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## Monitoring the Influence of Acid Deposition on Soil and Implications to Forest Health in the Daniel Boone National Forest

Tyler M. Sanderson  
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Dr. David Wagner, Director of Graduate Studies

MONITORING THE INFLUENCE OF ACID DEPOSITION  
ON SOIL AND IMPLICATIONS TO FOREST HEALTH IN  
THE DANIEL BOONE NATIONAL FOREST

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THESIS

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A thesis submitted in partial fulfillment of the  
requirements for the degree of Master of Science in  
the College of Agriculture, Food and Environment  
Department of Forestry at the University of  
Kentucky

By

Tyler Monroe Sanderson

Lexington, Kentucky

Director: Dr. Chris Barton, Professor of Forest Hydrology

2014

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## ABSTRACT OF THESIS

### MONITORING THE INFLUENCE OF ACID DEPOSITION ON SOIL AND IMPLICATIONS TO FOREST HEALTH IN THE DANIEL BOONE NATIONAL FOREST

Combustion of fossil fuels has contributed to many environmental problems including acid deposition. The Clean Air Act (CAA) was created to reduce ecological problems by cutting emissions of sulfur and nitrogen. Reduced emissions and rainfall concentrations of acidic ions have been observed since the enactment of the CAA, but soils continue to receive some acid inputs. Soils sensitive to acid deposition have been found to have low pH, a loss of base cations and a shift in the mineral phase controlling the activity of  $\text{Al}^{3+}$  and/or  $\text{SO}_4^{2-}$ . If inputs continue, soil may be depleted of base cations and saturated with Al and could cause low forest productivity. Soil solutions from lysimeters were taken in the Daniel Boone National Forest to evaluate potential impacts of acid deposition. In addition, tree-ring growth and chemical analysis created a timeline of forest health and ion accumulation. Physicochemical characteristics of the soils revealed that sites were very low in base saturation and pH and high in exchangeable acidity. Soil solution data indicated that sites periodically received high acid inputs leading to saturation of Al in soils and the formation of Al-hydroxy-sulfate minerals. Given these conditions, long-term changes in soil chemistry from acid deposition are acknowledged.

KEYWORDS: Acid deposition · Soil solution chemistry · Aluminum · Solubility control  
· Forest health

Tyler M. Sanderson

October 16, 2014

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## CHAPTER ONE

### Evaluation of soil and soil solution chemistry in the Daniel Boone National Forest.

#### **Introduction:**

The chemistry of the pedosphere provides insight on the processes involved and environmental changes caused by acidic atmospheric deposition. Within the soil environment, interactions between the lithosphere, atmosphere and hydrosphere take place and water extracted from this critical zone has been used to observe element cycling, nutrient availability, mineral transformation and mobility and transport of aluminum (Al) (Barton et al. 2002). Thus, soil solution chemistry may be utilized to assess the condition of ecological resources and to identify stressors contributing to ecosystem deterioration (Karathanasis 1989; Lawrence and David 1996; Kaiser and Kaupenjohann 1998).

Acid deposition is created by compounds reacting with water in the atmosphere to create acids that return to the Earth's surface. Acidification of water in the atmosphere occurs naturally when it reacts with carbon dioxide to create carbonic acid. However, the strength of this acid is weak and reduction of pH by this reaction is limited to 1.3 units from neutrality (i.e. pH 5.7) (Reuss and Johnson 1986). Other acidifying reactions that can drive pH levels below 5.7 are derived from sulfur or nitrogen oxides and ammonia reacting with atmospheric water to create strong sulfuric and nitric acids and ammonium. Naturally derived nitric and sulfuric acids normally do not cause rainwater pH levels of concern, however, anthropogenic emissions of these oxides exceeded natural rates in the middle of the twentieth century, and today are as high as eight times greater than natural rates (Galloway 1996). In some regions of the world, namely large urban areas or industrial hubs, human induced acidification of the atmosphere is one hundred times greater than natural rates, significantly contributing to the acidification of rainwater (Galloway 2001). The burning of fossil fuels increases emissions of sulfur dioxide (SO<sub>2</sub>) and nitrous oxides (NO<sub>x</sub>), which accelerates the acidification process (NAPAP 1987).

Acidic ions reach the Earth's surface via two methods of deposition, dry and wet. Wet deposition is when dissolved ions fall to surface in precipitation (i.e. rain, snow,

sleet, hail and fog). Dry deposition occurs by way of ions in the atmosphere collecting on plants, buildings and all other surfaces. In the forest, dry deposition can be taken in through stomata of vegetation (Matzner 1986), can leach cations from leaf surfaces,  $H^+$  ions can be exchanged for cations on inner leaves (Ulrich 1983) or deposition otherwise remains on vegetation until washed away by precipitation. Forests have a large amount of surface area produced by plant leaves which acts as an accumulator for atmospheric deposition above the surface of the soil. Dry deposition per unit area of forested land is greater than deposition collected in open land (Mayer and Ulrich 1974, 1976, 1980; McColl and Bush 1978). Precipitation contacts the surface of leaves and branches washing the accumulated dry deposition and leached leaf ions with it. These ions enter the soil by way of stemflow or throughfall, not necessarily corresponding to total deposition onto the canopy due to interaction before reaching the soil (Bredemeier 1988). Canopy interaction has been found to alter precipitation chemistry, usually resulting in higher concentrations of both cations and anions, and under coniferous canopies, lower pH in throughfall (Cronan and Reiners 1983). Ion concentrations in throughfall were also found to be higher under pine or spruce forests than in oak or beech (Mayer and Ulrich 1977a and b, Singer et al. 1996, Bredemeier 1988, Oulehle and Hruska 2005).

Acidic inputs to soils can potentially deplete base cations, mobilize Al on exchange complexes, leach heavy metals and pollutants into solution, and increase weathering of clay minerals (Reuss 1983). Base cations, namely plant available nutrients from exchange sites, are depleted by their replacement with Al or by pairing with leached sulfate ( $SO_4^{2-}$ ) and nitrate ( $NO_3^-$ ) and  $H^+$  in solution to maintain charge equilibrium (Cronan and Schofield 1990). Al is more available for exchange in an acid impacted soil because acids dissolve some clay minerals consequently replacing Ca and Mg with Al on soil exchange sites and leading to Al saturated soils (Thomas 1996), followed by a possible increase in soil solution Al (Reuss and Johnson 1986). If base saturation is below 20%, then acid deposition will mobilize and leach Al, and soils will be unable to neutralize acidity (Cronan and Schofield 1990). An increase in the proportion of acidic to basic cation exchange capacity (CEC) means greater amounts of acid ions available for exchange, a decrease in soil pH and an additional acidification of soil solution (Ulrich 1980). Similarly, the adsorption of both  $H^+$  and  $SO_4^{2-}$  in soils will increase permanent

CEC, reduce pH, base saturation and pH dependent CEC, but have no effect on net nutrient loss (Johnson et al. 1982).

Lower base saturation, from acidification and leaching, reduces the capacity of the soil to resist changes from continued acid inputs (Wilkländer 1980a). Soil base replenishment is an important process in the recovery of a soil system. Re-supply of base cations comes from weathering of soil minerals and organic matter, and from throughfall inputs. Unfortunately base cation input from soil weathering and throughfall is not sufficient to replenish that lost as output (Johnson et al. 1988; Knoepp and Swank 1994). Several studies have reported a net export of exchangeable Ca (Huntington 2000; Johnson and Lindberg 1992; Malek et al. 2005).

In 1970 the United States Environmental Protection Agency (USEPA) enacted the Clean Air Act (CAA) in an effort to minimize air pollution. A revision of the CAA in 1990 addressed the issue of acid rain. Ambient air quality standards required in the 1990 Amendments addressed utility emissions of SO<sub>2</sub> and NO<sub>x</sub> and proposed market-based cap and trade measure for controlling emissions (CAA 1990). The CAA set goals for the year 2000 of reducing annual SO<sub>2</sub> emissions by 10 million tons and reducing NO<sub>x</sub> emissions by 2 million tons from 1980 levels. The initial phase started in 1995 and was set for large coal-fired power plants. In 2000, smaller and differently fueled plants were added and compliance has been 100% (CAA 2012). The National Atmospheric Deposition Program (NADP) has measured SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> concentrations throughout the United States for decades. A monitoring site at Lilley Cornett Woods in Letcher County, Kentucky (NADP KY 22) has seen a 62.3% decrease in SO<sub>4</sub><sup>2-</sup> and a 33.9% decrease in NO<sub>3</sub><sup>-</sup> wet deposition since monitoring began in 1984 (Figure 1.1).

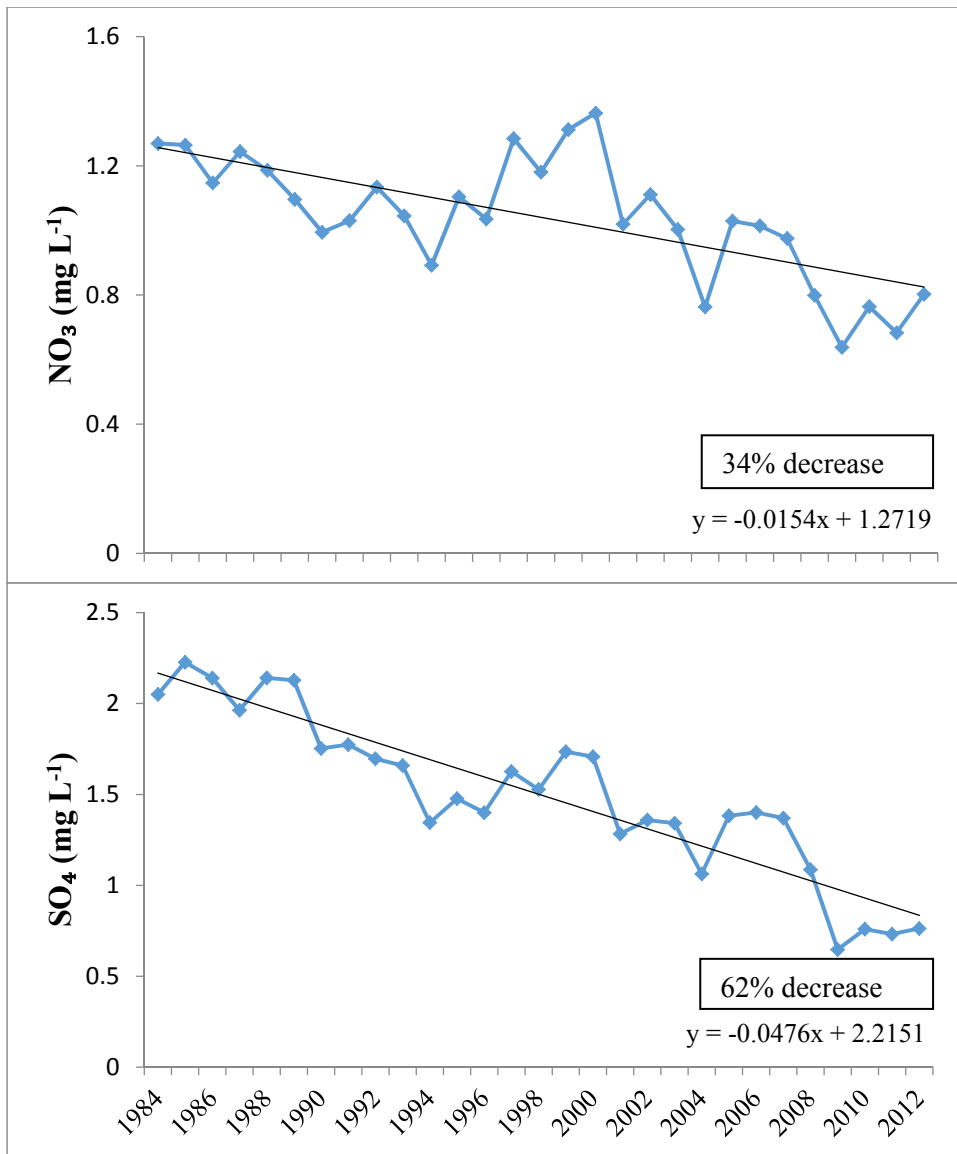


Figure 1.1: Average annual concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  from precipitation at NADP site KY 22, Lilley Cornett Woods (1984-2012).

Averages of three NADP monitoring sites located in eastern Kentucky report a 55% and 30% reduction in SO<sub>4</sub> and NO<sub>x</sub> deposition, respectively. Despite emission and wet deposition reductions, Kentucky is still a major contributor of SO<sub>2</sub> and NO<sub>x</sub> emissions.

The effect of acid deposition on soils and soil solution chemistry has been studied widely for over thirty years. Most of that work was conducted in areas with evident or strongly suspected impacts from acid rain. Forest ecosystems in the Appalachian region are among the most threatened by acid deposition due to an exposure to large amounts of acidic inputs (Herlihy et al. 1993), but impacts may not be as evident as in locations with lower soil buffering. A preliminary study conducted by the University of Kentucky (Barton et al. 2002) addressed the influence of acid deposition on the soil solution chemistry within the Daniel Boone National Forest (DBNF) and reported that the forest continues to be exposed to levels of atmospheric deposition that could, over time, become detrimental to forest soils and forest productivity. Monitoring within the DBNF was reinitiated (2012-2013) to examine current trends and determine whether changes in the CAA have worked to limit impacts from acid deposition.

### **Materials and Methods:**

#### *Daniel Boone National Forest:*

The Daniel Boone National Forest (DBNF) is located in portions of central, eastern and southeastern Kentucky. The U.S. Forest Service manages 290,000 hectares of forest within an 850,000 hectare proclamation boundary (USFS). Private land within the boundary includes residential, farming, forest and logging. DBNF is one of the most heavily used forests in the South, with over 5 million visitors annually. The land is characterized by steep forested ridges dissected by narrow ravines. The forest type is generally a mixed mesophytic hardwood forest (Braun 1950). The climate is temperate with moderately cold winters and warm, humid summers. Precipitation is fairly well distributed throughout the year, with an average yearly rainfall of 121 cm; October being the driest and July representing the wettest month (USDA 2013). Precipitation in the region is greater than levels of evapotranspiration, meaning that water reaching the forest is greater than can be used and taken up by vegetation leading to soil solution reaching waterways. Prevailing wind patterns are primarily from the South and West.



The DBNF is in close proximity to urban and industrial areas. The Appalachian and Ohio River valley regions are home to a high concentration of coal-fired power plants. There are twenty-one coal-fired power plant locations in Kentucky (Figure 1.2) and forty-five more plants in the vicinity within the surrounding states of Indiana, Ohio, Tennessee, Virginia and West Virginia.

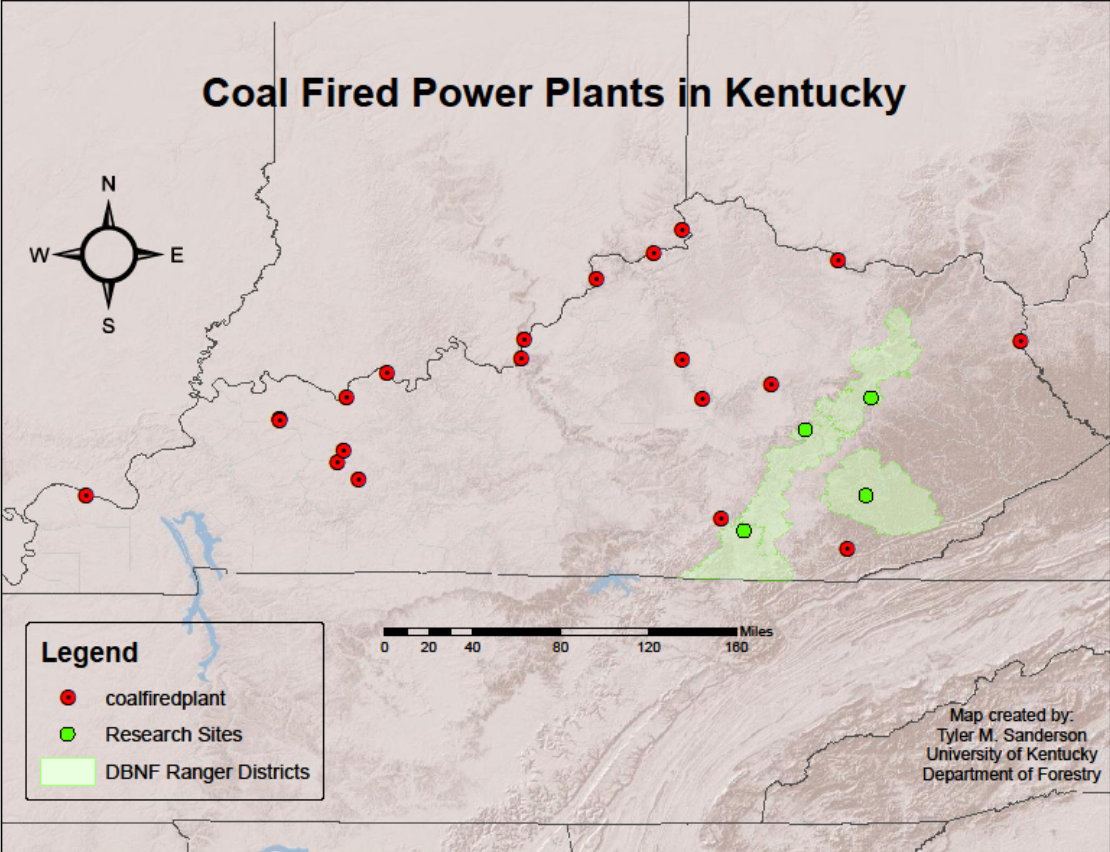


Figure 1.2: Major coal fired power plant locations within Kentucky (2012), Kentucky Geography Network ([kygeonet.ky.gov](http://kygeonet.ky.gov)).

Kentucky ranked in the top six states for coal-fired power production in 2013. Ohio, Indiana, and West Virginia were also in the top ten in 2011 (USEIA 2012). The DBNF's close proximity to major industrialization along with prevailing winds, landscape and other factors threaten the forest due to potential acid deposition inputs.

*Site Descriptions:*

The sites investigated are within the DBNF and represent each of the four Ranger Districts on the forest. They are located in Clay, Estill, McCreary and Wolfe counties, Kentucky, USA, and represent the Redbird, London, Stearns, and Cumberland ranger districts, respectively (Figure 1.3). Each site is positioned on subxeric, ridge-tops of the Cumberland Plateau and is within an uneven-age mixed pine-hardwood forest stand (Table 1.1).

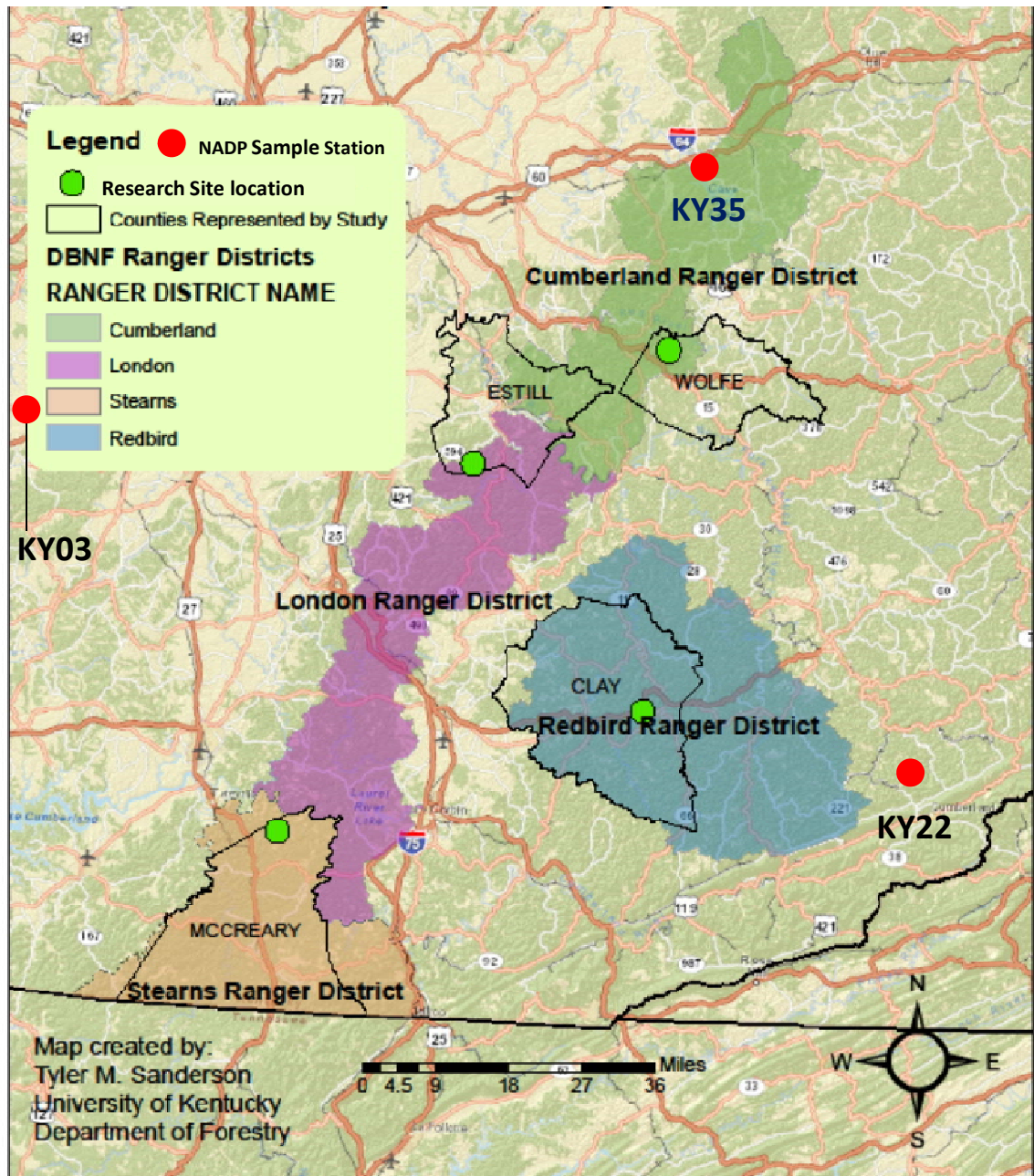
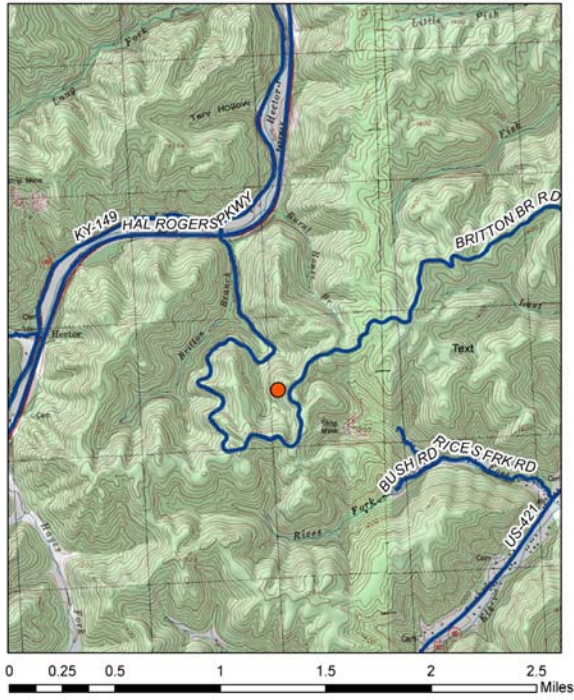


Figure 1.3: Site locations, Daniel Boone National Forest boundaries and eastern Kentucky NADP monitoring stations KY03, KY22, and KY35.

Table 1.1: Coordinates, slope, aspect and elevation of research sites.

| <b>Site Location</b> | <b>Coordinates</b>                   | <b>Slope</b> | <b>Aspect</b>                 | <b>Elevation</b> |
|----------------------|--------------------------------------|--------------|-------------------------------|------------------|
| Clay                 | 37° 08' 49.56" N<br>83° 38' 18.80" W | 8%           | Southwest<br>~215°            | 485 meters       |
| Estill               | 37° 34' 53.63" N<br>84° 01' 43.88" W | 8%           | West to<br>Northwest<br>~300° | 427 meters       |
| McCreary             | 35° 54' 58.19" N<br>84° 26' 13.28" W | 8%           | West to<br>Northwest<br>~294° | 335 meters       |
| Wolfe                | 37° 47' 41.60" N<br>83° 36' 0.95" W  | 9%           | Southwest<br>~218°            | 355 meters       |

The Clay, Estill and Wolfe sites contain soils representative of the Rayne silt loam (fine-loamy, mixed, active, mesic Typic Hapludult) series. The McCreary site contains soils representative of the Gilpin silt loam (fine-loamy, mixed, active, mesic Typic Hapludult) series. All soils are deep, well-drained with moderate permeability and formed of material weathered from shale, siltstone, and/or sandstone. Clay, Estill and McCreary are located a short distance (approx. 25-35 meters) from USFS access roads and the Wolfe County site is located slightly less than 1 km off Kentucky 715 (Figure 1.4). All sites are in close proximity (<100 km) of coal-fired power plants.



### Clay County Lysimeter Site



- Clay County Lysimeter Site
- Daniel Boone National Forest
- Forest or Public Road



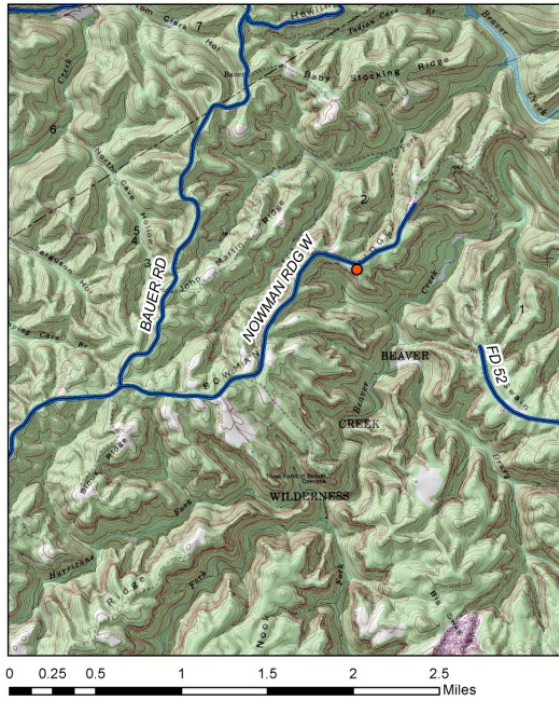
### Estill County Lysimeter Site



- Estill County Lysimeter Site
- Daniel Boone National Forest
- Forest or Public Road



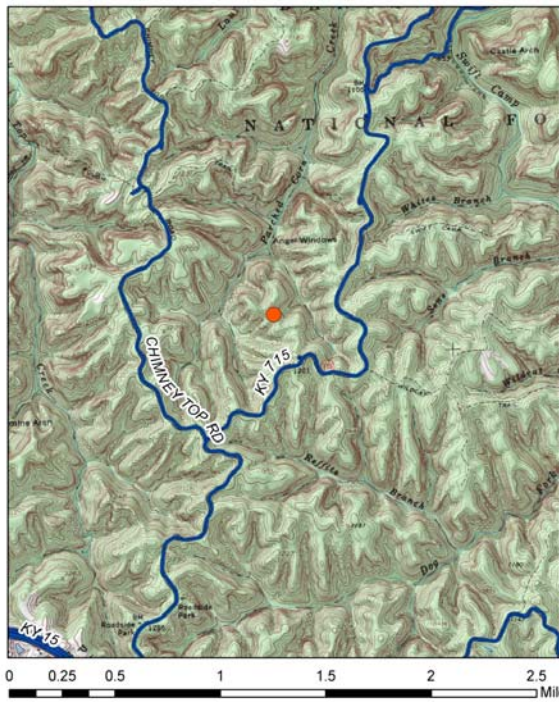
Figure 1.4: Clay and Estill sampling site locations.



### McCreary County Lysimeter Site



- McCreary County Lysimeter Site
- Daniel Boone National Forest
- Forest or Public Road



### Wolfe County Lysimeter Site



- Wolfe County Lysimeter Site
- Daniel Boone National Forest
- Forest or Public Road



Figure 1.4 (cont.): McCreary and Wolfe individual sampling site locations.



Databases from three weather monitoring programs were used in conjunction with on-site throughfall collectors and rain gauges to gather wet deposition information for the region of study. Nationwide precipitation chemistry data is compiled by the NADP. The program has many sampling sites across the nation, but three sites were used as reference for this research; NADP sites KY 03 in Mackville, KY 22 at Lilley Cornett Woods, and KY 35 at Clark State Fish Hatchery (Figure 1.2). Local precipitation data was also derived from the Kentucky Mesonet monitoring network ([www.kymesonet.org](http://www.kymesonet.org)).

*Lysimeter Establishment:*

Locating research sites involved finding a place in each of the four regions of the forest with the following characteristics: atop a ridge with similar elevations, within a stand of mixed pine-hardwood forest, exhibiting minimal human disturbance to forest and soil structure, located far enough away from high-use roads and trails, and located on similar soil series with a soil depth of at least 1 meter. Ridges were used because higher elevations have been found to receive greater acid deposition rates (Lovett and Lindberg 1993; Knoepp et al. 2008). Mixed pine-hardwood stands were sought rather than strictly deciduous because coniferous throughfall and soil chemistry tend to show more evidence of acidification and affects thereof (Mayer and Ulrich 1977a and b, Singer et al. 1996, Bredemeier 1988, Oulehle and Hruska 2005).

At each site a pit was excavated with approximate dimensions of 1.5 m x 1.2 m x 1 m (Figure 1.5).

