DETERMINATION OF CALCIUM, MAGNESIUM, AND ALUMINUM IN RED SPRUCE (*Picea rubens*) FOLIAGE AND SURROUNDING SOIL FROM THE GREAT SMOKY MOUNTAINS NATIONAL PARK AND RICHLAND BALSAM USING ICP-OES

By

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Abstract

DETERMINATION OF CALCIUM, MAGNESIUM, AND ALUMINUM IN RED SPRUCE (*Picea rubens*) FOLIAGE AND SURROUNDING SOIL FROM THE GREAT SMOKY MOUNTAINS NATIONAL PARK AND RICHLAND BALSAM USING ICP-OES

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The southern Appalachian spruce-fir forest is a unique ecosystem in North America which consists of red spruce (*Picea rubens*) and Fraser fir (*Abies Fraseri*). Found at elevations above 4500' and inhabiting 26,609 hectares in North Carolina, Tennessee and Virginia, these boreal forests are remnants of the last ice age.

The co-dominant Fraser fir has been enduring an exotic predator since the 1960s, the balsam woolly adelgid (*Adelges picaea*), which has caused heavy mortality. Bruck and Robarge have reported a decline of the red spruce in the southern Appalachians and attributed the decline to acid deposition. Regional fossil fuel combustion accelerates acid deposition (SO_4^{2-} and NO_3^-). As the natural buffering capacity of the soil is exceeded, nutrients such as calcium and magnesium combine with the sulfates and nitrates and become less available to root uptake. It is the increase in mobility of the nutrients calcium and magnesium and the toxic aluminum that has been adversely affecting the red spruce. By determining Ca, Mg, and Al in soils and foliage, a characterization of the effects of acid deposition on forest health can be achieved. Sample sites include Balsam High Top, Clingman's Dome, Double Spring Gap, Mt. LeConte, Mt. Sterling, and Spruce Mountain in the Great Smoky Mountains National Park (NC, TN), and Richland Balsam on the Blue Ridge Parkway (NC).

Foliar samples were collected from 30 red spruce at each site. The red spruce was then divided into three categories by height: 10 mature (above 4 meters), 10 saplings (2 to 4 meters), 10 seedlings (less than 2 meters). A soil sample was also collected for each tree. The samples were digested and analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). A statistical (*t*-test) analysis was performed on the results.

Due to the large standard deviations found at each sample site, there is insufficient evidence to indicate that elevation or geography affects the rate of acid deposition in the spruce-fir forest of the southern Appalachians. There was also little significant evidence suggesting that regional sulfur dioxide and oxides of nitrogen emissions affect the health of the red spruce.

INTRODUCTION

The Spruce-Fir Forest

The red spruce (*Picea rubens*) is a medium-sized conifer with a native range extending along the Appalachian Mountains of North America and into Canada. In southeastern Canada and northeastern United States, the red spruce can be found at elevations from near sea-level up to 1370 m (4,500 ft) and is it associated with many forest types (1).

At the southern extent of its native range, the red spruce is a co-dominant species with the Fraser fir (*Abies fraseri*) in the spruce-fir forest ecosystem. It has a narrow distribution in the Appalachian Mountains of Virginia, Tennessee and North Carolina and also corresponds to the limited native range of the Fraser fir.

The spruce-fir forests of the southern Appalachian Mountains are remnants of the last ice age which occurred approximately 18,000 years ago. During this cooling, the boreal forests now found in Canada migrated to lower latitudes as they were more adapted to the cooler climate. As the planet has warmed, these forests have receded to the high peaks of the southern Appalachians where the climate emulates that of higher latitudes (2). Currently, the southern Appalachian spruce-fir forest has retreated to elevations above 1676 m (5,500 ft) but can be found as low as 1372 m (4,500 ft) on north slopes and protected coves (3). These elevations receive 1900 to 2540 mm of precipitation per year and maintain an average summer temperature below 16 °C (2). With a more humid atmosphere and greater rainfall during the growing season, the red spruce of the southern Appalachians exhibit their maximum development (4). The spruce-fir ecosystem of the southern Appalachians is comprised of approximately 26,609 hectares and can be found within seven regions: 74% in Great Smoky Mountain National Park (NC, TN), 11% in the Black Mountains (NC), 10% in Balsam and Plott Balsams (NC), 2% in Roan Mountain (NC, TN), 1% in Grandfather Mountain (NC), and 2% in Mount Rogers (VA) (5).

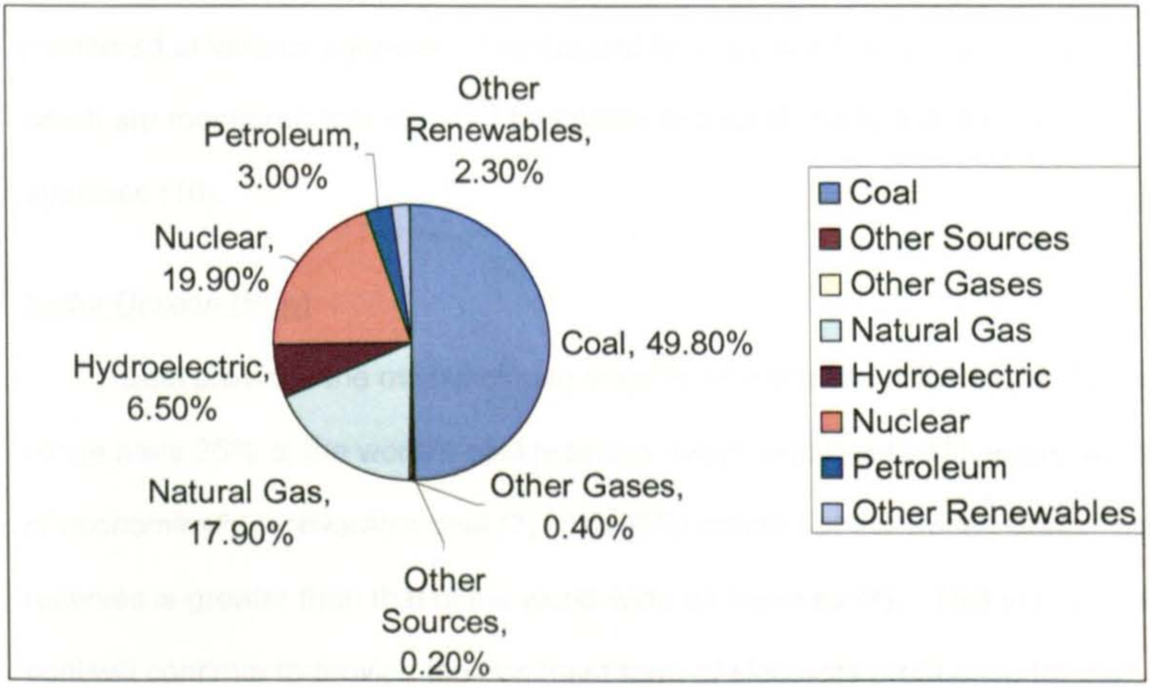
During the latter part of the 20th century, the spruce-fir forests in the United States have been declining. Since the 1960s, the balsam wooly adelgid (BWA) (*Adelges picaea*) has caused a great decline in the mature Fraser fir population of the southern Appalachians (3, 4).

Acid Deposition

In the United States, fossil fuels have been the dominant source of energy. The use of fossil fuels as an energy source has been accelerating for the past 150 years, as demand has also increased. With approximately 5% of the world's population, the U.S. consumes approximately 23% of the world's energy (6). With fossil fuel combustion at such rates, the United States, along with other high energy use countries, has potentially accelerated acid deposition beyond the buffering capacity of natural systems. The voluminous combustion of coal as a source of electricity and oil for transportation also emits many adverse byproducts into the atmosphere where they undergo chemical reactions and are redeposited. See Figure 1 for the electricity production by source in the U.S (7).

Two significant byproducts of fossil fuel combustion, sulfur dioxide (SO_2) and oxides of nitrogen (NO, NO_2) lead to acid precipitation. These compounds form their corresponding acids, sulfuric, sulfurous, nitrous and nitric acid, which, when deposited, decrease soil and surface water pH and leech nutrients from the soil column. Acid precipitation adversely affects nutrient levels in forest ecosystems which can lead to a decline of vegetation and aquatic life.

Figure 1
United States Electricity Production by Source (2004)



In Germany and the Northeastern United States, acid precipitation has been associated with the decline of the Norway spruce and red spruce, respectively, since the 1970s (8). In 1984, a decline in red spruce health was recorded at Mt. Mitchell, North Carolina, in the southern Appalachians (9). Acid deposition is currently being investigated as the primary cause of Norway and red spruce decline. There is no evidence of spruce decline due to predation, as in the Fraser fir.

Sources of SO_2 and NO_x

With the creation of the Clean Air Act, limits and reduction goals were placed on many of the major air pollutants. The Clean Air Act defined NO_x and SO_2 as criteria air pollutants. Criteria air pollutants are required to comply with two types of limits. The first limit involves ambient air concentration levels monitored at various agencies. The second limit is placed on actual emissions which are monitored and reported by utilities and local, state, and federal agencies (10).

Sulfur Dioxide (SO_2)

Coal provides the overwhelming majority of electricity in the United States as we have 25% of the world's coal reserves, which equates to 450 years' worth of economically recoverable coal (7). The BTU content of the United States' coal reserves is greater than that of the world-wide oil reserves (7). This implies that coal will continue to provide the dominant form of electricity production for the foreseeable future. See figure 1 for total electricity production by source in the United States.

There are two primary types of coal used in electricity production in the U.S., bituminous and anthracite. Bituminous coal is cheaper and easier to recover, however it is considered sour due to this relatively higher sulfur content. Anthracite coal is more expensive to recover. This "sweet" coal is a cleaner fuel source which contains less sulfur. The national average of sulfur in coal is 1% by weight (7). In the combustion process, sulfur reacts with oxygen to give SO_2. There are systems in place to reduce SO_2 emissions from coal combustion such as wet scrubbers; however, they do not operate at 100% efficiency (10).

According to the EPA, in 2003, 67% of SO_2 emissions originated from coal-fired power plants, 18% from other industries, 5% from vehicles, 3% from metal processing and 7% from other sources. In 1970, 31.2 million tons of SO_2 were emitted nationwide (10). In 2003, through legislative reductions and improvements in technology, total emissions have been reduced to 15.8 tons. While these nationwide reductions are mitigating acid deposition, sulfur dioxide emissions are concentrated in the eastern United States, primarily due to the vast coal reserves located in West Virginia, Kentucky and Pennsylvania. Forty-five of the top 50 SO_2 emitting point sources reside east of the Mississippi river (11). The overwhelming concentration of SO_2 emitters located in the east provides a source for accelerated regional sulfate deposition.

Oxides of Nitrogen, NO_x

NO_x refers to NO_2 and NO, both compounds are byproducts of combustion. During the year 2003, the EPA announced that 55% of NO_x emissions came from motor vehicles, 22% from industrial, commercial and residential sources, 22% from utilities and 1% from other sources (12).

Before the 1970s, the pollutants derived from fossil fuel combustion were viewed as an acceptable consequence. With the creation of the Clean Air Act, limits and reduction goals were placed on NO_x and SO_2. As time has progressed, stronger environmental laws and better technology have reduced the adverse effects of fossil fuel combustion.

Due to the inability to control non-point source pollution, the reduction in NO_x emissions is not as significant at SO_2. In 1970, 26.9 million tons of NO_x were emitted. Through reductions legislated by the Clean Air Act, by 2003, 20.5 tons of NO_x were emitted (10).

Sulfate & Nitrate Deposition

The following are two simplified mechanisms for the atmospheric conversion of SO_2 and NO_x to sulfates and nitrates, respectively (13).

$$2\,\mathbf{SO_2} + O_2 \rightarrow 2SO_3 \quad (1)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (2)$$

$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + \mathbf{SO_4^{2-}} \quad (3)$$

$$\mathbf{NO} + O_3 \rightarrow O_2 + NO_2 \quad (1)$$

$$\mathbf{NO_2} + OH^\bullet + M^* \rightarrow HNO_3 + M^* \quad (2)$$

$$HNO_3 + H_2O \rightarrow \mathbf{NO_3^-} + H_3O^+ \quad (3)$$

*where M represents a 'third body' required to stabilize the product (N_2 or O_2)

Sulfates and nitrates are deposited via wet, dry and cloud/ fog deposition. Wet deposition can be various forms of precipitation including rain and snow. Dry deposition involves the adsorption of compounds to particulates traveling by wind. Cloud/fog deposition is a significant mode of deposition at sites above the cloud base of approximately 1800 meters, but can also occur during fog episodes at lower elevations (14). The elevation of forest sites has a significant impact on the amount of cloud/fog deposition.

