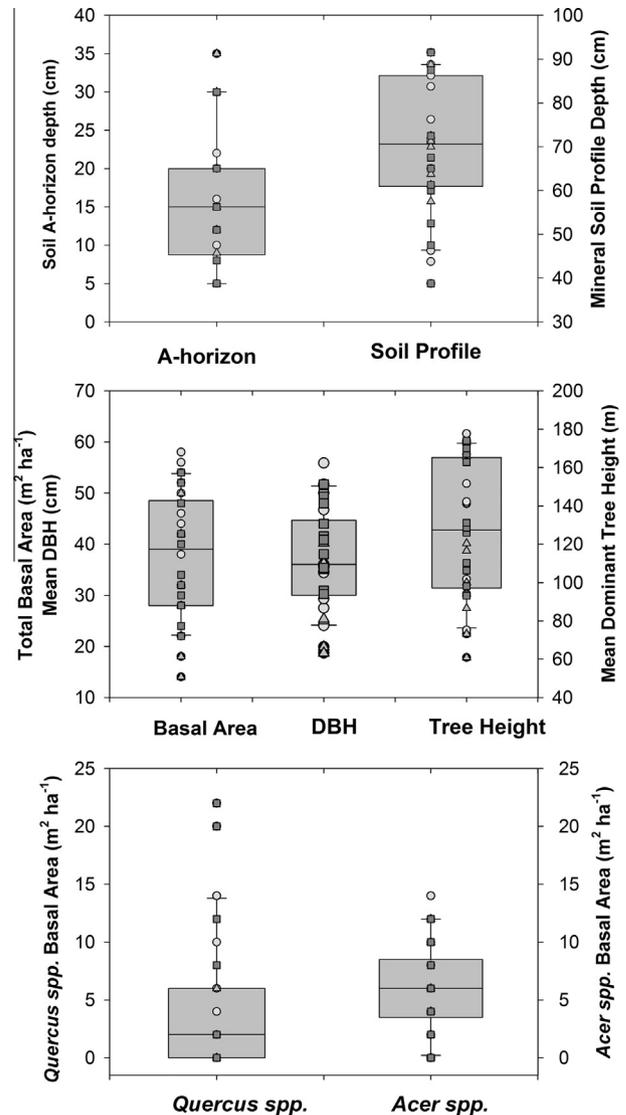

Fig. 2. Plot characterization variables were measured at each riparian and hillslope plots. A-horizon and total soil profile depth, basal area, diameter at breast height (DBH) and mean height of the 6 dominant overstory trees, and basal area of *Quercus* spp. and *Acer* spp. Plot values for each variable are shown with North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■). Box plots show watershed median value, along with the 10th, 25th, 75th and 90th percentiles.

watershed interaction were significant. As expected, the greatest Oi horizon mass was measured in fall (November) and the least in summer (July). Ca and Al concentrations differed significantly among watersheds (Ca, $F = 3.83$, $P = 0.04$; Al, $F = 3.47$, $P = 0.05$) and sample collection date (Ca, $F = 4.75$, $P < 0.01$; Al, $F = 5.39$, $P < 0.01$). Neither slope position nor watershed by date interaction were significant.

Oe + Oa horizon mass was significantly affected by watershed ($F = 16.17$, $P < 0.001$) and date ($F = 8.94$, $P < 0.001$). Mass was greatest in the spring (April 2013); watershed by date interaction was not significant. Collection date had a significant effect on total C and N concentration (C, $F = 3.35$, $P = 0.02$; N, $F = 3.36$, $P = 0.02$). Oe + Oa horizon Ca concentrations ranged from 0.89 to 5.0 g Ca kg^{-1} and differed among watersheds ($F = 9.39$, $P = 0.001$) and by date ($F = 7.84$, $P = 0.001$); there were no significant watershed by date interactions. Oe + Oa Al concentrations did not differ among watersheds but date effect was significant ($F = 4.25$, $P = 0.01$).

3.3. Variation in mineral soil chemistry

Mineral soil chemical characteristics in the surface soil depth varied significantly with both watershed and sample date; watershed by date interaction were significant for some variables (soil pH, total N and total C). Soil pH ranged from 3.1 to 4.4 (watershed, $F = 6.24$, $P = 0.01$; date, $F = 15.18$, $P < 0.001$) and %BS ranged from 2.3 to 42.2 $cmol_c\,kg^{-1}$ (watershed, $F = 7.51$, $P < 0.01$; date, $F = 6.02$, $P < 0.01$). Total C ranged from 10.9 to 153.2 $g\,kg^{-1}$ (watershed, $F = 28.44$, $P < 0.01$; date, $F = 5.04$, $P < 0.01$) and total N from 0.63 to 10.3 $g\,kg^{-1}$ (watershed, $F = 22.60$, $P < 0.01$; date, $F = 5.28$, $P < 0.01$).

Deep mineral soil pH, %BS, total N and total C concentrations showed a significant watershed and date effect; watershed by date interaction was significant for pH, total N and total C. Soil pH ranged from 4.1 to 4.7 (watershed, $F = 5.33$, $P = 0.01$; date, $F = 3.30$, $P = 0.03$) and %BS ranged from 1.2 to 14.7 $cmol_c\,kg^{-1}$ (watershed, $F = 7.49$, $P < 0.01$; date, $F = 11.00$, $P < 0.01$). Deep mineral soil total C ranged from 6.5 to 114.5 $g\,kg^{-1}$ (watershed, $F = 7.70$, $P < 0.01$; date, $F = 4.14$, $P < 0.01$) and total N from 0.51 to 7.4 $g\,kg^{-1}$ (watershed, $F = 9.92$, $P < 0.01$; date, $F = 4.84$, $P < 0.01$).

Mineral soil total Ca, K, and P in all mineral soil depths (surface, 0–10 cm; subsoil, 10–30 cm; deep soil, 30+ cm) differed among watersheds. Surface mineral soil total Ca concentrations ranged from 157 to 19,900 $g\,kg^{-1}$ ($F = 9.57$, $P < 0.01$) and total K concentrations ranged from 6900 to 24,300 $g\,kg^{-1}$ ($F = 8.93$, $P < 0.01$). The ratio of extractable Ca to total Ca (extractable Ca:total Ca) also differed significantly among watersheds ($F = 12.46$; $P < 0.001$) as did the Felsic:Mafic ratio ($F = 20.86$; $P < 0.01$) and the Fe:Al ratio ($F = 8.50$; $P < 0.01$).

3.4. Catchment soil nutrient availability characterization

We used nutrient concentrations in the November Oi horizon collection, a time when this horizon closely represents litterfall (hereafter, litterfall), and soil nutrient availability. None of the variables measured, litterfall mass, total N, Ca, Al concentrations, or the Ca:Al molar ratio showed significant differences among watersheds. Plot slope position had a significant effect on litterfall total Ca concentration ($F = 7.79$, $P = 0.02$).

3.5. Watershed variation in stream chemistry

Stream ANC varied significantly among watersheds; ANC values ranged from 6 $\mu eq\,L^{-1}$ to 84 $\mu eq\,L^{-1}$ at NR, from -5 $\mu eq\,L^{-1}$ to 42 $\mu eq\,L^{-1}$ at SC, and -7 $\mu eq\,L^{-1}$ to 51 $\mu eq\,L^{-1}$ at FB (Table 2 and Fig. 3). Sample collection date had no significant effect on stream ANC. Stream pH did not vary among watersheds or sample dates (Table 2). Mean stream pH values ranged from 6.1 to 6.7 in NR, from 5.4 to 6.3 in SC, and 5.8 to 6.4 in FB (Fig. 3). Watershed and date had a significant effect on stream Ca:Al molar ratio; there was no watershed by date interaction (Table 2). Stream Ca:Al molar ratio was lower in the summer compared to fall and spring.