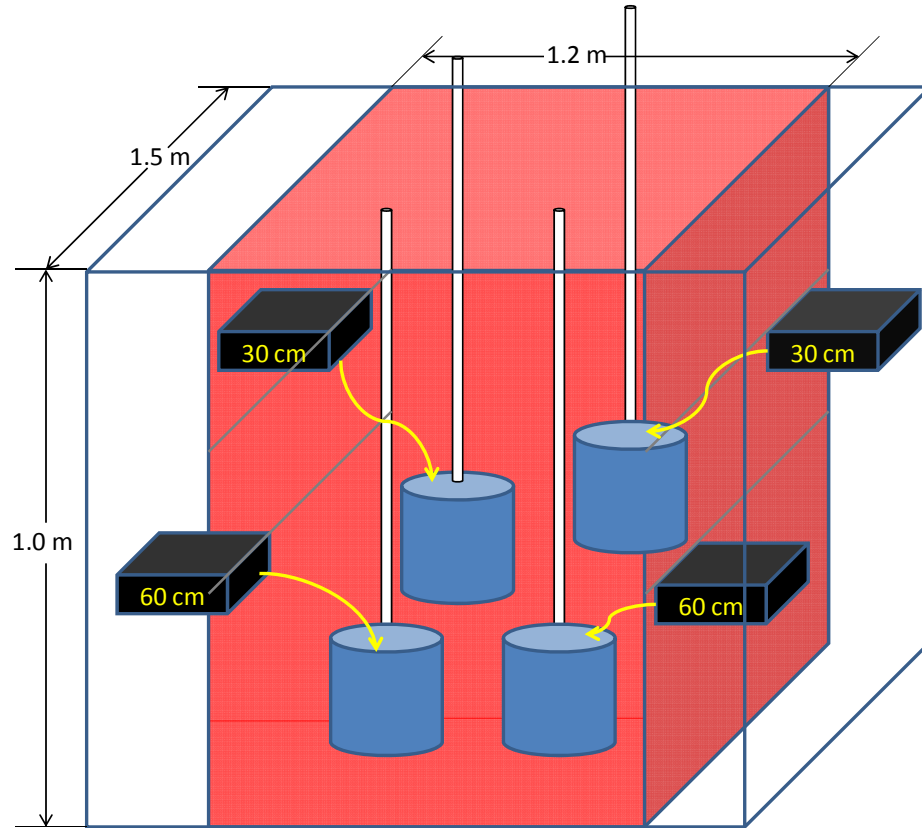


Figure 1.5: Schematic depicting pan (gravity) lysimeter placement in soil pit.

Area shaded in red is the area of pit excavation; blue cylinders are collection carboys; black boxes are the pans; yellow arrows are drainage tubes and white columns are PVC piping.

Soil profile descriptions were conducted according to the procedures of the Natural Resource Conservation Service (NRCS 1996). Soils were sampled by horizon from each pit and returned to the University of Kentucky Regulatory Services for laboratory characterization. Four zero-tension (pan) lysimeters were installed, two at 30- and two at 60-cm depths at each site. Four cavities were created in the sidewalls of the pit (2 in one side and 2 in the opposing side) to insert pans. The cavities were created in the sidewall so as not to disturb the soil above the desired depth, allowing for the column of soil above the pans to be undisturbed and natural. The cavity created was large enough to fit a shallow (32 x 28 x 5- cm) pan. A male hose fitting was screwed into a threaded nut that was welded into the bottom of the pan and window screen material was placed over the pan drain before being filled with pea gravel. A 9.5-mm-diameter polyethylene hose was attached to each pan and extended into 18.8 liter, polyethylene carboys placed at the bottom of the soil pit. Each carboy was altered to fit a 5-cm-diameter PVC pipe that extended from the bottom of the inside of the carboy to at least 50- cm above the forest floor. A notch was cut at the bottom of the PVC to allow water collected in the carboy to enter the pipe permitting the solution to be sampled. Plumbing contact adhesive was applied around the exit hole in the carboy and extending PVC creating a complete seal so solution entering the carboy came only from the hose of the pan lysimeter. Geofabric material was placed over each cavity and stapled into the sidewall of the pit to limit the entrance of disturbed soil. PVC caps were placed over the pipes and the pit was carefully backfilled with the excavated soil.

Two Tru-Check® (Edwards Manufacturing Co., Albert Lea, MN) rain gauges were installed within twenty meters of the pit at each site. Metal fence stakes were driven into the ground and rain gauges were mounted so that the top of the gauge was the highest point. Two throughfall collectors were also installed within twenty meters of the pit at each site. Metal fence stakes were driven into the ground and a milk crate basket was mounted to each stake. A 26.6-cm-diameter, heavy duty, polyethylene funnel was attached to a 3.8 liter, square Nalgene bottle and mounted into the basket so that the top of the funnel was the highest point. Funnel necks were stuffed with fiberglass glass wool to filter throughfall before entering the collection bottles. All PVC pipes from the pits, collection devices and fence stakes were spray painted with forest green and tan paint for

camouflage in order to minimize human influence at each site. GPS coordinates, elevation, aspect and slope were recorded for each pit location.

*Soil Characterization:*

Soil samples from each site were taken by horizon, bagged separately and analyzed for pH, buffer pH, Ca, Mg, K, Na, soil organic matter (OM), total N, soil texture (percent sand, silt and clay), cation exchange capacity (CEC), base saturation (BS), total exchangeable bases (TEB), and extractable acidity (EA) following methods of the University of Kentucky Regulatory Services. Soil was oven-dried at 38°C and ground to pass a 2-mm screen. A glass electrode measured pH of a soil slurry, and a slurry with Sikora buffer was added to measure buffer pH (Sikora 2006). Soil samples were saturated with ammonium acetate solution, then filtered and the solution was measured for exchangeable Ca, Mg, K, and Na (TEB) via inductively coupled plasma spectroscopy (ICP). Remaining soil was leached with NaCl to determine CEC. BS was determined as  $TEB/CEC * 100$  (SPAC 2000). Total organic carbon (%C) and total N were measured with a LECO dry combustion instrument (LECO Corp., St. Joseph, MI). OM was calculated as  $\%C \times 1.72 = OM$  (% of air dried soil) (Nelson and Sommers 1982).  $N_2$  gas emitted upon combustion (%N) was measured for total N. Soil texture (particle size analysis) was determined using the micropipette method (Miller and Miller 1987; Burt et al. 1993). EA was measured by titration, using the BaCl<sub>2</sub>-triethanolamine method (NRCS 1996).

Soil mineralogical composition was determined using a PANalytical X' Pert Pro diffractometer (PANalytical Inc., Westborough, MA) equipped with a copper X-ray tube, operated at 45 kV and 40 mA, and a Bragg-Bretano goniometer. A scanning rate of 2 degrees per 2 theta min<sup>-1</sup> from 2-40 degrees per 2 theta was used for Mg-saturated clay slides, and from 2-20 degrees per 2 theta for all other clay slides. Powder (sand - silt) samples were ran from 2-60 degrees per 2 theta.

*Solution Sampling:*

Soil solution was collected from the lysimeters from January 2012 – December 2013. Bi-weekly sampling was performed except during periods of light to no rainfall where sampling was delayed until approximately 2.5 cm was recorded at near-by Mesonet monitoring stations. Water was collected using an SKC Airchek Sampler (SKC

Inc., Eighty Four, PA) air pump connected to a 1000 mL Buchner suction flask. Water was collected into the Buchner flask from each carboy and transferred to 250 mL Nalgene bottles. Excess water in the carboys was pumped out and discarded down slope from the soil pit. The sampler was cleaned between each lysimeter to prevent cross contamination by pumping deionized water through the pump apparatus. Water in the throughfall collectors was transferred to 250 mL Nalgene bottles, rain gauge readings were recorded, and all devices were emptied, cleaned and returned to their places. In situ levels of pH, conductivity, temperature and dissolved oxygen were recorded for each collected sample (two 30-cm, two 60-cm, and two throughfall) using a YSI 556 (YSI Inc., Yellow Springs, OH) environmental monitor. All samples were then placed on ice in a cooler and transported back to the lab for further analysis.

In the lab, solution samples were filtered through a 1.0- $\mu\text{m}$  filter and refrigerated until analysis. Handling and analysis followed procedures from the Standard methods for the examination of water and wastewater (APHA 1989). Base cations (Ca, Mg, K and Na) were measured using a GBC (GBC Scientific Equipment, Braeside Australia) atomic absorption spectrophotometer. Total organic carbon was measured using a Shimadzu (Shimadzu Corp., Kyoto, Japan) TOC analyzer.  $\text{NO}_3^-$  and ammonium was measured colorimetrically with a Bran +/- Luebbe autoanalyzer. Chloride and  $\text{SO}_4^{2-}$  were measured with a Dionix (Thermo Scientific, Sunnyvale, CA) ion chromatograph. Electrical conductivity was measured with a YSI (YSI Inc., Yellow Springs, OH) conductivity bridge. An Orion (Thermo Scientific, Sunnyvale, CA) pH meter was used to measure solution pH, and alkalinity was measured colorimetrically by titration using the methyl orange method. A 50 mL centrifuge tube was filled for each sample taken and 250  $\mu\text{L}$  of 1:1 nitric acid was added, acidifying each sample so ions could remain in solution until Al analysis could be conducted. Acidified samples were filtered using 0.45  $\mu\text{m}$  syringe filters and taken to the University-of Kentucky Environmental Research Training Laboratory (ERTL) for Al analysis. Al was determined using a Varian Vista Pro (Varian Inc., Palo Alto, CA) inductively coupled plasma optical emission spectrometry (ICP-OES). Samples were ionized with inductively coupled plasma and Al was separated and quantified, calibrated with certified reference material. Mercury (Hg) content of soils and soil solution samples were tested using a Nippon MA-2 (Nippon Instruments Corp.,

Tokyo, Japan) direct Hg analyzer by methods of Ogorek et al. (2010). SAS 9.3 software was used to conduct means procedures and students T-tests to compare solution and throughfall data between sites. Frequencies and percentages were calculated for categorical variables and chi-square tests were used for comparison between groups. Means and standard deviations and tukey's groupings were determined for continuous variables. Univariate analysis was used to determine significant difference.

### **Results and Discussion:**

#### *Soil Physiochemical and Mineralogical Attributes:*

Soil physiochemical properties from the four studied sites are shown in Table 1.2.

Table 1.2: Physicochemical properties of soils by site and pedon.

| Pedon           | Depth (cm) | Textural Class           | pH  | Ca <sup>a</sup> | TEB <sup>b</sup> | CEC <sup>c</sup> | EA <sup>d</sup> | BS <sup>e</sup> | OM <sup>f</sup> |
|-----------------|------------|--------------------------|-----|-----------------|------------------|------------------|-----------------|-----------------|-----------------|
| <b>Clay</b>     |            | <b>Rayne silt loam</b>   |     |                 |                  |                  |                 |                 |                 |
| A               | 3 to 8     | sandy-loam               | 3.0 | 1.2             | 2.1              | 12               | 10              | 17              | 15              |
| AB              | 8 to 18    | sandy-loam               | 3.3 | 0.39            | 0.76             | 8.4              | 7.6             | 9.0             | 4.0             |
| BE              | 18-25      | sandy-loam               | 3.6 | 0.18            | 0.64             | 6.9              | 6.3             | 9.4             | 2.0             |
| 2Bt             | 25-56      | sandy-clay loam          | 3.6 | 0.22            | 0.36             | 6.4              | 6.0             | 5.6             | 1.5             |
| 2BC             | 56-94      | sandy-clay loam          | 3.3 | 0.41            | 0.76             | 10               | 9.4             | 7.5             | 0.84            |
| 2C              | 94-132     | sandy-clay loam          | 3.4 | 0.17            | 0.62             | 9.1              | 8.4             | 6.9             | 0.26            |
| <b>Estill</b>   |            | <b>Rayne silt loam</b>   |     |                 |                  |                  |                 |                 |                 |
| A               | 3 to 15    | silt loam                | 4.5 | 2.0             | 2.8              | 8.6              | 5.8             | 33              | 2.1             |
| AB              | 15-29      | silt loam                | 4.1 | 1.2             | 1.8              | 7.0              | 5.2             | 26              | 1.1             |
| Bt1             | 29-63      | loam                     | 3.8 | 1.8             | 2.9              | 8.3              | 5.4             | 35              | 0.6             |
| Bt2             | 63-85      | loam                     | 3.5 | 1.1             | 1.9              | 7.6              | 5.7             | 25              | 0.36            |
| C               | 85-150     | loam                     | 3.5 | 0.54            | 1.0              | 6.2              | 5.2             | 16              | 0.24            |
| <b>McCreary</b> |            | <b>Gilpin sandy loam</b> |     |                 |                  |                  |                 |                 |                 |
| A               | 2 to 7     | Sandy loam               | 3.5 | 0.16            | 0.51             | 12               | 11              | 4.5             | 5.4             |
| BA              | 7 to 24    | sandy loam               | 4.0 | 0.03            | 0.30             | 7.0              | 6.7             | 4.3             | 1.6             |
| Bt1             | 24-39      | sandy clay loam          | 3.8 | 0.03            | 0.34             | 7.9              | 7.5             | 4.3             | 0.71            |
| 2Bt2            | 39-69      | clay                     | 3.6 | 0.17            | 0.77             | 14               | 14              | 5.4             | 0.41            |
| 2Cr             | 69-125     | silty clay               | 3.2 | 0.05            | 0.67             | 18               | 17              | 3.8             | 0.21            |
| <b>Wolfe</b>    |            | <b>Rayne silt loam</b>   |     |                 |                  |                  |                 |                 |                 |
| A               | 2 to 6     | silt loam                | 3.2 | 0.06            | 0.59             | 14               | 13              | 4.3             | 5.1             |
| BA              | 6 to 16    | silt loam                | 3.9 | 0.02            | 0.14             | 8.2              | 8.0             | 1.8             | 2.2             |
| BE              | 16-28      | Silt loam                | 3.9 | 0.01            | 0.13             | 7.5              | 7.4             | 1.7             | 1.2             |
| Bt1             | 28-41      | silt loam                | 3.7 | 0.02            | 0.36             | 7.2              | 6.9             | 4.9             | 0.57            |
| Bt2             | 41-66      | clay loam                | 3.5 | 0.02            | 0.30             | 8.9              | 8.6             | 3.3             | 0.29            |
| CB1             | 66-108     | loam                     | 3.5 | 0.02            | 0.41             | 7.9              | 7.4             | 5.1             | 0.17            |

\* <sup>a</sup>Exchangeable calcium (cmol<sub>c</sub> kg<sup>-1</sup>); <sup>b</sup>Total exchangeable bases (cmol<sub>c</sub> kg<sup>-1</sup>); <sup>c</sup>Cation exchange capacity (meq 100g<sup>-1</sup>);

<sup>d</sup>Exchangeable acidity (meq 100<sup>-1</sup>); <sup>e</sup>Percent base saturation (%); <sup>f</sup>Percent organic matter (%)

Three of the four sites contained soils from the Rayne soil series. The Clay County site had a sandy loam texture from the surface to 25-cm depth and a slight increase in clay between 25- and 60-cm. This site has the highest percent sand and lowest percent clay between the surface and the 60-cm depth, with clay distribution slightly increasing and sand slightly decreasing with depth. The Estill County (Estill) site exhibited a silt loam texture in the top 30-cm and transitions to loam between 30- and 60-cm. The Wolfe County (Wolfe) site exhibited silt loam texture in the top 40-cm with an increase in clay content between 40- and 60-cm depth. McCreary County (McCreary) contained soils from the Gilpin soil series. The first 30-cm of depth was dominated by a sandy loam texture, and clay content increased from sandy clay loam to clay between 30- and 60-cm depth.

Clay County had the most acidic (pH 3.0) surface horizon, underlain by slightly less but still acidic (pH 3.4-3.6) lower horizons to the 60-cm depth. Estill had the least acidic (pH 4.5) surface horizon, but soil increased in acidity (pH 4.1-3.8) to 60-cm depth. McCreary soil ranged from pH 3.5 to 4.0 throughout 60-cm of depth. Wolfe soil ranged from pH 3.2 in the surface horizon to pH 3.9 in the top 30-cm, but pH dropped slightly (pH 3.7-3.5) to the 60-cm depth. Soil characterized in 1965 as Rayne silt loam from Coshocton County, OH describes the soils to have a surface pH between 5.5 and 6.5 with pH gradually decreasing to about 4.5 with depth (Kelly et al. 1975). The NRCS Web Soil Survey (WSS) ([websoilsurvey.nrcs.gov/](http://websoilsurvey.nrcs.gov/)) describes the Gilpin silt loam series (formerly Wernock) as having a pH of 5.5 in the top 10-cm decreasing to 4.6 at 60-cm depth. Even though the soil types represented in our research are expected to be acidic in nature, our soils exhibited pHs that were lower than described elsewhere for these series types. Estill was the only site to be least acidic in the surface horizon, and gradually become more acidic with depth. Surface soil acidity in the other three sites was probably influenced by the dense litter layer and high percent organic matter. Organic acids are found in forest litter and soil humus and have been found to decrease pH by contributing  $H^+$  ions to exchange sites (Johnson et al. 1982; Johnson et al. 1977). The high (>5%) OM content in the A horizons of Clay, McCreary and Wolfe resulted in low pH of A horizons (Table 1.2). Estill had lower OM content (2.12%) and the highest pH (4.5). OM levels at Clay, McCreary and Wolfe are above the expected percentage of 1.8-2.3% from WSS



descriptions of both Wernock and Rayne/Gilpin complex soils, which could be because of a dense forest overstory.

Forest soils, especially shallow, well drained, ridge-top soils where excess weathering has taken place, are especially sensitive to nutrient depletion (Huntington 2000). Soils are found to be acid sensitive when they have a percent base saturation below 10% (Sullivan et al. 2004), which was the case for many of our soil horizons. BS and TEB varied greatly among the sites. Estill had the highest BS (33-16 %) and TEB (2.9-1.0 cmolc kg<sup>-1</sup>) with levels more than double to eight times greater than other sites. Clay County had a relatively high BS (17 %) and TEB (2.1 cmolc kg<sup>-1</sup>) in the A horizon, and exhibited higher concentrations of TEB and BS than both McCreary and Wolfe in all horizons. Clay County had the lowest CEC (12-6.4 meq 100g<sup>-1</sup>) from the surface throughout the top 60-cm. Wolfe, which had the lowest BS (4.9-1.7 %) and TEB (0.59-0.13 cmolc kg<sup>-1</sup>), had the highest CEC (14-7.2 meq 100g<sup>-1</sup>) in most soil horizons. CEC values at our sites are within the range of WSS reported CEC for Wernock and Rayne/Gilpin complex soils, which was between 22 and 7.2 meq 100g<sup>-1</sup>. However, BS values for Rayne soil from Kelly et al. (1975) are higher (70-21%) than all of our sites. A high CEC coinciding with lower BS and TEB, as seen in McCreary and Wolfe, can be an indication that the two sites have already been weathered and leached of significant amounts of base cations. This leaves acid cation replacement from high EA to be the driver of buffering in those systems and potentially leads to greater acidification of soil and solution. Table 1.2 shows highest clay content in the McCreary subsoil coinciding with highest recorded EA in all sites indicating the weathering of clay minerals and enrichment of acid cations such as Al, Fe and H<sup>+</sup> and mineral exchange sites. Clay and Estill have not been significantly leached of major base cation pools, and therefore have not yet reached a tipping point at which buffering capacity is low and dominated by acid ions.

Mineralogical compositions of the <2- $\mu$ m clay fraction are recorded in Table 1.3.

Table 1.3: Mineralogical composition of the <2 $\mu$ m clay fraction by site and pedon.

| Site     | Pedon | Depth (cm) | V-HIV | INT | K  | MI | Q | GI | GO | F |
|----------|-------|------------|-------|-----|----|----|---|----|----|---|
| Clay     | A     | 3 to 8     | 24    | 4   | 66 | 4  | 2 |    |    |   |
|          | AB    | 8 to 18    | 30    |     | 66 | 3  |   |    | 1  |   |
|          | BE    | 18-25      | 29    |     | 67 | 3  | 1 |    |    |   |
|          | 2Bt   | 25-56      | 26    | 4   | 67 | 2  |   |    | 1  |   |
|          | 2BC   | 56-94      | 23    | 4   | 54 | 15 |   |    | 2  | 2 |
|          | 2C    | 94-132     | 14    | 16  | 48 | 20 | 2 |    |    |   |
| Estill   | A     | 3 to 15    | 34    | 4   | 47 | 6  | 7 |    | 2  |   |
|          | AB    | 15-29      | 41    |     | 47 | 6  | 5 |    |    | 1 |
|          | Bt1   | 29-63      | 41    | 5   | 44 | 3  | 5 |    | 2  |   |
|          | Bt2   | 63-85      | 42    |     | 47 | 5  | 4 |    | 2  |   |
|          | C     | 85-150     | 45    |     | 47 | 4  | 2 |    | 2  |   |
| McCreary | A     | 2 to 7     | 41    |     | 50 | 4  | 5 |    |    |   |
|          | BA    | 7 to 24    | 36    |     | 54 | 4  | 4 |    | 2  |   |
|          | Bt1   | 24-39      | 39    |     | 53 | 4  | 2 |    | 2  |   |
|          | 2Bt2  | 39-69      | 31    |     | 53 | 9  |   | 5  | 2  |   |
|          | 2Cr   | 69-125     | 23    |     | 54 | 21 | 2 |    |    |   |
| Wolfe    | A     | 2 to 6     | 54    | 5   | 33 | 3  | 4 |    |    | 1 |
|          | BA    | 6 to 16    | 46    |     | 42 | 6  | 6 |    |    |   |
|          | BE    | 16-28      | 31    | 4   | 45 | 9  | 4 | 5  | 2  |   |
|          | Bt1   | 28-41      | 25    | 5   | 54 | 9  | 4 |    | 3  |   |
|          | Bt2   | 41-66      | 16    | 4   | 65 | 11 |   |    | 4  |   |
|          | CB1   | 66-108     | 12    |     | 68 | 19 |   |    | 1  |   |

\* *V-HIV* vermiculite/hydroxyl-interlayered vermiculite; *INT* interstratified mica-vermiculite; *K* kaolinite; *MI* mica; *Q* quartz; *GI* gibbsite; *GO* goethite; *F* feldspars

Results are reported in percentages. The accuracy of results is  $\pm 3\%$ .

All soils contained a mix of aluminosilicate clay minerals dominated by hydroxy-interlayered vermiculite (V-HIV) and kaolinite. Clay County soil contained approximately 66% kaolinite and 24-30% V-HIV in the clay fraction, consistent from the surface to 60-cm depth. The Estill clay fraction had more kaolinite than V-HIV at all depths; approximately 47% and 34-41%, respectively. Wolfe was dominated by V-HIV near the surface (2-16 cm) and kaolinite at depths below (16-60 cm). McCreary clay fraction was dominated by kaolinite in each pedon and was the only site interstratified mica-vermiculite could not be found. All four sites contained some mica and quartz and low levels of goethite. Feldspars were found in very small amounts and only in the top 6 cm in Wolfe and 15-29 cm in Estill. Only Wolfe and McCreary contained gibbsite.

Hg content of soils and soil solution were found to be very low, and most samples resulted in levels below the detection limit. Therefore, Hg results were not used in evaluation of soil and soil solution chemistry at our research sites.

*Soil Solution Composition:*

Zero tension pan lysimeters collect only gravimetric water from the overlying soil column. As water infiltrates from the surface through the soil it leaches ions along the way. Chemical analysis of soil leachate is used to assess the impacts of precipitation inputs on soil properties and contributions to ecosystem deterioration (Karathanasis 1989). Soil solution pH of all sites displayed acidifying trends over the course of study with the exception of the 30-cm lysimeter depth at Clay County, which fluctuated but remained at a consistent level (Figure 1.6).

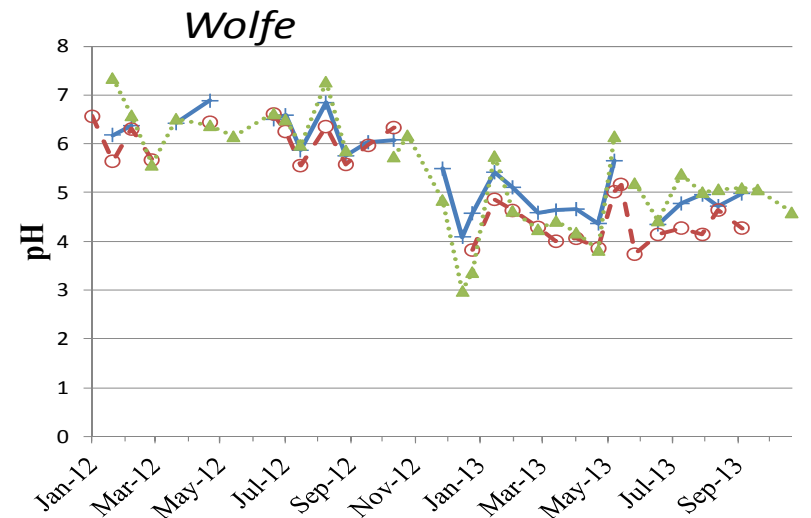
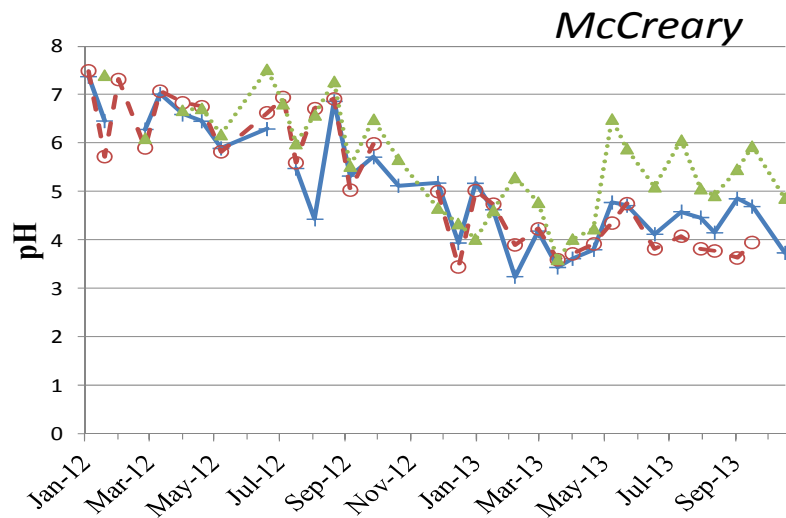
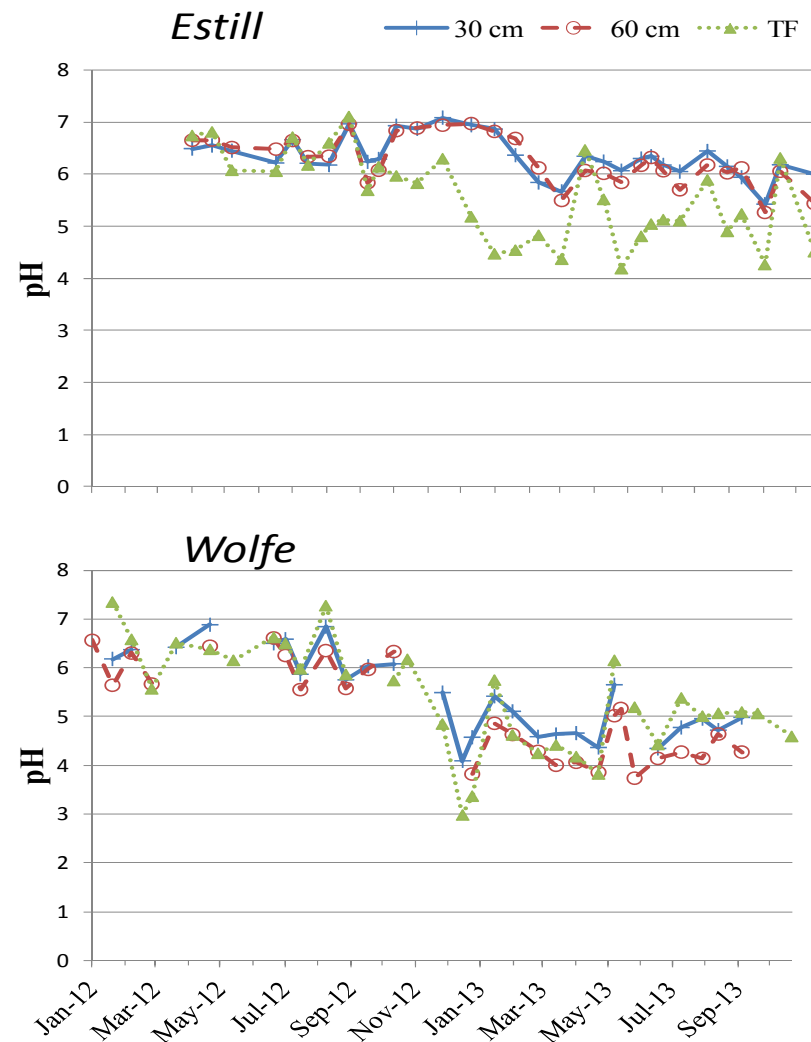
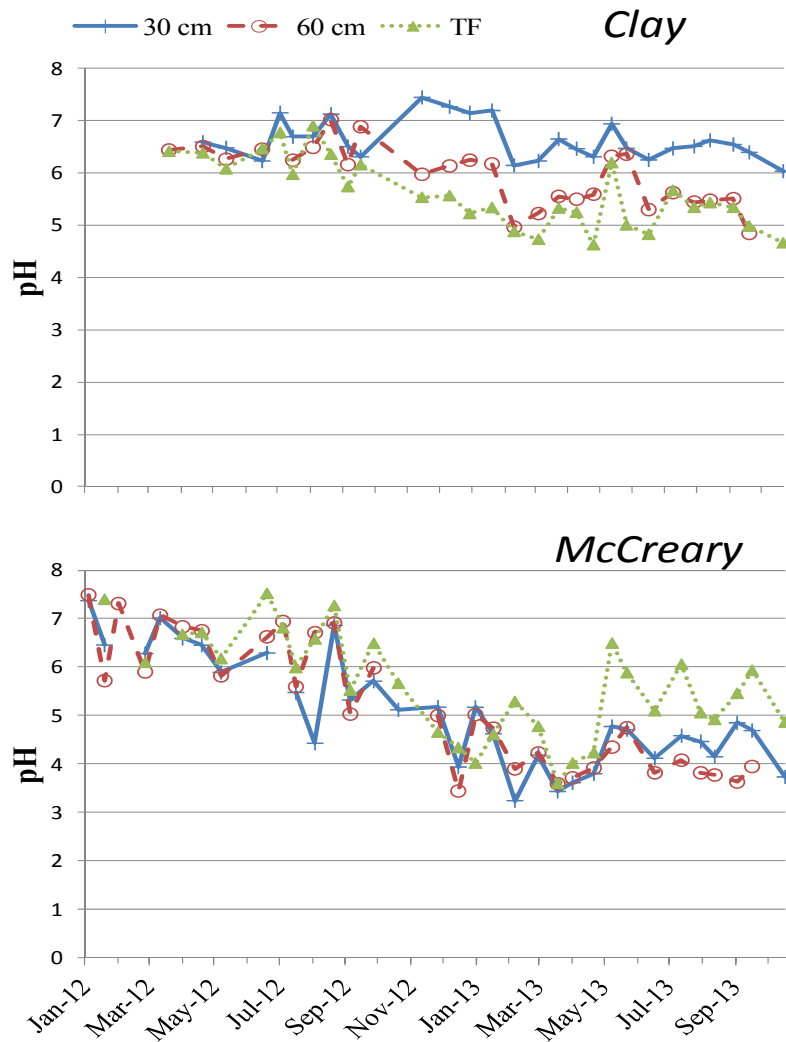


Figure 1.6: Throughfall (TF) and soil solution pH values for samples collected at sites in pan lysimeters at 30-, and 60-cm depths.