Saxena and Lin (14), studying on Mt. Mitchell, NC, found that direct cloud deposition was 2 to 5 times that of wet deposition and that cloud episodes averaged 258 days per year. Saxena and Lin also found that sulfate deposition accounted for 65% of the acidity in cloud water, which contributed 2 to 3 times that of nitrates.

According to an air quality pamphlet published by the Great Smoky Mountains National Park, high elevation sites receive over 100 pounds of sulfates per acre annually. (15)

Bruck and Robarge (9), at Mt. Mitchell, NC, found that above 1935 m, there was a four-fold decrease in the annual ring growth of red spruce between 1960 and 1990, compared to lower elevations.

These findings suggest that high elevation sites are likely to be the first to be affected by acidic deposition, due to the frequency of precipitation events, as well as the incidence of cloud/fog deposition.

Johnson, et al. (16) developed a hypothesis for the mechanism of red spruce decline by acidic deposition. Acidic deposition increased through the middle of the 20th century due to increased fossil fuel emissions. Oxides of sulfur and oxides of nitrogen (SO_x, NO_x) deposit the corresponding acidic anions (SO_4^{2-} and NO_3^-). These anions affect soil chemistry by increasing cation mobility. These cations include calcium (Ca^{2+}), magnesium (Mg^{2+}) and aluminum (Al^{3+}). Bondietti, et al. has reported that cation mobility reduces nutrient availability to red spruce and Fraser fir by leaching the nutrients away from the root zone (17). Saxena and Lin reported that the peaks of the Black Mountains were exposed to high quantities of acidic fog. Red spruce located amongst these peaks exhibited lower foliar calcium and magnesium than those at lower sites, indicating that peaks are more vulnerable and the first affected by acidic deposition (14).

Soil Chemistry

Trees, along with other vegetation exchange protons with nutrients as free cations that are adsorbed to negatively charged clay particles; these compounds include potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}). Monovalent cations (K^+) and divalent cations (Mg^{2+}, Ca^{2+}) act as natural buffers to naturally deposited sulfates and nitrates; however, anthropogenic sulfates and nitrates (anions) affect soil chemistry. Upon initial deposition, sulfates and nitrates act as fertilizers which increase growth; however, as time progresses, the anions begin to exceed the buffering capacity of the soil. The buffering capacity is exceeded when the deposition of acidic anions exceeds the natural ability of monovalent and divalent cations to neutralize (13). The buffering capacity is also hindered when accelerated deposition of acidic anions combine with cations to form soluble products which are leached out of the soil, out of the reach of fine root hair which occupy the shallow soil horizons. When buffering capacity is exceeded, trivalent aluminum becomes mobilized due to the lack of monovalent and divalent cations. Aluminum is toxic to plants and is normally bound too tightly to soil to be available to roots. Soil health can be quantified by analyzing the calcium to aluminum ratios. This ratio between divalent and trivalent cations is a general indicator of soil health because it allows soils of various compositions to be compared.

Hypotheses

The goal of this thesis project was to characterize high elevation sites in the Great Smoky Mountains National Park and Richland Balsam on the Blue Ridge Parkway by analyzing metals in red spruce foliage and surrounding soil. The metals chosen for this project include calcium (Ca^{2+}), magnesium (Mg^{2+}) and aluminum (Al^{3+}) analyzed by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). These metals were used by Bondietti, et al. (12) to determine if acid deposition reduced nutrient availability and results in a decline of spruce-fir forest health. A secondary goal of this project is to obtain trace metals data that can be compared with data collected by our research group in the mid 1990s.

We hypothesize that the sites located near the Northern and Eastern boundaries of the park will exhibit lower nutrient levels and higher aluminum levels, due to their proximity to regions in which many coal-fired power plants operate. Although all of our sample sites are above the cloud base of 1800 m, we also hypothesize that the sites higher in elevation will exhibit lower nutrient levels and higher aluminum levels based on the frequency of cloud deposition.

EXPERIMENTAL

Sample Sites

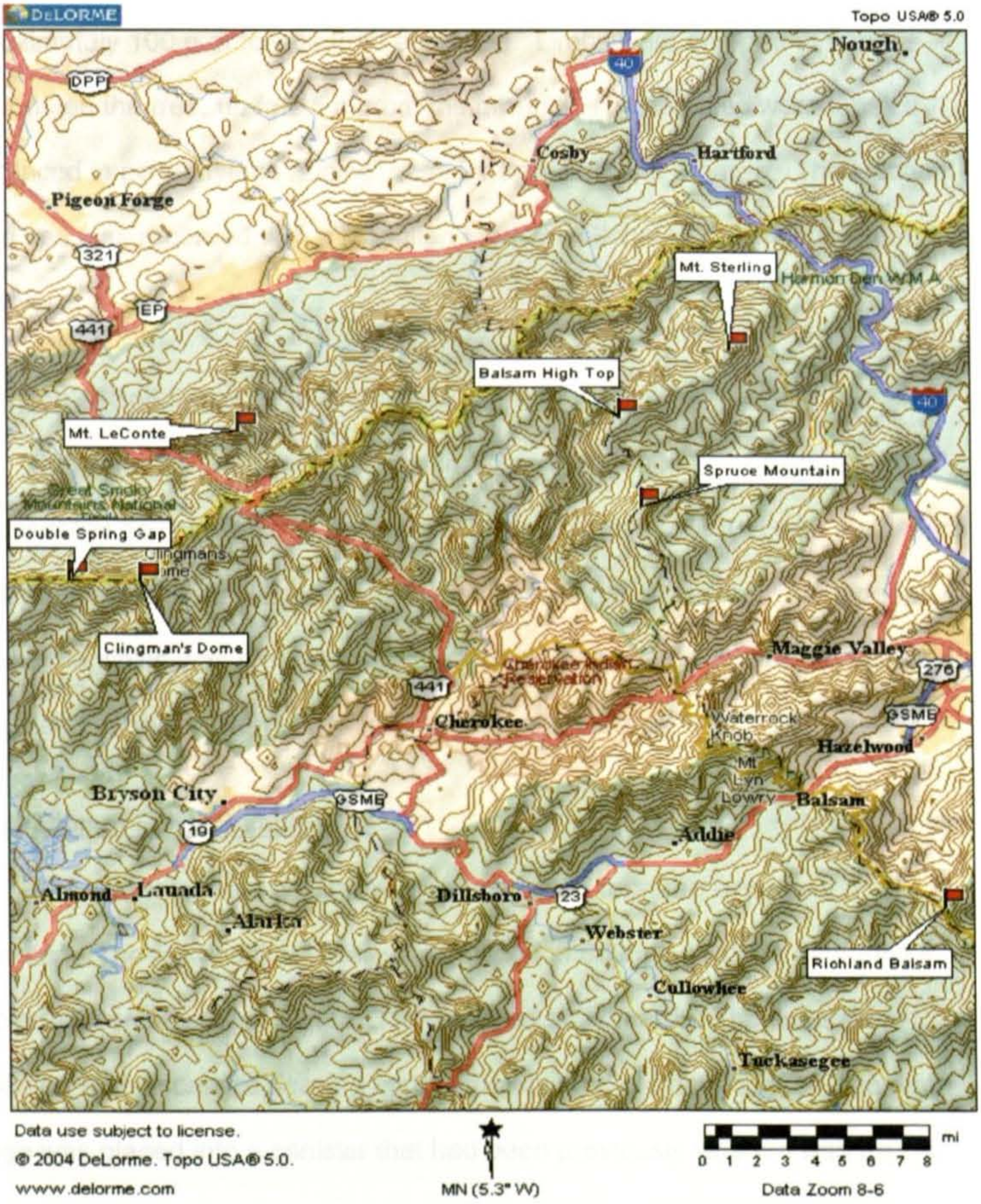
Seven sites were selected for this thesis project. Six sites reside within the Great Smoky Mountains National Park; the seventh site is Richland Balsam, at mile marker 431 on the Blue Ridge Parkway. The criteria used in selecting the sample sites include:

- spruce-fir forest
- a north-west slope aspect
- within 10 km of the trailhead
- broad distribution
- elevations from 5500 ft – 6600 ft

Table 1
Sample Site Coordinates, Elevations, Owners and Aspects

Site	Slope	Elevation (ft)	Latitude	Longitude	Owner
Mt. LeConte	NW	6593	N35° 39' 9.39"	W83° 26' 7.73"	GSMNP
Mt. Sterling	NW	5811	N35° 42' 8.80"	W83° 07' 20.78"	GSMNP
Clingman's Dome	NW	6625	N35° 33' 46.50"	W83° 29' 55.20"	GSMNP
Spruce Mountain	NW	5560	N35° 36' 30.26"	W83° 10' 44.25"	GSMNP
Balsam High Top	NW	5683	N35° 39' 56.05"	W83° 11' 46.25"	GSMNP
Double Spring Gap	NW	5505	N35° 33' 54.84"	W83° 32' 34.60"	GSMNP
Richland Balsam	NW	6367	N35° 22' 3.23"	W82° 59' 25.37"	BRP

Figure 2
Map of Sample Sites



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Collection of Foliar Samples

Foliar samples were collected using stainless steel pruning shears to cut approximately 100 g of foliage from each tree. Limbs were snipped at various locations on the tree, up to 2.5 m from the ground. The samples were labeled and placed in polyethylene "Ziploc" bags for transport and storage. The location of the tree was recorded with a Magellan Meridian Global Positioning System Receiver.

Collection of Soil Samples

Soil samples were collected within 3.3 m from the base of each tree to represent the soil available to the root system. Soil was collected with a stainless steel hand trowel. Leaf litter was displaced to obtain a 10 cm^2 by 15 cm deep soil sample which was removed with the trowel. The samples were then labeled and placed in polyethylene bags for transport and storage.

Preparation of Foliar Samples

The current year's new growth was removed from the limbs and discarded. The foliated limbs were then placed in 600 mL beakers and dried in a Precision Economy Oven at 110°C for a period of 24 hours. The limbs were defoliated and discarded, leaving approximately 10 g of dried foliage. The dried foliage was placed into a canister that had been previously washed with an Alconox solution, rinsed with NANOpure filtered water and dried. The canister was placed in a Spex mixer/mill 8000 and milled until fully homogenized (typically 5 to 30 minutes).

Preparation of Soil Samples

Soil samples were air-dried for approximately one month. Once dried, they were sieved in No.10, 2 mm and No.18, 1 mm sieves. The sieves were Alconox washed, rinsed with NANOpure filtered water and oven dried U.S.A. Standard Testing Sieves made by Fisher Scientific. The dried, homogenized soil was placed in polyethylene Ziploc bags for storage.

Soil and Foliar Digestion Procedure

The soil and foliar samples were wet-digested using the same procedure which was given by Embrick (18).

The samples were weighed out to 0.2000g ± 0.01 g in triplicate with a stainless steel spatula that was washed with a 1% Alconox solution. The samples were placed into 16 X 150 mm borosilicate disposable culture tubes and 5 mL of concentrated nitric acid (Fisher A200-c212) was added using a mechanical pipette. The solution was vortexed and heated in a proprietary heating block at 110°C for 2 hours. The solution was cooled to room temperature and 0.5 mL of 30% H_2O_2 (Fisher, BP2633-500) was added. The solution was heated at 110°C for 1 hour.

The digested samples were transferred to 100 mL volumetric flasks and diluted with NANOpure water from a Barnstead NANOpure water purification unit. The soil samples were gravity filtered to remove the undigested particles.

All glassware was washed with a 1% Alconox solution, rinsed with distilled water, washed in a 20% nitric acid solution and rinsed with NANOpure water.

Standards Preparation

The calcium and magnesium and aluminum standards were prepared using commercially purchased 1,000 µg/mL stock solutions.

Instrumental Analysis

The samples were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) Perkin-Elmer Optima 4100 DV. ICP-OES can qualitatively and quantitatively determine multiple elements simultaneously with detection limits between 1-10 ppb. ICP affords a rapid multi-elemental analysis with little chemical interference due to the inert nature of the argon environment (19).

Samples were aspirated and nebulized. The nebulized sample is carried by argon gas through a heated tube, where the solvent evaporates. The stream then passes through a refrigerated zone in which solvent condenses and is removed. The sample reaches the plasma flame as an aerosol of dry, solid particles (19).

Argon gas was fed into the inlet system of the plasma and was ionized by a 27 MHz Tesla coil that created a radio frequency field (19). The plasma produces temperatures between 6,000 -10,000°C, as chemical compounds enter the plasma, their bonds are broken and the atoms become electronically excited. As the atoms return to their ground state, they emit unique wavelengths of light which can be qualitatively detected. The intensity of the unique wavelength(s) can then be quantified.

The detector in the ICP-OES used in this experiment was a charge-coupled device (CCD). A CCD is a solid-state detector exhibiting high sensitivity; two monochromators were oriented at 90° to obtain high resolution (19).