3.6. Catchment variables as indicators of stream chemistry

Nested split-plot analyses of biotic and physical catchment characteristics identified stream elevation ($P = 0.02$) as the only significant covariate for stream ANC (Table 3 and Fig. 4); basal area of Quercus spp. was a marginally positive covariate ($P = 0.08$). Biotic and physical characteristics that were significant in covariates in analysis of stream pH were depth of mineral soil A horizon ($P = 0.001$) and total catchment basal area ($P = 0.01$), both with positive coefficients (Table 3 and Fig. 4). Vegetation characteristics were also significant covariates for analysis of stream Ca:Al molar

ratio; mean height of the dominant trees ($P = 0.01$) was a positive coefficient (Table 3 and Fig. 3).

Nested split-plot analysis of catchment chemical characteristics identified total soil Ca content (kg ha^{-1}) ($P < 0.001$), as a significant negative covariate for stream ANC (Table 3 and Fig. 5). The extractable Ca:total Ca in the surface soil ($P = 0.02$) was the only significant catchment chemical characteristic (positive coefficient) that varied with stream pH (Table 3 and Fig. 5). Analysis of stream Ca:Al molar ratio identified two significant covariates, surface soil Fe:Al ratio ($P = 0.01$) and litterfall Ca:Al ratio ($P = 0.02$), both had negative coefficients (Table 3 and Fig. 5).

O-horizon physical and chemical characteristics were included in repeated measures analysis of stream chemistry variability. Stream ANC analyses identified total N concentration (negative coefficient) in the Oe + Oa horizon as a significant covariate ($P = 0.05$). Oi horizon mass (g m^{-2}) was a significant covariate in stream pH analysis ($P = 0.001$) with a negative coefficient (Table 3 and Fig. 6). Al concentration in the Oi horizon ($P = 0.01$) was a positive covariate for stream Ca:Al molar ratio (Table 3 and Fig. 6).

Repeated measures analysis of soil chemical characteristics identified two significant covariates for stream ANC, deep mineral soil total C concentration ($P < 0.001$) and surface mineral soil Al concentration ($P = 0.02$); both had negative coefficients (Table 3 and Fig. 7). Deep mineral soil total C concentration ($P = 0.002$) was also identified as a significant covariate in stream pH analysis. Analysis of stream Ca:Al molar ratio identified subsoil (30+ cm) % BS ($P = 0.05$) as a significant covariate with a positive coefficient (Table 3 and Fig. 7).

We also examined the effect of only the riparian plot measurements of non-chemical, O-horizon physical and chemical, and soil physical and chemical characteristics on stream chemistry (Table 4). Nested split plot analysis identified stream elevation ($P = 0.02$) as a significant covariate with stream ANC (Table 4), and A horizon depth as a significant covariate for both pH ($P < 0.001$) and Ca:Al molar ratio ($P < 0.01$). Analysis of stream pH with riparian plot chemical characteristics included the Felsic: Mafic ratio of the deep mineral soil ($P < 0.001$) as well as extractable K:total K ($P = 0.001$) and surface soil total Ca concentration ($P = 0.001$) as significant covariates. Both Felsic:Mafic and extractable K:total K had positive coefficients while total surface soil Ca was negative (Table 4). There were no significant soil chemistry covariates in the riparian plot analysis of stream Ca:Al molar ratio. Repeated measures analysis of stream chemistry and riparian plot O-horizon chemistry identified no significant covariates for stream ANC or pH, whereas Al concentration of the Oi horizon ($P < 0.01$)
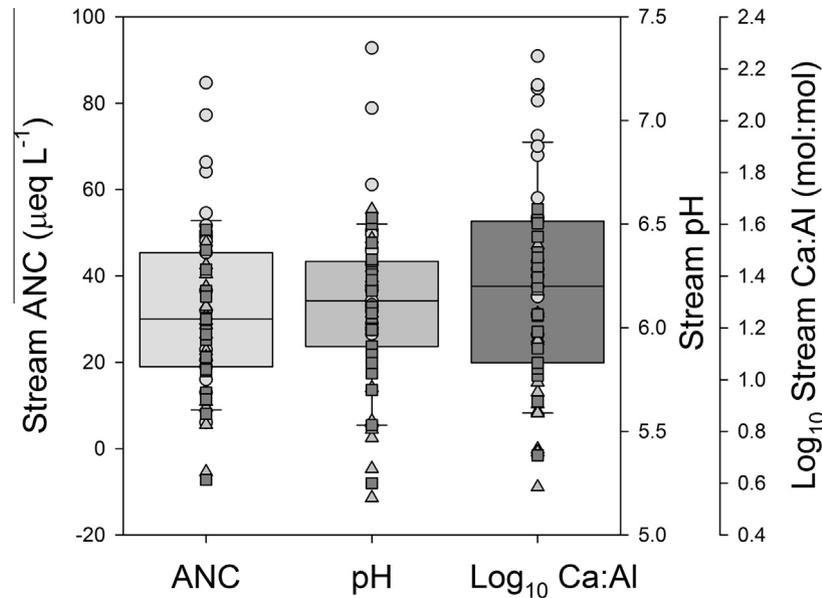
Table 2

Stream chemistry statistical analyses of acid neutralizing capacity (ANC ($\mu eq\,L^{-1}$) = $\sum$ base cations (Ca + Mg + Na + K) $- \sum$ acid anions (SO_4 + NO_3 + Cl)), pH, and the molar ratio of calcium to aluminum (mmol Ca:mmol Al). (A) Repeated measures analysis including effects of watershed (fixed), date (fixed), watershed by date interaction, and catchment within watersheds (random effect); (B) nested split-plot experimental design included watershed (fixed) and catchment within watersheds (random effect). Presented are F-value, degrees of freedom (DF), probability (P) of a value greater than F in parentheses, and the estimated R^2 of the model. Significant relationships are highlighted in bold.

	DF	ANC ($\mu eq\,L^{-1}$) F-value (P)	pH F-value (P)	Molar Ca:Al F-value (P)
A. Repeated measures experimental design				
WS	2	**6.50 (0.01)**	2.20 (0.15)	**14.72 (<0.001)**
DATE	3	1.55 (0.22)	0.71 (0.55)	**9.39 (<0.001)**
WS × D	6	**5.84 (<0.001)**	1.76 (0.14)	0.14 (0.99)
Model R^2		0.56	0.26	0.63
B. Nested split-plot experimental design				
WS	2	**3.75 (0.05)**	2.28 (0.14)	**15.17 (<0.001)**
Model R^2		0.38	0.28	0.72

Fig. 3. Catchment stream chemistry including all sample dates (early summer, mid-summer, fall and spring) for acid neutralizing capacity (ANC), pH, and log$_{10}$ molar Ca:Al ratio. Shown are catchment values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■). Box plots show watershed median value, along with the 10th, 25th, 75th and 90th percentiles.