McCreary and Wolfe had the largest decline in pH over the period, dropping from a range of pH 6-7 in early and mid-2012 to a range of pH 3.5-5 in 2013. McCreary had the greatest range in pH, starting around pH 7.5 at both the 30- and 60-cm depths and dropping below pH 3.5. Clay and Estill did not have as large of a soil solution pH range which was around pH 7.5-5.0 and 7.0-5.4 respectively. Clay County 60-cm lysimeters revealed a trend of greater acidification than Estill, but yielded consistent pH levels at the 30-cm depth. This might be explained by high OM along with low soil pH (<3) for Clay County surface soils, which provides some buffering potential in the top 30-cm. Additional acidity in solution can come from the decomposition of litter layers and incorporation to soil humus (Johnson et al. 1982). Soil humus produces humic acids which can naturally acidify the soil. Humus production contributes to the CEC by increasing the % H saturation and causing a decrease in the proportion of base cations to H<sup>+</sup> ions available for exchange but allowing buffering to remain (Ulrich 1980). Mayer and Ulrich (1977a) found that buffering of the soil solution takes place in the upper 20 to 30 cm of the soil and is most evident in the upper 1-2 cm of the mineral soil. They observed soil pH values as low as 3 at that depth and still reported 80% of precipitation acidity neutralized with Al forming the buffer system, supporting claims that at low pH and low BS, Al<sup>3+</sup> controls buffering.

Soil base cations contribute to the buffering potential of a soil, and are leached as the soil environment is acidified. Not only is an acidic soil generally less capable of pH buffering, losses in important base cations will continue until reserves are low (Stevens et al. 2009). All four sites had statistically similar average throughfall pH over the course of the study, but did not have similar solution pH. Table 1.4 shows average throughfall pH for McCreary and Wolfe to be 5.6 and 5.4, respectively.

Table 1.4: Means and standard deviations of soil solution (30- and 60-cm depths) and throughfall (TF) chemistry.

|  | Sample Depth | Clay               |      | Estill             |      | McCreary           |      | Wolfe              |      |
|--|--------------|--------------------|------|--------------------|------|--------------------|------|--------------------|------|
|  |              | Mean               | Stdv | Mean               | Stdv | Mean               | Stdv | Mean               | Stdv |
| <b>pH</b>  | TF           | 5.6 <sup>a</sup>   | 0.86 | 5.6 <sup>a</sup>   | 0.66 | 5.6 <sup>a</sup>   | 1.1  | 5.4 <sup>a</sup>   | 1.1  |
|  | 30 cm        | 6.3 <sup>a</sup>   | 0.39 | 6.6 <sup>a</sup>   | 0.38 | 5.1 <sup>b</sup>   | 1.1  | 5.5 <sup>b</sup>   | 0.86 |
|  | 60 cm        | 6.3 <sup>a</sup>   | 0.47 | 6.0 <sup>a</sup>   | 0.57 | 5.2 <sup>b</sup>   | 1.3  | 5.1 <sup>b</sup>   | 0.99 |
| <b>EC</b><br>( $\mu\text{S cm}^{-1}$ )                       | TF           | 22.8 <sup>a</sup>  | 12   | 35.5 <sup>a</sup>  | 21   | 30.7 <sup>a</sup>  | 64   | 27.9 <sup>a</sup>  | 16   |
|  | 30 cm        | 152 <sup>b</sup>   | 58   | 277 <sup>a</sup>   | 65   | 46.8 <sup>c</sup>  | 120  | 32.3 <sup>c</sup>  | 10   |
|  | 60 cm        | 150 <sup>a</sup>   | 73   | 106 <sup>b</sup>   | 72   | 22.7 <sup>c</sup>  | 7.9  | 32.2 <sup>c</sup>  | 14   |
| <b>NO<sub>3</sub><sup>-</sup></b><br>( $\text{mg L}^{-1}$ )  | TF           | 0.14 <sup>b</sup>  | 0.15 | 0.15 <sup>b</sup>  | 0.20 | 0.14 <sup>b</sup>  | 0.11 | 0.34 <sup>a</sup>  | 0.36 |
|  | 30 cm        | 0.71 <sup>a</sup>  | 1.1  | 0.41 <sup>a</sup>  | 0.44 | 0.41 <sup>a</sup>  | 0.85 | 0.48 <sup>a</sup>  | 0.66 |
|  | 60 cm        | 0.65 <sup>a</sup>  | 1.2  | 0.47 <sup>a</sup>  | 1.2  | 0.52 <sup>a</sup>  | 1.2  | 0.27 <sup>a</sup>  | 0.48 |
| <b>SO<sub>4</sub><sup>2-</sup></b><br>( $\text{mg L}^{-1}$ ) | TF           | 2.8 <sup>a</sup>   | 1.8  | 4.9 <sup>a</sup>   | 9.9  | 2.3 <sup>a</sup>   | 2.5  | 2.3 <sup>a</sup>   | 1.4  |
|  | 30 cm        | 8.0 <sup>b</sup>   | 5.3  | 12 <sup>a</sup>    | 7.6  | 3.9 <sup>c</sup>   | 2.8  | 4.2 <sup>c</sup>   | 2.0  |
|  | 60 cm        | 7.8 <sup>a</sup>   | 5.3  | 9.3 <sup>a</sup>   | 5.6  | 3.3 <sup>b</sup>   | 2.3  | 5.3 <sup>b</sup>   | 2.1  |
| <b>Al</b><br>( $\text{mg L}^{-1}$ )                          | TF           | 0.05 <sup>a</sup>  | 0.05 | 0.051 <sup>a</sup> | 0.05 | 0.04 <sup>a</sup>  | 0.07 | 0.06 <sup>a</sup>  | 0.05 |
|  | 30 cm        | 1.0 <sup>a</sup>   | 1.6  | 0.29 <sup>b</sup>  | 0.28 | 0.48 <sup>ab</sup> | 0.35 | 0.54 <sup>ab</sup> | 0.35 |
|  | 60 cm        | 1.1 <sup>a</sup>   | 2.6  | 0.31 <sup>a</sup>  | 0.37 | 1.1 <sup>a</sup>   | 2.1  | 0.29 <sup>a</sup>  | 0.29 |
| <b>Ca</b><br>( $\text{mg L}^{-1}$ )                          | TF           | 0.99 <sup>ab</sup> | 2.1  | 1.8 <sup>a</sup>   | 3.2  | 0.44 <sup>b</sup>  | 0.32 | 0.79 <sup>b</sup>  | 0.56 |
|  | 30 cm        | 17 <sup>b</sup>    | 5.1  | 24 <sup>a</sup>    | 4.2  | 1.0 <sup>c</sup>   | 0.84 | 1.7 <sup>c</sup>   | 1.1  |
|  | 60 cm        | 17 <sup>a</sup>    | 6.7  | 8.8 <sup>b</sup>   | 5.6  | 0.91 <sup>c</sup>  | 0.60 | 1.1 <sup>c</sup>   | 1.2  |

Means with the same letter are not significantly different ( $p = 0.05$ ) among sites at the same depth.

McCreary 30-cm lysimeters had a lower pH (5.1) than Wolfe (5.5), but 60-cm had a higher pH (5.2) than Wolfe (5.1). This is surprising because McCreary in general had higher soil BS, more TEB and lower levels of EA. Reasoning for higher solution pH in Clay and Estill could be greater BS and lower levels of EA allowing stronger buffering from pH changes compared to Wolfe and McCreary.

A concern with using pan lysimeter was that soil chemistry could be altered by the installation of the monitoring equipment and care was given to minimize these effects. Examination of the data suggested that pH trends between throughfall and soil solution were similar for all sites and showed an acidifying trend for the duration of the study. Peaks and troughs in throughfall pH were also evident in the majority of soil solution trends. Throughfall collectors are very inefficient collectors of gases, fine particles, and cloud droplets, underestimating total deposition (Lindberg et al. 1986), but can be indicators of major changes in precipitation and compared to changes occurring in soil solution. Acidifying trends during 2012 were also seen at local NADP weather stations (Figure 1.7) but pH showed a larger upward trend in 2013.

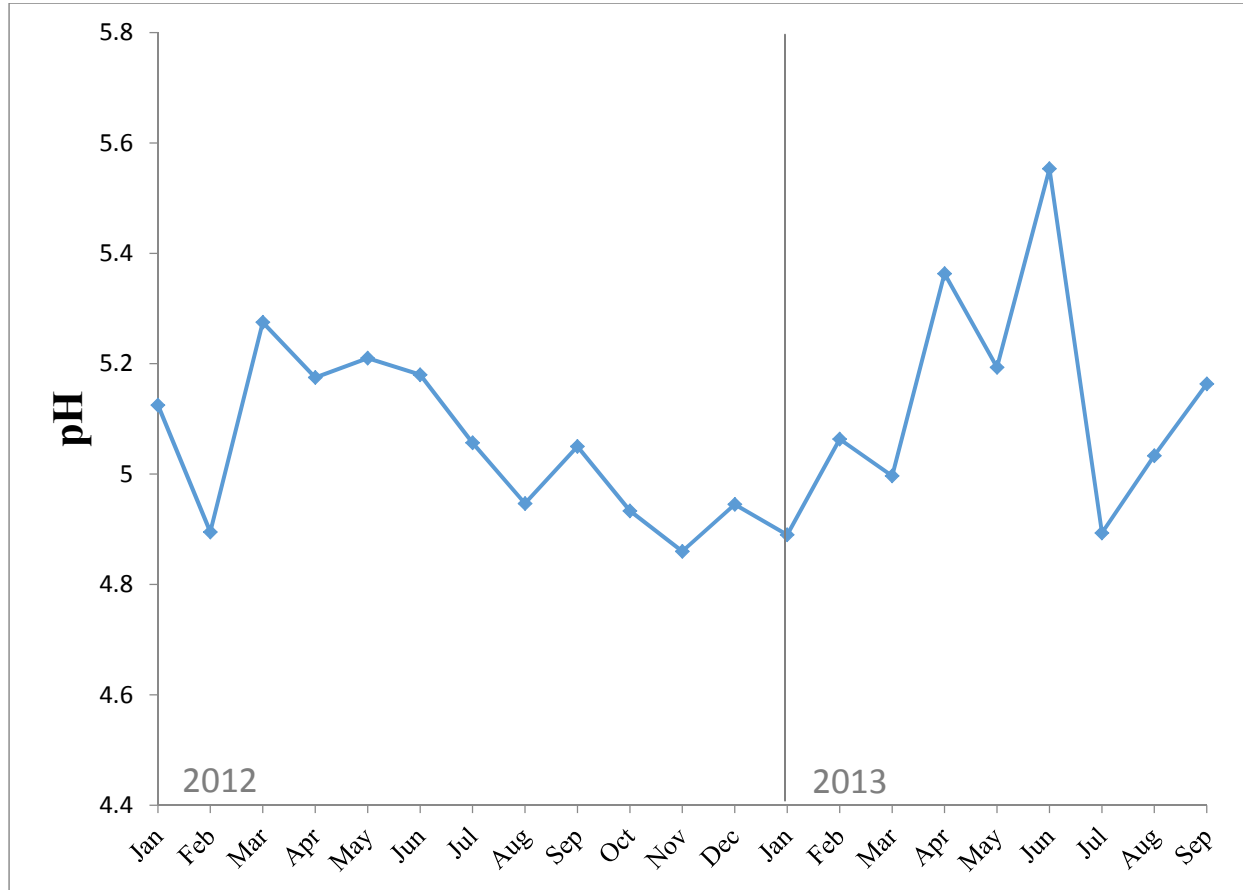


Figure 1.7: Average pH of precipitation from NADP sites KY03, KY22, and KY35.



In most occurrences, trends in throughfall more similarly matched solution trends than those collected by the NADP. The collection of dust, fine particles and dry deposition on canopy surfaces has an apparent influence on the chemistry of the water reaching the forest floor. Thus, NADP data cannot be related to throughfall or soil solution chemistry because dry deposition plays such a major role in the end product.

$\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  entering soil is influenced by the activity of microbes and plants found within the soil environment. Assimilation or uptake of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  consumes acidity by either taking up a cation ( $\text{H}^+$ ) or excreting an anion ( $\text{OH}^-$ ), neutralizing the strong acids to the extent of use by plants and microbes (Binkley et al. 1989). Nitrogen reduction from  $\text{NO}_3^-$  to  $\text{NH}_4^+$  and immobilization to organic matter consumes electrons increasing the pH of the environment (Coyne 2008). Inputs exceeding biotic use can either be adsorbed in soil increasing soil acidity, leached increasing solution acidity, or transformed to other compounds by organisms. Excess  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  contribute to the acidification of soils, leaching of base cations and mobilization of Al from soil minerals (McLaughlin et al. 1998; Shortle and Smith 1988).

$\text{NO}_3^-$  concentrations from soil leachate were highly variable, and generally low ( $< 0.5 \text{ mg L}^{-1}$ ) for all sites but occasionally peaked to levels above  $3.5 \text{ mg L}^{-1}$  at all but Wolfe (Figure 1.8).

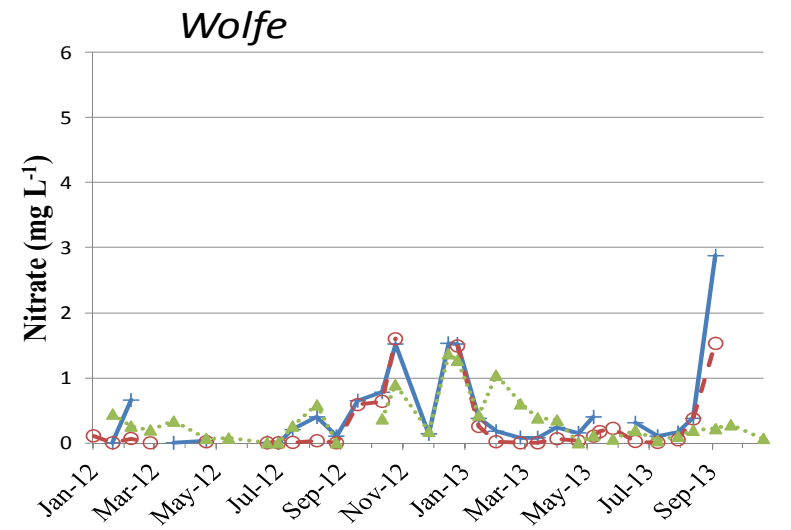
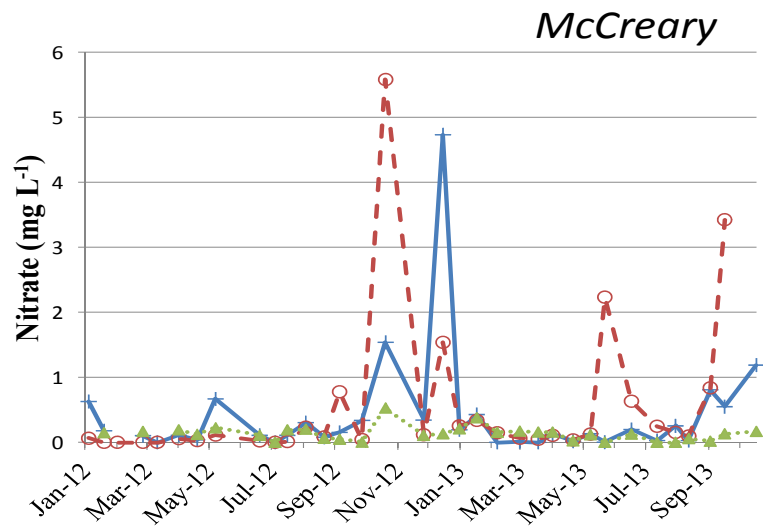
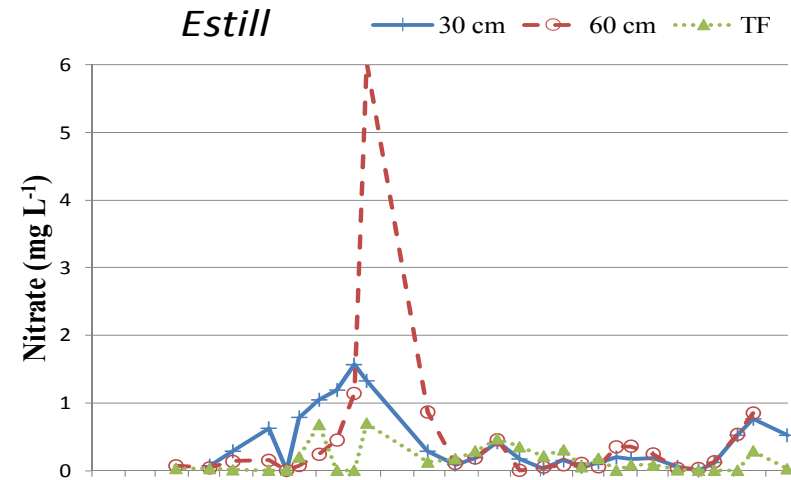
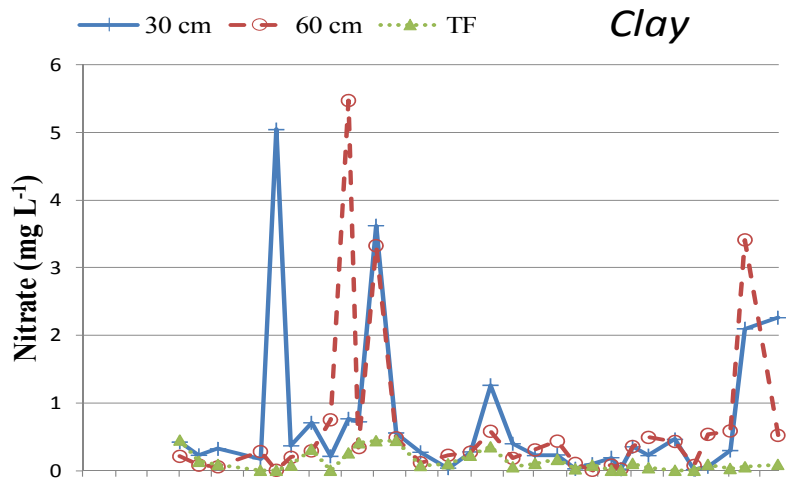


Figure 1.8: Throughfall (TF) and soil solution  $\text{NO}_3^-$  concentration for samples collected at sites in pan lysimeters at 30-, and 60-cm depths.

Spikes in  $\text{NO}_3^-$  levels were distributed throughout all seasons between the sites. Clay County saw major peaks during the late summer and early fall of 2012 and again in late fall, 2013. Estill had higher concentrations during the same time periods as Clay County. McCreary and Wolfe had higher peaks of  $\text{NO}_3^-$  concentrations during the late fall and early winter months of 2012-13, late June, 2013 and again in late September. Each site had relatively high throughfall concentrations in late November and mid-February and soil solution at all sites but Wolfe exhibited a corresponding peak in solution  $\text{NO}_3^-$  in February, 2013. Table 1.4 shows that all sites at each depth were statistically similar, but Clay County had the highest mean  $\text{NO}_3^-$  concentrations and Wolfe had the lowest, even though Wolfe throughfall showed a mean  $\text{NO}_3^-$  concentration significantly higher than the other sites.

De Vries et al. (2003) found most variation in  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in solution was related to atmospheric input and not as much to rainfall amount. However, they related  $\text{NO}_3^-$  in solution to  $\text{NH}_4^+$  rather than  $\text{NO}_3^-$  in precipitation; suggesting a strong influence of soil nitrification processes. Edwards et al. (2002) recognized biological assimilation of N in the topsoil to be a contributor to results of higher  $\text{NO}_3^-$  in subsurface soil solution than surface soils. Studies have shown seasonal differences in solution  $\text{NO}_3^-$ , with peak periods usually in the summer months (Johnson et al. 1999; McDowell et al. 2004). In other studies, including most of our DBNF sites, no significant monthly differences were found (Knoepp et al. 2008). Nitrogen in southern forests is often a limited nutrient readily used by organisms and much of the  $\text{NO}_3^-$  is utilized by plant uptake (Binkley et al. 1989). Even N saturated soils undergo biological interaction with the N cycle, therefore,  $\text{NO}_3^-$  may not be the best strong mobile acid anion to use when evaluating soil solution.

$\text{SO}_4^{2-}$  may be more representative of deposition trends (Binkley et al. 1989). Naturally derived  $\text{SO}_4^{2-}$  is typically below 10% of total  $\text{SO}_4^{2-}$  in precipitation for inland areas (Dovland et al. 1976). Chao et al. (1964) and Harward and Reisenauer (1966) found that free Fe and Al in soil adsorbs  $\text{SO}_4^{2-}$ . Soils having low  $\text{SO}_4^{2-}$  sorption at  $\text{pH} < 4$  are characterized by high Al contents and low Fe contents (Courchesne and Hendersot 1989; Xue and Harrison 1991; Kaiser and Kaupenjohann 1998). Soils with Al compounds dominating  $\text{SO}_4^{2-}$  retention could cause greater increases in  $\text{SO}_4^{2-}$  output and decreased pH of solution which can lead to higher rates of weathering on clay minerals

and increased release of Al (Nordstrom 1982). As  $\text{SO}_4^{2-}$  in soil increases, soil pH decreases, and adsorption sites become outnumbered by  $\text{SO}_4^{2-}$ . Contrarily,  $\text{SO}_4^{2-}$  may desorb from soil when precipitation concentrations are lowered and a concomitant increase in soil pH and acidification of solution is likely. Johnson et al. (1999) and Watmough et al. (2005) saw a rapid response of soil solution  $\text{SO}_4^{2-}$  to reduced S deposition and determined that it reflected a low buffering of  $\text{SO}_4^{2-}$  inputs due to low adsorption ability. When the solution reaches or goes below the pH of minimum solubility for Al hydroxides of clay minerals, which is approximately pH 6.7 for gibbsite (May et al. 1979), soils are weathered and Al concentrations in solution increase (Binkley et al. 1989). Johnson et al. (1999) concluded that S and N deposition is the major factor affecting soil solution Al concentrations.

Solution  $\text{SO}_4^{2-}$  levels in Clay and Estill fluctuated significantly during the sampling period, exhibiting a slight reducing trend with periods of spikes throughout (Figure 1.9).

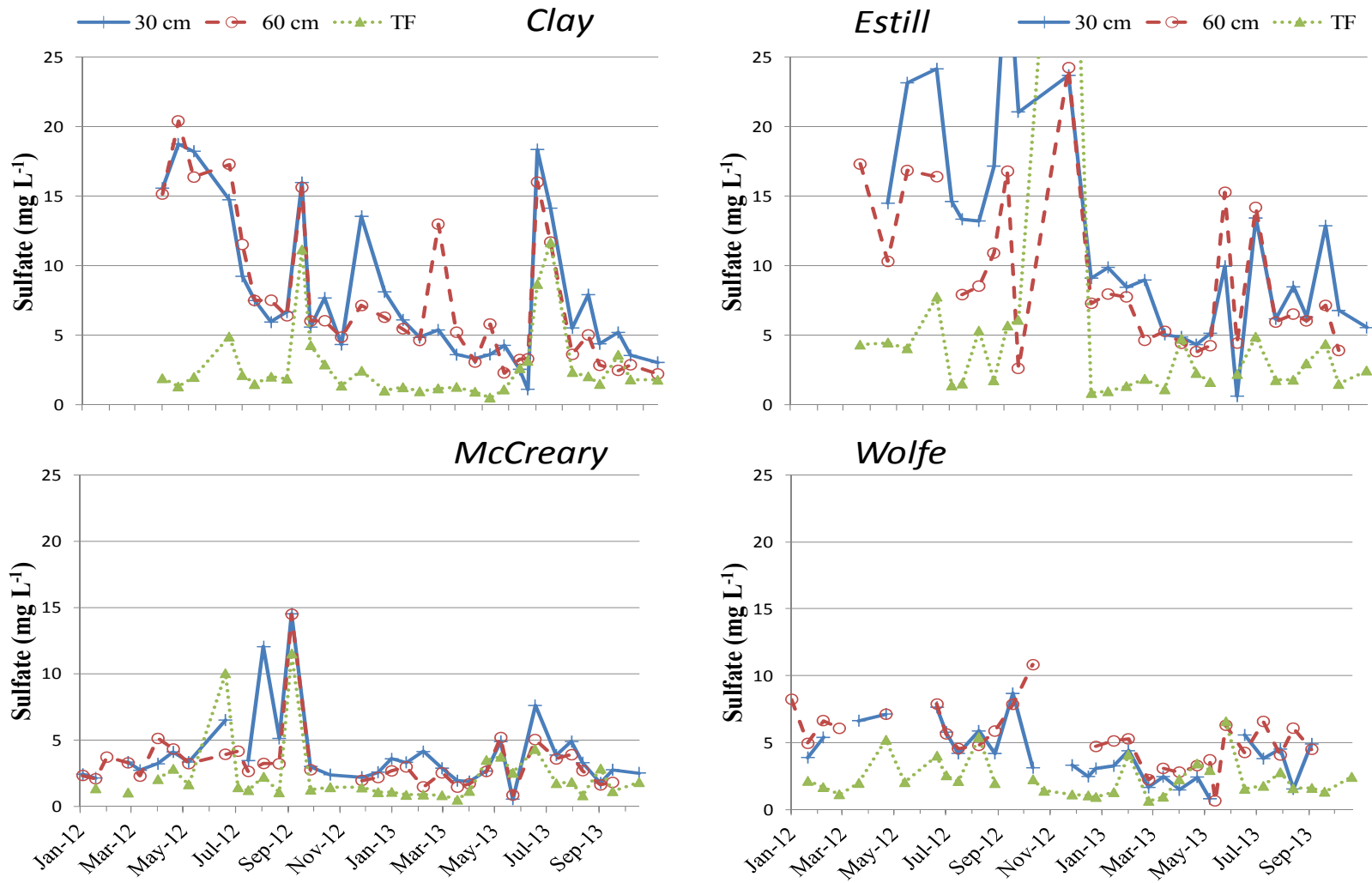


Figure 1.9: Throughfall (TF) and soil solution  $\text{SO}_4^{2-}$  concentration for samples collected at sites in pan lysimeters at 30-, and 60-cm depths.

Estill recorded the highest levels of  $\text{SO}_4^{2-}$ , with greatest concentrations during 2012. Estill 30-cm depth  $\text{SO}_4^{2-}$  concentrations were significantly higher than Clay County and might be explained by higher mean  $\text{SO}_4^{2-}$  concentrations found in throughfall samples. Mean  $\text{SO}_4^{2-}$  levels for Clay and Estill solution at both depths were significantly higher than in McCreary and Wolfe which were statistically similar to each other (Table 1.4). McCreary solution and throughfall samples revealed a trend that was expected for all sites.  $\text{SO}_4^{2-}$  concentrations were highest from late spring to early fall and peaks in solution matched peaks in throughfall concentrations. The summer of 2012 was much warmer and dryer than 2013. Temperatures, averaged over the whole year, were lower in 2013 compared with the warmest year in Kentucky on record, 2012 (NOAA), thus more power may have been generated to cool buildings in 2012. Trends from McCreary corresponded well to these expected increases in power production, this could be due to the site's close proximity (~16 km) to the Cooper Power Station in Burnside, KY, allowing for more direct seasonal changes to be observed.

Electrical conductivity (EC) is often used as an index for ionic strength which is the concentration of ionic charge in solution. Changes in ionic composition could bring about changes in communities and shifts in ecosystem function (Ziegler et al. 2012). Barton et al. (2002) revealed that  $\text{SO}_4^{2-}$  inputs at McCreary and Wolfe had a positive relationship with EC, while Kaiser and Kaupenjohann (1998) found increased ionic strength coinciding with decreasing release of  $\text{SO}_4^{2-}$ . Recent solution trends for each site show similarities between EC and  $\text{SO}_4^{2-}$  concentrations (Figures 1.9 and 1.10).