Analytes, Wavelengths and Conditions

Wavelengths were chosen based on the best intensity and lowest detection limit for the species to be analyzed. The conditions of the ICP-OES were given in Embrick (18). Refer to Table 2 for the selected analytes, wavelengths and conditions used in this analysis.

Table 2
Selected Analytes, Wavelengths and Conditions

Analyte	Wavelength
Calcium	317.933
Calcium	315.887
Calcium	396.847
Aluminum	309.271
Aluminum	308.215
Aluminum	394.401
Magnesium	280.271
Magnesium	279.553
Magnesium	279.077
Radio Frequency (watts)	1300
Pump Rate (mL/min)	1.70
Aux. Gas Flow (L/min)	0.2
Nebulizer Gas Flow (L/min)	0.80
Plasma Gas Flow (L/min)	15
View Distance	15.0
Plasma View	Axial

RESULTS AND DISCUSSION

Maps containing the approximate sample locations can be found in Appendix 1. Concentration values, coordinates, standard deviations for individual samples can be found in Appendix 2. The Site ID, Elevation and population sizes for each sample site can be found in Table 3.

This chapter will be divided into five sections: mean foliar concentrations at each site, mean soil concentrations at each site, comparison of seedlings, saplings, and mature samples at individual sites, soil Ca:Al ratios at each site, and comparison to previous data.

Table 3
Site Key and Sample Populations

SITE ID	SITE	Elevation (ft)	SOIL POP.	FOLIAR POP.
BT	Balsam High Top	5683	12	30
CD	Clingman's Dome	6642	17	30
DS	Double Spring Gap	5505	11	29
LC	Mt. LeConte	6593	12	30
MS	Mount Sterling	5811	10	30
RB	Richland Balsam	6367	12	30
SM	Spruce Mountain	5560	10	30

Considering the mean concentration of all red spruce (*Picea rubens*) at each site, higher elevation sites LC, CD and RB should be most affected by acid deposition, in that soil and foliar Ca and Mg levels should be the lower than the lower elevation sites. The soil Ca:Al ratio and foliar and soil Al concentrations should be higher than the low elevation sites. Richland Balsam should be the healthiest high elevation site because it is the farthest south. For the low elevation sites, Spruce Mountain should be the healthiest site as it is farthest south. Mt. Sterling should be the unhealthiest site as it is the most north-eastern sample site. Double Spring Gap should exhibit the second unhealthiest concentrations because it resides on the main ridge of the Great Smoky Mountains. Balsam High Top should exhibit the second healthiest concentrations as it is south of the main ridge.

Sample Sites from hypothesized healthiest to unhealthiest:
Spruce Mountain, Balsam High Top, Double Spring Gap, Richland Balsam, Mt. Sterling, Clingman's Dome, and Mt. LeConte

In the comparison of foliar concentrations of seedlings versus saplings versus mature red spruce at individual sites, we expect to see the seedlings the most affected by acid deposition as they are the most vulnerable. The mature trees should be least affected by acid deposition. Trends in seedling, sapling and mature tree foliar concentrations should follow the same order of overall health previously discussed.

Figure 3
Mean Foliar Ca Concentrations of Red spruce at All Sample Sites

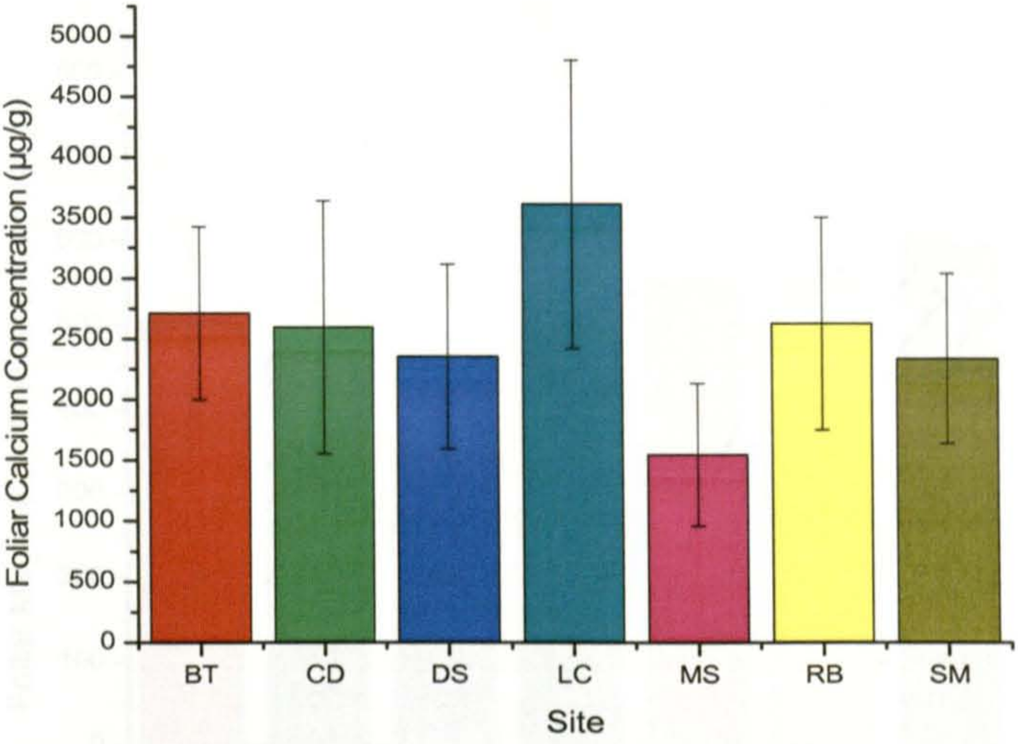


Figure 3 Key - BT = Balsam High Top, CD = Clingman's Dome, DS = Double Spring Gap, LC = Mt. LeConte, MS = Mt. Sterling, RB = Richland Balsam, SM = Spruce Mountain

Comparison of mean foliar calcium concentrations shows that all sample sites are statistically the same with the exception of Mt. LeConte and Mt. Sterling. Elevation and geography does not seem to affect foliar Ca levels. Mt. Sterling and Mt. LeConte were hypothesized to have the lowest foliar Ca due to their locations in the park.

Figure 4
Mean Foliar Mg Concentrations of Red spruce at All Sample Sites

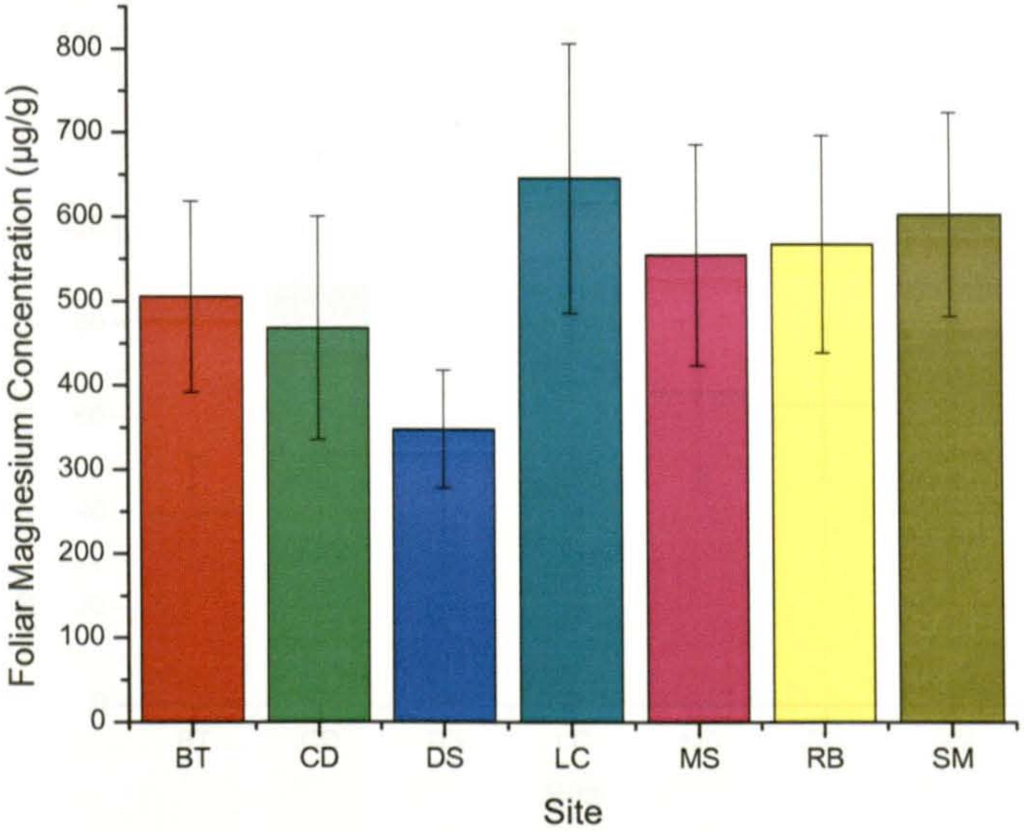


Figure 4 Key - BT = Balsam High Top, CD = Clingman's Dome, DS = Double Spring Gap, LC = Mt. LeConte, MS = Mt. Sterling, RB = Richland Balsam, SM = Spruce Mountain

Comparison of mean foliar magnesium concentrations shows that all sample sites are statistically the same. Elevation does not seem to affect foliar Mg levels. Double Spring Gap, at 5505 ft, was hypothesized to exhibit higher Mg concentrations than higher elevation sites due to the less frequent cloud deposition episodes.

Figure 5
Mean Foliar Al Concentrations of Red spruce at All Sample Sites

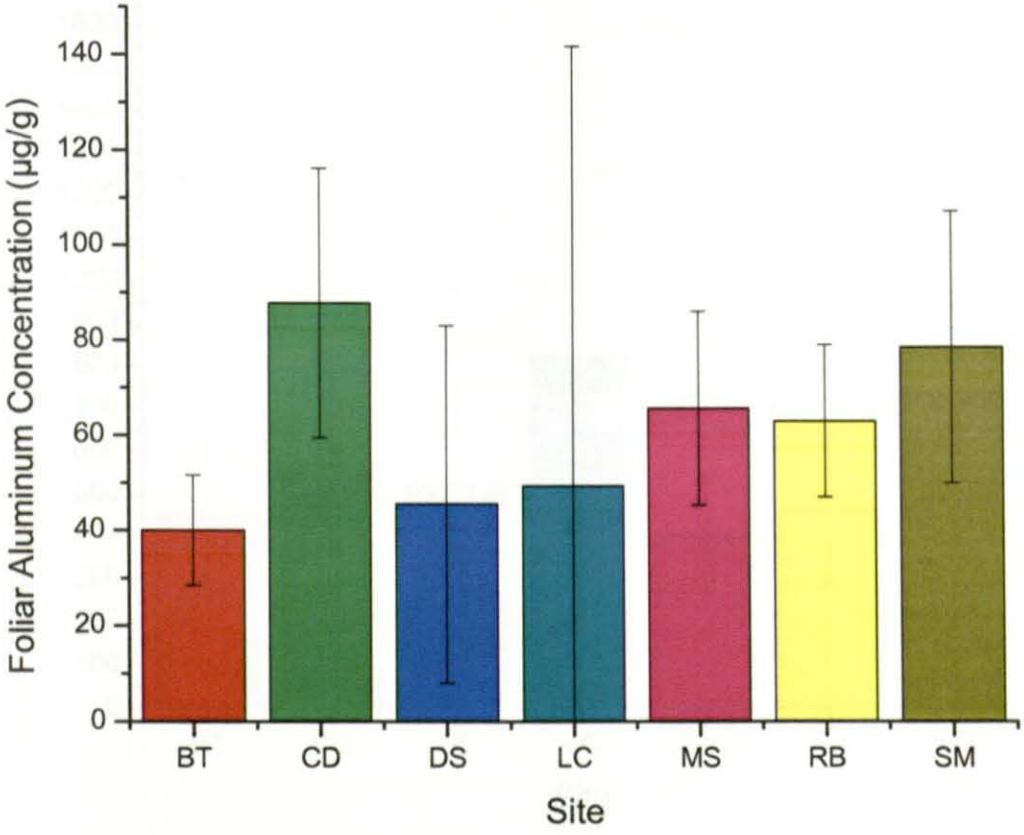


Figure 5 Key - BT = Balsam High Top, CD = Clingman's Dome, DS = Double Spring Gap, LC = Mt. LeConte, MS = Mt. Sterling, RB = Richland Balsam, SM = Spruce Mountain

A comparison of foliar Al concentrations at all sample sites indicates all sample sites are statistically the same. The high standard deviation at Mt. LeConte is due to several sample results with concentrations of 0.6 ppm up to 167 ppm.