Table 3
Catchment variables included as covariates in the statistical models examining the variability in stream chemistry for ANC, pH and molar Ca:Al ratio. Covariates listed were included in the model with P-value ⩽ 0.05. Covariate variables designated '*' were significant in the split plot experimental design and '**' in the repeated measures analysis. The estimated model R^2 incorporates the nested split-plot or repeated measures models as presented in Table 2 with the improvement in predictions by including covariate(s).

Variables	Stream ANC		Stream pH		Stream molar Ca:Al	
Catchment characteristics*	Stream elevation (m) (−) Model R^2 = 0.64		A Hzn depth (cm) (+) Model R^2 = 0.83	Basal area[a] (m^2 ha^{-1}) (+)	Mean tree height[b] (m) (+) Model R^2 = 0.86	
Catchment geochemical characteristics*	Total Ca[c] (kg ha^{-1})[d] (−) Model R^2 = 0.71		Ext Ca:Total Ca[e] 0–10 cm[f] (+) Model R^2 = 0.55		Fe:Al[g] 0–10 cm (−) Model R^2 = 0.89	Litterfall[h] Ca:Al (−)
O-horizon**	N (g kg^{-1}) Oe + Oa Hzn (−) Model R^2 = 0.64		Mass (g m^{-2}) Oi Hzn (−) Model R^2 = 0.46		Al (g kg^{-1}) Oi Hzn (+) Model R^2 = 0.75	
Mineral soil chemistry**	C (g kg^{-1}) 30+ cm[i] (−) Model R^2 = 0.65	Al (g kg^{-1}) 0–10 cm (−)	C (g kg^{-1}) 30+ cm (+) Model R^2 = 0.21		%BS 30+ cm (+) Model R^2 = 0.68	

[a] Plot basal area m^2 ha^{-1}.
[b] Mean tree height of the six dominant trees per plot.
[c] Total elemental Ca.
[d] Total mineral soil profile content (0–30+ cm).
[e] Ratio of NH$_4$Cl extractable to total Ca.
[f] Mineral surface soil (0–10 cm).
[g] Ratio of total elemental Fe to total elemental Al.
[h] Litterfall chemistry estimated as November Oi-horizon collected immediately after leaf-fall.
[i] Mineral deep soil (30+ cm).

and C:N of the Oe + Oa horizon (P = 0.02) were significant positive covariates for stream Ca:Al molar ratio. Deep mineral soil total C concentration was a significant soil chemistry characteristic, providing a negative coefficient for ANC (P < 0.001) and a positive coefficient for stream pH (P = 0.01) analyses.

3.7. Lime requirement

We conducted laboratory analyses to estimate the lime application required to increase soil to pH 5.5 for each soil layer (Fig. 8). Watershed did not have a significant effect on lime requirement;

however, slope position was significant for both surface mineral soil (0–10 cm) (F = 13.72, P < 0.001) and mineral soil 0–30 cm (F = 8.46, P = 0.005), hillslope plots required greater lime inputs to reach the pH 5.5 target than riparian plots. Lime required to increase the soil to pH = 5.5 varied among catchments, ranging from 5.2 Mg ha^{-1} to 9.5 Mg ha^{-1} for the surface mineral soil (Fig. 8) and 11.6 Mg ha^{-1} to 21.1 Mg ha^{-1} for the surface soil mineral plus subsoil (Fig. 8). Lime requirement was initially included in statistical analyses as a catchment chemical characteristic, but was not identified as a significant covariate for any of the stream chemistry variables.
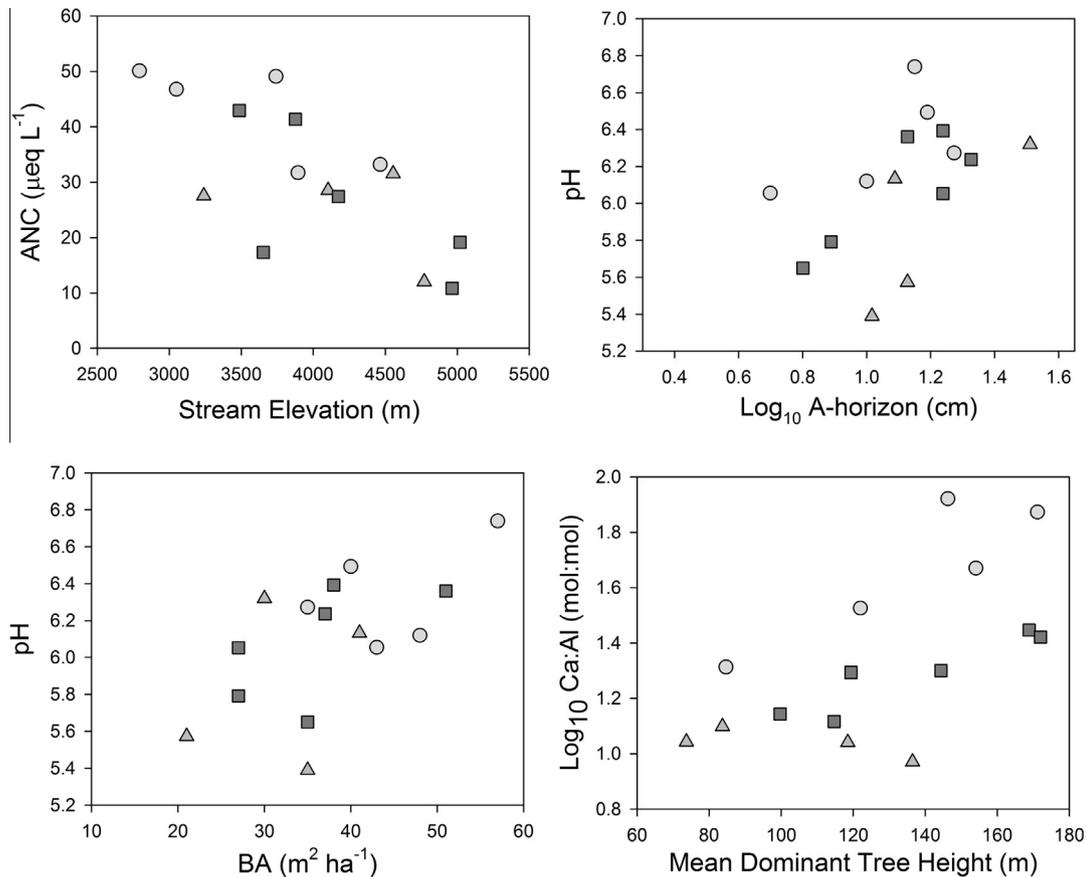
Fig. 4. Relationship between catchment non-chemical characteristics that significantly inform stream chemistry variability and stream chemistry: elevation versus ANC, $\log_{10}$ mineral soil A-horizon depth and catchment basal area versus pH, and mean dominant tree height versus $\log_{10}$ molar Ca:Al. Data shown are mean catchment values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■).