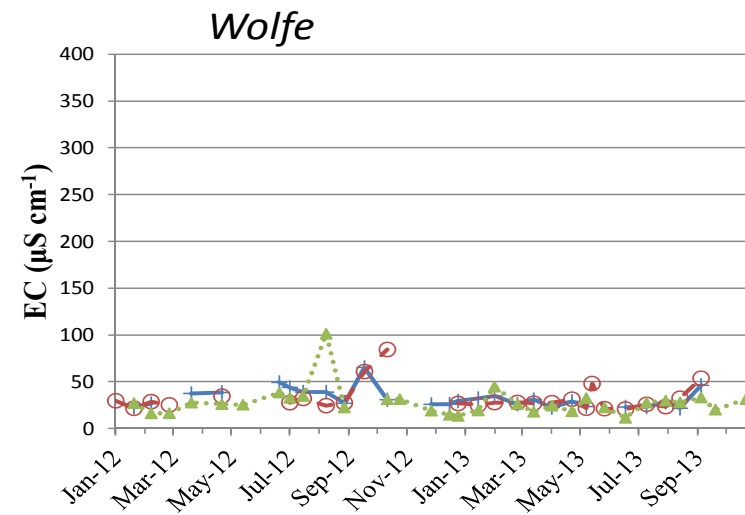
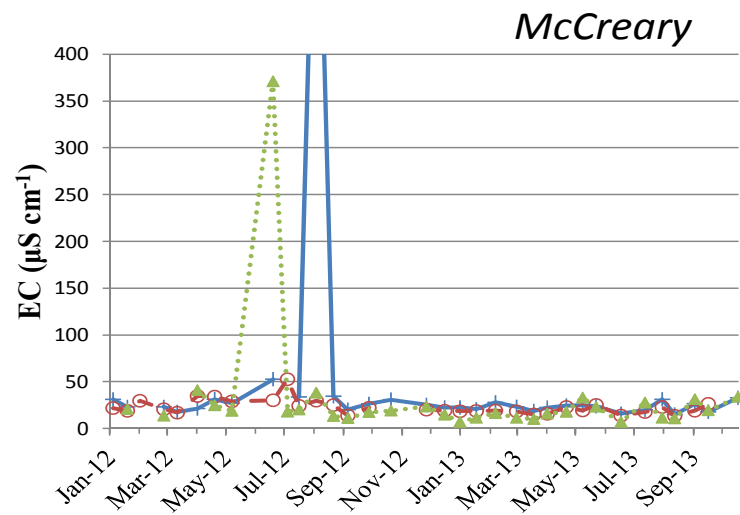
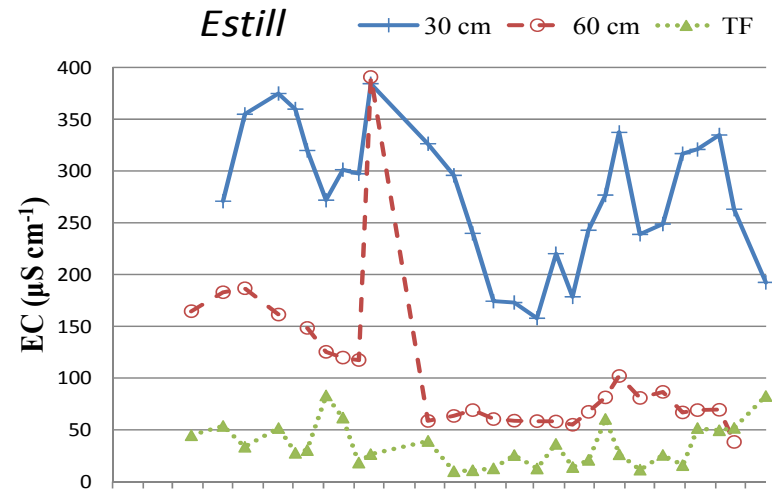
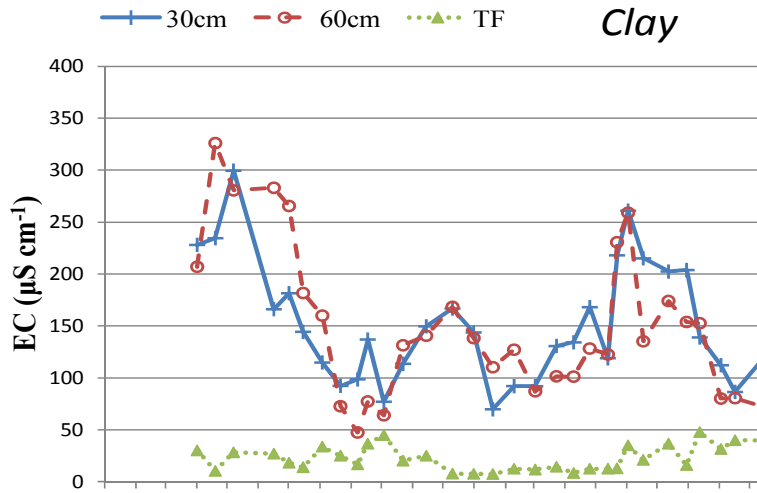


Figure 1.10: Throughfall (TF) and soil solution EC values for samples collected at sites in pan lysimeters at 30-, and 60-cm depths.

Both EC and  $\text{SO}_4^{2-}$  for both depths at each site exhibit a slight reducing trend with peaks throughout. Summer months recorded the largest, and the summer of 2012 recorded higher peaks than 2013. Early sampling at Clay and Estill revealed high initial values of both parameters which could either be from disturbance from installation or the fact that sampling began in the spring, delayed four months from McCreary and Wolfe. Mean EC levels during sampling show a clear difference in sites that is similar to mean concentrations of  $\text{SO}_4^{2-}$  (Table 1.4). Estill 30-cm solution yielded higher EC and  $\text{SO}_4^{2-}$  than Clay County. At the 60-cm depth, Clay County EC was higher than Estill while  $\text{SO}_4^{2-}$  levels were similar.  $\text{SO}_4^{2-}$  and EC levels at Clay and Estill were statistically higher than McCreary and Wolfe at both depths. These similarities in EC and  $\text{SO}_4^{2-}$  levels, along with differences among sites provide evidence that  $\text{SO}_4^{2-}$  concentration is likely linked to ionic strength in soil solution.

EC and  $\text{SO}_4^{2-}$  levels may influence Al in soils by increasing solubility with increased ionic strength and concentration (Barton et al. 2002; Kaiser and Kaupenjohann 1998). Al is very important in acid affected ecosystems because it has been found to be toxic to both terrestrial and aquatic vegetation (Wolt 1994). Al might contribute to soil nutrient imbalances and decline in vegetative productivity by being directly toxic to roots or by inhibiting Ca and Mg uptake (Shortle and Smith 1988; Bondietti et al. 1990). Bailey et al. (2005) found decreases in pH and exchangeable Ca and Mg in soils in the Allegheny National Forest in Pennsylvania and increases in exchangeable Al was a result. They concluded that acid deposition was the main driver of these changes and may cause reductions in forest productivity. Table 1.4 shows Estill had very low soil solution mean concentrations of Al ( $<0.3 \text{ mg L}^{-1}$ ) at both the 30- and 60-cm depths. Average Al concentrations are high ( $1.0$  and  $1.1 \text{ mg L}^{-1}$ ) in Clay County at both the 30- and 60-cm depths, respectively, and high in the McCreary County 60-cm ( $1.1 \text{ mg L}^{-1}$ ) and moderate at 30-cm ( $0.48 \text{ mg L}^{-1}$ ). Mean concentration at the 60-cm depth in Wolfe was below  $0.3 \text{ mg L}^{-1}$ , but was relatively moderate ( $0.54 \text{ mg L}^{-1}$ ) at 30-cm. Wolfe was the only site to have lower solution concentrations of Al at 60-cm compared to 30-cm depth indicating an accumulation of soil Al, while Clay, Estill and McCreary appears to be leaching soil Al as solution moves through the column.



Acid ions available for exchange on soil colloids (EA) may explain some Al trends by site (Table 1.2 and 1.4). Solution Al and soil EA are both higher at 30-cm and lower at 60-cm at the Wolfe site. EA also matches McCreary moderate 30-cm and high 60-cm Al concentrations. Estill has the lowest EA and showed evidence of lower mean Al at both depths. Clay County average Al concentrations do not match EA trends as well as other sites. Clay County had the highest Al concentrations in solution, but relatively low or normal comparative EA. This may be due to more highly weathered soils from high precipitation and inputs. Greater amounts of kaolinite compared to 2:1 clay minerals in Clay County indicates that soils are probably more highly weathered than other sites. Kaolinite is more abundant in highly weathered, mature soils because it is stable mineral and less prone to weathering (Karathanasis 2006). Clay County soil pH is also lowest throughout the soil column, and the site was the wettest site throughout the study which could lead to more weathering and leaching.

There were very few spikes in solution Al concentrations that matched up with either spikes in  $\text{SO}_4^{2-}$  or spikes in  $\text{NO}_3^-$  at any of the observed sites (Figure 1.11).

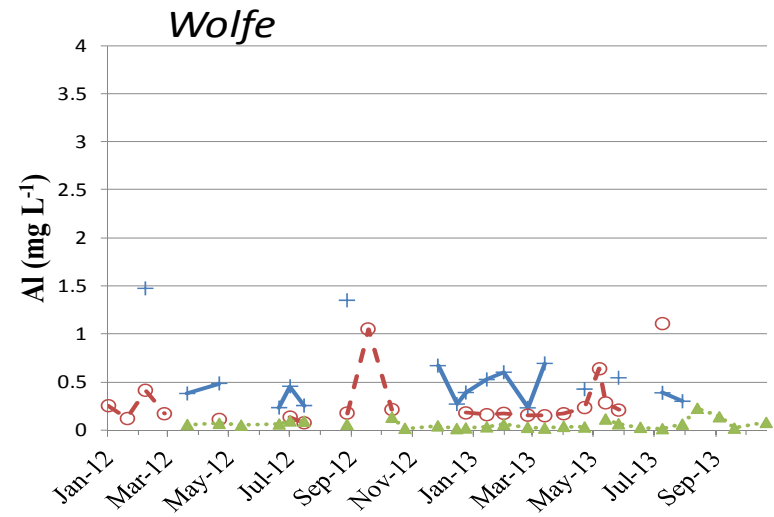
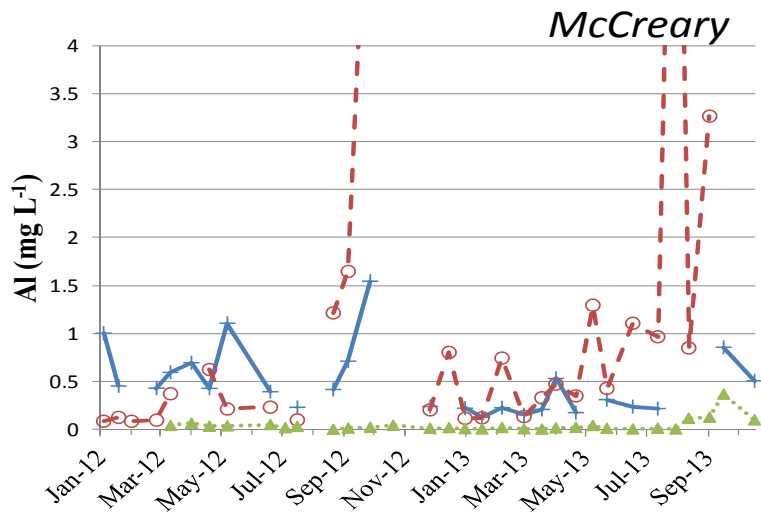
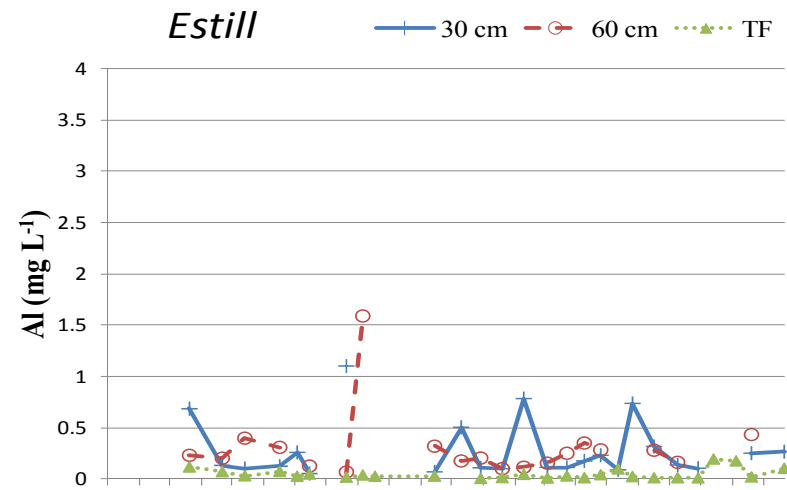
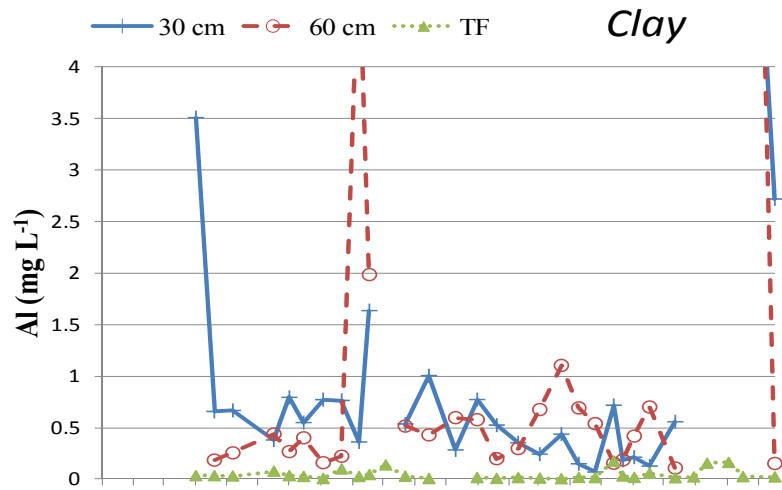


Figure 1.11: Throughfall (TF) and soil solution Al concentration for samples collected at sites in pan lysimeters at 30-, and 60-cm depths.

Clay County  $\text{NO}_3^-$  concentration had spikes in October of 2012 and 2013 which corresponded to Al peaks. A peak in  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  at Estill in September and October, 2012 matches a slight increase in Al concentration during the same time. There are no evident peaks of  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  matching peaks in Al at either the McCreary or Wolfe County sites. There was not enough contrast in Al levels at Wolfe to determine peaks or any trends. Water samples from August 2012 to January 2013 were not large enough in quantity to allow for all analyses to be completed.

Important base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) and exchangeable acid ions ( $\text{H}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Cl}^-$ ) make up the total CEC of a soil. Soils with higher CEC, especially exhibiting high TEB and low EA, will yield higher buffering capacity and resist changes that can occur with increasing acid inputs; slowing the acidification of soils and mobility of Al into solution. This trend is evident when observing soil and soil solution chemistry among the four research sites. Both Wolfe and McCreary had fewer TEB, but higher EA than Clay and Estill. Much more calcium was found in the leachate of Clay and Estill (Figure 1.12) but less of a drop in pH of solution was seen as well.

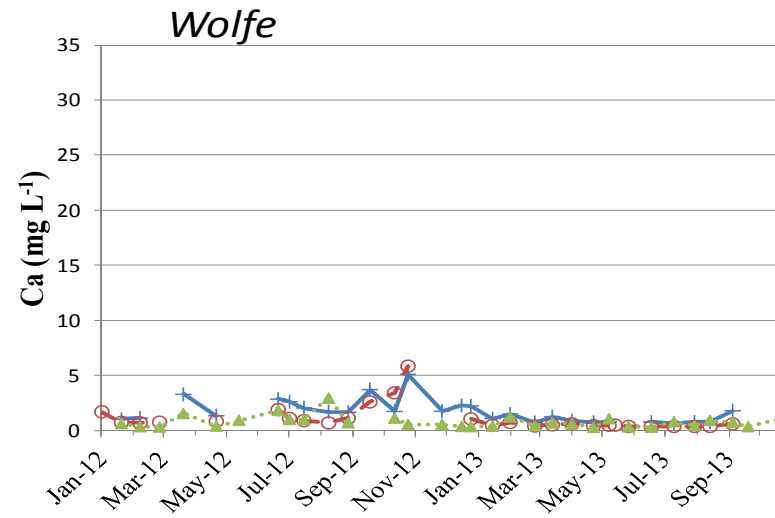
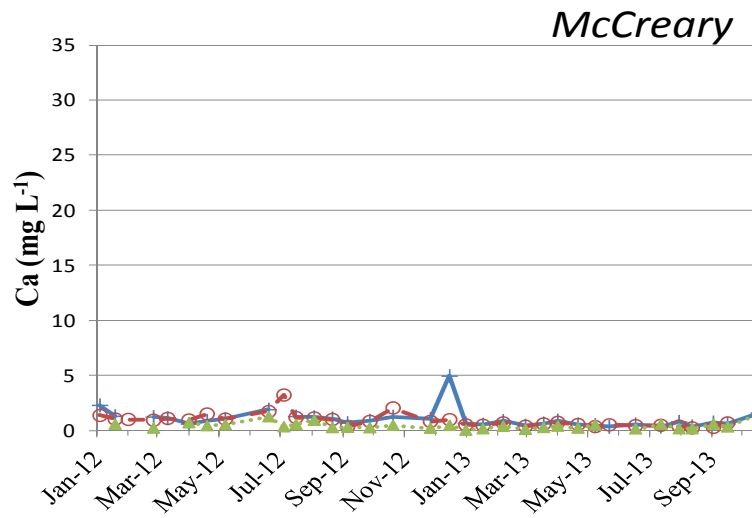
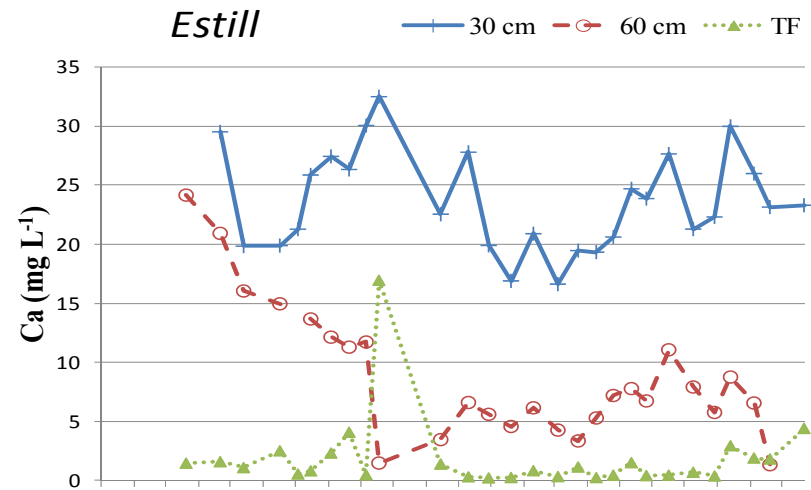
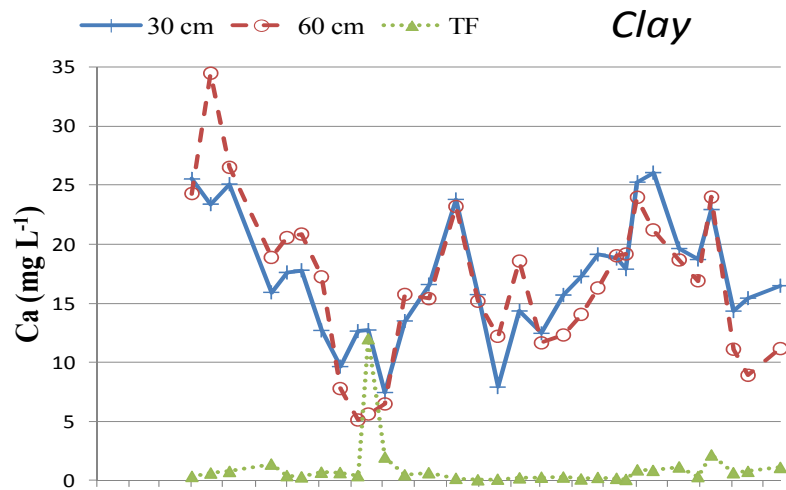


Figure 1.12: Throughfall (TF) and soil solution Ca concentration for samples collected at sites in pan lysimeters at 30-, and 60-cm depths.

This suggests that the high TEB, namely calcium, in the clay fraction of Clay and Estill soils remains a buffer for pH of solution. However, calcium exchanged and lost in solution, potentially due to acid inputs and replacement on exchange sites, will continue to be lost with further acid inputs. Fenn et al. (2006) discuss similar results from North America, explaining that soil acidification increased the rate of weathering, but Ca release was likely to be small in already acidic soils. This supports the possibilities that continued weathering could deplete base cations further and increase Al solubility. Al concentrations in leachate were lower in Estill as a result of its soils' buffering capacity. The soil appeared to lose more base cations, especially calcium, instead of solubilizing Al. However, Clay County has higher TEB and BS, allowing for potentially strong buffering, but soil pH, especially in the A horizon, was much lower than other sites, therefore more Al was observed in solution. Soils with mid-range pH (4.6-6.0) would be most sensitive to pH changes. Soils with lower pH will be buffered by high levels of Al, and soils with higher pH will be buffered by high base saturation (Wilkländer 1980b). All soils were at or below the mid- to low-range boundary, but Clay County soils were well below pH 4.6 and greater amounts of Al was observed.

Evaluation of data from three NADP sampling stations (KY 03, 22 and 35) supports evidence of depositional differences across space within central and eastern Kentucky. Averages of the three monitoring sites from 2012 indicate this variability with  $\text{NO}_3^-$  equaling 0.75, 0.80 and 1.0  $\text{mg L}^{-1}$  at KY 03, 22 and 35, respectively.  $\text{SO}_4^{2-}$  concentrations in rainfall equaled 0.73, 0.76 and 1.2  $\text{mg L}^{-1}$  at KY 03, 22 and 35, respectively. pH average measurements were not very different between sites during 2012, but the slight variability of most parameters indicate location as a potential factor. Variability could be due to many factors, but distance from and direction to major urban areas and power plants could be one of the major drivers. NADP sites during the study sampling period did not reveal any trends in concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and pH. Study sites did however reveal an acidifying trend over time in both throughfall and soil solution samples. This could be an indication of tree canopy interactions, including dry deposition in canopies, as a factor influencing the chemistry of water reaching forest soils.

Soil solution and throughfall chemistry is highly erratic and has proven to be influenced by a multitude of variables. Variations in soil properties and throughfall quality are site specific, and co-linearity of variables created difficulty comparing between research sites. However, Tukey's T-test comparing means between sites concluded that variation in soil solution pH is explained 40% by site alone.

**Conclusion:**

The four sites studied in the DBNF exhibited significant variation in soil and solution chemistry. Soil solution data taken at various depths in Gilpin and Rayne soils suggested that there were sporadic periods of high acid anion inputs into these systems. As a result, the input of acidity from anthropogenic acid deposition may be accelerating the weathering and depletion of base cations within these systems. Even though soils were classified as the same or similar soil series', differences in sites' soil and solution chemistry suggest different degrees of weathering across the DBNF. Evidence that McCreary and Wolfe are further depleted of BS supports the conclusion that the forest is experiencing different rates of weathering. McCreary and Wolfe soils may be so far depleted of base cations, that they possess inherently weak pH buffering capacity. Clay and Estill soils may have not yet reached the level of BS depletion at which buffering capacity is limited. Therefore, to assess the effects of acid deposition on soil buffering capacity and weathering continued monitoring of soil and soil solution in the DBNF is important. Further analysis is necessary to develop a clear understanding of the future health of these forest soils and suggestions for resource management.

## CHAPTER TWO

Long-term evaluation of acidic atmospheric deposition on soils and ridge-top stands in the Daniel Boone National Forest.

### **Introduction:**

Ecosystem impacts from the deposition of acidic precipitation are an issue of global concern. Initially, impacts from acid rain were observed in locations downwind from major industrialized areas containing soils with limited buffering capacity (Oden 1968; Ulrich 1989). Today, the effects of acid rain are widespread and not just considered a localized issue. Acidified waterways (Schindler 1980; Schofield 1980; Reuss and Johnson 1985; Driscoll et al. 2001; Sullivan et al. 2004), impacted soils (Johnson et al. 1986, Nilsson 1986; Tamm and Hallbacken 1986; Binkley et al. 1989) and decline of growth and/or survival of tree species (Joslin et al. 1992; Nellemann and Thomsen 2001; Nellemann and Esser 1998; Duchesne et al. 2002) from acid rain have been documented around the globe. Even in healthy forest stands with soils that exhibit moderate buffering capacity continued acid inputs could tip the balance and long-term forest productivity declines may occur (Huntington 1996; Barton et al. 2002).

The Clean Air Act (CAA) was enacted in 1970 and administered by the United States Environmental Protection Agency. Revisions to the CAA were made in 1990 to provide further control on emissions of pollutants known to cause acid rain (CAA 1990). The initial phase of the provisions started in 1995, placing limits on major coal-fired power plants in the U.S. In 2000, emission caps were set for smaller power plants. Between 1990 and 2009, coal-fired power plants in Kentucky have increased electricity generation by almost 20,000 Gigawatt hours. However, during the same period the electric power sector of Kentucky has reduced sulfur dioxide (SO<sub>2</sub>) and nitrogen oxide (NO<sub>x</sub>) emissions by 72 and 75 percent respectively (KY Energy Profile 2011). Mining of low sulfur coal and installation of emission controlling technology, such as scrubbers, has proven to reduce emissions of SO<sub>2</sub> and NO<sub>x</sub> even with increases in power plant production. Emissions reductions following implementation of the CAA are also reflected in the chemistry of precipitation collected in Kentucky. Precipitation

concentrations of nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) have decreased and pH has increased since the 1980s (NADP 2013), so it is likely that there would be a response at the forest stand level.

Monitoring soil solution chemistry is one method for evaluating the impact of acid deposition on forest ecosystem dynamics. Soil solution is the medium within which many important soil reactions occur, and information gathered is critical for understanding the chemical processes controlling element cycling, nutrient uptake and availability, mineral transformation, and pollution transport processes within the subsurface environment (Harter and Naidu 2001). Acidic anion inputs of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  have the potential to deplete soil base cation pools, increase weathering of soil minerals, mobilize soil aluminum (Al) and hinder vegetative productivity (Reuss 1983). Prolonged base cation depletion reduces a soil's ability to buffer against pH changes and can form Al-saturated soils (Reuss and Johnson 1986). Over time, soils may be impacted by even small concentrations of acid anions entering the system. As such, reductions in anthropogenic emissions and improved precipitation chemistry may not be reflected in soil solution chemistry. Malek et al. (2005) noted that the depletion of soil base cations can delay ecosystem recovery from acidification; however, many forces in soil can reduce the final effect of acid precipitation. Johnson et al. (1982) found that acid substances are neutralized by basic substances which can come from leaching of living plant tissue and soils, and can be found in precipitation. Unfortunately, base cation inputs in the eastern US from natural weathering, acid deposition, and leaching from living plant tissue are currently insufficient to outweigh losses from anthropogenically-induced soil exchange processes (Johnson et al. 1988; Knoepp and Swank 1994).

A soil's ability to adsorb or retain  $\text{SO}_4^{2-}$  complicates an assessment of the impacts from reduced emissions and acid deposition.  $\text{SO}_4^{2-}$  can be adsorbed to clay minerals or incorporated into the formation of Al-hydroxy-sulfates or amorphous Al and iron (Fe) hydroxides (Johnson 1984). The result of sorption is displacement of  $-\text{OH}$  and/or  $-\text{OH}_2^+$  from clay minerals, which creates an overall negative charge and a cation exchange site provided by the sulfate ion (Rajan 1978; Parfitt and Smart 1978). Sulfate retention is difficult to measure, but large amounts of sulfate have been found in acid impacted soils (Alewell 2001; Cai et al. 2010). As sulfur emissions and the related deposition decreases,



adsorbed sulfate will slowly shift to solution, consuming  $\text{-OH}$  and providing  $\text{H}^+$  to solution. Generally, the process of desorption is slow and gradual (Parfitt and Smart 1978), causing lag time or delayed response to reduced atmospheric acidity.

Aluminum (Al) is important to observe when addressing effects of acid deposition on soils because of its increasing solubility and mobility in soil with increased acidity in precipitation (Norton 1976; Johnson N.M. et al. 1981; Nordstrom 1982). In its available form, Al is toxic to most plant species because it reduces root growth and development and interferes with nutrient uptake (Foy et al. 1978). Al is the third most abundant element found in the Earth's crust and the clay fraction of soil is made up of a variety of aluminosilicate, oxyhydroxide, and nonsilicate minerals containing Al (Barnhisel and Bertsch 1982). Aluminum solubility is usually controlled by dissolution-precipitation of soil mineral phases in well-drained soil with prolonged contact between water and the soil mineral phase (Barton et al. 2002). It is often proposed that the solubility of crystalline forms of gibbsite  $[\text{Al}(\text{OH})_3]$  or kaolinite  $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$  control the  $\text{Al}^{3+}$  concentration in soil solution (Jones et al. 1974; Barnes 1975), but a watershed level study in the Adirondack mountains indicated that soil solution  $\text{Al}^{3+}$  levels are higher than expected based on the abundance and solubility of these minerals for this to be the case (David and Driscoll 1984). Roberson and Hem (1969) suggested that Al can form soluble complexes with hydroxide, fluoride, and sulfate, which could lead to more  $\text{Al}^{3+}$  in solution. Nordstrom (1982) found evidence indicating sulfate-induced acidification creates a tendency for  $\text{SO}_4^{2-}$  and Al to be retained in soil as soluble Al-hydroxy-sulfate minerals. In this case, relatively insoluble gibbsite and kaolinite minerals become more soluble in conditions of  $\text{pH} < 4.5$  and form Al-hydroxy-sulfate compounds. Basaluminite  $[\text{Al}_4\text{SO}_4(\text{OH})_{10}]$ , alunite  $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$ , and jurbanite  $[\text{AlSO}_4\text{OH} \cdot 5\text{H}_2\text{O}]$  were recognized as Al-hydroxy-sulfate minerals that have stability in acidic soils and are able to act as both source and sink of Al in solution (Nordstrom 1982).