Figure 6
Soil Ca Concentrations of Red spruce at All Sample Sites

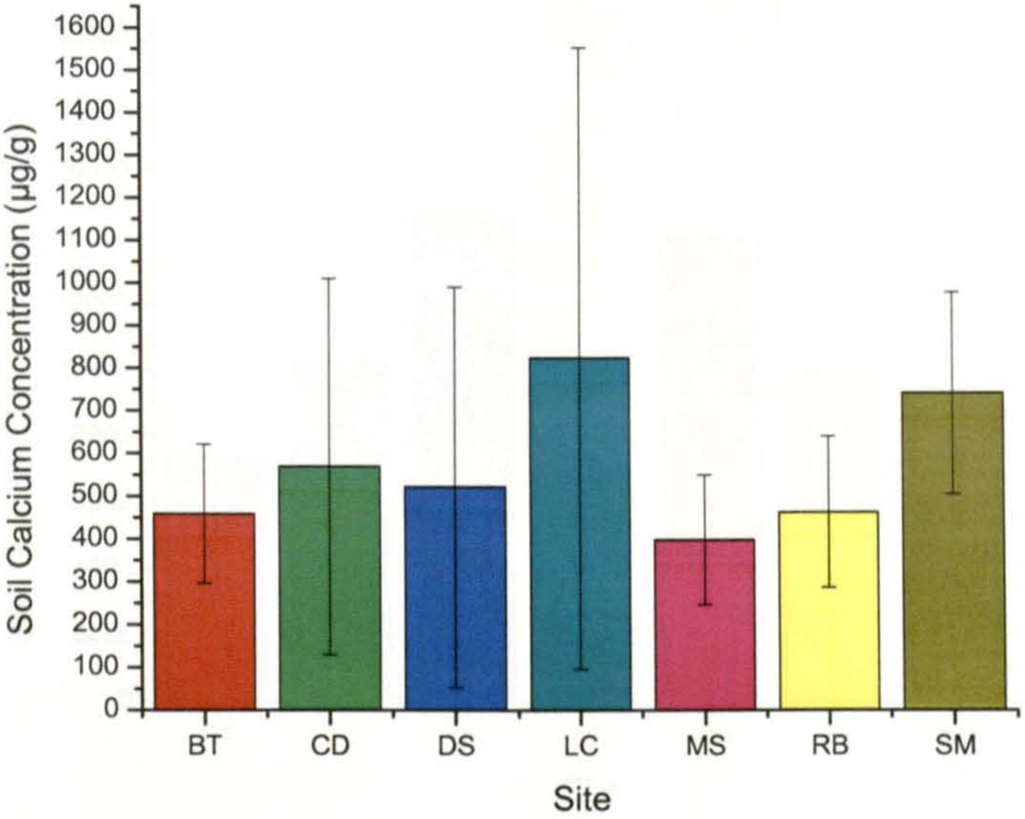


Figure 6 Key – BT = Balsam High Top, CD = Clingman's Dome, DS = Double Spring Gap, LC = Mt. LeConte, MS = Mt. Sterling, RB = Richland Balsam, SM = Spruce Mountain

A statistical analysis of soil Ca concentrations shows no statistical difference in the results.

Figure 7
Soil Al Concentrations of Red spruce at All Sample Sites

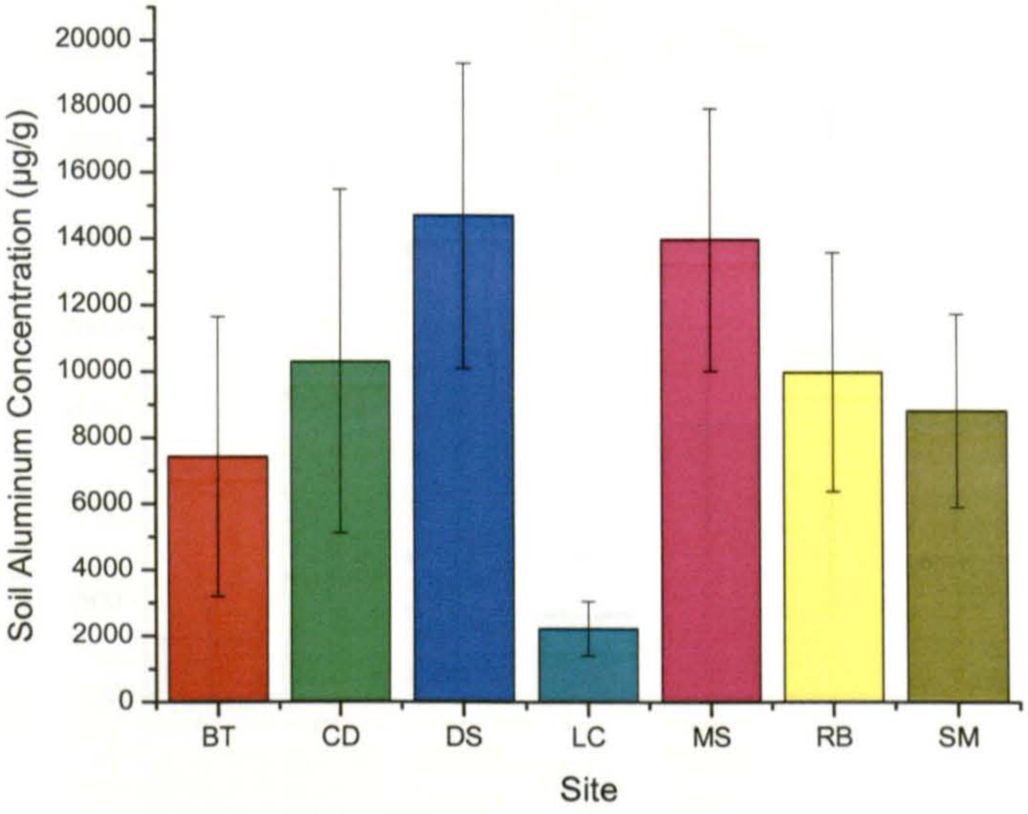


Figure 7 Key – BT = Balsam High Top, CD = Clingman's Dome, DS = Double Spring Gap, LC = Mt. LeConte, MS = Mt. Sterling, RB = Richland Balsam, SM = Spruce Mountain

Comparison of extractable soil Al concentrations indicate BT, CD, DS, MS, RB and SM are statistically the same. The soil Al concentrations on Mt. LeConte are significantly different than all other sites and relatively much lower which is contrary to our hypothesis. This difference may involve the soil type and sample location. Elevation does not seem to affect soil aluminum concentrations.

Figure 8
Soil Mg Concentrations of Red spruce at All Sample Sites

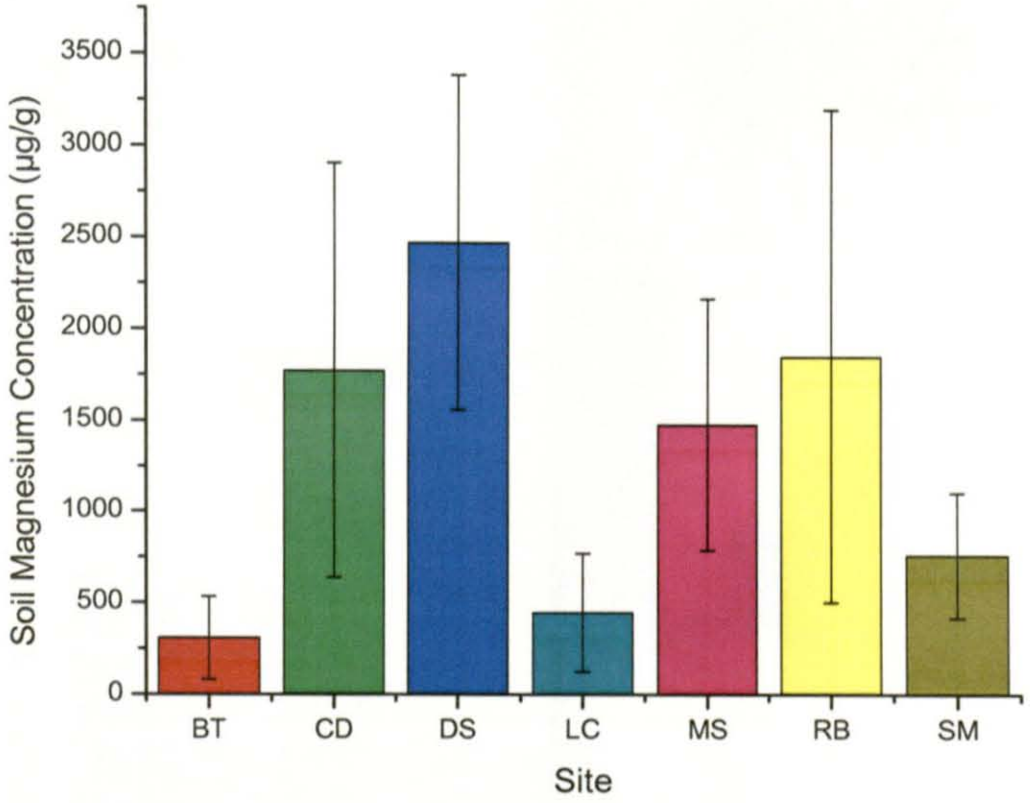
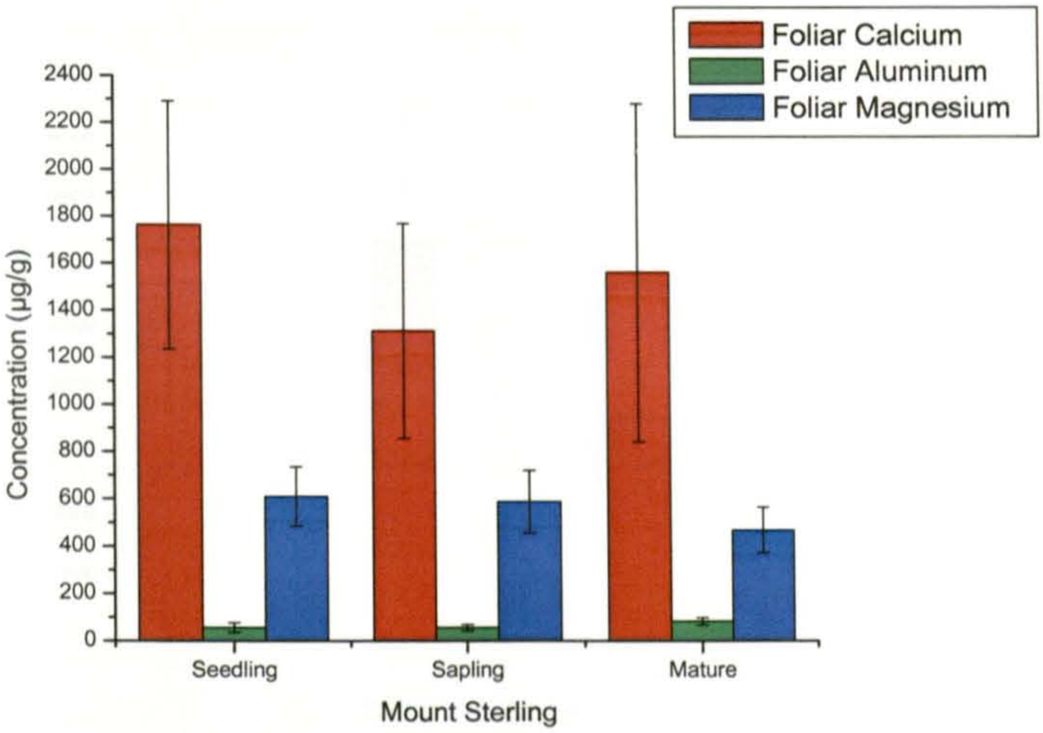


Figure 8 Key – BT = Balsam High Top, CD = Clingman's Dome, DS = Double Spring Gap, LC = Mt. LeConte, MS = Mt. Sterling, RB = Richland Balsam, SM = Spruce Mountain

Comparison of soil magnesium concentrations at all sample sites shows that SM, RB, MS, and CD are all statistically the same. DS is significantly different than SM, LC, and BT, but the same as CD, MS, and RB. These results indicate that there is little correlation between soil Ca and Al concentrations and soil Mg concentrations. SM, BT and DS were hypothesized to be the highest, while LC, CD and RB should have been the lowest.