4. Discussion

Despite a 40% decrease in wet SO_4 deposition across the eastern United States high elevation streams in the southern Appalachian have been identified as acidic with ANC values <50 μeq L^{-1} (NADP, 2007; Burns et al., 2011). We measured catchment biotic, physical, and chemical characteristics that were potential indicators of stream chemistry. The catchments represented a broad range of all characteristics allowing us to evaluate potential indicators of stream acidity and to help identify catchments where stream acidity could be mitigated with liming. The relationships between indicators and stream chemistry were complex and in some cases opposite of the expected patterns. For example, stream ANC was negatively correlated with total soil Ca, and stream Ca:Al was negatively correlated with litterfall Ca:Al. These unexpected patterns may be partially due to insufficient sample size (either too few catchments or too few plots within a catchment to capture the full range of variation), seasonally varying patterns of stream/soil connectivity, or as yet undescribed patterns of stream and soil recovery from acidic deposition (Lawrence et al., 2015). Long-term forest soil sampling efforts in the 1980s and 1990s showed declining exchangeable Ca and increasing soil acidity linked to forest growth and leaching losses (Johnson et al., 1991; Knoepp and Swank, 1995; Lawrence et al., 1995; Likens et al., 1998). Implementation of the CAA in 1970 resulted in the recovery of stream chemistry in Hubbard Brook Experimental Forest (Likens and Buso, 2012). However, since 2007 streams show a declining trend of both acid anions and base cations resulting in a decline in both stream ANC and stream Ca concentrations. Likens and Buso (2012) suggested that this response was due to changes in the stream

ion balance from being historically dominated by Ca(HCO$_3$)$_2$, then shifting to CaSO$_4$, and currently toward NaHCO$_3$. In another study, Lawrence et al. (2015) examined soil recovery in 27 sites across the NE USA and eastern Canada by resampling soils after 8–24 years. They found that site specific decline in SO_4 deposition was correlated with increased base saturation and decreased exchangeable Al in the O-horizon. However, base saturation in B horizon soils had not increased, and actually decreased at 33% of the sites. These examples of declining soil and stream Ca following reductions in acidic deposition demonstrate the value of long-term stream and soil sampling. Thus, one time collections (or one year of collections) may not reveal all of the interactions between forest growth and nutrient uptake, soil nutrient processes, and stream ion balance, particularly if acidic deposition is expected to continue to decline.

4.1. Physical parameters

High elevation catchments in the southern Appalachians are sensitive to acidic deposition not only due to the high rates of input, but also physical factors such as steep topography and soil depth. As expected (Swank and Vose, 1997; Sullivan et al., 2011) (Knoepp, unpublished data), our data show a significant negative linear correlation between stream elevation and measures of stream acidity such as ANC, pH, and Ca:Al molar ratios (Fig. 9); however, we also identified other physical catchment characteristics that could be used to explain variability in stream chemistry. For example, we found significant positive relationships between mineral soil A-horizon depth and stream pH and Ca:Al molar ratio (Fig. 3). The formation and depth of the A-horizon is the result of
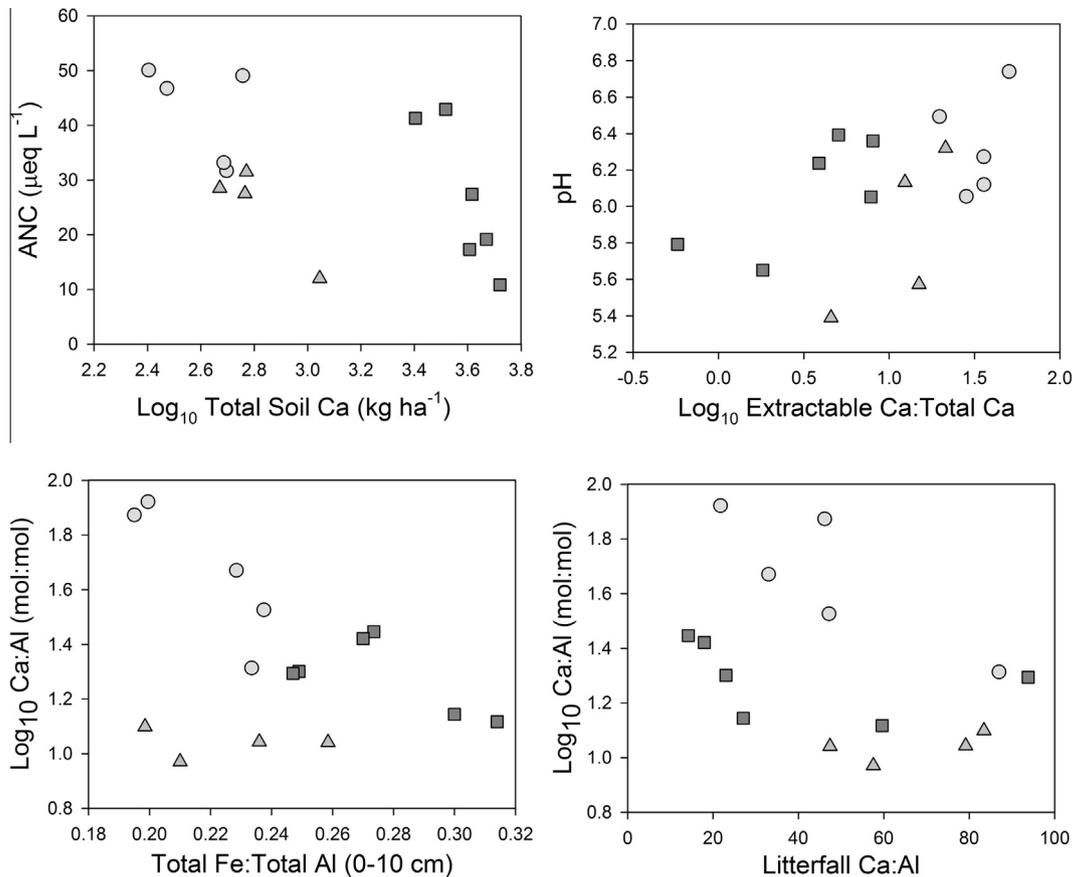
Fig. 5. Relationship between catchment geochemical characteristics that significantly inform stream chemistry variability and stream chemistry: soil profile total Ca content versus ANC, $\log_{10}$ ratio of extractable to total Ca in surface mineral soil versus pH, and surface mineral soil Fe:Al ratio and litterfall Ca:Al versus $\log_{10}$ molar Ca:Al. Data shown are mean catchment values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■).

vegetation, topography, parent material and other factors of soil formation (Ramann, 1928; Jenny, 1941; Buol et al., 2011); hence, the relationship between soil A-horizon depth and stream chemistry is not surprising due to the movement of organic material, dissolved and exchangeable nutrients, and water through the soil profile. We also expected total soil profile depth would be an indicator of stream chemistry due to its effect on stream/soil connectivity, which directly affects stream chemistry. However, in this study, soil profile depth was not identified as a significant indicator of stream chemistry. Some studies have shown that the movement of chemical constituents to the stream varies with its location in the profile. For example, Lutz et al. (2012) found evidence that NO_3 is transported to the stream via subsurface pathways across a range of precipitation event sizes, whereas surface soil DOC is only mobilized when soils become connected with the stream after large precipitation events. Research has also shown that seasonal differences in stream chemistry are often due to differences in hydrologic flow paths and soil/stream connectivity (Christopher et al., 2006; Murdoch and Shanley, 2006a,b). We conducted our stream collections seasonally to account for the differences in soil/stream connectivity that are evident due to greater stream baseflow in March–May in the southern Appalachians (Swift et al., 1988).