Tree productivity as it relates to air pollution (Ashby and Fritts 1972; Benoit et al. 1982; Fox et al. 1986) and acid rain (Johnson A.H. et al. 1981; Thomas et al. 2013) has been studied, but results are often questionable because other climatic and environmental factors may have a more pronounced effect on growth (Fritts 1976). It is especially difficult to relate productivity to pollution in locations that are not receiving large, direct

inputs of pollution into the ecosystem. However, the comparison of growth before and after the onset or offset of pollution, coupled with historical climate variables, is a promising strategy for the study of forest decline (Fritts and Swetnam 1989). For instance, Fox et al. (1986) studied pollution effects on ring-width chronologies and found that trees growing downwind from point pollution sources showed increases in ring-width after emission controls were installed.

Chemical concentrations in tree-rings may enhance our ability to explain impacts on forest productivity as affected by air pollution. Dendrochemistry measures concentrations of specific ions within growth rings to estimate a relationship between elemental availability, uptake, and forest productivity (Bondietti et al. 1989b). Dendrochemistry, as it relates to soil solution, has been examined (McClenahan et al. 1987; Guyette and McGinnes 1987; Bondietti et al. 1989a, b; Guyette and Cutter 1994) and may offer additional techniques for examining acid deposition effects. McLaughlin et al. (1987) stated that fluctuation in soil solution chemistry may be a factor in growth trends of red spruce (*Picea rubens*) in the Great Smoky Mountains National Park. Research on eastern red cedar (*Juniperus virginiana*) trees in West Virginia (Thomas et al. 2013) found that basal area increment (BAI) has increased significantly since the enactment of the CAA and increases in atmospheric CO<sub>2</sub> and NO<sub>x</sub> emissions along with decreases in SO<sub>2</sub> emissions explain the growth trends best. Hence, soils, soil solution chemistry and historical weather data may be useful in comparing tree-ring growth and chemistry as an environmental indicator.

Barton et al. (2002) examined soil solution from two ridge-top locations in the Daniel Boone National Forest (DBNF), Kentucky between 1994 and 1999. Suction (tension) and gravity (pan) lysimeters were used to collect naturally infiltrated water from various depths. This research determined that a major effect sensitive soils experience from acid deposition is a shift in mineral solubility phase sequences, which control Al activity in soil solution. Study sites appear to favor transfers of Al solubility control from gibbsite or kaolinite to the Al-hydroxy-sulfate minerals jurbanite and/or alunite. They also found that anthropogenic acid inputs may accelerate the depletion of base cations in soil. Since this study was conducted, no direct effects of acid deposition on soil and vegetation have been observed in the DBNF, and more detailed analysis of soil and soil

solution is needed to evaluate changes over time. Therefore, this study was designed with the following objectives: 1) to re-examine the sites between 2012 and 2013 to 2) investigate long-term changes that may have taken place during the last 15-20 years; 3) to explore soil physicochemical and mineralogical alterations coupled with soil solution ionic concentrations as indicators of changes accelerated by continued acidic inputs; finally, 4) to examine the impact these changes have had on forest productivity in the DBNF through tree-ring growth and ionic concentrations.

### **Materials and Methods:**

#### *Site Descriptions and Sampling Design:*

The two research sites are located in McCreary and Wolfe Counties, KY. Both sites are within the Daniel Boone National Forest (DBNF) and represent the Stearns and Cumberland Ranger Districts, respectively. There are two time periods of data collection in this study. The initial study was conducted from 1994 to 1999 (P1) and a twenty-two month reevaluation period (P2) was finished in November, 2013. Both McCreary and Wolfe sites were located on ridge-top positions within mixed pine-hardwood stands in the Cumberland Plateau physiographic section. The McCreary site is located in the Beaver Creek Wildlife Management Area within a two-aged stand dominated by Virginia pine (*Pinus virginiana*), red maple (*Acer rubra*) and scarlet oak (*Quercus coccinea*). The Wolfe site is located in the Red River Gorge Geological Area within an uneven-aged stand dominated by Virginia and shortleaf pine (*Pinus virginiana and echinata*), red maple (*Acer rubra*), and scarlet and chestnut oak (*Quercus coccinea and prinus*). Small prescribed burns occurred near both sites in the 1980s and 1990s and both sites have suffered damage from southern pine beetle (*Dendroctonus frontalis* Zimmermann) infestation beginning in the early 1990s.

Thirteen years spanned between sampling periods, and the original lysimeters used during P1 were no longer functioning. Soil pits were dug within the same two ridges as previously investigated to keep the spatial location and forest and soil qualities similar. However, excavation was offset from the original locations to avoid sampling backfill from the original pits. At each site a pit was excavated with approximate dimensions of 1.5x1.2x1.0 meters. Soil profile descriptions were conducted by the same personnel who characterized the soils in 1994 following procedures of the Natural

Resource Conservation Service (NRCS 1996). Soils were sampled by horizon from each pit and returned to the laboratory for analysis. Both sites were sub-xeric and contained deep, well drained, and moderately permeable soils. In 1994, the McCreary soil was classified as Wernock silt loam (fine, silty, mixed mesic Typic Hapludults), while the 2012-soil was re-classified as Gilpin silt loam (fine-loamy, mixed, active, mesic Typic Hapludult). The Wolfe soil, from both sampling periods, was characterized as Rayne silt loam (fine-loamy, mixed, active, mesic typic Hapludult).

Four zero-tension (pan) lysimeters were installed, two at 30- and two at 60-cm depths at each site. Four cavities were created in the sidewalls of the pit (2 in one side and 2 in the opposing side) to insert 32x28x5 centimeter pans. The cavities were created in the sidewall so as not to disturb the soil above the desired depth, allowing for the column of soil above the pans to be undisturbed and natural. A male hose fitting was screwed into a threaded nut that was welded into the bottom of the pan and window screen material was placed over the pan drain before being filled with pea gravel. A 9.5-mm-diameter polyethylene hose was attached to each pan and extended into 18.8-L, polyethylene carboys placed at the bottom of the soil pit. Geofabric material was placed over each cavity and stapled into the sidewall to limit the entrance of disturbed soil. Each carboy was altered to fit 5-cm-diameter PVC pipe from the bottom of the inside of the carboy, out the top and extended at least 50-cm above the forest floor. A notch was cut in the bottom of the PVC to allow water collected in the carboy to enter the pipe permitting the solution to be sampled. The contact around the exit hole in the carboy and extending PVC was sealed using plumbing contact adhesive creating a complete seal so solution entering the carboy came only from the hose of the pan lysimeter. PVC caps were placed over the pipes and the pit was carefully backfilled with soil.

Soil water sampled during P1 was conducted approximately quarterly using a diaphragm hand pump to evacuate water. Water was collected bi-weekly during P2. The first 6 months of P2 was sampled using a diaphragm hand pump. During the growing season, sample volume in the carboys was too small to evacuate with a large hose (2.5-cm diameter) so an SKC Aircheck Sampler (SKC Inc., Eighty Four, PA) with a 8-mm diameter tube was used. Once evacuated, samples were placed in polyethylene bottles, packed in ice and transported to laboratory refrigerators where they remained until

analyzed. Excess lysimeter solution was discarded downslope. Precipitation quantity was measured on-site using Tru-Check® (Edwards Manufacturing Co., Albert Lea, MN) rain gauges. Throughfall was collected below the canopy at both sites using a funnel attached to a 1-L polyethylene bottle. Glass wool was placed in the funnel to prevent debris and insects from entering the container. Long-term meteoric data was acquired from the National Atmospheric Deposition Program (NADP) which has three weather sampling stations near the research sites; KY 03 in Mackville, KY 22 at Lilley Cornett Woods, and KY 35 at Clark State Fish Hatchery (Figure 1.2).

All three sites have deposition chemistry data conforming to protocols of the National Acid Precipitation Assessment Program (NAPAP) for the period 1984 to present. NADP rainfall chemistry data was used as a timeline of historic deposition and compared to soil and soil solution data from P1 and P2 study sites. Average annual precipitation chemistry (pH, EC, NO<sub>3</sub>, and SO<sub>4</sub>) from NADP sites were compared to Kentucky emissions trends to exemplify possible impacts and changes brought by the CAA from 1984 to present. Precipitation data was also averaged for the separate timeframes of P1 and P2 to recognize differences in precipitation quality between periods. Data from NADP and on-site throughfall precipitation during P2 was compared to evaluate differences between open-air and closed-canopy precipitation reaching the soil surface.

#### *Soil Characterization and Solution Analysis:*

Physicochemical properties of soils collected from each site were analyzed similarly for both study periods. Soil samples from each site and period were taken by horizon, bagged separately and taken to the University of Kentucky for laboratory analyses. Soil was oven-dried at 38°C and ground to pass a 2-mm screen. Both periods analyzed extractable bases (TEB) and cation exchange capacity (CEC) using the 1 M ammonium acetate (NH<sub>4</sub>Oac), pH 7.0 (Buchner funnel) (5B1) (5A1b) methods, respectively (NRCS 1996). P1 analysis of calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) was performed by atomic adsorption spectroscopy using an Instrumentation Laboratory model S11 AA/AE spectrophotometer. P2 measured exchangeable Ca, Mg, Na, and K (TEB) via inductively coupled plasma (ICP). Base saturation (BS) was determined as  $TEB/CEC * 100$  (SPAC 2000). Ammonium (NH<sub>4</sub><sup>+</sup>)

was measured using a Technicon Auto-Analyzer II. Organic carbon (TOC) was determined using a Leco Carbon Analyzer (LECO Corp., St. Joseph, MI), Model CR-12. Organic matter (OM) was calculated as  $\%C \times 1.72 = OM$  (% of air dried soil) (Nelson and Sommers 1982). Particle size analysis was determined using the pipette method (NRCS 1996). Soil pH was measured in a 1:1 soil-water suspension with an Orion pH meter. Extractable acidity (EA) was measured by titration, using the  $BaCl_2$ -triethanolamine method (NRCS 1996). P2 measured total Nitrogen using a LECO dry combustion instrument, where  $N_2$  gas emitted upon combustion (%N) was measured for total N. Mineralogical composition was determined similarly between periods. During P1 a Phillips PW 1840 diffractometer interfaced with a PW 1729 X-ray generator was used. The diffractometer was equipped with a cobalt X-ray tube, operated at 40 kV and 30 mA, and a Bragg-Bretano goniometer. A scanning rate of  $2^\circ$  per  $2\Theta$   $min^{-1}$  from  $2-60^\circ$  per  $2\Theta$  was used for Mg-saturated clay slides, and from  $2-30^\circ$  per  $2\Theta$  for all other slides. Mineralogical composition during P2 was performed using a PANalytical X' Pert Pro diffractometer equipped with a copper X-ray tube, operated at 45 kV and 40 mA, and a Bragg-Bretano goniometer. Scanning rates changed to  $2^\circ$  degrees per  $2\Theta$   $min^{-1}$  from  $2-40^\circ$  per  $2\Theta$  for Mg-saturated clay slides, and from  $2-20^\circ$  per  $2\Theta$  for all other clay slides. Powder (sand - silt) samples were ran from  $2-60^\circ$  per  $2\Theta$ .

Handling, storage and characterization procedures for soil solution samples during both periods followed methods outlined in the standard methods for examination of water and wastewater (APHA 1989). P1 solution samples were filtered through  $0.2\text{-}\mu\text{m}$  filters, P2 samples were filtered through a  $1.0\text{-}\mu\text{m}$  filter, and all samples were refrigerated until analysis. Base cations (Ca, Mg, K and Na) were measured using a GBC atomic absorption spectrophotometer (GBC Scientific Equipment, Braeside Australia). Total organic carbon was measured using a Shimadzu (Shimadzu Corp., Kyoto, Japan) TOC analyzer. During P1,  $NO_3^-$  was measured by ion chromatography using a Technicon Auto-Analyzer II, and  $SO_4^{2-}$  was determined turbidimetrically using the barium chloride method. P2 measured  $NO_3^-$  and  $NH_4^+$  colorimetrically with a Bran +/- Luebbe autoanalyzer, and measured  $SO_4^{2-}$  and chloride (Cl) using a Dionix ion chromatograph (Thermo Scientific, Sunnyvale, CA). Electrical conductivity (EC) was measured with a YSI conductivity bridge (YSI Inc., Yellow Springs, OH). An Orion pH meter (Thermo

Scientific, Sunnyvale, CA) was used to measure solution pH, and alkalinity was measured colorimetrically by titration using the methyl orange method (APHA 1989). Al was determined colorimetrically by the eriochrome cyanine-R method and measured with a Bio-Tek Instruments spectrophotometer microplate autoreader during P1. Aluminum was analyzed during P2 with a Varian Vista Pro inductively coupled plasma optical emission spectrometry (ICP-OES). Samples were ionized with inductively coupled plasma and Al was separated and quantified calibrated with certified reference material. ICP-OES results reported multiple wavelengths for each parameter. The most fitting wavelength results were determined with QA/QC guideline calculations based on method blanks, duplicate samples for precision, and matrix spike samples and laboratory control sample curves (LCS) for accuracy of readings. Data was reduced to one wavelength for each parameter and one value ( $\text{mg L}^{-1}$ ) was reported for individual samples. Geochemical modeling of P1 aqueous-phase chemical equilibria was performed with the MINTEQA2 computer program (Allison et al. 1990) and P2 results were superimposed in the model.

#### *Tree-ring Analysis:*

Two separate methods were used for the analysis of tree rings. The first, whole-tree method, involved cutting two trees at both McCreary and Wolfe sampling sites. One Virginia pine (*Pinus virginiana*) and one scarlet oak (*Quercus coccinea*) were chosen because they were well represented at each site. The second, increment corer method, compiled tree rings from core samples of nineteen Virginia pines found on the ridgetops near the lysimeters. Virginia pine was chosen because conifers tend to exhibit greater potential for reconstructing chronologies of elemental uptake and storage over hardwoods (Legge et al. 1984).

#### Method 1: Whole-tree

Trees were selected that met project objectives with regards to age and species and were deemed to inflict minimal ecological damage by their felling. No trees were selected that could impact potential bat roost trees or snags during felling. Once the trees were felled, three 8-cm thick cross sections (cookies) were cut from breast height (~4.5-ft/1.4-m). The cookies were taken to the University of Kentucky Department of Forestry where they were dried in an oven at 56°C for approximately two weeks.

Once dried, one cookie from each tree was sanded with a series of increasing grit sand paper up to 1000 grit extra-fine paper to make rings and ring boundaries more visible. Samples were then evaluated on a Velmex TA UniSlide tree ring dissecting microscope system, which measured radial growth of each year and calculated the age of the tree. Radial growth was measured for opposite sides of the tree from the two side-slope portions and averages between the two measurements for each year of growth were calculated. Upslope and downslope sides of trees tend to have tension and compression wood causing wider ring widths to one side and narrower widths on the opposing side. Conifers produce compression wood with wider rings on the tilt, or downslope, side of the tree, while tension wood with narrow rings are formed on the side opposite the tilt (Fritts and Swetnam 1989).

The remaining oven-dried cookies were used for elemental analysis. Sections of the cookies from the same two sides that radial measurements were taken were portioned using a stainless steel wedge. Each portion was separated under microscope into three year increments starting from the bark (2013) and working toward the pith. The 3-yr increments were ground to a pulp using a Wiley mill equipped with a 20- $\mu$ m screen and placed in scintillation vials prior to digestion.

#### Method 2: Increment corer

Four 5-mm cores were taken using an increment borer from each of nineteen dominant and co-dominant Virginia pine trees located within 100-m of the P2 lysimeters. Cores were taken from the upslope, downslope and both sides perpendicular to the slope of the ridge each 90° apart from the next. Cores were transported to the laboratory where three from each tree were oven dried at 90°C for 3 days. The fourth core from each tree was mounted on blocks with wood glue and sanded with increasing grit sandpaper up to 1000 grit and measured on the tree ring dissecting microscope system, measuring radial growth of each year and calculating the age of the tree. It was important to choose one of the two cores taken perpendicular to the slope for radial growth measurements because those were the cores with minimal influence from tension and compression wood growth patterns.

The dendrochronology program library in R (dplR) reads files of width measurements, detrends and converts them to a series of ring-width indices (RWI), and



builds standard chronologies based on differing tree age (Bunn 2008). The chron function in dplR builds a mean value chronology reflecting age and size differences. A smoothing spline approach takes into account dataset statistics and produces one chronology value, or RWI, for each growth year, which indicates within-tree and between-tree correlations. For the purpose of this research, the resultant RWI curve was used as a unitless standardized growth sequence. The result was one radial growth measurement for each year for each site.

Oven-dried cores were separated into 3-yr increments beginning with 2013 and working to the pith. Increments were separated under microscope with a stainless steel wedge and scalpel. Corresponding year increments from each core were combined with other cores from the same site and ground to pulp using a Wiley mill with a 20- $\mu\text{m}$  screen, creating a single sample for each three year period at each site. Samples were handled, ground, and analyzed using the same methods as the whole-tree samples.

#### *Digestion Methods:*

Three methods of digestion were used for elemental analysis. A Microwave Accelerated Reaction System (MARS 5) was used to digest whole-tree samples in nitric acid ( $\text{HNO}_3$ ). Approximately 0.3-g of wood dust sample was placed into a Teflon lined microwave vessel and 2-mL of ultra pure deionized water was added. Subsequently, 4-mL of concentrated, metals grade  $\text{HNO}_3$  and 4-mL of 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were mixed thoroughly with the solution. Vessels were loaded into a carousel and placed in the microwave. Microwave digestion procedures followed the EPA method for Plant Tissue Analysis (USEPA 1996). When the program run completed, samples were cooled and poured through a funnel with Whatman #40 filter paper into a 50-mL volumetric flask and brought to volume with ultrapure water. Samples were analyzed at the University of Kentucky Environmental Research Training Laboratory (ERTL) for Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, and Zn via a Varian Vista Pro ICP-OES calibrated with certified reference material.

A second digestion method was used for increment corer samples. This alternate method involved weighing 0.3-g of sample into 50-mL plastic digestion tubes, adding 8-mL of concentrated metals grade  $\text{HNO}_3$  to the tubes, and capping with diaphragm reflux caps to allow the release of vapors from the tube while inhibiting liquids from escaping.

Samples were heated on a thermal block at 95°C and swirled by hand approximately every hour for 5.5 hours, then removed and cooled to room temperature. Each sample was filtered using an Environmental Express Flipmate 50 suction filtration systems with 0.45-µm filters and analyzed by ICP-OES. All ICP-OES runs followed QA/QC guidelines and used method blanks, duplicate samples for precision, and matrix spike samples and laboratory control sample curves (LCS) for accuracy of readings.

A third digestion technique, block digestion, was used for analysis of total nitrogen in the sample. Approximately 0.5-g of sample material was added to a 75-mL volumetric test tube with stepwise additions of selenized (selenium coated) boiling chips, 7-mL of concentrated H<sub>2</sub>SO<sub>4</sub>, and 3-mL of 30% H<sub>2</sub>O<sub>2</sub>. Tubes were vortexed between the acid and H<sub>2</sub>O<sub>2</sub> additions, and again after addition of H<sub>2</sub>O<sub>2</sub> to mix thoroughly. Tubes were capped and placed on a thermal block for 1 hour at 375°C until solid sample was fully digested into solution. Samples were then analyzed at the University of Kentucky Department of Plant and Soil Sciences for total N using a colorimetric Nitrogen Auto-analyzer (AA) with a 5-cm flow-cell.

Differentiating heartwood from sapwood boundaries was determined by applying a 10% ferric chloride (FeCl<sub>2</sub>) solution to tree samples, producing a green color in the sapwood because of the presence of living cells and a brown/blue to black color in heartwood due to the lack of living cells (Kutscha and Sachs 1962).

Changes in leachate samples, element concentration in tree rings and variation between sites over time were evaluated using SAS 9.3 software for statistical analyses. Student's T-tests and Tukey's grouping were used to compare solution and throughfall data between sites and the two time periods. Means and standard deviations were determined for continuous variables. Univariate analysis was used to determine significant difference. Linear regression was used for the continuous variables.

## **Results and Discussion:**

### *Nearby Weather Station Precipitation*

Data from three nearby NADP weather stations was used to compare precipitation chemistry during the two sampling periods. Average annual precipitation trends from the NADP stations indicated changes in precipitation chemistry from 1984 to 2012 (Figure 2.1).

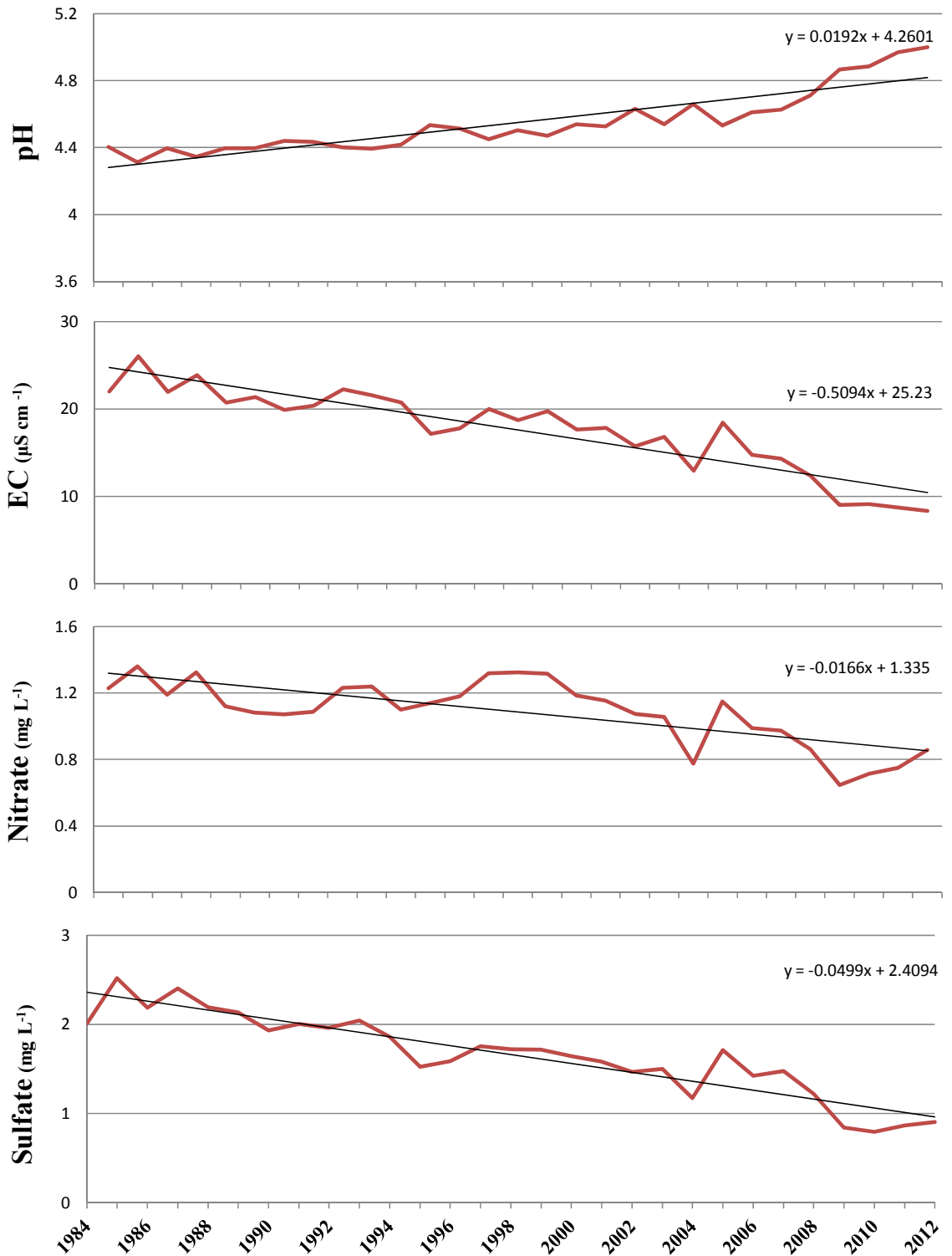


Figure 2.1: Average annual precipitation chemistry with regression lines for eastern Kentucky NADP sites KY 03, 22 and 35.

Annual precipitation pH increased from pH 4.4 in 1984 to pH 5.0 in 2012; a 14% increase. Average annual  $\text{NO}_3^-$  concentration decreased from  $1.23 \text{ mg L}^{-1}$  in 1984 to  $0.86 \text{ mg L}^{-1}$  in 2012; a 30% reduction. Swank and Vose (1997) reported an increase in N deposition from 1972 to 1994 at the Coweeta Hydrologic Laboratory in western North Carolina, while Knoepp et al. (2008) found no significant change in nitrate concentrations from 1995-2004 at the same location. Average annual  $\text{SO}_4^{2-}$  concentration decreased from  $2.0 \text{ mg L}^{-1}$  in 1984 to  $0.91 \text{ mg L}^{-1}$  in 2012; a 55% reduction. Likens et al. (2002) measured annual, volume weighted concentrations of  $\text{SO}_4^{2-}$  at the Hubbard Brook Experimental Forest in New Hampshire from 1964 to 1998 and determined a 50% decrease could largely be attributed to the positive correlation between sulfate in precipitation and emissions of  $\text{SO}_2$  (Likens et al 2005). EC levels have decreased from  $22 \text{ }\mu\text{S cm}^{-1}$  in 1984 to  $8.3 \text{ }\mu\text{S cm}^{-1}$  in 2012; a 62% decrease. Over the twenty-eight years of collection, the three NADP monitoring sites near the DBNF have exhibited changes reflecting the atmospheric reductions sought by the CAA.

Precipitation data from the combined NADP weather stations were averaged for our two sampling periods (Figure 2.2).

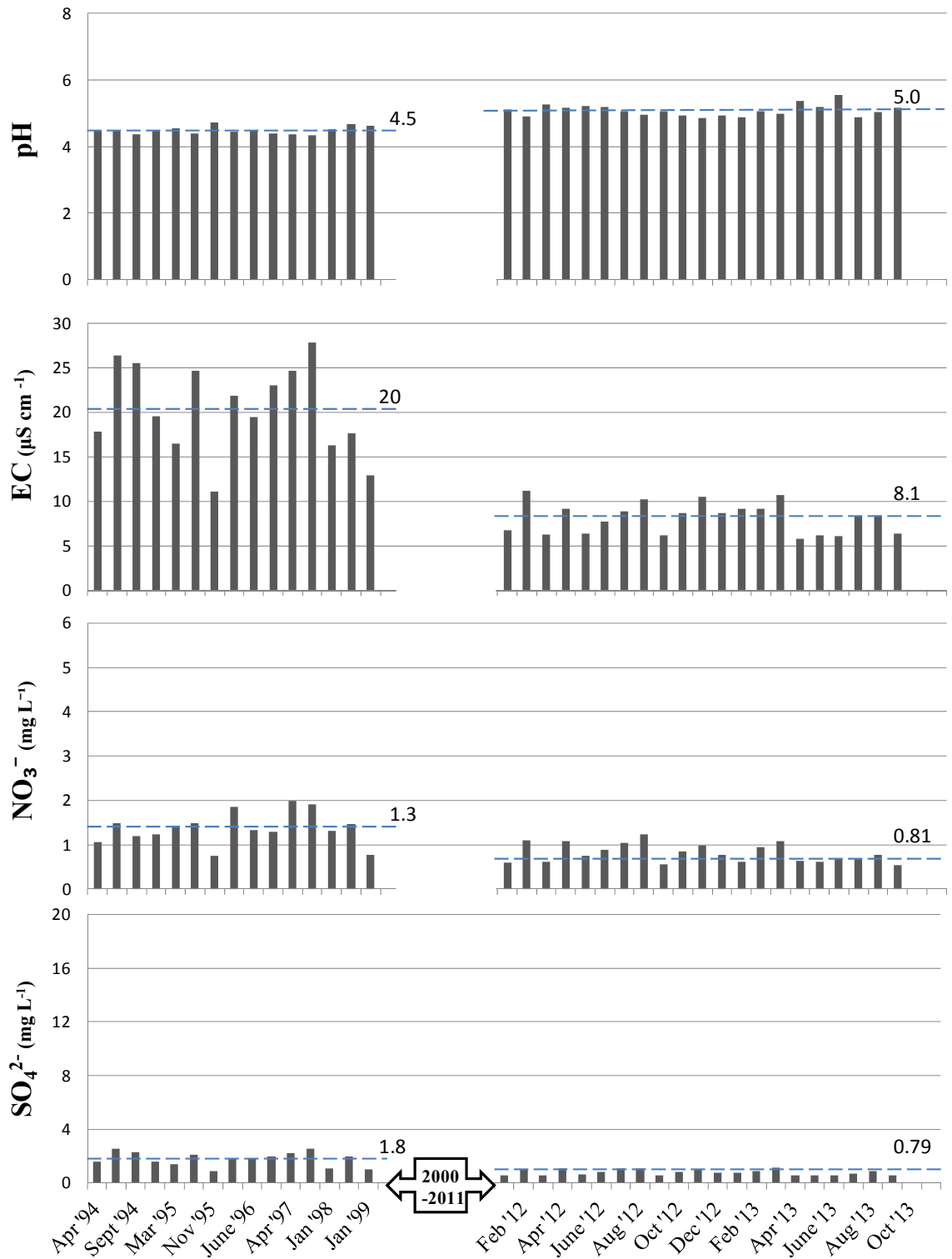


Figure 2.2: Average monthly precipitation chemistry and average P1 and P2 precipitation chemistry (dotted line) for eastern Kentucky NADP sites KY 03, 22 and 35. X-axis represents monthly averages for sampling event months within study periods and does not represent real time (P1=6 yrs.; P2=2 yrs.).