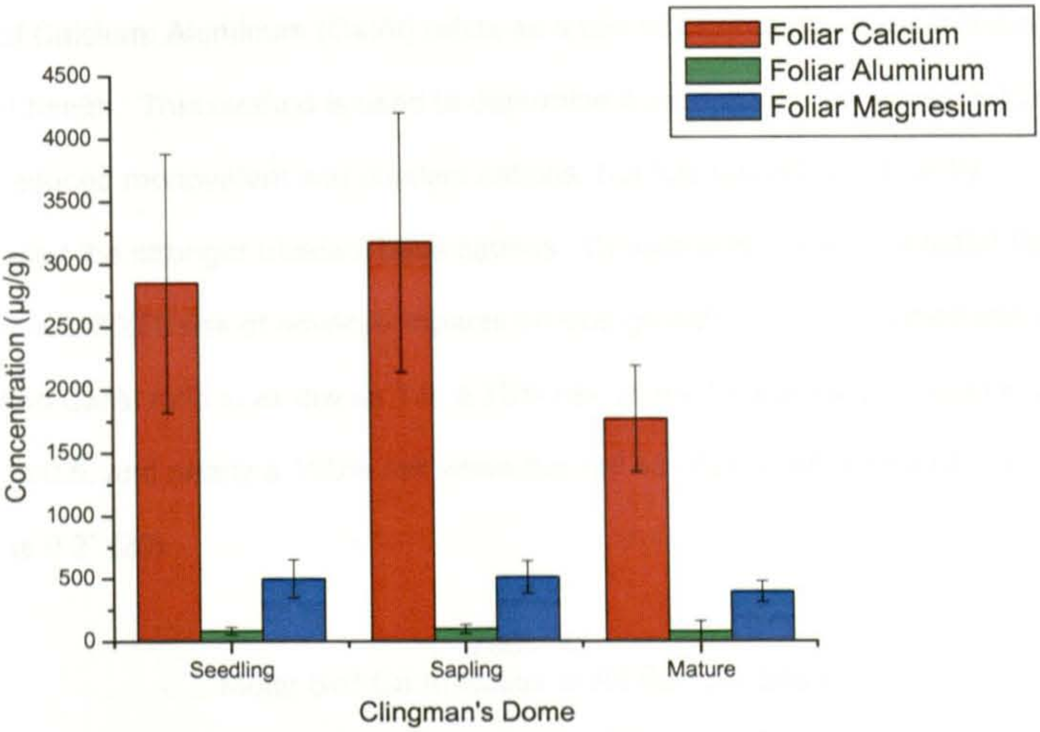
Figure 9
Comparison of Seedlings, Saplings and Mature Trees at Mount Sterling



Due to the large standard deviations, foliar concentrations for each analyte in each life stage are not statistically different. All sample sites except Clingman's Dome exhibit this trend; therefore, it is not necessary to discuss sample sites by foliar concentrations versus life stage.

Figure 10

Comparison of Seedlings, Saplings and Mature Trees at Clingman's Dome



Clingman's Dome is the only sample site that displayed results that were statistically different when comparing concentrations between life stages. For foliar calcium concentrations, mature trees exhibited lower results than seedlings and saplings. For foliar magnesium, mature trees exhibited lower results than seedlings. The results for foliar aluminum were statistically the same. This data suggests mature trees at Clingman's Dome exhibit lower calcium and magnesium concentrations than younger life stages.

Calcium: Aluminum Ratios in Soil

Cronan and Grigel (20) performed a critical literature review regarding the use of Calcium: Aluminum (Ca:Al) ratios as a tool to estimate adverse impacts on forest health. This method is used to determine if excessive anionic deposition has reduced monovalent and divalent cations, but has not yet significantly impacted the stronger trivalent base cations. Cronan and Grigel concluded that "there is a 50:50 risk of adverse impacts on tree growth or nutrition when the soil solution Ca/Al ratio is as low as 1.0, a 75% risk when the soil solution ratio is as low as 0.5, and nearly a 100% risk when the soil solution Ca/Al molar ratio is as low as 0.2" (20).

Table 4
Molar Soil Ca:Al Ratios at All Sample Sites

SITE	Molar Ca:Al Ratio	RSD
Balsam High Top (BT)	0.094	66%
Clingman's Dome (CD)	0.084	92%
Double Spring Gap (DS)	0.053	95%
Mt. LeConte (LC)	0.567	95%
Mount Sterling (MS)	0.070	47%
Richland Balsam (RB)	0.070	52%
Spruce Mountain (SM)	0.128	45%

According to the criteria set by Cronan and Grigel (20), Mt. LeConte has a 75% risk of adverse forest health effects based on the soil Ca/Al ratios. All other sites, including Spruce Mountain, exhibit a 100% risk of adverse health effects due to the soil molar Ca/Al ratios below 0.2.

Results Comparison with Previous Work

McLaughlin, et al. (21) reported Ca:Al ratios for soil surrounding red spruce saplings at Mt. LeConte, Clingman's Dome and Mount Sterling. Tables 5 and 6 depict the comparison of Ca:Al ratios found by McLaughlin with those found in this project. In Table 5, the soil Ca:Al concentrations do not show any significant trends. The Ca:Al ratio at Clingman's dome has decreased by 50%, Mt. LeConte has increased four-fold and Mt. Sterling has remained the same.

Table 5
Comparison of Soil Ca:Al Ratios Between
McLaughlin (1988) and Bintz (2005)

Ca:Al Concentration in Soil	McLaughlin (1988)	RSD	Bintz (2005)	RSD
Clingman's Dome	0.10	NR*	0.05	92%
Mt. LeConte	0.08	NR*	0.37	95%
Mount Sterling	0.03	NR*	0.03	47%

NR* - Not Reported

Table 6 displays the foliar Ca:Al ratio in red spruce. In this medium, the values have slightly increased; however, without the reported standard deviations a t-test cannot be performed. Overall, no conclusions can be made from the analysis of Ca:Al ratios between McLaughlin's work in 1988 and this project.

Table 6
Comparison of Foliar Ca:Al Ratios Between
McLaughlin (1988) and Bintz (2005)

Ca:Al Concentration in Red Spruce	McLaughlin (1988)	RSD	Bintz (2005)	RSD
Clingman's Dome	20	NR*	30	51%
Mt. LeConte	46	NR*	73	190%
Mount Sterling	14	NR*	24	48%

NR* - Not Reported

Richland Balsam Mountain on the Blue Ridge Parkway in Haywood County, North Carolina, was sampled to compare data with results from 1994 and 1969 (22). Table 7 depicts the comparison between this project, Weaver (1969) and Shepard (1994) (22). A t-test analysis of foliar Ca and Mg concentrations obtained by the three researchers indicates that each researcher's data is statistically different from the others. The t-test comparison of Shepard and Weaver were obtained by Shepard (22). The foliar Ca, 0.05 critical value for Weaver (n=14) and Bintz (n=30) is 2.029; for Shepard (n=10) and Bintz (n=30), the critical value is 2.025. The foliar Mg, 0.05 critical value for Weaver (n=12) and Bintz (n=30) is 2.021; for Shepard (n=10) and Bintz (n=30), the critical value is 2.025.

The results of the comparisons between Weaver (1969), Shepard (1994) and Bintz (2005) indicate that at Richland Balsam, foliar nutrient levels decreased between 1969 and 1994. Since 1994, foliar nutrient levels have increased, but are still not at the levels observed in 1969. This trend could be due to the increase in fossil fuel consumption between 1970 and 1994. The increase in foliar nutrient levels of the red spruce between 1994 and 2005 may be a result of federal acid rain reduction legislation introduced in the early 1990s.

Table 7
Comparison of Foliar Ca and Mg Concentrations Between Bintz, Shepard and Weaver at Richland Balsam, NC

Researcher	Foliar Ca (µg/g)	t-test w/ Bintz	RSD	Foliar Mg (µg/g)	t-test w/ Bintz	RSD
Weaver (1969) n =14 Ca n =12 Mg	4164±388	8.15	6.4%	788±62	5.65	7.9%
Shepard (1994) n = 10	1932±712	2.26	37%	330±68	5.47	21%
Bintz (2005) n = 30	2627±878	X	33%	567±129	X	23%

CONCLUSIONS

This project set out to accomplish two goals. The first goal was to determine calcium, magnesium and aluminum in red spruce foliage and surrounding soil and compare these values with data collected at the same sites (Clingman's Dome, Mount LeConte, Richland Balsam, Mount Sterling) in the past. The results obtained from the analysis, and any significant trends, would yield a better understanding of the effects of acid deposition in geographically vulnerable regions, such as the peaks of the Great Smoky Mountains National Park, which are above the 1800m cloud base. These high peaks are subject to cloud/ fog deposition at rates much higher than lower elevations as revealed by Saxena and Lin (14).

If anthropogenic acceleration of the deposition of the acidic anions, sulfates and nitrates was affecting forest health, these sites would be the first affected. As the Frasier fir has been infected by the Balsam Wooly Adelgid (BWA), this species would not be a reliable gauge of forest health due to the external pressure of the BWA. In addition, red spruce attains its maximum development in the southern Appalachians (1). Bruck and Robarge (9) discovered a decline in red spruce growth, beginning in the 1960s, at Mt. Mitchell State Park, North Carolina. Their data concluded that red spruce health worsened with elevation, implying that higher altitudes were more affected. The red spruce, as well as a similar species, the Norway spruce, have exhibited decline in other areas of high acid deposition. The data obtained in this study will allow a comparison of forest health between the southern Appalachians and other affected regions as well as any future analyses. This is also the second goal of this project, which is to establish new data for new sites (Balsam High Top, Spruce Mountain and Double Spring Gap) to further characterize the soil and foliar nutrient concentrations of the red spruce in the southern Appalachians.

The data was analyzed in various ways to establish any correlation or trends that may be present. The lack of the ability to do so rests primarily with the large standard deviations which exist at the individual level. These large standard deviations render a statistical analysis of the results to be rejected due to the chance in which the numbers may be found in the same population. In sampling thirty trees (10 seedlings, 10 saplings and 10 mature) and at least 10 soil samples at each sample site, great variations of foliar and soil nutrient levels will most likely be present.

We analyzed the data as a function of elevation, the higher elevation sites should exhibit lower nutrient levels; however this is not the case. Mt. LeConte, which has an elevation of 6593 ft above m.s.l. exhibited the healthiest Ca:Al ratio. The sample sites were statistically the same at all elevations indicating that elevation does not have an effect on nutrient levels. This also indicates that acid deposition does not have a significant impact on foliar and soil base cation concentration. Perhaps the sample sites chosen, all of which were near the 1800 m cloud base (accelerated cloud/ fog deposition) exhibit the same characteristics which are indistinguishable. Future research may choose another component of the spruce-fir ecosystem that can be found at very low elevations to explore the effects of elevation.

The sample sites were also analyzed geographically; it was hypothesized that the sites that were farther north and east would be the most affected do to their closer proximity to a high concentration of coal-fired power plants in operation to the north. Although Mt. Sterling exhibited lower nutrient levels, they were not statistically significant enough to support the hypothesis. Mt. LeConte should have also exhibited relatively lower nutrient levels; however it appears to be relatively healthy which contradicts the stated hypothesis. Future research should consider choosing sample sites that are relatively farther apart to analyze the significance of geography.

By using the conclusions drawn by Cronan and Grigel (20), the Calcium:Aluminum ratios obtained in this study indicate that Mt. LeConte has a 75% risk of adverse effects of forest health. All other sample sites have a 100% risk of adverse effects of forest health. The comparison between this project and the Ca:Al ratios given in McLaughlin (21), indicate no conclusion can be drawn on the effects of time on foliar and soil Ca:Al ratios at Clingman's Dome, Mt. LeConte, and Mt. Sterling, although foliar Ca:Al increased in all three locations.

Research that spans over three decades on Richland Balsam, beginning with Weaver in 1969 concludes that foliar Ca and Mg decreased between 1969 and 1994 (22) but has increased between 1994 and 2005. The results obtained in this comparison are statistically significant. The data suggests that at Richland Balsam, foliar nutrient levels have been improving in the last decade. Further research could look at Richland Balsam and other sites along the Blue Ridge Parkway.

The data obtained in this project allows for no overall conclusion that acid deposition significantly affects the health of red spruce. Elevation and geography also do not appear to have an impact on the effects of acid deposition. Further research could involve the specific mechanisms in which acid deposition affects soil chemistry, as well as the plant physiology and chemistry that involves base cations. Perhaps determining total foliar and soil Ca, Mg and Al may require manipulation due to large variability that can be found within populations. The large population size (n=30) allowed for greater variability which affects the statistics of analysis. A method to normalize individual traits to reduce the large standard deviation would be useful in ascertaining the effects of acid deposition on red spruce.