4.2. Vegetation parameters

The effects of vegetation composition on stream chemistry have been noted in several ecosystems (Knoepp and Swank, 1998; Lovett and Mitchell, 2004; Christopher et al., 2006; Wurzburger

and Hendrick, 2007; Knoepp et al., 2008). For example, Christopher et al. (2006) found that the presence of base rich tree species (*Acer saccharum* Marsh., *Tilia americana* Mill., *Ostrya virginiana* (Mill.) K. Koch) resulted in greater stream Ca and NO_3 concentrations; whereas, concentrations were lower in the watershed dominated by *Fagus grandifolia* Ehrhart and *Pinus strobus* L. McLaughlin (2014) found that although hardwood sites contained significantly greater pools of Ca compared to mixed hardwood-conifer sites, they also lost a greater amount of Ca from the O-horizon and to stream export. In addition, vegetation that stimulates nitrification, resulting in increased soil and soil solution NO_3, can also result in increased cation leaching (Lovett and Mitchell, 2004; Christopher et al., 2006). We identified catchment *Quercus* spp. basal area as a marginally significant covariate in our model of stream ANC at the catchment scale; where ANC increased with increasing *Quercus* basal area. Previous work in the southern Appalachians has shown lower N cycling rates and N leaching (i.e., lower NO_3 in soil solution and lower potential cation leaching) and greater O-horizon accumulation in *Quercus* dominated sites compared to northern hardwood forests (Knoepp and Swank, 1998; Knoepp et al., 2000, 2008). Other significant vegetation characteristics in our models were mean catchment basal area of all species (positive covariate with stream pH) and mean tree height of all species (positive covariate with stream Ca:Al molar ratio). Because catchment basal area is related to site productivity (e.g., nutrient availability and soil pH) and species composition (e.g., species specific nutrient uptake and requirements) (Searcy et al., 2003; Hahm et al., 2014), it is not surprising that basal area, tree height, and mean DBH were positively related to
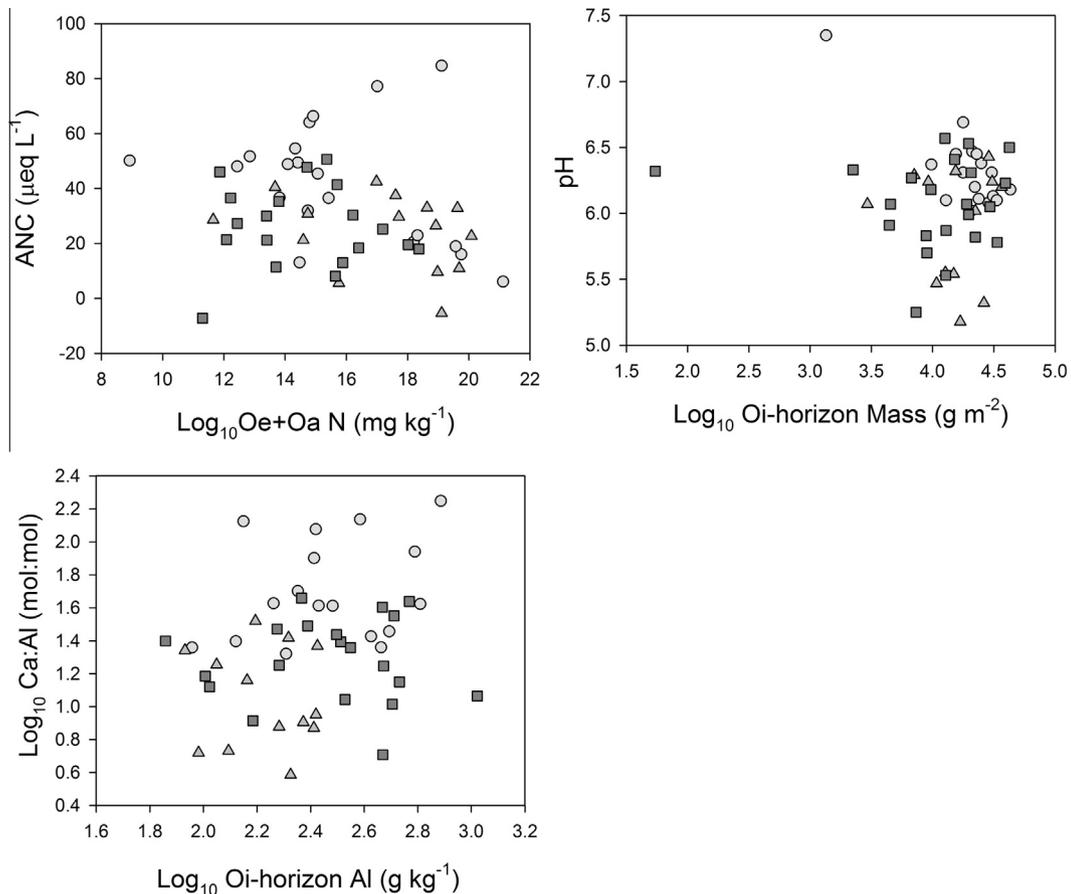
Fig. 6. Relationship between catchment O-horizon physical and chemical characteristics that significantly inform stream chemistry variability and stream chemistry: total N concentration in the Oe + Oa horizon versus ANC, $\log_{10}$ Oi horizon mass versus pH, and $\log_{10}$ total Al concentration in the Oi horizon versus $\log_{10}$ molar Ca:Al. Data shown are mean catchment values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■) for all sample dates (early summer, mid-summer, fall and spring).

stream pH. This suggests that relatively simple forest stand measurements, such as tree heights, diameters, and total basal area, could be useful indicators of sensitive streams (i.e., those with low Ca:Al or pH). For example, although soil pH and extractable Ca:Al molar ratio were not significant covariates in our stream chemistry models we found significant positive relationships between surface mineral soil pH and Ca:Al molar ratio and mean tree height ($r^2 = 0.29$, $P = 0.002$ and $r^2 = 0.18$, $P = 0.02$, respectively) and mean DBH ($r^2 = 0.33$, $P = 0.001$ and $r^2 = 0.28$, $P = 0.002$, respectively).

4.3. Soil O-horizon and litterfall

Soil O-horizon physical and chemical characteristics were significant covariates in models examining catchment variability in stream chemistry (Tables 3 and 4). Past research has examined how overstory litter input and root turnover provide nutrient inputs to unfertilized forest ecosystems (Hursh, 1928; Alban, 1982; Knoepp et al., 2011), and how inputs are affected by site nutrient availability (Knoepp et al., 2000; Ordoñez et al., 2009). In general, O-horizon formation is the result of inputs and turnover rates which are regulated by the interactions among site nutrient availability, temperature, precipitation, and micro- and macrofauna and microbial populations. In some forest ecosystems the Oa-horizon plays an important role in nutrient availability with many tree roots occupying that layer (Perala and Alban, 1982; Rauland-Rasmussen and Vejre, 1995; Joergensen et al., 2009). The Oa-horizon has been examined as a surrogate for total

deposition, as it represents the accumulation of all mineral input sources, litterfall, root turnover, and fungal activity, as well as wet and dry deposition (Weathers et al., 2006; Joergensen et al., 2009). In our study, O-horizon Al concentrations and C:N ratios had a positive relationship with stream Ca:Al molar ratio; however, increasing O-horizon total N concentrations resulted in declining stream ANC. This finding is similar to studies examining the declining SO_4 deposition. Pannatier et al. (2011) found that SO_4 deposition declines in ecosystems where N deposition was dominant had no effect on improving soil solution chemistry. Lawrence et al. (2012) measured increased exchangeable Al concentrations in B horizon soils in some red spruce forests after years of SO_4 decline.