The NADP reported an average pH of precipitation during P1 to be 4.5 and P2 revealed an increase in average pH to 5.0; an increase of 12% between periods (or a 72% decrease in  $H^+$  concentration). NADP average annual  $NO_3^-$  and  $SO_4^{2-}$  concentrations were variable during sampling periods. P1 had an average  $NO_3^-$  concentration of  $1.3 \text{ mg L}^{-1}$  and decreased to  $0.81 \text{ mg L}^{-1}$  during P2; a 39% reduction.  $SO_4^{2-}$  average from P1 was  $1.8 \text{ mg L}^{-1}$  and dropped to  $0.79 \text{ mg L}^{-1}$  during P2; a 56% reduction. Average concentrations of  $NO_3^-$  and  $SO_4^{2-}$  from NADP weather stations match what was expected based on reductions in Kentucky electrical utilities emissions of both parameters. Reduced acid anion concentrations can partially explain the increase in precipitation pH between periods. Average EC in precipitation during P1 was  $20 \text{ } \mu\text{S cm}^{-1}$ . Conductivity decreased 60% in P2 to an average of  $8.1 \text{ } \mu\text{S cm}^{-1}$ .

*Throughfall Chemistry:*

Throughfall collectors in P2 provided an on-site record for local input chemistry of water entering the soil and were utilized to assess chemical differences between open-air and closed-canopy systems. The McCreary site had an average throughfall pH of 5.6 and the Wolfe site had an average pH of 5.4, which were higher than the average pH of 5.0 from the three regional NADP open air stations. It is possible that precipitation/canopy interactions increased pH in throughfall opposed to bulk precipitation due to ion fluxes from the canopy and by the buffering of  $H^+$  by cation exchange from inner leaf surfaces (Ulrich 1983; Mayer and Ulrich 1980). Oulehle and Hruška (2005) reported lower pH in bulk precipitation than in throughfall under beech forests. Throughfall collectors had average  $NO_3^-$  concentrations of 0.14 and  $0.34 \text{ mg L}^{-1}$  for the McCreary and Wolfe sites, respectively, which was lower than the average NADP  $NO_3^-$  concentration of  $0.81 \text{ mg L}^{-1}$ . Kristensen et al. (2004) stated that low levels of N deposition  $< 5 \text{ kg N ha}^{-1} \text{ y}^{-1}$  may directly assimilate precipitation N in the canopy thus decreasing throughfall N relative to bulk precipitation, while higher levels may rinse canopy collected dry deposition N or leach N from leaf surfaces and cause higher concentrations in throughfall. Average  $SO_4^{2-}$  concentrations for both McCreary and Wolfe was  $2.3 \text{ mg L}^{-1}$ , which is higher than the average of  $0.79 \text{ mg L}^{-1}$  measured at NADP sites. Singer et al. (1996) found that  $SO_4^{2-}$  concentrations were higher in throughfall and stemflow than in bulk precipitation because of the interaction between

wet and dry deposition within the forest canopy. They also noted that the highest  $\text{SO}_4^{2-}$  concentrations were measured in throughfall after a long dry period. Average EC was 31 and 28  $\mu\text{S cm}^{-1}$  for McCreary and Wolfe sites, respectively, while NADP sites averaged 8.1  $\mu\text{S cm}^{-1}$  during P2, which also suggests increased ionic strength from canopy surfaces and leaching of ions from leaves. There are evident differences in precipitation between the open-air stations of the NADP and our closed-canopy throughfall collectors. Results indicated that the forest canopy at our sites has some influence on precipitation chemistry before reaching the forest floor, therefore throughfall concentrations are considered to be more representative than bulk precipitation of soil solution chemistry.

*Soil Properties and Mineralogy:*

McCreary soil properties are given in Figure 2.3 and Table 2.1.

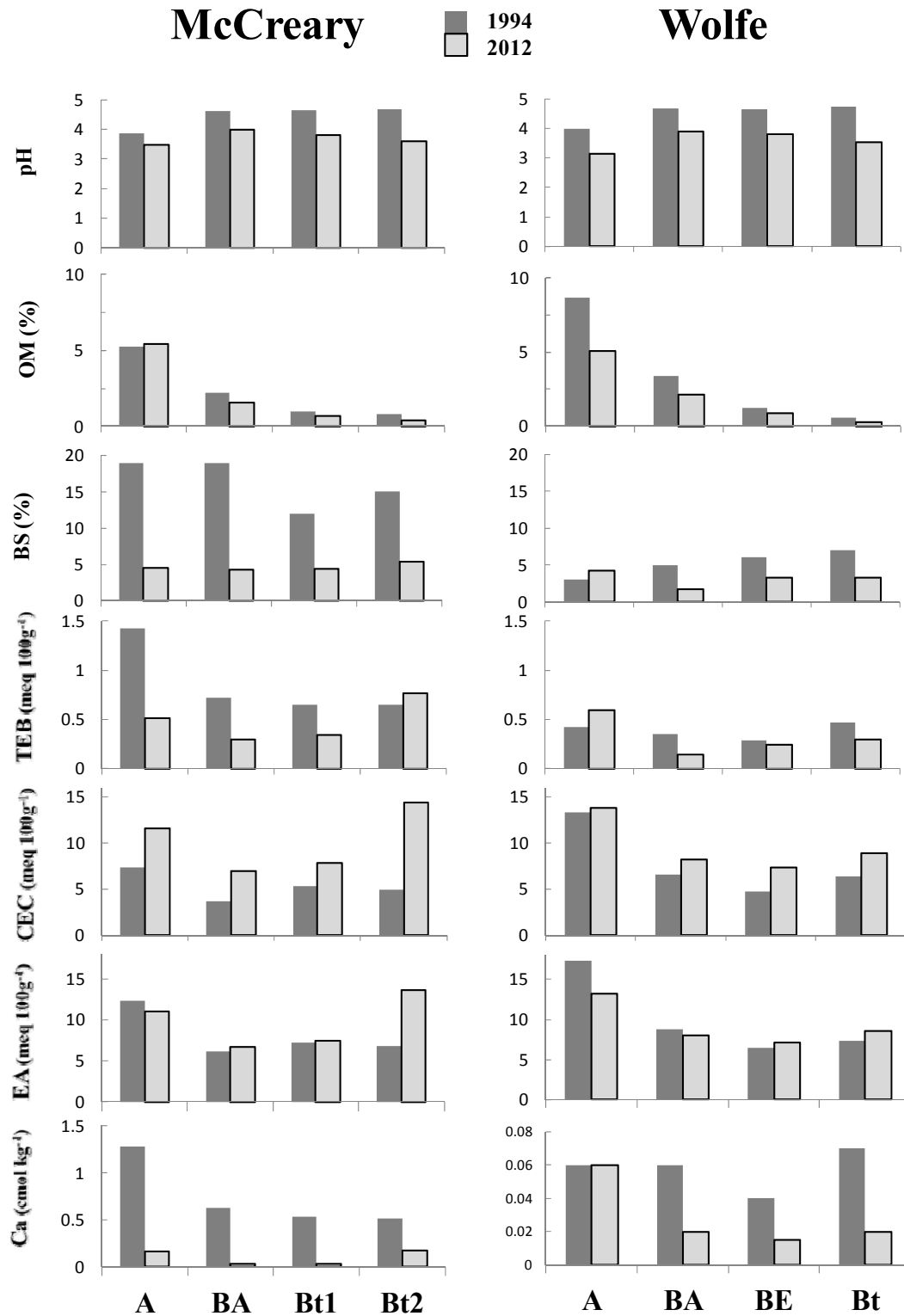


Figure 2.3: Physicochemical properties by pedon of the soils included in the study from P1 and P2.



Table 2.1: Physicochemical properties of the soils from sites included in P1 and P2 sampling.

| Site<br>Pedon   | pH   |      | Ca <sup>a</sup> |      | TEB <sup>b</sup> |      | CEC <sup>c</sup> |      | EA <sup>d</sup> |      | BS <sup>e</sup> |      | OM <sup>f</sup> |      |
|-----------------|------|------|-----------------|------|------------------|------|------------------|------|-----------------|------|-----------------|------|-----------------|------|
|                 | 1994 | 2012 | 1994            | 2012 | 1994             | 2012 | 1994             | 2012 | 1994            | 2012 | 1994            | 2012 | 1994            | 2012 |
| <b>McCreary</b> |      |      |                 |      |                  |      |                  |      |                 |      |                 |      |                 |      |
| A               | 3.9  | 3.5  | 1.3             | 0.16 | 1.4              | 0.51 | 7.4              | 12   | 12              | 11   | 19              | 4.5  | 5.3             | 5.4  |
| BA              | 4.6  | 4.0  | 0.63            | 0.03 | 0.72             | 0.30 | 3.7              | 7.0  | 6.2             | 6.7  | 19              | 4.3  | 2.2             | 1.6  |
| Bt1             | 4.7  | 3.8  | 0.53            | 0.03 | 0.65             | 0.34 | 5.4              | 7.9  | 7.2             | 7.5  | 12              | 4.3  | 0.99            | 0.71 |
| Bt2             | 4.7  | 3.6  | 0.51            | 0.17 | 0.65             | 0.77 | 4.9              | 14   | 6.8             | 14   | 15              | 5.4  | 0.81            | 0.41 |
| <b>Wolfe</b>    |      |      |                 |      |                  |      |                  |      |                 |      |                 |      |                 |      |
| A               | 4.0  | 3.2  | 0.06            | 0.06 | 0.42             | 0.59 | 13               | 14   | 17              | 13   | 3.0             | 4.3  | 8.7             | 5.1  |
| BA              | 4.7  | 3.9  | 0.06            | 0.02 | 0.35             | 0.14 | 6.6              | 8.2  | 8.8             | 8.0  | 5.0             | 1.8  | 3.4             | 2.2  |
| BE              | 4.7  | 3.8  | 0.04            | 0.02 | 0.29             | 0.25 | 4.7              | 7.4  | 6.5             | 7.2  | 6.0             | 3.3  | 1.3             | 0.91 |
| Bt              | 4.8  | 3.5  | 0.07            | 0.02 | 0.47             | 0.30 | 6.4              | 8.9  | 7.3             | 8.6  | 7.0             | 3.3  | 0.57            | 0.29 |

\* <sup>a</sup>Exchangeable calcium (cmol<sub>c</sub> kg<sup>-1</sup>); <sup>b</sup>Total exchangeable bases (meq 100g<sup>-1</sup>); <sup>c</sup>Cation exchange capacity (meq 100g<sup>-1</sup>);  
<sup>d</sup>Exchangeable acidity (meq 100g<sup>-1</sup>); <sup>e</sup>Percent base saturation (%); <sup>f</sup>Percent organic matter (%)

Surface soil pH was acidic (pH <4.0) and subsoil was moderately acidic (~pH 4.6) during P1. Soils became more acidic by P2 with all horizons having pH <4.0. Surface soil in P2 is still the most acidic and pH slightly rises with depth in the profile. As noted by Barton et al. (2002), the acidic nature of the surface horizon is probably due to organic acids and the acidity associated with elevated organic matter content, which did not change greatly between P1 and P2. Soils exhibited a large loss in percent base saturation (BS) between periods. Each soil horizon exhibited a decrease in BS by at least 66% from 1995 to 2012. Total exchangeable bases (TEB) also decreased between periods. However, the Bt2 horizon saw an increase in TEB, indicating that exchangeable ions may have been lost from the upper horizons and accumulated in the Bt2 horizon. Reasons for loss of base cations could be due to normal leaching by rainfall and soil development, enhanced leaching by acid deposition, organic matter decomposition, nutrient uptake and release by vegetation, erosion, slow rates of base input from parent material weathering and slow cycling of nutrients (Farr et al. 2009). The large decrease in soil BS and TEB is likely attributed to a very significant loss of exchangeable calcium between periods. It is evident that exchangeable Ca levels have been depleted which could be a result of continued inputs from atmospheric deposition. Cation exchange capacity (CEC) increased over time at all depths. Unsatisfied charges on clay particles could be a result of weathering of clay minerals, increasing surface area and exchange sites. Base cation leaching due to increased input acidity also exposes more negative exchange sites. Both cases indicate elevated weathering between periods.

Mineralogical compositions of the McCreary soils are reported in Table 2.2.

Table 2.2: Mineralogical composition of the <2µm clay fraction from sites included in P1 and P2 sampling.

| Site            | V-HIV |      | INT  |      | K    |      | MI   |      | Q    |      | GI   |      | GO   |      | F    |      |
|-----------------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|                 | 1994  | 2012 | 1994 | 2012 | 1994 | 2012 | 1994 | 2012 | 1994 | 2012 | 1994 | 2012 | 1994 | 2012 | 1994 | 2012 |
| <b>McCreary</b> |       |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| A               | 38    | 41   |      |      | 40   | 50   | 3    | 4    | 12   | 5    | 5    |      |      |      |      | 2    |
| BA              | 32    | 36   | 6    |      | 42   | 54   | 7    | 4    | 8    | 4    | 6    |      | 2    |      |      | 2    |
| Bt1             | 30    | 39   | 5    |      | 45   | 53   | 5    | 4    | 6    | 2    | 6    |      | 2    |      |      | 3    |
| 2Bt2            | 26    | 31   |      |      | 57   | 53   | 3    | 9    | 6    |      | 6    | 5    | 2    |      |      | 2    |
| <b>Wolfe</b>    |       |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| A               | 41    | 54   | 6    | 5    | 28   | 33   | 5    | 3    | 17   | 4    | 4    |      |      |      | 5    | 1    |
| BA              | 32    | 46   | 4    |      | 30   | 42   | 10   | 6    | 16   | 6    | 5    |      |      |      |      | 3    |
| BE              | 30    | 28   | 5    | 5    | 42   | 49   | 10   | 9    | 6    | 4    | 4    | 2    | 3    |      |      | 3    |
| Bt              | 10    | 16   |      | 4    | 60   | 65   | 15   | 11   | 6    |      |      |      | 4    |      |      | 3    |

\* *V-HIV* vermiculite/hydroxy-interlayered vermiculite; *INT* interstratified mica-vermiculite; *K* kaolinite; *MI* mica; *Q* quartz; *GI* gibbsite; *GO* goethite; *F* feldspars

Results are reported in percentages. The accuracy of results is ±3%.

Kaolinite was the dominant aluminosilicate in the clay fraction in both periods and was found in greater abundance in P2 compared to P1. Kaolinite is common in weathered soils, accumulating from the weathering of feldspars, micas, vermiculite and smectite and remaining in the clay fraction because of its stability (Karathanasis 2006). A corresponding reduction in quartz and feldspars may also be an indication of weathering over time. While quartz is relatively stable in the sand fraction, clay fraction quartz is relatively unstable, and weatherable into amorphous, soluble silica, where it can be lost via leaching (Wolt 1994). Feldspars typically weather to kaolinite and are important sources of K and Ca in soils (Karathanasis 2006). Increased kaolinite in our soils may be explained by reductions in feldspars. Mica contents were about the same between periods, with some reduction in the BA and Bt1 horizon and an increase in the Bt2 horizon. Micas may be weathering into vermiculite, kaolinite and gibbsite in the middle horizons, and accumulating lower in the soil column over time.

When feldspars, kaolins, smectites and micas are dissolved, silica is released to solution as silicic acid while Al is conserved in the solid phase as an oxyhydroxide (Wolt 1994). Therefore, silica is mobilized more rapidly than Al as soils are weathered and become more acid. If leaching continues, gibbsite is left as the dominant mineral and Lindsay (1979) states that gibbsite controls soil pH buffering and control of Al activity in solution. Gibbsite content was found to be 5-6% of clay minerals in each horizon during P1 but was detected only in the Bt2 horizon at 5% during P2. Gibbsite is a soluble mineral associated with the latter stages of weathering (Schulze 1989) and, even with additions from weathering of micas and kaolinite, appears to have been lost from the McCreary soil. In an environment experiencing intense leaching, kaolinite and gibbsite are usually the most common products (Karathanasis 2006).

Goethite is a highly stable iron bearing hydroxide mineral that may remain in soil for long periods of time, and large amounts in well-aerated soils in association with gibbsite and kaolinite indicate advanced weathering (Schulze 1989). Goethite was not found in soils from P1, but was present from the 6-60 cm depth in P2, indicating some degree of weathering. Vermiculite (V) and hydroxyl-interlayered vermiculite (HIV) are most common in Alfisols and Ultisols and are most abundant near the surface decreasing with depth (Schulze 1989). Percentages of V and HIV were between 3 and 9% lower in

P1 than P2, which is not significantly different, but could be an indication of weathering from micas and chlorite. In summary, McCreary clay fraction mineralogy indicates some level of weathering of unstable to more stable minerals, potentially due to pH of soil and solution solubility controls. Wolt (1994) states that soil weathering results in Si mobilization and Al accumulation and mineral activity is controlled by the dissolution of unstable primary minerals, formation of stable secondary minerals, and the rate of mineral removal via leaching and plant uptake. The author also affirms that weathering and mineral activity is pH dependent, and a drop in pH results in the accumulation of Al-enriched and secondary aluminosilicate minerals. Therefore, as soil and solution pH decreases, it can be expected that weathering and a shift in mineral phases would occur.

Wolfe soil properties are given in Figure 2.3 and Table 2.1. The Wolfe soils exhibited acidic to moderately acidic pHs from the surface down in P1 and became even more acidic at all depths by P2. All horizons in P2 were lower than that observed in P1 with values dropping from pH 4.0 to 3.2 in the A horizon, pH 4.7 to 3.9 in BA, pH 4.7 to 3.8 in BE, and pH 4.8 to 3.5 in the Bt horizon. OM contents also decreased from P1 to P2. The Wolfe soil exhibited large losses in BS and small losses in TEB for all layers except the A horizon. A decrease of BS and TEB in the underlying soil is likely because of significant losses in Ca at those depths due to vegetative uptake, substitution and leaching. CEC increased slightly at each depth, but changed the least in the A horizon. The subsoil exhibited rather significant reductions in Ca, TEB and BS and very little change in EA.

Mineralogical compositions of the Wolfe soils are reported in Table 2.2. HIV is the dominant clay mineral in the surface soil but decreases with depth, and kaolinite is appreciable in abundance with depth. P2 showed between 4-14% higher V/HIV content than P1 except for a slight (2%) decrease in BE soil. Kaolinite content was between 5-12% higher in P2 at all depths. Mica, quartz, gibbsite and feldspar levels were lowered from P1 to P2. In P1 gibbsite was 4-5% in the top three horizons, but was only identified in the BE horizon in P2, while feldspars were only found in very small amounts in the top 6 cm in P2. Much like McCreary, Wolfe soils show evidence of prolonged weathering of feldspars, mica and quartz creating minor increases in V/HIV and kaolinite content.

Gibbsite also appears to be lost due to solubility, and goethite has accumulated from 0% to 2-4% in the subsoil over time.

McCreary soils exhibited greater depletion of Ca and other base cations than Wolfe soils. The pH values for both sites during both periods were similar, and increases in soil acidity occurred at similar rates among sites. The A horizon in Wolfe has experienced greater reductions in EA, OM and pH, which may be why BS, TEB and Ca either improved or remained constant at all depths. Wolfe soil saw greater losses in OM in upper horizons over time, bringing OM to similar levels as McCreary at the start of P2. The reduced OM and EA in Wolfe topsoil may be a control on the base cations, while minimal changes in McCreary OM and EA could explain large reductions in Ca and other base cations. In this case, OM and EA would act as a buffer for the loss of soil cations (Bot and Benites 2005). Instead of losing base cations in soil, acid cations may be lost or base cations could be transferred from OM exchange sites. Pohlman and McColl (1986) have shown rapid release of base cations from forest soils when leached with naturally occurring organic acids which had higher rates of release than mineral acids. Trends in mineralogy over time were very similar at both sites. Weathering of clay minerals has occurred at both sites with similar frequency, and mineral solubility controls appear to be an important driver of these systems.

Several studies within the Appalachian region have reported changes in soil properties over an extended period of time. Many soils within eastern US forests are prone to base cation depletion because they are old, highly weathered soils where base-bearing minerals have been lost (Daniels and Hammer 1992; Markewich et al. 1994). The Panola Mountain Research Watershed near Atlanta, GA recorded concentrations of exchangeable Ca in the A horizon to be 80% greater than B horizons, while other exchangeable base cations decreased only slightly with soil depth (Huntington et al. 2000). This is similar to our results (Table 2.1). Research plots in the Allegheny National Forest in northwestern Pennsylvania show a long-term decrease in pH, exchangeable Ca and Mg, and an increase in exchangeable Al from 1967 to 1997 (Bailey et al. 2005). Studies in West Virginia (Adams 1999; Farr et al. 2009) and North Carolina (Knoepp and Swank 1994) have documented base cation depletion in soils due to acid deposition and forest re-growth. Similar to these and our current research, Markewitz et

al. (1998) found significant decreases in pH and TEB, and increases in EA to a depth of 60-cm in South Carolina, suggesting that acid deposition may have altered the entire soil profile in highly weathered soils. However, other studies found most pH and cation depletion to be in the Oa and A horizons in the Northeast US (Drohan and Sharpe 1997; Johnson et al. 1994).

The failure of many soils and streams to recover after major reductions in emissions and deposition can be partially attributed to depletion of exchangeable base cations (Likens et al. 1996). Another major influence on speed of recovery observed is due to years of accumulated N and S in forest soils. These ions may be slowly released from soil, even after reductions in deposition have been observed, and continue to deplete soil of exchangeable base cations (Driscoll et al. 2001; Knoepp and Swank 1994). Several studies conclude that re-supply of base cations via mineral weathering and precipitation inputs is exceeded by base cation leaching, suggesting that re-supply rates are not enough to outweigh rates of loss (Bailey et al. 1996; Huntington 2000; Binkley et al. 1989).

#### *Soil Solution Composition:*

Soil solution chemistry focuses on the available fraction of water occurring in the soil environment and is critical for understanding chemical decomposition from soil weathering and for assessing elemental availability (Wolt 1994). Mean values and standard deviations are reported for each parameter in Table 2.3. Soil solution pH for McCreary during P1 remained relatively stable for the duration of the study (Figure 2.4).

Table 2.3: Soil solution composition means and standard deviations for samples collected from gravity lysimeters at 30- and 60-cm depths between sites and sampling periods (P1 and P2).

|  |              | McCreary    |             |             |             | Wolfe       |             |             |             |
|--|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|  |              | P1*         |             | P2          |             | P1          |             | P2          |             |
|  |              | <i>Mean</i> | <i>Stdv</i> | <i>Mean</i> | <i>Stdv</i> | <i>Mean</i> | <i>Stdv</i> | <i>Mean</i> | <i>Stdv</i> |
| <b>pH</b>  | <i>30 cm</i> | 5.2         | 0.49        | 5.1         | 1.1         | 5.4         | 0.96        | 5.5         | 0.86        |
|  | <i>60 cm</i> | 5.5         | 0.54        | 5.2         | 1.3         | 5.4         | 0.67        | 5.1         | 0.99        |
| <b>EC</b><br>( $\mu\text{S cm}^{-1}$ )                       | <i>30 cm</i> | 47.1        | 21          | 46.8        | 120         | 57.3        | 73          | 32.3        | 10          |
|  | <i>60 cm</i> | 59.7        | 28          | 22.7        | 7.9         | 54.7        | 77          | 32.2        | 14          |
| <b>NO<sub>3</sub><sup>-</sup></b><br>( $\text{mg L}^{-1}$ )  | <i>30 cm</i> | 0.093       | 0.07        | 0.41        | 0.85        | 1.0         | 1.8         | 0.48        | 0.66        |
|  | <i>60 cm</i> | 0.056       | 0.06        | 0.53        | 1.2         | 0.25        | 0.32        | 0.27        | 0.48        |
| <b>SO<sub>4</sub><sup>2-</sup></b><br>( $\text{mg L}^{-1}$ ) | <i>30 cm</i> | 5.9         | 8.5         | 3.9         | 2.8         | 4.5         | 4.9         | 4.2         | 2.0         |
|  | <i>60 cm</i> | 5.5         | 3.3         | 3.3         | 2.3         | 4.7         | 5.1         | 5.3         | 2.1         |
| <b>Al</b><br>( $\text{mg L}^{-1}$ )                          | <i>30 cm</i> | 0.68        | 1.1         | 0.48        | 0.35        | 0.84        | 0.86        | 0.54        | 0.35        |
|  | <i>60 cm</i> | 0.41        | 0.59        | 1.1         | 2.1         | 0.74        | 1.2         | 0.29        | 0.29        |

\* P1 = 1994 – 1999; P2 = 2012 – 2013.

No means were significantly different between periods or sites.



# McCreary

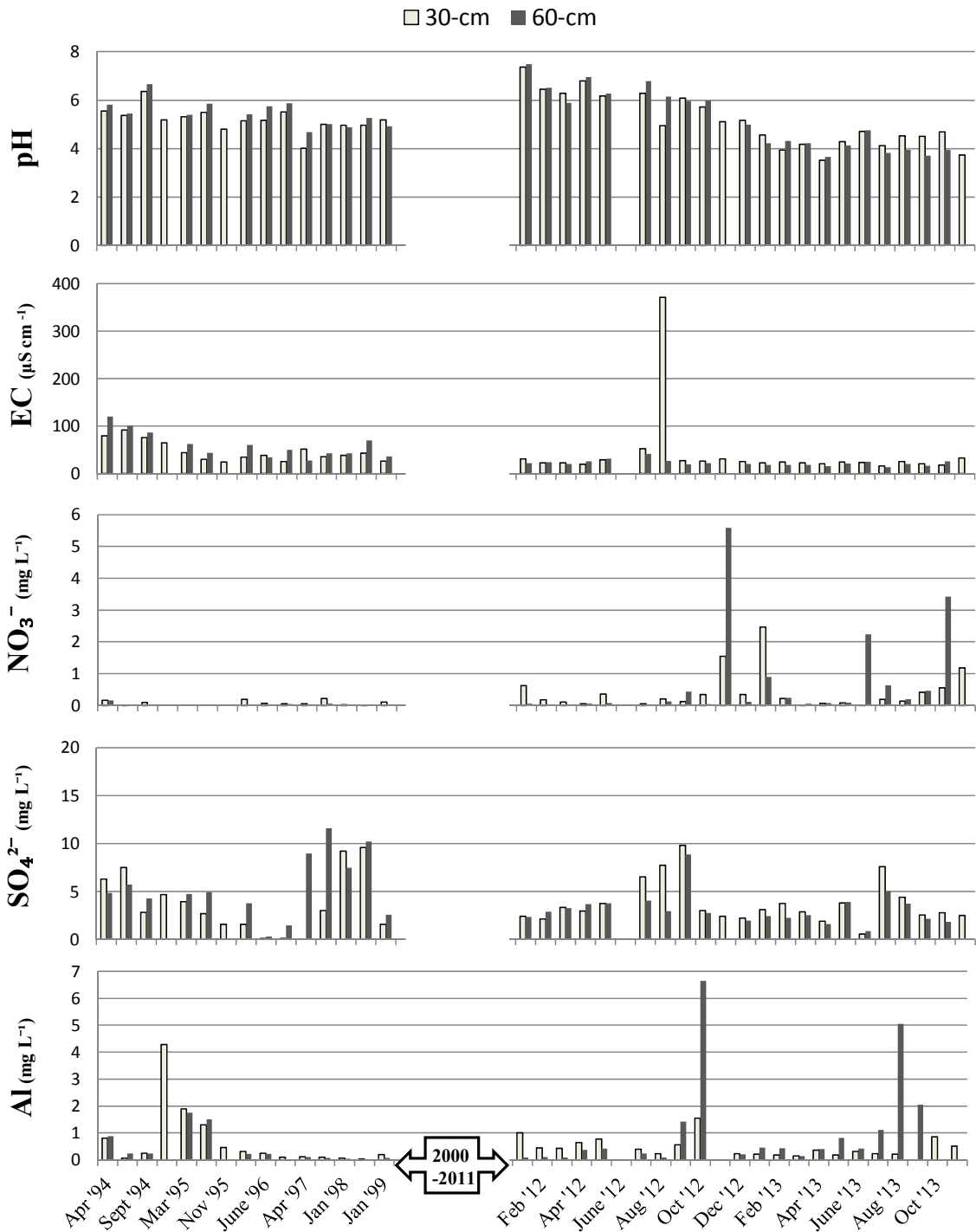


Figure 2.4: Soil solution composition for samples collected at McCreary from gravity lysimeters at 30- and 60-cm depths between P1 and P2. X-axis represents sampling events during study periods and does not represent real time (P1=6 yrs.; P2=2 yrs.).

Average pH increased slightly from the 30- to 60-cm depths (pH 5.2 to 5.5 respectively), which may be due to increased organic acids in upper horizons associated with higher OM content. Sampling during P2, however, revealed an acidifying trend through the duration of the study. Solution pH started between pH 6-7 in the winter/spring of 2012, but dropped below pH 5.0 as time progressed. Average pH values by sampling period revealed a slight acidification of soil solution over time. Samples from the 30-cm depth dropped from pH 5.2 to 5.1, a 26% increase in  $H^+$  concentration, and the 60-cm solution dropped from pH 5.5 to 5.2, 100% increase in  $H^+$  concentration (Table 2.3). Wilkländer (1980b) hypothesized that soils with pH values between 4.5 and 6.0 would be most sensitive to acidic precipitation and soil pH change. More basic, circum-neutral soils are buffered by a high degree of base saturation and more acidic soils have higher levels of Al, potentially buffering against further soil acidification. Based on this hypothesis, it is evident that McCreary soils are within the pH range of the most sensitive soils, and over time may become increasingly acidic and Al saturated to levels that may affect vegetative productivity.

Aluminum concentrations in soil solution are used as an indication of Al mobilization. Al values were highly variable during both sampling periods (Figure 2.4). Mean Al concentration was low ( $0.68 \text{ mg L}^{-1}$ ) at the 30-cm depth and slightly lower ( $0.41 \text{ mg L}^{-1}$ ) at 60-cm depth during P1. P2 Al concentrations decreased ( $0.48 \text{ mg L}^{-1}$ ) at 30-cm depth and increased ( $1.1 \text{ mg L}^{-1}$ ) at 60-cm depth, suggesting Al mobilization lower in the profile over time. Al peaks in P2 occurred during the fall months of 2012 and 2013 at both depths, but P1 exhibited only an Al peak in the '94-'95 winter. Even though pH levels remain higher at 60-cm opposed to 30-cm the percent reduction over time is greater at the 60-cm depth. Soil pH values decreased greater at lower depths, also suggesting Al mobilization with depth. The pH might be a control on Al in solution, showing a negative relationship between change in pH and quantity of Al in solution. In general, the Al in soil is important in acid reactions, especially in the vulnerable pH range of 4.5-6.0. Al becomes soluble and behaves as a base at low pH (Norton 1976). Kinraide (2003) concluded that  $Al^{3+}$  activity in soil solution increased with decreasing pH to about pH 4.1, then declined as pH dropped below 4.1. This supports the Wilkländer (1980b)

hypothesis that more acidic soils are buffered by relatively high levels of Al because it may act as a base at low pH values.