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Appendices

Appendix 1: Maps

Figure 11
Map of Sample Sites

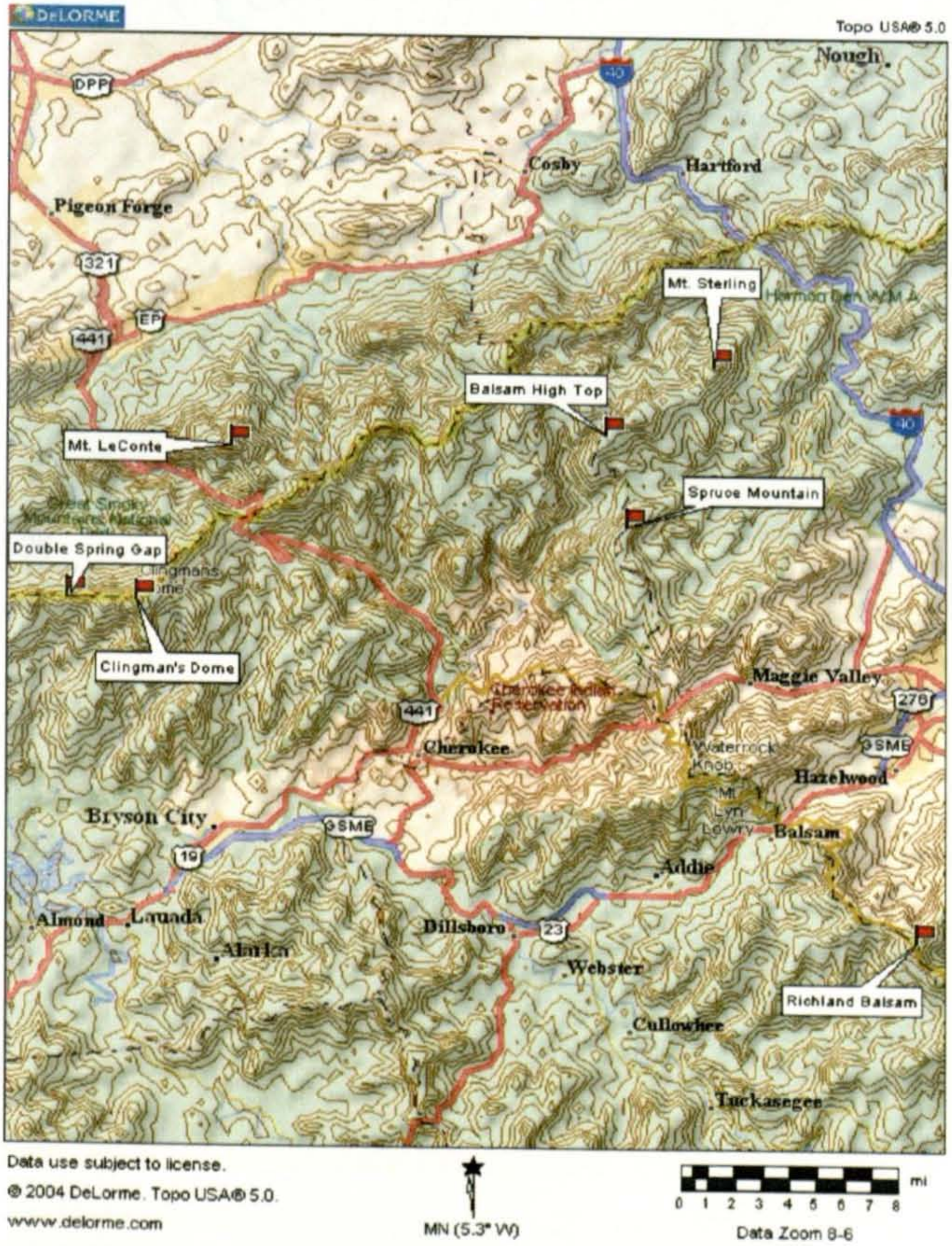

Figure 12
Map and Approximate Sampling Area at Richland Balsam

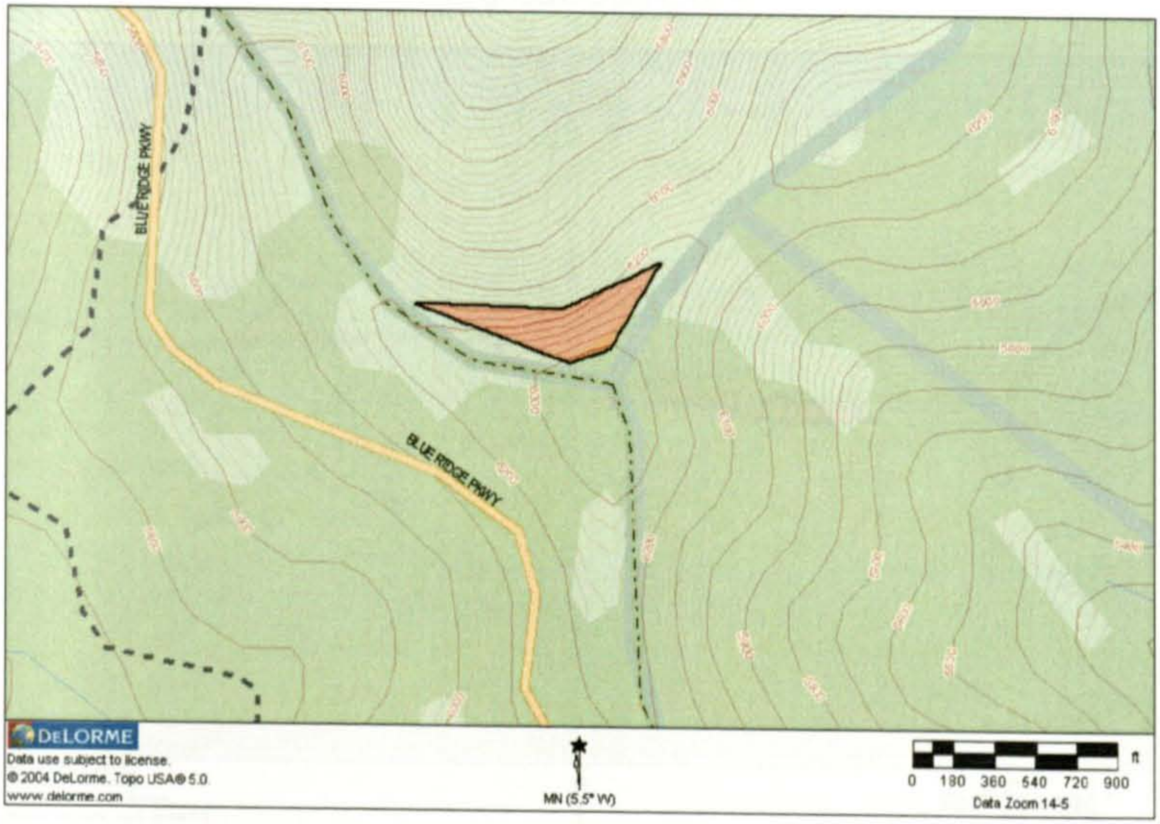

Figure 13
Map and Approximate Sampling Area at Clingman's Dome
and Double Spring Gap