We used the November Oi horizon collection to represent litterfall chemistry as a proxy for plant available soil nutrients. We found that litterfall Ca:Al ratio was a significant negative covariate in stream Ca:Al molar ratio. Examination of the relationship between litterfall Ca:Al ratios and soil chemistry and found a weak but positive correlation with soil extractable Al ($r^2 = 0.18$, $P = 0.02$) but not with extractable soil Ca. On the other hand, litterfall Ca concentration was significantly correlated with both soil extractable Ca ($r^2 = 0.35$, $P = 0.001$) and the proportion of extractable Ca (i.e., available to plants) to total elemental Ca ($r^2 = 0.47$, $P < 0.001$). Additionally, seasonally collected Oi-horizon Al concentration was identified as having a positive relationship with stream Ca:Al molar ratio. Hallet and Hornbeck (1997) found that soils in both red oak and white pine forests exhibited Ca depletion while Al accumulated in the O-horizon. Our data suggest a complex
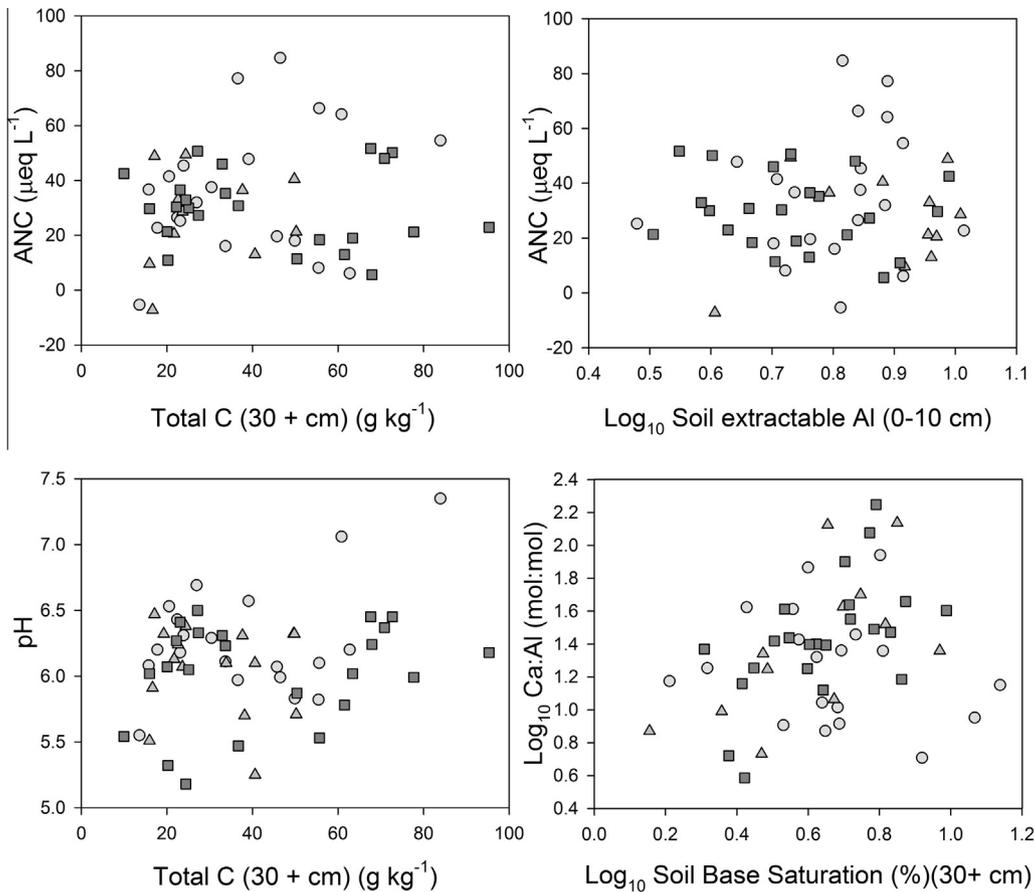
Fig. 7. Relationship between catchment mineral soil chemical characteristics that significantly inform stream chemistry variability and stream chemistry: total C concentration in the deep mineral soil and $\log_{10}$ extractable Al in the surface mineral soil versus ANC, total C concentration in the deep mineral soil versus pH, and $\log_{10}$ %base saturation in deep mineral soil versus $\log_{10}$ molar Ca:Al. Data shown are mean catchment values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■) for all sample dates (early summer, mid-summer, fall and spring).

interaction between nutrient availability, plant uptake and litterfall, and O-horizon formation, and ultimately stream Ca:Al molar ratio. Oi-horizon Ca:Al ratio was greatest in fall (November) and least in summer (July). As litterfall material transitions from the Oi- to the Oe + Oa-horizon the Ca:Al molar ratio declined 5-fold (Oi horizon Ca:Al = 35, Oe + Oa horizon Ca:Al = 6) suggesting a preferential loss of Ca or accumulation of Al during decomposition and O-horizon formation. The presence of *Quercus* spp. was positively correlated with ANC, perhaps due to its effect on O-horizon accumulation (Knoepp et al., 2008). Other researchers have documented the linkage between understory vegetation, O-horizon decomposition, and soil nutrient availability (Qiao et al., 2014; Elliott et al., 2015), however, we did not include measurement of leaf litterfall decomposition rates or herbaceous plant surveys in this study.

4.4. Mineral soil chemistry

The interaction of soils with soil water and ultimately stream water is determined not only by mineral soil exchangeable chemistry but also by parent material which controls the release of cations and anions through weathering processes (Velbel, 1985, 1988). We used mineral soil total elemental cation concentrations (Ca, Mg, K and Na) as a proxy for parent material and found that soil total elemental Ca content was negatively related to stream ANC (Table 3) at the catchment scale, while surface soil total Ca was related to stream pH within the riparian zone alone (Table 4). Other mineral soil total cation parameters (Fe:Al ratio, Felsic:Mafic,

extractable K:total K), at both the catchment and riparian zone scale, were significantly related to stream pH and Ca:Al molar ratio (Tables 3 and 4). The role of riparian zone characteristics differs among stream acidity indices, perhaps due to differences in location of exchangeable cations and anions within the soil profile (Fölster et al., 2003; Lutz et al., 2012) or differences among watersheds and catchments (Christopher et al., 2006; Talhelm et al., 2012). Elliott et al. (2008) and Sullivan et al. (2011) modeled sensitivity of wilderness areas in western North Carolina USA to SO₄ deposition, they found that sites with soils derived from parent material with low base cation concentrations were more sensitive to SO₄ deposition. This agrees with the conclusions of other studies (Rice et al., 2006; Sullivan et al., 2007) that suggest that stream ANC is largely regulated by watershed geology. However, soil parent material and stream chemistry relationships are not always predictable due to variation in the regulation of mineral weathering (Velbel and Price, 2007). For example, Grieve (1999) tested the response of mineral soils from three different parent materials (basalt, sandstone sediments, and metamorphosed schists) to leaching with an acidic solution in laboratory experiments. In this case, leachate chemistry could not be explained simply by soil chemical characteristics such as ion exchange capacity or weathering potential. Searcy et al. (2003) examined the influence of parent material and aspect on soil and vegetation distribution in mountains of Massachusetts USA. They found that only 51% of the variance in soil chemistry was due to parent material differences while differences in vegetation composition were due to both parent material and aspect.

Table 4

Riparian plot variables from that were included as covariates in the statistical model examining the variability in stream chemistry, for ANC, pH and molar Ca:Al ratio. Covariates listed were included in the model with P-value $\leqslant 0.05$. 'NS' indicates analyses in which no significant covariates were identified. Covariate variables designated '*' were significant in the nested split-plot experimental design and '**' in the repeated measures analysis. The estimated model R^2 incorporates the split-plot or repeated measures models as presented in Table 2 with the improvement in predictions by including covariate(s).