Soil solution  $\text{NO}_3^-$  concentrations were low in P1 compared to P2 (Figure 2.4). P1 mean  $\text{NO}_3^-$  concentrations were below  $0.10 \text{ mg L}^{-1}$  and no sample was above  $0.25 \text{ mg L}^{-1}$ . Mean P2 concentrations were higher exhibiting  $0.41$  and  $0.53 \text{ mg L}^{-1}$  at the 30- and 60-cm depths, respectively. P2 concentrations were variable, but peaks were observed during both winter of 2012-13 and fall 2013 at both depths. Differences between periods could be due to many factors, but it is possible that vegetation may have a strong influence. It is possible that the vegetation was more efficient in uptake of N during P1 than P2. This could be from reduced vigor over years or changes in root morphology from aging or blockage of receptors by accumulating Al. Solution  $\text{NO}_3^-$  trends during P2 sampling show higher concentrations during months outside the growing season when soil temperatures are lower. Trends could reflect the increased water infiltration due to decreased evapotranspiration as well as decreased microbial nitrifying activity preventing fixation, uptake and use of nitrogen which occurs when soil temperatures are higher (Kristensen et al. 2004). Cai et al. (2012) discovered that N cycling in the Great Smoky Mountains National Park soils was primarily controlled by biological transformations rather than acid deposition because high levels of organic N in surface soils allow for high rates of mineralization and nitrification. Seasonal differences in  $\text{NO}_3^-$  concentrations in throughfall were observed by Knoepp et al. (2008), with highest concentrations noted during summer months when emissions were highest. Walna (2007) concluded that soil solution  $\text{NO}_3^-$  was higher in the fall than in the spring, and concentrations declined with increasing depth, while Edwards et al. (2002) found increasing  $\text{NO}_3^-$  concentrations in solution during summer months and concentrations also decreased with increasing depth. Results suggest that biological activity in the upper soil horizons have a large impact on soil solution concentrations. Differences in depth are similar to our results; however seasonal variation in soil solution has given mixed results.

Variable  $\text{NO}_3^-$  concentrations found in solution as well as biological activity and use of N often makes sulfate the more reasonable anion to consider with respect to base cation depletion and Al mobility. Solution  $\text{SO}_4^{2-}$  was variable throughout both sampling

periods (Figure 2.4). The highest concentrations were observed during the winter and summer of 1998 at 30-cm depth and during summers of 1997 and 1998 for 60-cm lysimeters. The P2  $\text{SO}_4^{2-}$  concentration trends revealed peaks during growing seasons with highest concentrations occurring in the summer and fall of 2012. Mean  $\text{SO}_4^{2-}$  concentrations were 5.9 and 5.5  $\text{mg L}^{-1}$  for P1 and 3.9 and 3.3  $\text{mg L}^{-1}$  for P2 at 30- and 60-cm depths, respectively. It is difficult to relate solution  $\text{SO}_4^{2-}$  to solution Al during the sampling periods, but the summer of 1997 displayed peaks in both Al and  $\text{SO}_4^{2-}$ , and one large peak in Al during P2 was observed during a sampling event immediately following a large  $\text{SO}_4^{2-}$  peak. The two recorded occurrences possibly indicate a delayed Al mobilization effect triggered by high sulfate inputs (Barton et al. 2002).

$\text{SO}_4^{2-}$  in soil is preferentially adsorbed because of greater exchange selectivity for sulfate (Donn and Menzies 2005). Sulfate retention can cause mixed results when observing soils due to the complex processes involved in sorption/desorption of S in forested ecosystems (Garten et al. 1988; Alewell 2001). Cai et al. (2012) found that soils in the Great Smoky Mountains National Park were a  $\text{SO}_4^{2-}$  sink, but desorption may be expected as reductions in  $\text{SO}_4^{2-}$  deposition and increased soil pH are anticipated in the future. However, it should be noted that desorption of sulfate may be a slow process even with decreasing inputs, because acidified soils have high sulfate retention, thus low reversibility (Shanley 1992). Sulfate retention also controls base cation pools, as Ca can be readily leached in association with  $\text{SO}_4^{2-}$  (Reuss and Johnson 1986).

Electrical conductance (EC) measurements in soil solution are used as an indicator for ionic strength, with higher EC relating to higher solution ionic strength (Gillman 1981). Figure 2.4 shows results of solution EC levels between both sampling periods. EC levels were more variable at the 60-cm depth during P1. EC levels at the 30-cm depth were not significantly different between periods, but measurements from the 60-cm depth saw a reduction in average EC from 60 to 23  $\mu\text{S cm}^{-1}$  between P1 and P2. Increased EC in precipitation and soil solution attributed to greater acid ion concentrations have influenced  $\text{SO}_4^{2-}$  sorption (Donn and Menzies 2005). Generally, increased precipitation EC levels will increase the positive charge density of soil minerals and result in greater adsorption of acid anions. In contrast, reduced positive charge

density from lower EC in precipitation will cause the adsorbed ions to leach. This may become the case at the 60-cm depth if reduced EC continues. Leaching of these anions will result in greater amounts in solution in the short-term but lesser amounts in soil and solution in the long-term.

Solution pH measurements for Wolfe reveal an acidifying trend during both sampling periods. Solution from early sampling events for both periods was circumneutral and decreased slightly over each period (Figure 2.5).

# Wolfe

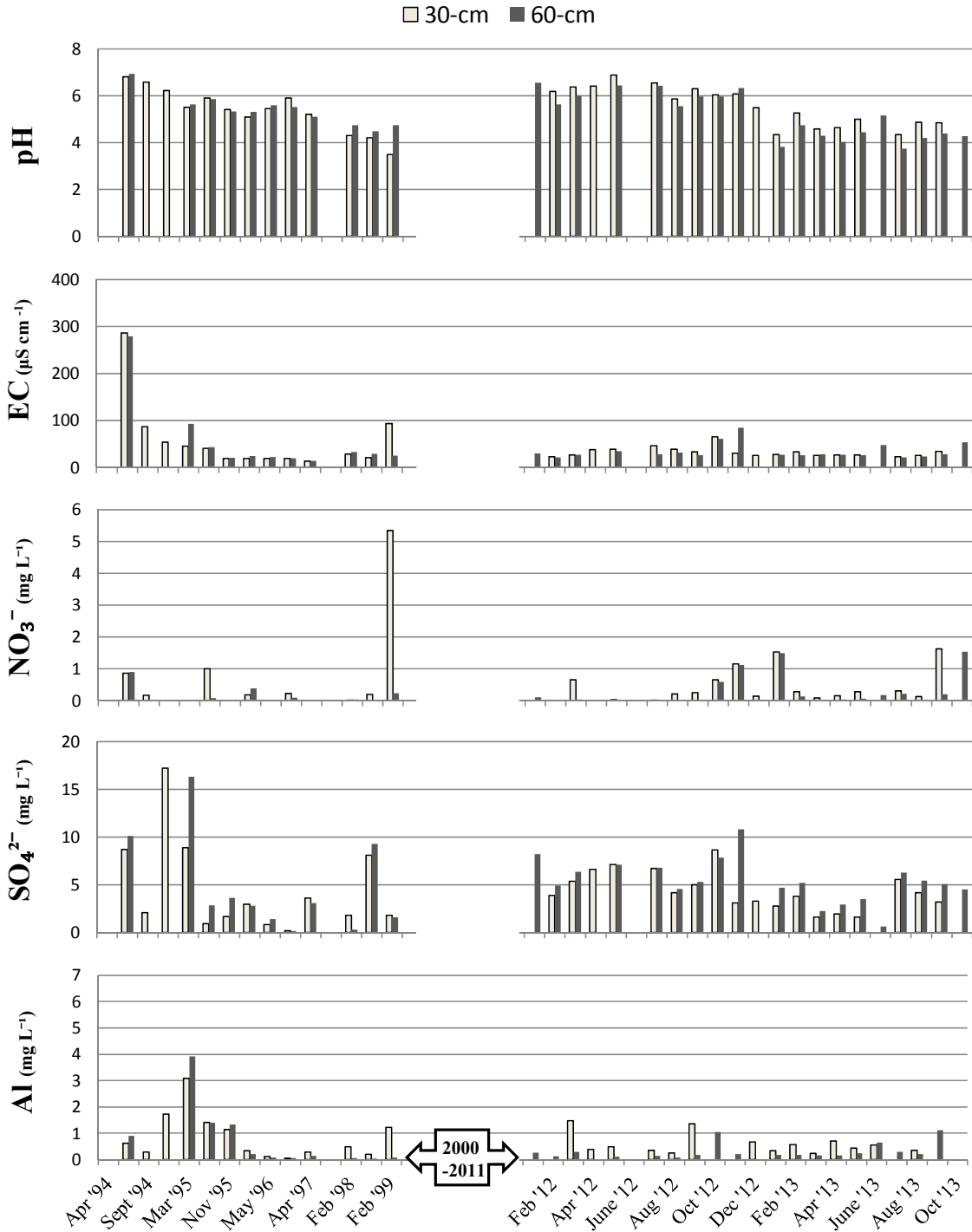


Figure 2.5: Soil solution composition for samples collected at Wolfe from gravity lysimeters at 30- and 60-cm depths between P1 and P2. X-axis represents sampling events during study periods and does not represent real time (P1=6 yrs.; P2=2 yrs.).

Mean pH for both depths in P1 was 5.4. Mean pH for P2 was 5.5 at 30-cm and 5.1 at 60-cm depths, a 21% decrease and 100% increase in  $H^+$  concentration, respectively (Table 2.3). Even though mean pH did not change between P1 and P2, acidifying trends within both sampling periods were observed. Soil disturbance during site installation was investigated as a driver of this trend, but throughfall measurements from P2 (discussed in chapter 1) show a similar trend as seen in the soil solution.

Much like the McCreary Al results, Wolfe Al values are highly variable (Figure 2.5). Al concentrations were highest in 1995 and peaks at both depths corresponded to each other. Average Al in solution dropped from 0.86 to 0.54  $mg L^{-1}$  and from 1.2 to 0.29  $mg L^{-1}$  at 30- and 60-cm depths, respectively, between periods. P2 Al ( $<1.5 mg L^{-1}$ ) deviated less than P1 ( $<4.0 mg L^{-1}$ ). Trends are not evident when comparing 30- to 60-cm depths in P2.

Nitrate data was often below detection in P1. When measurable, values were low throughout both depths, with the exception of the 30-cm sample in the winter of 1999, which had a concentration of 5.3  $mg L^{-1}$  (Figure 2.5). Trends from P2, however, show elevated concentrations in fall months of sampling in both 2012 and 2013.

Decomposition of leaf litter on the forest floor contributes to N availability (Knoepp et al. 2005), and fall months are the time when leaf litter content is greatest. Average  $NO_3^-$  concentrations decreased from 1.0 to 0.48  $mg L^{-1}$  at 30-cm depth and little change was observed (0.25 to 0.27  $mg L^{-1}$ ) at the 60-cm depth between periods. Compared to McCreary, the Wolfe site had greater concentrations of  $NO_3^-$  in both periods. This may be because the vegetation at Wolfe was less efficient at utilizing N both in P1 and P2, causing more to be lost in solution. Soil chemistry was more similar between sites in P2, which could be an indication of the changes in nutrient availability. In P1, McCreary had much higher TEB and BS than Wolfe, but levels dropped to a similar level in P2. As TEB and BS were depleted in McCreary, the health and ability of vegetation to take up nutrients may have been affected, resulting in a loss of N use efficiency.

Mean  $SO_4^{2-}$  concentrations were similar between periods, dropping from 4.5 to 4.2  $mg L^{-1}$  at 30-cm and jumping from 4.7 to 5.3  $mg L^{-1}$  at 60-cm depth, indicating little overall change in solution  $SO_4^{2-}$  over time (Figure 2.5).  $SO_4^{2-}$  concentrations during P1 were variable in Wolfe, and trends from P2 are not obvious, but may indicate some

seasonality with concentrations showing somewhat of an increase from winter to fall during both years. EC levels were more variable during P1 sampling than P2 (Figure 2.5). Trends in EC at the Wolfe site are difficult to ascertain, and offer little help in understanding developments in mineral solubility controls.

During P1, McCreary experienced minimal change in solution pH, while Wolfe exhibited a slight acidification over time. During P2, both sites experienced acidification over time, however there were no obvious differences in mean pH of solution between sampling periods at either site. Aluminum concentrations in solution were higher in McCreary than Wolfe. The 60-cm lysimeters at McCreary saw increased Al in solution between periods while Wolfe exhibited lowered concentrations. Nitrate concentrations were higher in P2 at McCreary and trends of higher concentrations were seen at both sites during the fall of 2012 and 2013. Sulfate concentration trends are not comparable between sites, but McCreary experienced a lowering of sulfate in solution from P1 to P2 while Wolfe experienced little to no change. As  $\text{SO}_4^{2-}$  levels remained similar and  $\text{NO}_3^-$  increased over time at Wolfe, solution pH declined. Increased solution  $\text{NO}_3^-$  and reduced  $\text{SO}_4^{2-}$  at McCreary coincided with minimal pH change. Introduction of strong mobile acid ions into these systems may enhance soil acidification (Barton et al. 2002); however reductions in  $\text{SO}_4^{2-}$  over time still lead to reduced pH. This is an indication that soils at our sites are unable to buffer against acid anion inputs even when concentrations are lowered.

Precipitation data from the NADP revealed no trends in acidification during either period, which is different from our soil solution data that saw acidification of McCreary solution during the course of sampling in P2 and Wolfe soil solution during both sampling periods. Soil solution pH averages by sampling period showed no changes over time in pH, while precipitation data saw an increase of average pH over time. NADP precipitation data reflects changes sought by revisions of the CAA. Rainfall pH increased, and sulfate, nitrate and conductivity of precipitation decreased over time. Evidence supports ideas that reductions in power plant emissions of sulfur and nitrogen oxides brought about by the CAA are having favorable outcomes for atmospheric environments. Based on soil solution data gathered during the two sampling periods, it is not evident that revisions in the CAA have led to any changes in soil solution chemistry



or reduced effluent impacts on waterways. There are too many factors influencing soil solution chemistry to make any claims that the CAA improvements on precipitation chemistry have altered the soil system. It is evident though that the soils at McCreary and Wolfe sampling sites are acidifying, continuing to weather, and losing base cations over time. This supports Barton et al. (2002) claims that further input of acid anions, no matter the concentration, will continue to deplete base cations and limit the already weak pH buffering capacity of these systems.

*Mineral Solubility Control Sequences:*

Barton et al. (2002) examined the mineral phases of gibbsite, alunite, jurbanite, and basaluminite with associated log K values of -33.95, -85.4, -17.2, and -117.5, respectively (Reuss and Johnson 1986) and created stability diagrams from corresponding dissolution reactions and composition points from the solution chemistry of the study sites. The area above a solubility line indicates supersaturation with respect to the mineral, while area below the line indicates undersaturation. Composition points falling anywhere along the graph can illustrate saturation, supersaturation or undersaturation for the given minerals. Current soil solution chemistry was used to overlay new composition points into previous graphs for comparison (Figures 2.6 and 2.7).

McCreary  
Wernock / Gilpin

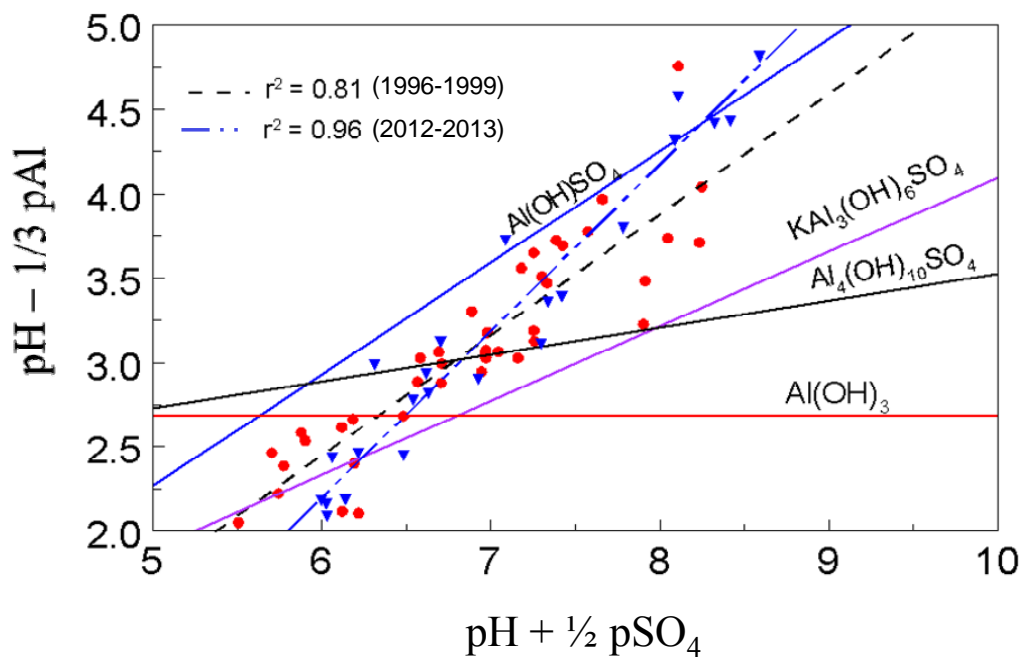


Figure 2.6: Soil solution composition points for Wernock/Gilpin series from P1 (red dots) and P2 (blue triangles) in reference to a mineral stability diagram depicting solubility lines of jurbanite [ $\text{Al(OH)SO}_4$ ], alunite [ $\text{KAl}_3(\text{OH})_6\text{SO}_4$ ], basaluminite [ $\text{Al}_4(\text{OH})_{10}\text{SO}_4$ ], and gibbsite [ $\text{Al(OH)}_3$ ].

Wolfe  
Rayne

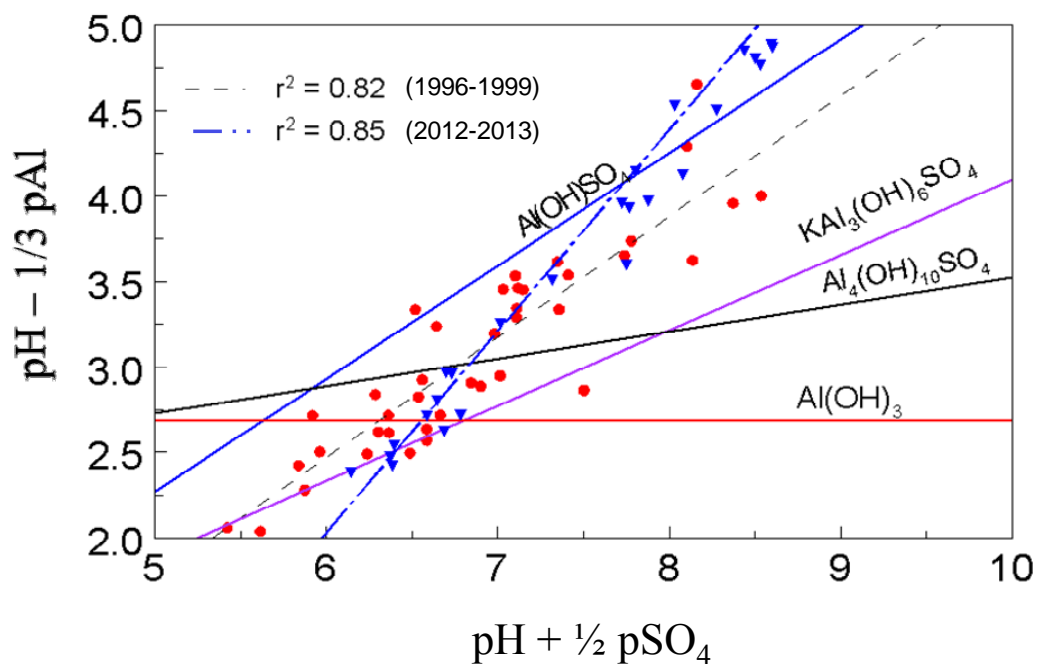


Figure 2.7: Soil solution composition points for Rayne series soil from P1 (red dots) and P2 (blue triangles) in reference to a mineral stability diagram depicting solubility lines of jurbanite  $[\text{Al(OH)SO}_4]$ , alunite  $[\text{KAl}_3(\text{OH})_6\text{SO}_4]$ , basaluminite  $[\text{Al}_4(\text{OH})_{10}\text{SO}_4]$ , and gibbsite  $[\text{Al(OH)}_3]$ .

Linear regression lines were constructed for both periods at each site and, in general, lie between the stability lines for alunite and jurbanite. All data points from each site and sampling period, with the exception of a few, are in equilibrium or supersaturated with respect to alunite, and undersaturated with respect to jurbanite. As noted in the previous study, the stability line for basaluminite still appears to cut the data points in half, with half of the points supersaturated with respect to the mineral and the other half undersaturated. McCreary (Wernock) solution also still has a clustering of points near equilibrium with basaluminite. Wolfe (Rayne) solution points tend to cluster on the lower end of the curves with a clustering between gibbsite and alunite.

Most importantly, as pointed out by Barton et al. (2002), the regression line slope of the solution data points in the Rayne soil is parallel to that of jurbanite, whereas the Wernock soil is not quite parallel to jurbanite and not parallel to any of the displayed minerals, but has a slope somewhere between that of alunite and jurbanite. Similar to Barton et al. (2002), this suggests that the chemical composition of the Al-controlling mineral phase is similar, but of a different solubility, to the investigated sulfate minerals, and definitely different than that of gibbsite. Regression lines for both McCreary and Wolfe showed no sign of shift, indicating a shift in solubility control, but instead exhibited a pivot to a steeper slope. None of the examined mineral solubility lines are parallel to the recent regression slopes and Wolfe solution had a greater increase in slope between sampling periods. The solubility line pivots suggest there is another mineral controlling the system. That mineral is likely an Fe-hydroxide, Fe-sulfate or an Al-hydroxy-sulfate that was not examined. There may be an interaction with iron affecting the solubility of S, therefore changing the way S binds with Al. This has some control on the acid in the system, and a pH drop could lead to the hydrolysis of Fe-hydroxide, thus leading to a change the slope of the solubility line.

#### *Tree-ring Growth Analysis:*

Dendroanalysis is a useful tool for evaluating forest stand growth as it relates to climate and pollution (Fritts 1976; Fritts and Swetnam 1989; Cook and Jacoby 1983; Bondietti et al. 1990; Guyette et al. 1992; McClenahan and Vimmerstedt 1993). Trees produce yearly growth rings with periods of early wood and late wood forming color and density differences, making it easy to identify and measure each year's growth. Radial

growth may be controlled by factors that include disturbance, competition, soil chemistry, precipitation and temperature (Cook and Innes 1989). Climate conditions are one of the major factors controlling the productivity of a tree in a given year (McClenahen and Vimmerstedt 1993). For example, an increase in the long-term ambient air temperature can increase forest productivity due to longer growing seasons, allowing for increased biomass production (McNulty and Boggs 2010). Easily observable tree-ring width sequences have been used to reconstruct records of past climatic changes (Fritts 1976; Fritts and Swetnam 1989; Cook and Jacoby 1977). Tree rings are the only widely available source of long-term, baseline data on forest growth and productivity that may predate monitoring programs and the present era of elevated atmospheric pollution (Cook and Innes 1989).

Radial ring-width measurements of individual trees from McCreary and Wolfe research sites showed slowed growth with age (Figure 2.8).

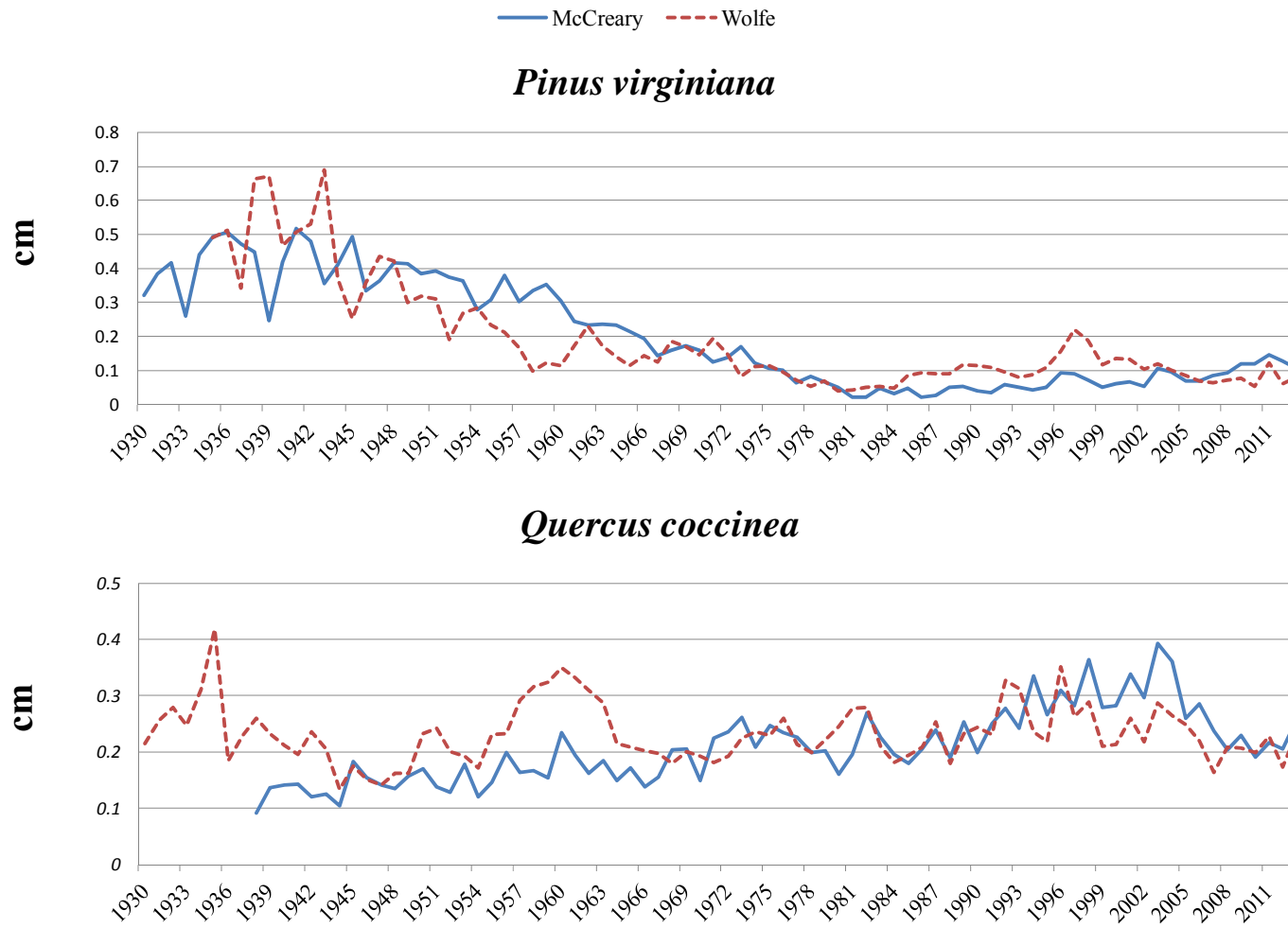


Figure 2.8: Annual radial growth (cm) of single-tree *Pinus virginiana* and *Quercus coccinea* samples from sites included in the study.

McCreary Virginia pine was approximately 88 and scarlet oak was 75 years old. Wolfe pine was approximately 78 and oak was 86 years old. McCreary pine had a period of high growth from the pith to 1950 followed by a steady decrease until it reached its lowest growth in the early 1980s. Since then, ring width gradually increased to the present. Wolfe had high growth from the pith to 1944 followed by a sharp decrease in the late 1940s. From 1950 to early 1980s the tree gradually declined to its lowest growth followed by slight productivity to the present. Both sample trees had largest ring-widths in the 1930s and 1940s with growth tapering off as the trees aged to the early 1980s, the lowest period of growth, only to improve slightly since. Oak tree samples did not display similar growth trends. Both McCreary and Wolfe oaks were consistent and between 0.4 and 0.1 cm of radial growth.

It is believed that the use of a single tree from each site as an environmental marker is not representative of the state of the forest (Watmough 1999). Therefore, the multi-tree aggregate sampling method was implemented and core samples from Virginia pines illustrated a different trend from the single trees (Figure 2.9).