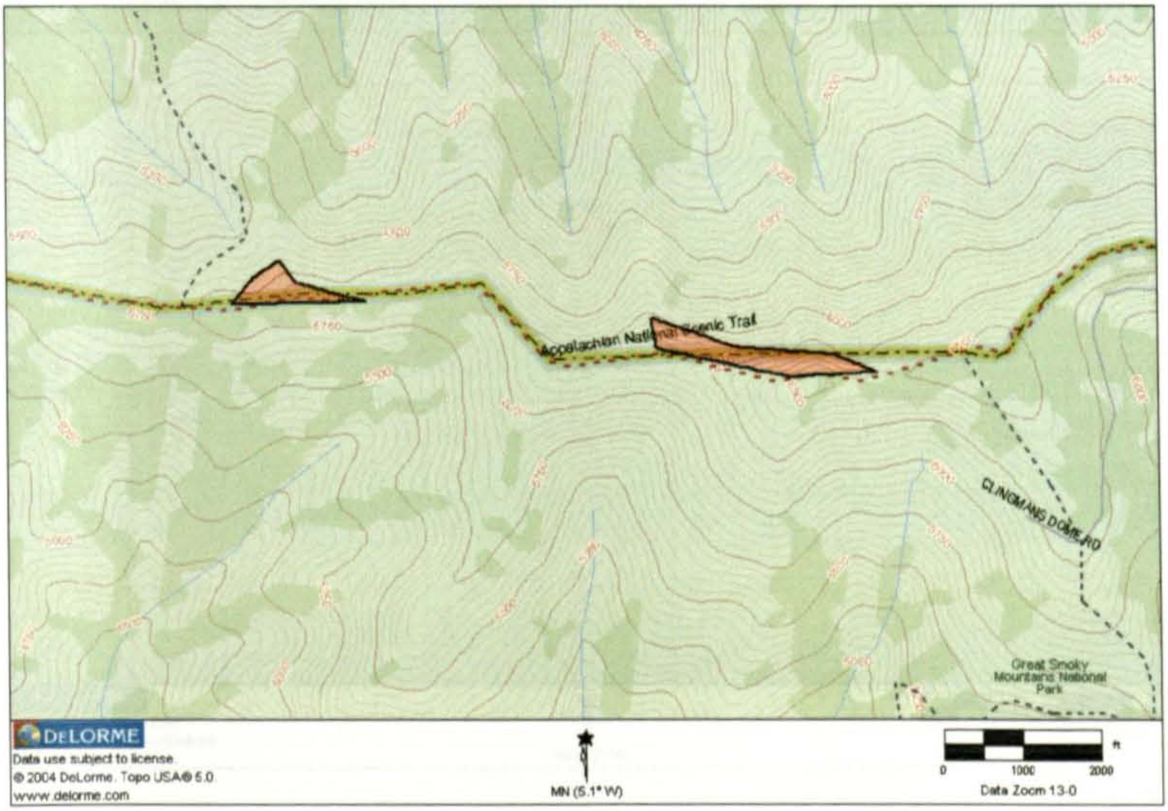

Figure 14
Map and Approximate Sampling Area at Mt. LeConte

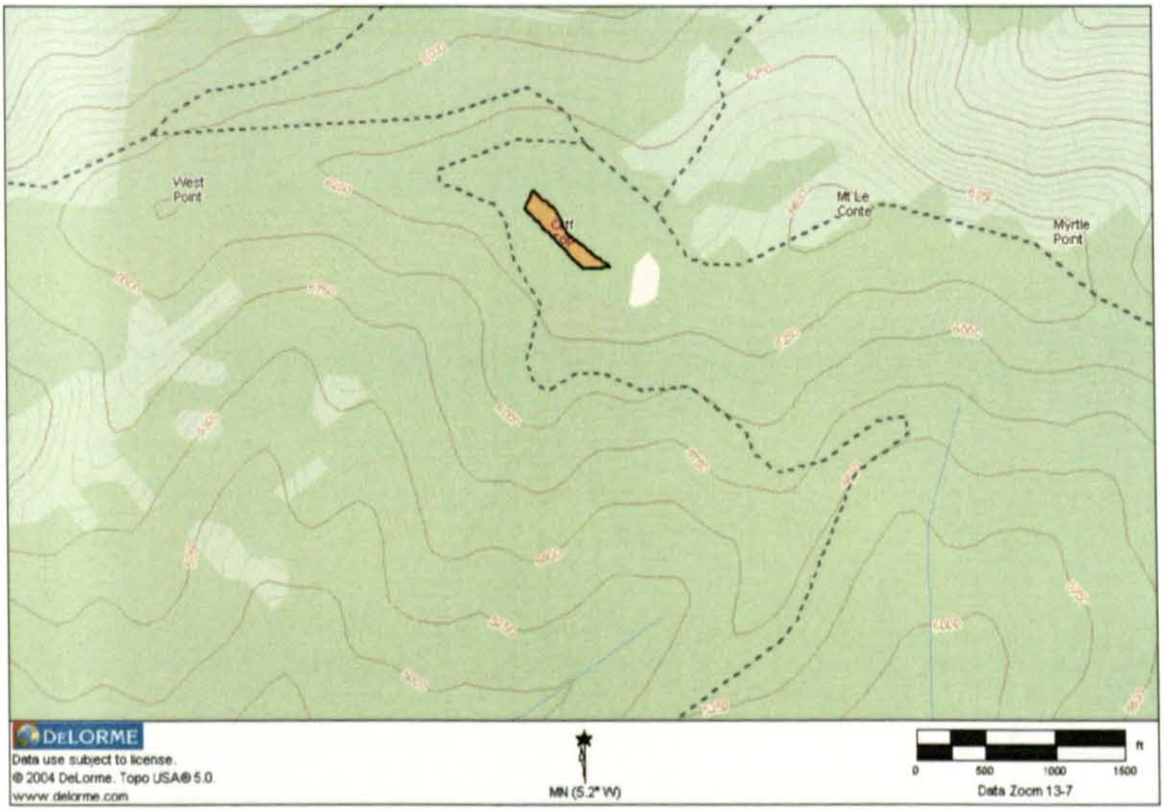

Figure 15
Map and Approximate Sampling Area at Mt. Sterling

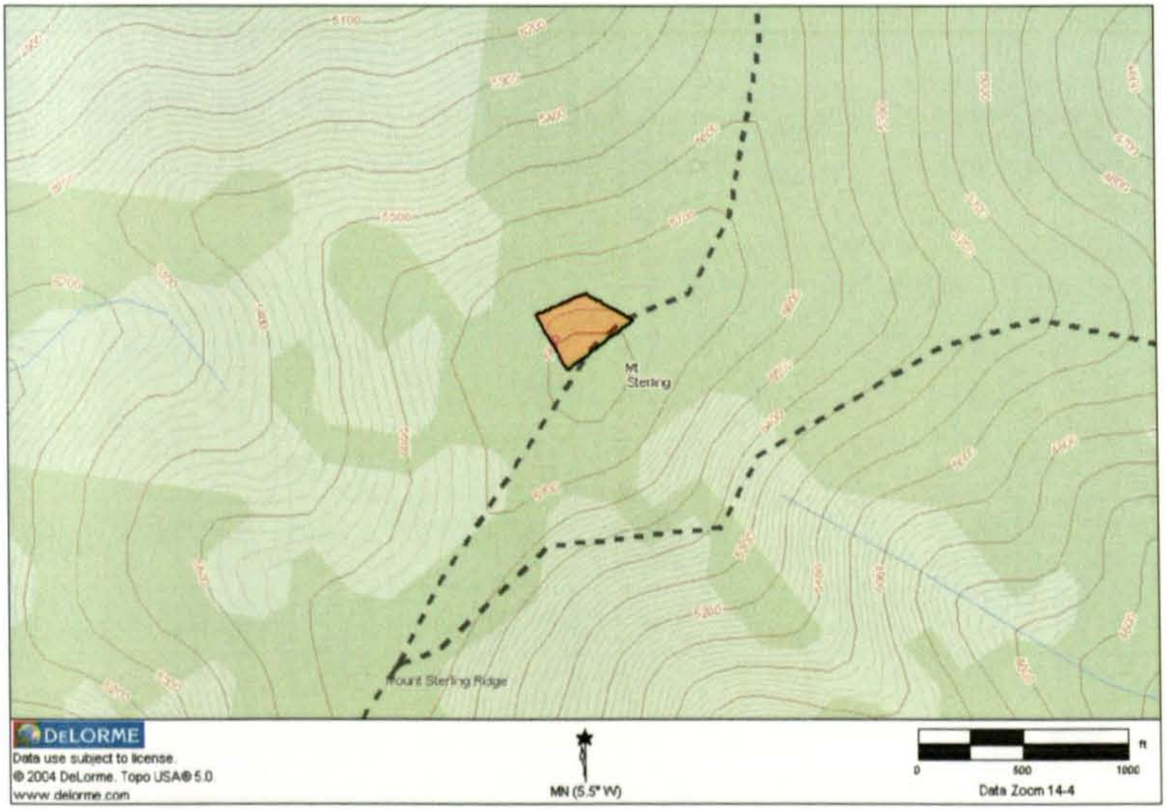

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Figure 16
Map and Approximate Sampling Area at Balsam High Top

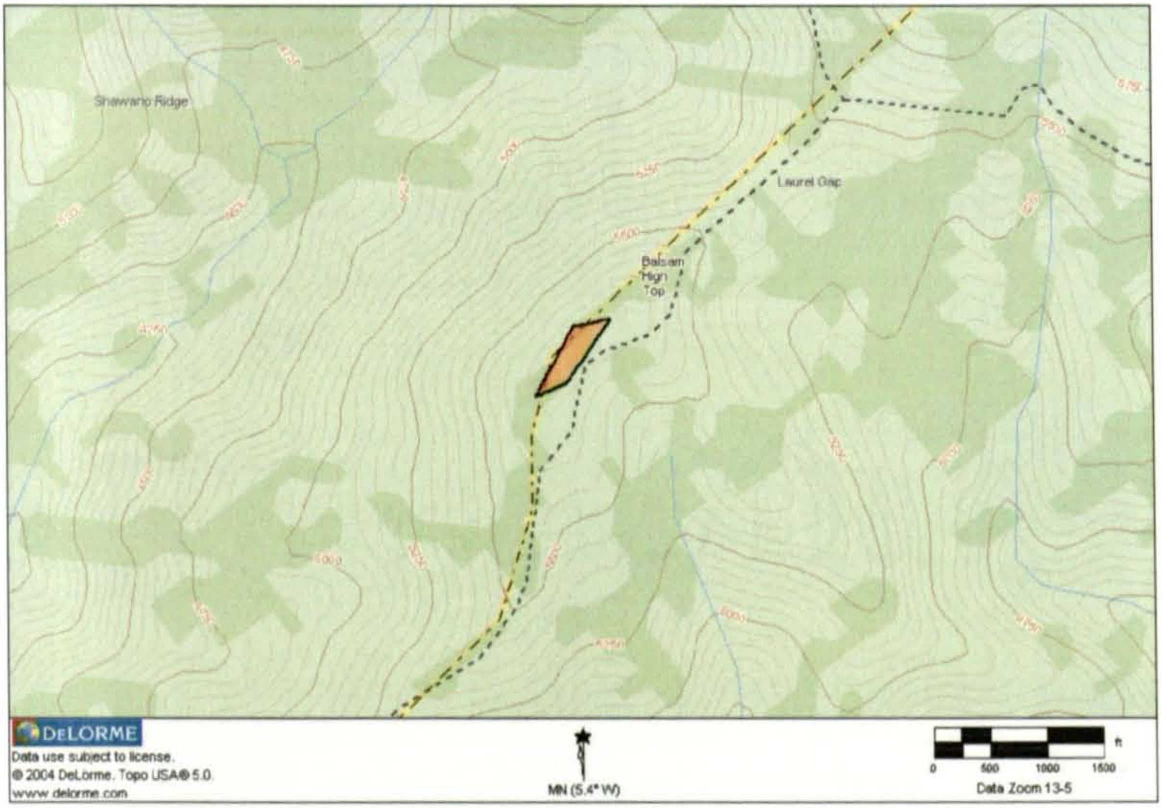
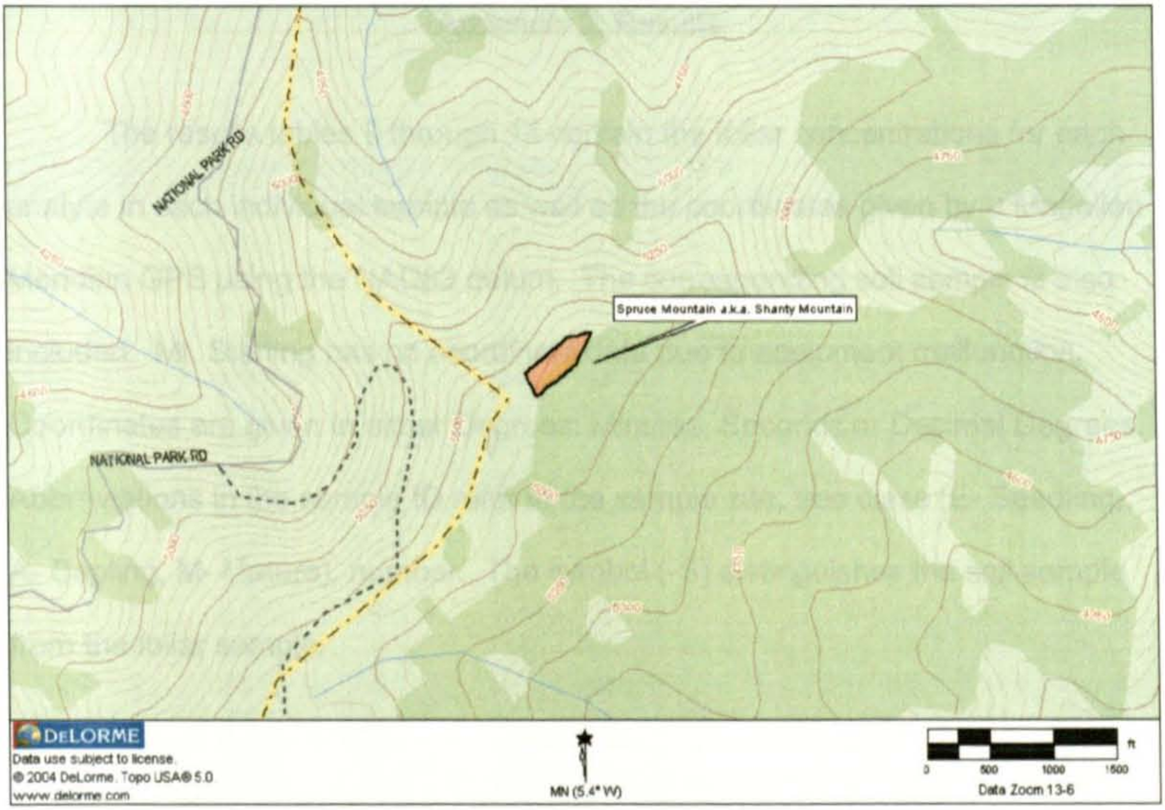


Figure 17
Map and Approximate Sampling Area at Spruce Mountain



Appendix 2: Results

The results tables 8 through 14 contain the foliar concentrations for each analyte in each individual sample as well as the coordinates given by a Magellen Meridian GPS using the NAD83 datum. The corresponding soil sample is also included. Mt. Sterling has no coordinate data due to equipment malfunction. Coordinates are given in either Degrees: Minutes, Seconds or Decimal Degrees. Abbreviations in the sample ID refer to the sample site, tree class (E- Seedling, A- Sapling, M- Mature), number. The symbol (-S) distinguishes the soil sample from the foliar sample.

FOLIAR RESULTS

Table 8
Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken at Balsam High Top

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)	Latitude	Longitude	Soil Sample
BT-M1	3250	64.7	436	35° 39' 72.1"	83° 11' 54.2"	BT-E1-S
BT-M2	2920	37.7	360	35° 39' 72.7"	83° 11' 54.7"	BT-E1-S
BT-M3	3290	64.4	510	35° 39' 72.3"	83° 11' 54.2"	BT-E2-S
BT-M4	3050	48.2	433	35° 39' 72.6"	83° 11' 56.0"	BT-A2-S
BT-M5	4090	35.4	455	35° 39' 72.1"	83° 11' 55.4"	BT-E4-S
BT-M6	2790	37.2	382	35° 39' 72.6"	83° 11' 56.6"	BT-A3-S
BT-M7	2770	42.6	556	35° 39' 72.4"	83° 11' 57.0"	BT-A3-S
BT-M8	2770	33.6	585	35° 39' 72.3"	83° 11' 58.0"	BT-A7-S
BT-M9	2060	53.7	389	35° 39' 70.9"	83° 11' 58.8"	BT-M9-S
BT-M10	2670	62.9	392	35° 39' 70.4"	83° 11' 58.5"	BT-A8-S
BT-A1	2750	39.9	535	35° 39' 72.9"	83° 11' 55.1"	BT-E2-S
BT-A2	3000	42.3	533	35° 39' 72.7"	83° 11' 55.8"	BT-A2-S
BT-A3	2330	35.3	451	35° 39' 72.6"	83° 11' 56.8"	BT-A3-S
BT-A4	1800	45.6	515	35° 39' 72.9"	83° 11' 56.9"	BT-E6-S
BT-A5	2820	50.5	561	35° 39' 72.9"	83° 11' 56.9"	BT-E6-S
BT-A6	2400	29.7	547	35° 39' 72.2"	83° 11' 58.1"	BT-A7-S
BT-A7	4510	22.4	753	35° 39' 72.2"	83° 11' 58.2"	BT-A7-S
BT-A8	2090	34.1	385	35° 39' 70.6"	83° 11' 58.5"	BT-A8-S
BT-A9	3480	45.2	506	35° 39' 70.4"	83° 11' 58.5"	BT-A8-S
BT-A10	1810	52.7	801	35° 39' 68.5"	83° 11' 61.4"	BT-E10-S
BT-E1	2120	29.2	477	35° 39' 72.4"	83° 11' 54.4"	BT-E1-S
BT-E2	2850	33.6	633	35° 39' 72.9"	83° 11' 55.1"	BT-E2-S
BT-E3	1090	45.1	297	35° 39' 72.7"	83° 11' 55.9"	BT-A2-S
BT-E4	1460	18.3	367	35° 39' 72.2"	83° 11' 56.1"	BT-E4-S
BT-E5	3430	35.1	576	35° 39' 72.3"	83° 11' 55.4"	BT-E4-S
BT-E6	2400	29.7	547	35° 39' 72.9"	83° 11' 57.0"	BT-E6-S
BT-E7	2580	37.7	505	35° 39' 70.6"	83° 11' 59.0"	BT-M9-S
BT-E8	3080	31.9	457	35° 39' 70.2"	83° 11' 59.5"	BT-E8-S
BT-E9	2810	32.6	569	35° 39' 69.6"	83° 11' 60.4"	BT-E9-S
BT-E10	2870	28.8	653	35° 39' 68.5"	83° 11' 61.3"	BT-E10-S
Std Dev.	712	11.6	113			
Mean	2710	40.0	506			
Mean E	2470	32.2	508			
Mean A	2700	39.8	559			
Mean M	2970	48.0	450			

Table 9
Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken at Clingman's Dome