Variables	Stream ANC	Stream pH			Stream molar Ca:Al	
Catchment characteristics*	Stream elevation (m) (−) Model R^2 = 0.64	A Hzn depth (cm) (+) Model R^2 = 0.81			A Hzn depth (cm) (+) Model R^2 = 0.87	
Catchment geochemical characteristics*	NS	Felsic: Mafic[a] 30+ cm[b] (+) Model R^2 = 0.94	ExtK:Total K[c] 0–10 cm (+)	Total Ca[d] 0–10 cm (−)	NS	
O-horizon**	NS	NS			Al (g kg^{-1}) Oi Hzn (+) Model R^2 = 0.74	C:N Oe + Oa Hzn (+)
Mineral soil chemistry**	C (g kg^{-1}) 30+ cm[e] (−) Model R^2 = 0.69	C (g kg^{-1}) 30+ cm (+) Model R^2 = 0.28			NS	

[a] Estimated ratio of felsic to mafic parent material; (total elemental K + Na)/(total elemental Ca + Mg).
[b] Mineral surface soil (0–10 cm).
[c] Ratio of NH$_4$Cl extractable to total elemental K.
[d] Total elemental Ca in the surface soil (g kg^{-1}).
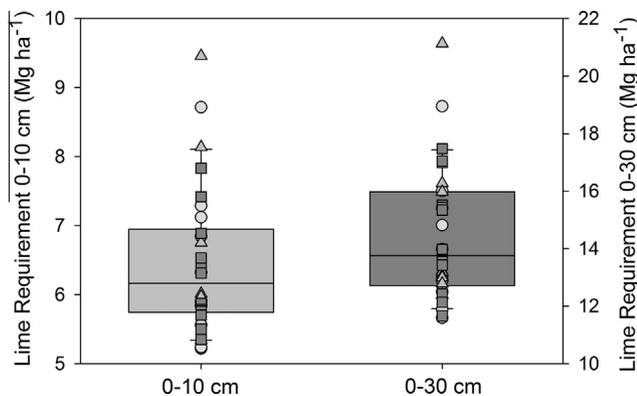[e] Mineral deep soil (30+ cm).

Fig. 8. Estimated lime required to increase mineral soil to pH 5.5 for the surface soil (0–10 cm) and surface plus subsurface soil (0–30 cm). Shown are plot values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■). Box plots show watershed median value, along with the 10th, 25th, 75th and 90th percentiles.

Factors of soil formation suggest that forest soils become increasingly acidic over time for a number of reasons including base cation uptake by vegetation, humus formation, soil leaching wherever precipitation exceeds mean annual evapotranspiration (Johnson, 1987), and base cation removal during forest harvesting (Federer et al., 1989; Knoepp and Swank, 1997). Cation losses have been accelerated by acidic deposition and Ca depletion has occurred in many forest ecosystems (Joslin et al., 1992; Knoepp and Swank, 1995; Graf Pannatier et al., 2004; Likens, 2004; McLaughlin, 2014). In high elevation red spruce, Joslin et al. (1992) showed that base cations Ca and Mg were preferentially leached out of surface soils, tree ring chemistry showed decreasing Ca:Al ratios over time, suggesting that soil acidity and Al solubility had increased. In Switzerland, Graf Pannatier et al. (2004) examined ratios of base cations to aluminum (BC:Al) in forest soils and soil solution to estimate acidic deposition response. Their data showed that the pH – Al relationship was curvilinear and that soils with %BS < 10 and BC:Al ratios <0.2 generally had soil solutions

with low BC:Al ratios and the potential for root toxicity. In our study, soil %BS was often <10% and mineral soil exchangeable Ca: Al ratio was <1.0 (mol:mol). Similar to the findings of Graf Pannatier et al. (2004), we found that %BS in deep soil was a significant covariate informing variability in stream Ca:Al molar ratio (Table 3).

Although decreasing atmospheric SO$_4$ deposition has resulted in decreasing soil solution and stream SO$_4$ in some studies (Fölster et al., 2003; Pardo and Duarte, 2007), we found no relationships between stream chemistry and soil total S or extractable SO$_4$ in any soil layer (data not shown). However, soil solution or stream SO$_4$ may not respond immediately to changes in deposition due to other sources of SO$_4$ within the soil profile and the watershed (Bailey et al., 2004; Morth et al., 2005; Mitchell et al., 2008; Pannatier et al., 2011; Rice et al., 2014). These sources include weathering of mineral S in bedrock, dry deposition inputs, mineralization of organic S, desorption of soil SO$_4$, and the oxidation of recently formed SO$_2$ in anoxic areas draining to the stream. Responses to declining SO$_4$ deposition may also vary within the soil profile. For example, Fölster et al. (2003) measured declining soil solution SO$_4$ in catchments in Sweden. They found greater SO$_4$ declines in soil E horizons compared to B horizons suggesting that desorption of previously accumulated SO$_4$ in B horizons was occurring more slowly in response to decreasing acid deposition.

Due to close proximity, we expected a high level of connectivity between the riparian zone soil chemistry and the stream, especially during sample dates with greater baseflow (i.e., spring and early summer) (Christopher et al., 2006; Lutz et al., 2012). However, we identified fewer significant covariates of stream acidity (ANC, pH, and Ca:Al molar ratio) from riparian zones (Table 4) compared to the catchment scale (Table 3) suggesting little riparian-stream connectivity. This could be due to sample collection during baseflow conditions. Other studies, for example, Murdoch and Shanley (2006a, b), have shown that sampling during baseflow or during a storm event can affect stream chemistry and observed trends in declining stream acidity. We collected stream samples seasonally and compared indicator sample collections at the riparian and catchment scale in order to evaluate soil-stream connectivity. Interestingly, we found strong relationships between
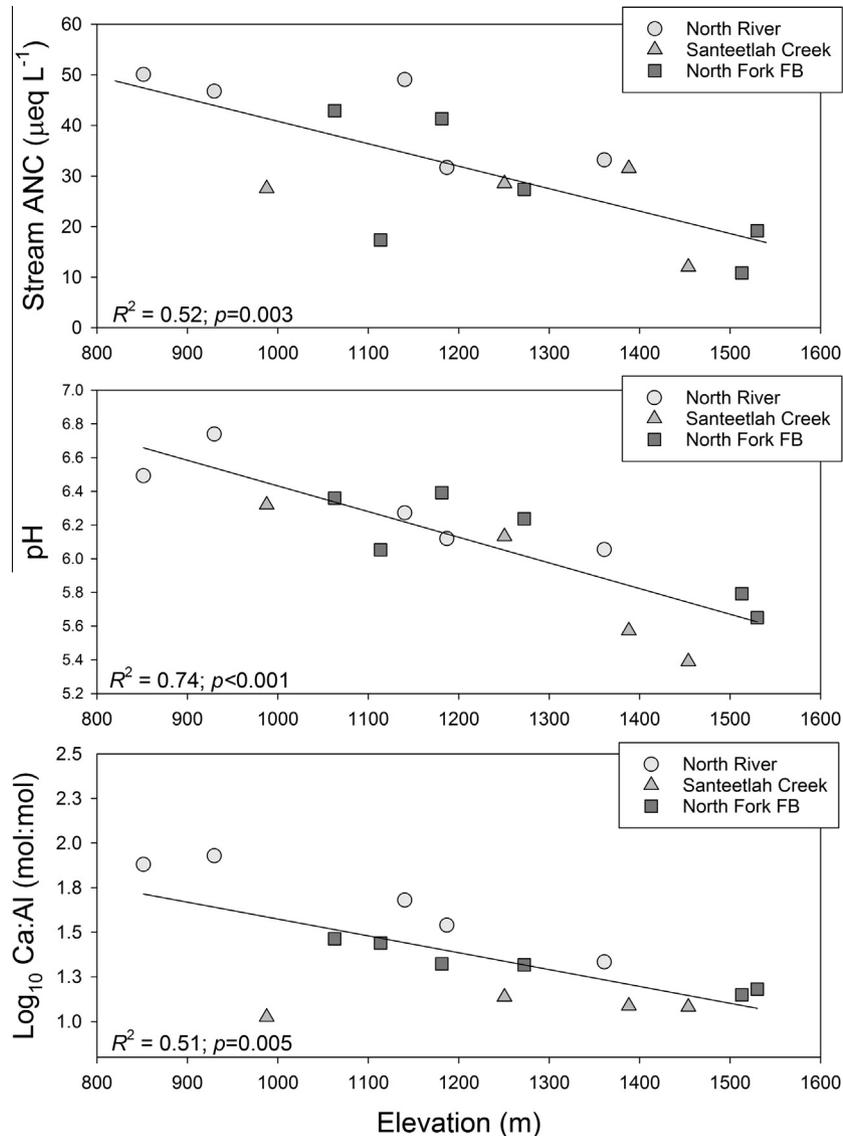
Fig. 9. Relationship between catchment stream elevation and stream chemistry: ANC, pH, and $\log_{10}$ molar Ca:Al. Data shown are mean catchment values for each watershed, North River (●), Santeetlah Creek (▲), and North Fork of the French Broad (■).