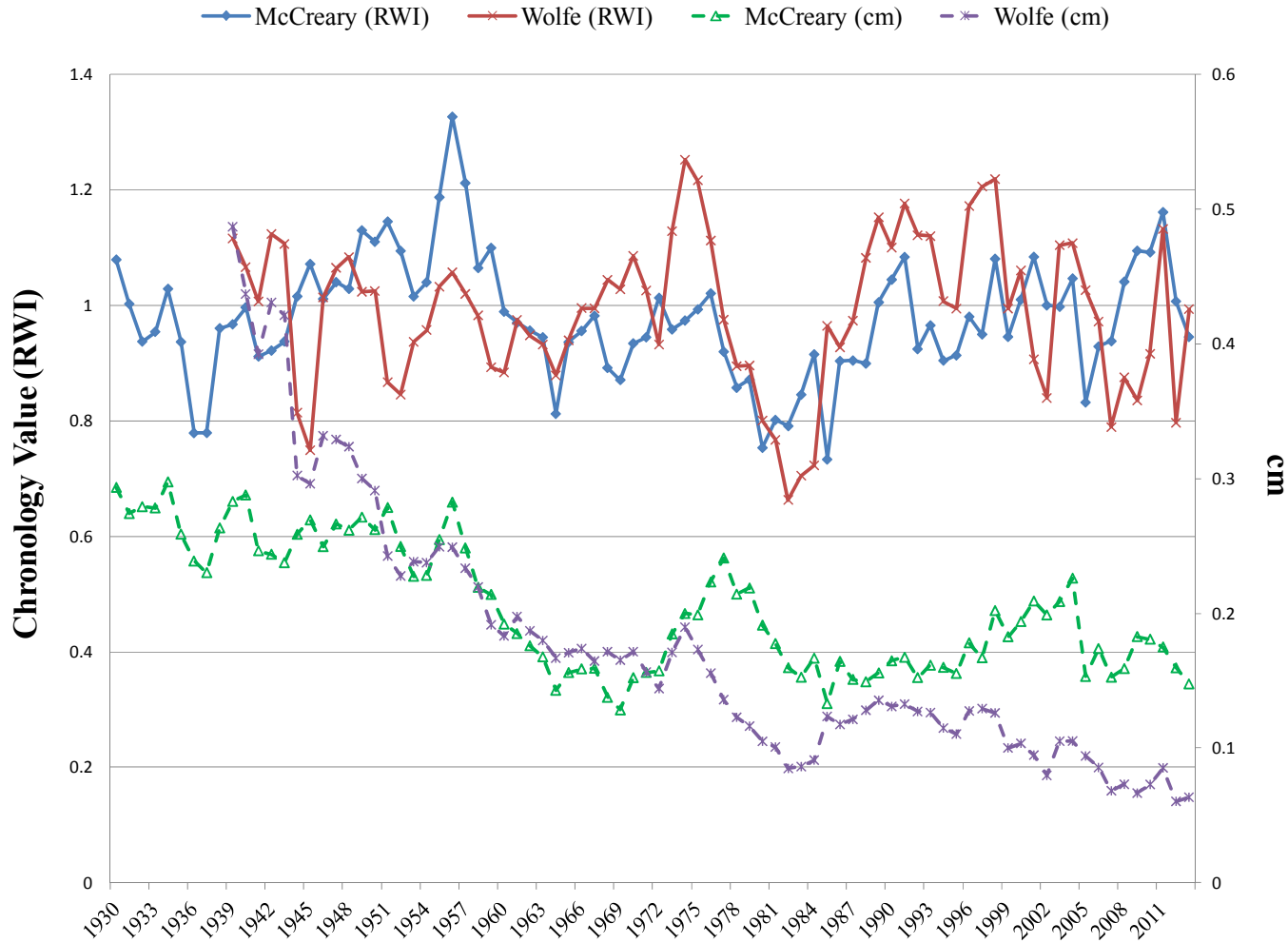


Figure 2.9: Average radial growth (RWI; cm) of *Pinus virginiana* core samples taken from sites included in the study. Solid growth trend lines are for ring width indice (RWI) values on the left axis and dashed trend lines are for measured widths (cm) on the right axis. The graph represents values for two separate methods for expressing growth of the same trees.



McCreary average tree age was 75 and median was 66 years, while Wolfe average tree age was 71 and median was 70 years. McCreary core samples exhibited a small decreasing trend in radial growth over time with periods of higher and lower growth. The cores showed steady growth between approximately 0.33 and 0.22 cm from 1919 to the late 1950s. However, radial growth dropped below 0.25 cm per year for all the years following. There was a spike in growth in the late 1970s and again in the early 2000s, but never reached productivity as high as before the late 1950s. Wolfe cores showed gradual decline in growth from pith to bark with the lowest period of growth taking place in recent years.

The increment corer method sampled trees (n=19) of different ages at both sites. As a tree ages, radial growth tends to decline with all other factors being equal (Ryan et al. 1997). The distance from photosynthetic centers in the canopy and diameter of tree boles increases over time causing ring widths to decrease in a curvilinear fashion, which must not be misinterpreted as decreases in productivity (Cook and Innes 1989). The RWI standardizes for the loss in productivity over time and gives a more representative average growth trend. McCreary RWIs had spikes in growth during the mid-1920s, 1950s and a more recent, smaller spike in growth in the late 2010s. Periods of lowest growth were in the late 1930s and 1980s. Wolfe RWI values had alternating periods of high and low growth spread throughout the trees' lives. Highest growth occurred in the mid-1970s followed by a very quick transition to the lowest chronology value in 1982. On average, both McCreary and Wolfe RWI values did not change significantly during the life of the trees and there is no apparent period of catastrophic decline in growth, but trends in periods of fast and slow growth were somewhat evident. There is no good expectation of what pollution effect looks like in tree rings other than tree-ring widths possibly decreasing in the presence of pollution (Cook and Innes 1989).

Kentucky historical precipitation and temperature data was compiled by the University of Kentucky Ag Weather Center and separated in four climate divisions. Both research sites are located in the East region climate division and data can be seen in Figure 2.10.

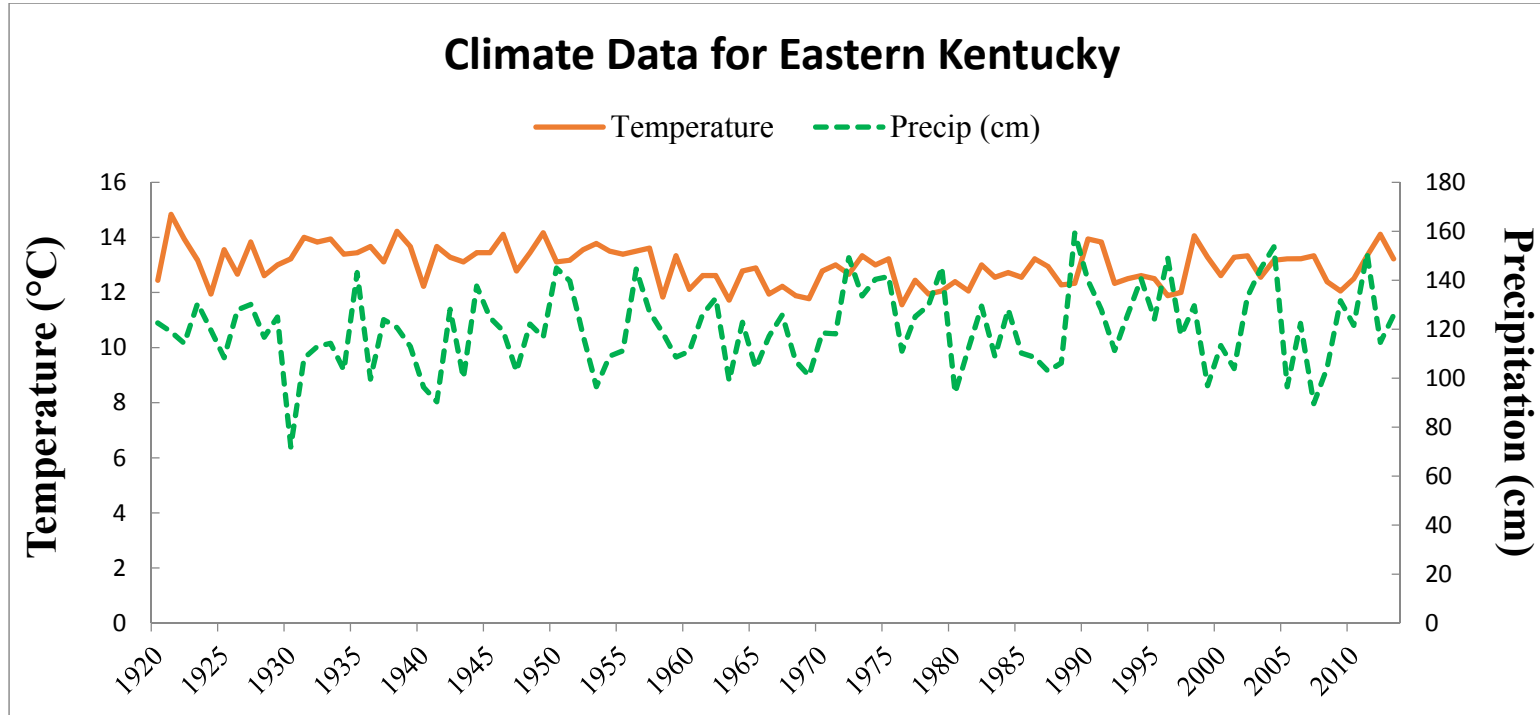


Figure 2.10: Kentucky east region average annual temperature (°C) and precipitation (cm) from the University of Kentucky Ag Weather Center ([www.agwx.uky.edu](http://www.agwx.uky.edu)).

There are possible relationships between rainfall and growth that can be seen when comparing trends. For example, years with reduced precipitation from the previous year (1998-1999, 2004-2005, and 2011-2012) resulted in reductions of tree growth between those years. A peak rainfall year in 2011 also resulted in elevated growth from the previous year. Temperature trends do not appear to have a major effect on core sample RWI values. Temperatures in Kentucky rarely reach high or low extremes, therefore may not have visible influence on tree growth.

McClenahan and Vimmerstedt (1993) discovered that ring width responses indicated periods of physiological stress from precipitation and temperature extremes and could be partly responsible for concentration levels of many elements. It can be assumed that there are other physiological and site-specific factors controlling tree growth, such as insect and disease infestation, competition, canopy gaps, forest succession and management. Radial growth, elemental storage and a relationship with soil chemistry may be an important aspect to consider as trees obtain nutrients, water and toxins via root uptake of soil solution.

#### *Tree-ring Chemical Analysis:*

There are many interrelated factors influencing elemental content in trees including climate, soil pH and composition, interception and leaching of ions in tree canopies, growth rate and redistribution of elements in tissue (Ruppert and Wischow 2006). Dendrochemical analyses have been used to investigate effects of atmospheric deposition on tree productivity (Ault et al. 1970; Baes and McClaughlin 1984; Bondietti et al. 1990; Guyette et al. 1989), but has proven to be extremely difficult (Penninckx et al. 2001) because little is known about the stability of elements to remain in rings after their formation (Hagemeyer et al. 1992). Ions may be used as indications of tree stress, relating soil and wood chemistry to growth during a specific period. Johnson et al. (1992) concluded that acid deposition increased red spruce (*Picea rubens*) sensitivity to injury, soil base cation loss, and Al mobilization. Irregular increases or decreases in ion concentration of tree-ring samples may be interpreted as soil ion mobilization from acid deposition inputs, or reduced nutrient availability from leaching after prolonged inputs, respectively (Bondietti et al. 1990). Slow tree productivity from low soil nutrient supply in the eastern US has been documented (Elias et al. 2009; Lovett et al. 2009; Huntington

2000). Extended soil exposure to acid deposition will eventually deplete ionic pools, resulting in altered ion concentrations found in trees (Shortle and Bondietti 1992). The current study does not have an extensive soil database, but soil properties from 1994 and 2012 are known, and large decreases in soil quality between sampling events was observed. Theoretically, it can be expected that degrading forest soils paired with acidic precipitation could be seen in the chemistry of tree tissue, resulting in lower nutrient concentrations and higher heavy metal pollutant concentrations.

Interpretation must be used with caution because wood tissue usually has low mineral concentration when compared to other tree organs (Woodwell et al. 1975), and elemental distribution is not homogeneous (Hillis 1987). In order to effectively analyze elemental concentrations, one must assume that conditions under which rings were formed have a consistent effect on chemical composition of the ring and that ions within rings are relatively static (Read 2009; Watmough 1997). However, this is not the case for all ions and tree species (Watmough and Hutchinson 2002). An important factor to consider is the heartiness of the tree. Some trees, such as Virginia pine, are able to thrive in nutrient poor, weathered or eroded soils (Fenton and Bond 1964). Many of the trees found at our sites are adapted to live in poor soil and may be why they are found on weathered ridges of the DBNF. The silvics of Virginia pine complicates nutrient analyses because periods of environmental stress may not be experienced by these trees. Nine genera of mycorrhizae are known to have association with Virginia pine roots (Carter and Snow 1990), allowing tree roots more surface area for nutrient uptake, thus minimizing reactions in growth to periods of stress.

There are strong differences in tree species that can determine the potential of ion binding and exchange. Hardwoods typically have a higher percentage of ray cells per wood and rays are usually two or more cells wide, allowing radial movement of ions across year rings. In contrast, conifers contain more primitive wood, possessing fewer and shorter ray cells that are usually one cell wide (uniseriate), suggesting a greater potential for reconstructing chronologies of elemental uptake and storage (Legge et al. 1984). Most cations in conifers are bound to cell walls in the xylem and are controlled by cation binding affinities of wood (Ferguson and Bollard 1976). Binding affinities generally increase with increasing valence ( $M^{3+} > M^{2+} > M^{+}$ ) and increasing ionic size

(Bondietti et al. 1989b). The magnitude sequence of concentration namely for nutrients is Ca, K > Mg, Na > P; and for trace elements it is Fe > Al > Mn > Zn, Cu > Pb > As > Cd (Chun and Hui-Yi 1992). Our results were similar to this sequence and were almost identical between sites, offering likelihood of significant results. McCreary yielded a magnitude sequence of nutrients Ca > K > Mg > P > Na; and trace elements Mn > Al > Fe > Zn > Sr > Cu > As > Cd. The only difference between McCreary and Wolfe was a reordering of Ba > Na > Zn > Fe.

Fluctuations in elemental concentrations can be strongly influenced by tree anatomy and is dependent on species (Lepp 1975). In conifers, outwardly decreasing concentrations of divalent cations have been found (Baes and McLaughlin 1986) and are attributed to decreasing binding affinities from pith to bark (Bondietti et al. 1990; Momoshima and Bondietti 1990). The heartwood-sapwood boundary has been found to be a location where elemental concentrations are highly variable (McClenahen et al. 1989; Penninckx et al. 2001). Increases in concentrations have been found on this border, and have been attributed to nutrient desorption and resorption from senescing sapwood rings (Penninckx et al. 2001). Toxic substances have been shown to be carried by rays into the heartwood where wood is no longer alive and toxins cannot affect tree health (Stewart 1966). Most trees show a decline in cation concentration with increasing tree age, which is linked to the binding exchange properties in the woody tissue diminishing with age (Prohaska et al. 1998). Radial translocation may occur in both directions and elements with high mobility are As, K, Na, Mg, and P; moderate mobility are Ca, Sr, Mn, Zn and Cu; and low mobility are Fe, Ni, Ba, Al and Cd (Cutter and Guyette 1993).

Ionic concentrations in tree tissue are reported in Figure 2.11 in mass of the elements per mass of wood sampled per chronology growth value for the given ring year increments ( $\text{mg kg}^{-1} \text{RWI}^{-1}$ ), giving concentrations as it relates to growth.

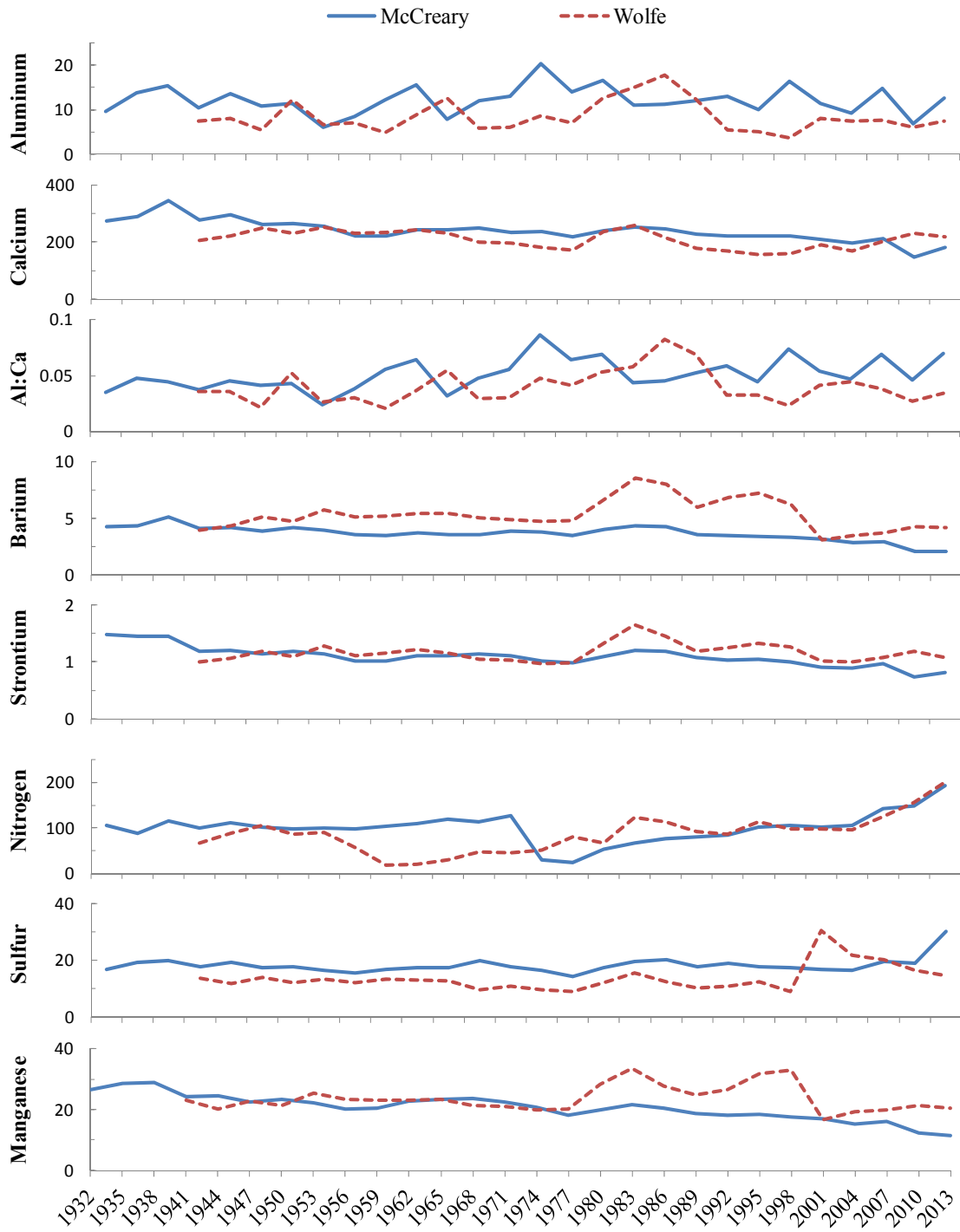


Figure 2.11: Average incremental elemental concentration reported in mass of element per mass dried wood per average tree growth ( $\text{mg kg}^{-1} \text{RWI}^{-1}$ ) from *Pinus virginiana* core samples taken from sites included in the study.

Our analysis is based on trends in cation ratios, and elemental concentrations in wood sampled at breast height, however, and does not represent a whole-tree perspective.

Aluminum may be a useful parameter to evaluate because of the potential shift in solubility as an effect of acid deposition. Al taken up by trees has low mobility in the wood and will most likely remain in rings from the year taken up (Cronan and Grigall 1995; Cutter and Guyette 1993), making it a reliable indicator. However, tree roots have the ability to exclude uptake at the root tip even when in high concentration in soil solution and may misrepresent the Al available for uptake (Smith and Shortle 1996). Aluminum was variable in concentration throughout time at both sites (Figure 2.11). McCreary Al concentrations were highest (~20 mg/kg/growth) in the early 1970s and lowest (~6 mg/kg/growth) in the early 1950s with periods of high and low concentration spread throughout. Wolfe Al concentrations were highest (~18 mg/kg/growth) in the mid-1980s and lowest (~4 mg/kg/growth) in the late 1990s. There are a few similarities in Al trends between sites and comparable concentrations indicate that they exhibit similar uptake and accumulation and perhaps have experienced similar atmospheric conditions.

Al phytotoxicity is more readily characterized by root morphology rather than tissue Al accumulation (Foy et al. 1978) and effects on tree growth may not be represented in Al concentrations. However, it is possible poor root morphology can alter nutrient and trace element uptake and result in certain trends as soil degrades. Evidence of soil nutrient pool depletion, especially of  $\text{Ca}^{2+}$ , threatens the long-term productivity of some US forest stands (Federer et al. 1989). Calcium is an important nutrient for trees because it is used for cell wall development, growth of roots and shoots, and elasticity and strength of cell walls and plants must obtain Ca from the soil (Tucker 1999). It is usually considered to have low mobility in xylem because of its high affinity for wood exchange sites (Cutter and Guyette 1993). Our research found Ca to be the most depleted soil nutrient between sampling periods at the two sites. Tree tissue concentration graphs (Figure 2.11) demonstrate gradual reductions over time. McCreary had steady concentrations (200-250 mg/kg/growth) from the mid-1950s to late 1990s and a small drop since the turn of the century. Wolfe trees also remained relatively steady through time, with lowest Ca concentrations occurring in the mid-1990s. Concentrations have

since increased to the present, which is an opposite trend of depleted soil Ca reserves between sampling periods. This finding may be explained by the susceptibility of Ca in tree tissue to dilution in years of favorable growth, where Ca is taken up in similar amounts even in years of slow growth (McClenahan and Vimmerstedt 1993). Ruppert and Wischow (2006) found concentrations of Ca, Sr and Ba tended to decrease with increasing tree-ring width. Bukata and Kyser (2008) found that during historic periods of stress, plant biomass concentrations of essential cations, including Ca, were found to increase while chemically similar non-nutrients, such as Ba and Sr did not change, indicating a physiological response within the tree rather than an actual change in elemental bioavailability.

Decrease in Ca content in the trees with time may have several explanations. Trees potentially impoverish the soil with growth, accumulating nutrients in tissue. If more Ca was taken out and leached from the system than was replaced, then it could explain the soil Ca loss at our sites as well as decreasing Ca in trees. Another explanation is that ongoing acidification of the soil will transport cations like  $\text{Ca}^{2+}$  out of the ecosystem and impoverish the soil (Åberg et al. 1990). Soil exchangeable Ca concentrations do not appear to have fallen beyond the point at which they become limiting to Virginia pine growth which, as found by Sucoff (1962), is below  $3 \text{ mg L}^{-1}$ . Therefore trees may be taking up just as much calcium as in previous years, despite the fact that Ca has leached from the system. While soil cation concentrations have declined from 1994 to 2012, no obvious decreases in RWI values and no major declines in wood Ca concentration were observed. Wolfe trees actually exhibited an increase in Ca between periods, suggesting that cations are not limiting growth (Read 2009). This may be true especially due to the use of nutrient efficient Virginia pine trees.

Evidence of Ca concentrations decreasing and Al increasing in wood during periods of high atmospheric deposition (mid 1900s) at Great Smokey Mountain National Park (GSMNP) (Baes and McLaughlin 1986) provokes opportunity to use Al:Ca ratios as indicators of high  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  levels in soil solution (Bondietti et al. 1989b). They noted as soil mineral acid anion concentrations increase, and/or BS decreases, the Al:Ca ratio in the soil solution will increase. Red spruce at GSMNP showed increases in tree tissue Al:Ca contemporaneous with large  $\text{SO}_2$  emissions from upwind sources and the



increases are consistent with soils which are sensitive to  $\text{Al}^{3+}$  mobilization by acid inputs. Tree tissue Al:Ca trends described by Baes and McLaughlin (1986) are not unique to GSMNP; in the last two to four decades, aluminum concentrations in trees growing in many other locations have also increased due to enhanced Al availability. The Al:Ca ratio in McCreary tree samples exhibit periods of high and low ratios with the largest peak beginning in the mid-1960s and peaking (0.086) in the early 1970s. Since, levels tapered off with a few periods of higher values in the late 1990s and early 2000s. Wolfe ratios peaked (0.082) in the mid-1980s and decreased to the present (Figure 2.11).

Calcium concentration trends may be misleading because radial concentrations of Ca tend to decline from pith to bark (Tendel and Wolf 1988). In general, the radial trends of the elements such as Ca, Mg, Sr, Mn, Ba and Zn are negative (Tendel and Wolf 1988; Baes and McLaughlin 1986; Orman and Will 1960). Ba and Sr act very similarly to Ca in trees because they are incorporated into woody tissue in a similar way (Momoshima et al. 1995). Ba concentrations have been found to vary with soil pH, with higher Ba in trees growing on acidic soils (Ruppert and Wischow 2006; Bukata and Kyser 2008). This suggests Ba concentrations in tree-rings may be related to soil pH and not concentrations in soil leachate. It is possible to make an estimation of Ca availability based on Sr isotopes, which has been shown to be a powerful tool in understanding environmental changes (Åberg et al. 1990). Ba and Sr concentrations in tree-rings from McCreary and Wolfe show very similar trends (Figure 2.11). McCreary exhibits slowly decreasing concentrations of both Ba and Sr over time with a small increase in the early to mid-1980s. Wolfe has steady concentrations of both ions, and a spike was seen in early 1980s and again in mid-1990s. In general, ion concentrations of Ba, Sr and Ca are similar for each site and may provide evidence that the three ions act similar in the soil environment and are taken up and stored by vegetation in similar ways.

Metals such as Mn have also been used as bioindicators in tree-rings. Sites with low soil pH generally have higher Mn concentrations from pith to bark (Bukata and Kyser 2008). This trend could be due to exhaustion of available Mn from a limited soluble Mn pool within the rooting depth spurred from long-term leaching. Based on its availability strongly increasing with decreasing pH, Mn concentration in wood has been proposed as a reliable indicator of variations in soil pH (Guyette et al. 1992). It is

important to observe trends in Mn over longer timeframes because it exhibits high radial mobility (Cutter and Guyette 1993; Penninckx et al. 1999). Tree-ring Mn concentrations from McCreary and Wolfe follow very similar trends as Ba and Sr (Figure 2.11). This could be evidence of pH changes in soils, possibly from effects of acid deposition. Wolfe concentrations indicate possible shifts in soil pH during the early 1980s and the mid-1990s, however, without historical soil pH values; it is difficult to determine the relationship between trace elements and soil acidity.

Nitrogen is a necessary macronutrient for trees and contributes to growth, structure, metabolism, and is one basic component of chlorophyll and the process of photosynthesis (Tucker 1999). Most cations have a limited role in living cells, but nitrogen concentrations are usually highest near the cambium where living cell volumes are greatest (Bondietti et al. 1989a). Nitrogen has increased in both site tree core samples from the early 1970s to 2013 (Figure 2.11), similar to increased emission rates for Kentucky. Tree-ring concentrations may reflect deposition concentrations, but could be controlled by other forces. Radial N distribution is not well documented, but it is known that N is often the limiting nutrient for forest growth in Appalachian forests and increased deposition probably has a fertilizing effect on forest growth (Solberg et al. 2004).

Sulfur (S) is an essential nutrient for tree growth and development and is found in amino acids that make up proteins (Tucker 1999). It is difficult to observe trends in S concentrations of tree ring samples and S is highly mobile in sapwood (Cutter and Guyette 1993). The mid-1980s shows small spikes in S for both sites, which was the only period where S trends are comparable (Figure 2.11). McCreary had a large spike in the last three years of growth while Wolfe saw a spike at the turn of the 21<sup>st</sup> century followed by reduction closer to the samples' normal level. Reduction of S seen in NADP atmospheric data since mid-1980s is not evident in ring samples at either site. The high concentrations in more recent years at both sites could be from accumulation of S in solution by the release of adsorbed S, but more likely is due to the mobility of S across xylem rings.

Our analysis does not reveal any trends in tree response to acidic input concentrations. Tree growth appears to remain “normal” in recent decades even with reduced acid deposition. This could be a result of several ecosystem controls including

biotic control, or by reductions in soil buffering and nutrient availability with time. Still missing is a useful understanding of how ambient levels of various air pollutants affect the soils and the growth of different tree species under natural forest conditions over time.

**Conclusion:**

Sampling from eastern Kentucky atmospheric monitoring stations revealed improvements in precipitation chemistry between our study intervals P1 and P2, including pH, EC,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Reduced concentrations of acid anions during that time may be the result of controls on emissions set by the amendments of the CAA. Soil from the two sites studied in the DBNF revealed changes in soil physicochemical and mineralogical properties between P1 and P2. Evidence of soil weathering, leaching of base cations and slight acidification was apparent at both sites, but loss of base cations was more evident at McCreary than Wolfe. Soil solution pH remained stable between periods and solution was chemically similar for all measured parameters, therefore definite conclusions cannot be drawn. However, analysis revealed that there are subtle changes in soil solution chemistry trends. Solution data suggested that both periods experienced sporadic times of high acid anion inputs into solution and decreasing pH. Soils, solution and mineral solubility at McCreary and Wolfe sites suggest a change has recently occurred in the soils. The soils are in a period of transition from having the ability to buffer against acid inputs to acid sensitive and depleted of base cations. It is evident that the system is still in flux, which would warrant continued monitoring in the near future to detect if and when nutrient depletions become a detriment. Monitoring outcomes would allow for decisions to be made regarding how intensive future management should become. If depletion continues in the future, it is expected that a change in vegetation will follow. Tree ring growth and chemical analysis was used to explore the state of the ridge-top forest stands' health based on differences in annual climate and the recent changes observed in soils, but analyses did not provide enough information to determine any relationships. Therefore, to assess the long-term effects of acid deposition on soils and forests atop ridges in the DBNF further monitoring of soils and soil solution is important and additional tree-ring methods must be developed.

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## Vita

Tyler M. Sanderson was born in Chapel Hill, NC, and raised in Cincinnati, OH, where he attended Turpin High School. He received a B.S. in Agricultural Economics from the University of Kentucky. Following graduation, he was a business and social entrepreneurship volunteer with the Peace Corps in the Republic of Georgia. Upon early program cancellation, Tyler worked as a volunteer for AmeriCorps and the Student Conservation Association as a New Hampshire Conservation Corps member. He returned to Kentucky and worked as a research assistant in a soils laboratory in the College of Agriculture, Food and Environment, which directed his path to the Department of Forestry. As a graduate student he earned a Master certificate in Stream and Watershed Science and the chapters of this thesis will be submitted as manuscripts.