stream chemistry and soil O-horizon and mineral surface and deep soils.

4.5. Catchment liming and mitigation

Our second objective was to make laboratory based estimates of catchment lime requirements and evaluate how liming at a catchment scale may improve stream chemistry. Soils and stream recovery from acidic deposition is a slow process that may be accelerated by land managers through liming. The specific goals of liming streams or catchments are to increase stream ANC, pH and Ca while decreasing SO_4 and Al. Restoration practices include adding lime directly to stream water or treating the entire catchment with reported lime additions ranging from 5 to 30 Mg ha^{-1} (Clair and Hindar, 2005). Our estimated lime additions fall within this broad range, with 11.6–21.1 Mg ha^{-1} CaCO$_3$ required to increase the top 30 cm of soil to pH 5.5. Our estimated lime requirement did not differ among the three watersheds we studied. However, as reported in the literature (Reid and Watmough, 2014), riparian zone soils which have greater organic C content, required less lime to increase soil pH to 5.5. Understanding stream

acidity responses to riparian zone or catchment level liming would require experimental lime addition, ideally in catchments with the low extractable Ca and high stream acidity such as, those in the Santeetlah Creek watershed.

In an extensive literature review, Clair and Hindar (2005) examined liming experiments conducted from the 1980s to 2000, including various chemical compounds and methods of application. Overall, their review found that directly adding lime to the stream channel significantly improved the stream pH, chemistry, and suitability for fish populations. Their review also presents research suggesting that while catchment level liming was effective at increasing stream pH and Ca concentrations the effects on inorganic Al concentrations were variable. Johnson et al. (1995) presented long term soil and stream chemistry results of a catchment level liming experiment in the southern Appalachians; 6.7 Mg ha^{-1} dolomitic limestone was added in a single application. They found liming increased Ca, Mg and percent base saturation in surface (0–15 cm) and subsurface (15–30 cm) mineral soils but there was little movement of the added lime to deep soils (30 + cm); stream Ca was increased for almost 20 years. A study by Long et al. (2015) examined soil responses to a liming treatment

on sugar maple stands in northern Pennsylvania; 22.4 Mg ha^{-1} dolomitic lime was added in a single application. They found increases in exchangeable Ca and Mg to soil depths of 45 cm along with increased foliar Ca, 21 years after treatment. Ormerod and Durance (2009) examined 25 year stream chemistry responses to reductions in acidic deposition and liming in moorland and forest catchments; 9–25 Mg ha^{-1} calcium carbonate added in a single application. Declining acidic deposition, without lime treatment, resulted in increased stream water pH with values increasing from 4.8 to 5.2 while liming increased stream pH to 5.9. Our estimated lime requirements for high elevation, mixed deciduous forests were greater than that applied by Johnson et al. (1995), but are within the range applied by others in the northeastern USA (Clair and Hindar, 2005; Long et al., 2015), suggesting that lime applications in these forests would result in long-term soil and stream responses.

Research studies have also examined base cation additions, specifically Ca, without pH adjustment, on soil chemistry, vegetation Ca, and stream chemistry. In the Hubbard Brook Experimental Forest, wollastonite ($CaSiO_3$) (0.85 Mg Ca ha^{-1}) was applied to a forested catchment with Ca depleted soils and the responses have been extensively studied (Juice et al., 2006; Nezat et al., 2010; Green et al., 2013). Juice et al. (2006) found that Ca addition increased the pH of the Oi + Oe horizons from 3.8 to 5.0 and the Oa horizon from 3.9 to 4.2 within 3 years of treatment; foliar and fine root Ca concentrations also increased. Nezat et al. (2010) found that it took 3–9 years for the applied Ca to infiltrate the deeper flow paths in the soil profile before it was exported to the stream. Within this same watershed, Green et al. (2013) found that stream flow was increased due to reduced rates of evapotranspiration for three years, before returning to pre-treatment levels. They attributed this to increased aboveground productivity due to the short term correction of a nutrient imbalance, as found in other studies (e.g., Kulmatiski et al., 2007).

5. Conclusions

We studied three watersheds in the southern Appalachian mountains, North River (NR), Santeetlah Creek (SC) and the North Fork of the French Broad (FB), in an effort to identify catchment (i.e., smaller 1st order catchments within the 3rd order watersheds) indicators of stream acidity (ANC, pH, and Ca:Al molar ratio) that would aid land managers in selecting catchments to focus restoration efforts. Catchments represented a broad range of stream acidity and indicators of sensitivity to acidic deposition. We found that vegetation (stand basal area, dominant tree height and tree diameter), soil A-horizon depth, deep soil C concentrations and indicators of soil parent material (total elemental Ca and extractable Ca:total Ca ratio) were significant covariates for stream ANC, pH, and Ca:Al ratio. O-horizon total N and Al concentrations were also strongly related to stream acidity.

Laboratory estimated lime requirements, which were within the broad range found in other studies, varied by as much as 8 Mg ha^{-1} among catchments due to differences in soil chemistry. Expected stream responses to lime application may also differ, depending on overstory species, soil-stream connectivity and other soil processes. Long-term lime application studies are recommended for these high elevation, mixed deciduous forests to evaluate how they will respond to lime application. Nonetheless, our initial estimates of lime requirement will help land managers target the catchments and streams where lime application would have the greatest probability of reducing stream acidity.

Our measures of how catchment biotic, physical and chemical indicators related to stream acidity could provide insight to selecting forested catchments for restoration treatments. However, full

understanding of the applicability of these indicators in targeting restoration efforts will require an effort that includes widespread regional sampling to capture a greater range of watershed conditions and recovery patterns.

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