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)	Latitude	Longitude	Soil Sample
CD-A1	3780	89.3	491	35° 33' 77.7"	83° 30' 00.9"	CD-A1-S
CD-A2	2820	76.8	334	35° 33' 73.1"	83° 30' 22.0"	CD-A2-S
CD-A3	4720	109	665	35° 33' 72.4"	83° 30' 27.3"	CD-A3-S
CD-A4	3030	78.4	646	35° 33' 75.7"	83° 30' 38.8"	CD-A4-S
CD-A5	3050	76.9	561	35° 33' 76.9"	83° 30' 39.1"	CD-A4-S
CD-A6	2790	90.9	611	35° 33' 17.1"	83° 30' 40.2"	CD-A4-S
CD-A7	1380	83.6	410	35° 33' 75.2"	83° 30' 38.7"	CD-E6-S
CD-A8	1960	167	342	35° 33' 75.6"	83° 30' 37.5"	CD-A8-S
CD-A9	3820	155	408	35° 33' 76.8"	83° 30' 37.1"	CD-E10-S
CD-A10	4360	61.7	641	35° 33' 77.0"	83° 30' 37.3"	CD-E10-S
CD-M1	1440	71.3	359	NA	NA	CD-M1-S
CD-M2	1280	78.1	334	35° 33' 80.4"	83° 30' 97.5"	CD-M1-S
CD-M3	2670	93.2	303	35° 33' 77.7"	83° 30' 98.8"	CD-M3-S
CD-M4	1970	95.7	385	35° 33' 77.7"	83° 30' 99.1"	CD-M3-S
CD-M5	1830	65.5	299	35° 33' 75.9"	83° 30' 02.9"	CD-E1-S
CD-M6	1760	67.0	439	35° 33' 76.7"	83° 30' 03.1"	CD-E1-S
CD-M7	1660	74.3	347	35° 33' 75.0"	83° 30' 07.4"	CD-M7-S
CD-M8	2180	70.2	427	35° 33' 75.2"	83° 30' 09.1"	CD-M8-S
CD-M9	1400	112	536	35° 33' 73.4"	83° 30' 17.2"	CD-M9-S
CD-M10	1480	66.8	516	35° 33' 73.0"	83° 30' 18.4"	NA
CD-E1	3020	47.5	457	35° 33' 76.5"	83° 30' 03.0"	CD-E1-S
CD-E2	2460	131	574	35° 33' 72.8"	83° 30' 19.5"	CD-E2-S
CD-E3	3560	88.9	785	35° 33' 72.8"	83° 30' 19.8"	CD-E2-S
CD-E4	2100	107	522	35° 33' 73.0"	83° 30' 29.7"	CD-E4-S
CD-E5	2160	64.0	415	35° 33' 73.9"	83° 30' 36.4"	CD-E5-S
CD-E6	2400	55.3	595	35° 33' 75.0"	83° 30' 38.6"	CD-E6-S
CD-E7	2180	60.3	642	35° 33' 75.1"	83° 30' 38.6"	CD-E6-S
CD-E8	5130	125	354	35° 33' 75.5"	83° 30' 38.1"	CD-E8-S
CD-E9	3730	96.6	369	35° 33' 75.9"	83° 30' 37.1"	CD-A8-S
CD-E10	1750	72.6	283	35° 33' 76.6"	83° 30' 37.0"	CD-E10-S
Std. Dev.	1040	28.4	132			
Mean	2600	87.8	468			
Mean E	2850	84.9	500			
Mean A	3170	99.0	511			
Mean M	1770	79.4	395			

Table 10

Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken Near Double Spring Gap

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)	Latitude	Longitude	Soil Sample
DS-M1	3740	50.9	301	35.56556	83.52329	DS-M1-S
DS-M2	3560	48.8	311	35.56552	83.52251	DS-M1-S
DS-M3	2980	39.3	490	35.56560	83.52253	DS-A2-S
DS-M4	765	46.7	333	35.56566	83.52236	DS-A2-S
DS-M5	3700	69.3	319	35.56565	83.52236	DS-E1-S
DS-M6	3740	30.3	379	35.56567	83.52227	DS-E2-S
DS-M7	2720	51.1	351	35.56578	83.52237	DS-A4-S
DS-M8	1760	29.6	302	35.56571	83.52253	DS-E5-S
DS-M9	1570	73.9	261	35.56557	83.52268	DS-M10-S
DS-A1	2630	49.8	547	35.56552	83.52245	DS-M1-S
DS-A2	1760	94.4	350	35.56564	83.52235	DS-A2-S
DS-A3	2440	32.8	328	35.56565	83.52239	DS-E1-S
DS-A4	2550	40.0	276	35.56572	83.52239	DS-A4-S
DS-A5	1400	30.2	302	35.56569	83.52244	DS-E3-S
DS-A6	2070	26.1	324	35.56573	83.52248	DS-E5-S
DS-A7	3170	32.6	221	35.56553	83.52256	DS-E6-S
DS-A8	1900	135	275	35.56550	83.52260	DS-E10-S
DS-A9	1890	31.7	362	35.56577	83.52269	DS-M10-S
DS-A10	2420	45.2	456	35.56577	83.52269	DS-M10-S
DS-E1	3360	30.9	412	35.56566	83.52234	DS-E1-S
DS-E2	2030	178	425	35.56565	83.52232	DS-E2-S
DS-E3	1790	23.2	340	35.56569	83.52243	DS-E3-S
DS-E4	2070	63.3	344	35.56569	83.52248	DS-E3-S
DS-E5	2070	4.6	319	35.56576	83.52252	DS-E5-S
DS-E6	2480	14.3	340	35.56551	83.52254	DS-E6-S
DS-E7	2070	8.1	335	35.56548	83.52256	DS-E7-S
DS-E8	1550	15.7	297	35.56548	83.52256	DS-E7-S
DS-E9	1890	8.4	372	35.56548	83.52256	DS-E7-S
DS-E10	2200	16.3	426	35.56549	83.52259	DS-E10-S
Std. Dev.	762	37.5	70			
Mean	2360	45.6	348			
Mean E	2150	36.3	361			
Mean A	2220	51.8	344			
Mean M	2730	48.9	339			

Table 11
Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken at Mt. LeConte

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)	Latitude	Longitude	Soil Sample
LC-E1	3180	55.5	1010	35° 39' 15.2"	83° 26' 39.0"	LC-A1-S
LC-E2	7030	17.8	697	35° 39' 15.2"	83° 26' 39.0"	LC-A1-S
LC-E3	4680	121	841	35° 39' 15.3"	83° 26' 38.4"	LC-M2-S
LC-E4	3970	2.1	722	35° 39' 14.9"	83° 26' 38.7"	LC-M3-S
LC-E5	3780	0.9	486	35° 39' 14.4"	83° 26' 37.8"	LC-E5-S
LC-E6	3900	36.5	662	35° 39' 14.3"	83° 26' 36.8"	LC-E5-S
LC-E7	3340	29.9	562	35° 39' 14.0"	83° 26' 37.8"	LC-E7-S
LC-E8	2510	9.2	599	35° 39' 14.1"	83° 26' 37.5"	LC-E8-S
LC-E9	2300	9.6	760	35° 39' 14.1"	83° 26' 37.5"	LC-E8-S
LC-E10	2500	5.4	512	35° 39' 13.3"	83° 26' 37.2"	LC-E10-S
LC-A1	2000	77.4	723	35° 39' 15.2"	83° 26' 39.0"	LC-A1-S
LC-A2	4330	8.5	582	35° 39' 14.9"	83° 26' 38.6"	LC-M3-S
LC-A3	5120	29.8	581	35° 39' 14.9"	83° 26' 38.7"	LC-M4-S
LC-A4	4450	1.4	917	35° 39' 14.8"	83° 26' 38.7"	LC-M4-S
LC-A5	2880	17.8	657	35° 39' 14.8"	83° 26' 38.6"	LC-A5-S
LC-A6	3150	3.6	725	35° 39' 14.0"	83° 26' 38.0"	LC-A6-S
LC-A7	1820	498	449	35° 39' 14.0"	83° 26' 37.8"	LC-A6-S
LC-A8	2830	38.2	452	35° 39' 14.0"	83° 26' 38.0"	LC-A6-S
LC-A9	2210	14.2	489	35° 39' 14.0"	83° 26' 37.9"	LC-A6-S
LC-A10	2890	19.5	466	35° 39' 14.1"	83° 26' 37.6"	LC-E7-S
LC-M1	3030	74.8	669	35° 38' 28.7"	83° 26' 79.1"	LC-M1S
LC-M2	2880	20.4	556	35° 39' 15.4"	83° 26' 38.4"	LC-M2-S
LC-M3	5360	23.0	728	35° 39' 15.2"	83° 26' 38.8"	LC-M3-S
LC-M4	4470	20.7	655	35° 39' 14.9"	83° 26' 38.6"	LC-M4-S
LC-M5	3920	25.2	524	35° 39' 14.8"	83° 26' 38.6"	LC-A5-S
LC-M6	4460	163	562	35° 39' 14.3"	83° 26' 37.7"	LC-E5-S
LC-M7	5710	35.9	1070	35° 39' 14.0"	83° 26' 37.6"	LC-E7-S
LC-M8	3050	17.5	554	35° 39' 14.0"	83° 26' 36.9"	LC-E10-S
LC-M9	2930	60.2	439	35° 39' 13.6"	83° 26' 36.9"	LC-E10-S
LC-M10	3770	45.2	742	35° 39' 13.6"	83° 26' 37.0"	LC-E10-S
Std. Dev.	1190	92.4	161			
Mean	3610	49.3	646			
Mean E	3720	28.7	685			
Mean A	3170	70.6	604			
Mean M	3960	48.7	650			

Table 12

Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken at Mt. Sterling

Sample ID	Ca ppm (μg/g)	Al ppm (μg/g)	Mg ppm (μg/g)	Latitude	Longitude	Soil Sample
MS-M1	706	87.6	397	NA	NA	MS-A1-S
MS-M2	1520	92.3	608	NA	NA	MS-A2-S
MS-M3	1020	95.3	365	NA	NA	MS-M2-S
MS-M4	1820	90.8	607	NA	NA	MS-M2-S
MS-M5	2250	91.1	461	NA	NA	MS-M3-S
MS-M6	2070	64.7	495	NA	NA	MS-A6-S
MS-M7	2930	53.1	497	NA	NA	MS-A6-S
MS-M8	863	67.9	460	NA	NA	MS-A6-S
MS-M9	1480	88.2	486	NA	NA	MS-E8-S
MS-M10	911	101	300	NA	NA	MS-E10-S
MS-A1	1340	48.8	358	NA	NA	MS-A1-S
MS-A2	1500	45.8	472	NA	NA	MS-A2-S
MS-A3	905	66.6	783	NA	NA	MS-M2-S
MS-A4	1170	49.4	604	NA	NA	MS-M2-S
MS-A5	707	84.4	578	NA	NA	MS-M3-S
MS-A6	1230	60.4	699	NA	NA	MS-A6-S
MS-A7	1350	44.4	738	NA	NA	MS-A6-S
MS-A8	2330	41.9	612	NA	NA	MS-A6-S
MS-A9	946	62.0	562	NA	NA	MS-E8-S
MS-A10	1630	63.1	463	NA	NA	MS-E10-S
MS-E1	1840	72.8	440	NA	NA	MS-A1-S
MS-E2	2070	45.8	413	NA	NA	MS-A1-S
MS-E3	1900	69.3	661	NA	NA	MS-M1-S
MS-E4	1280	40.5	512	NA	NA	MS-M1-S
MS-E5	901	66.8	590	NA	NA	MS-A2-S
MS-E6	1290	79.5	729	NA	NA	MS-A2-S
MS-E7	2250	85.1	747	NA	NA	MS-M3-S
MS-E8	1370	40.4	603	NA	NA	MS-E8-S
MS-E9	2540	25.0	783	NA	NA	MS-E8-S
MS-E10	2200	44.3	621	NA	NA	MS-E10-S
Std. Dev.	588	20.4	131			
Mean	1550	65.6	555			
Mean E	1760	56.9	610			
Mean A	1310	56.7	587			
Mean M	1560	83.2	467			

Table 13
Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken at Richland Balsam

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)	Latitude	Longitude	Soil Sample
RB-M1	2680	47.8	564	35° 22' 01.8"	83° 59' 44.5"	RB-A1-S
RB-M2	2810	72.6	769	35° 22' 01.4"	83° 59' 45.1"	RB-A3-S
RB-M3	2230	64.3	623	35° 22' 20.4"	83° 59' 45.0"	RB-A4-S
RB-M4	5350	63.7	667	35° 22' 02.6"	83° 59' 44.9"	RB-A4-S
RB-M5	1930	105	428	35° 21' 99.3"	83° 59' 45.0"	RB-M5-S
RB-M6	2640	112	759	35° 21' 98.7"	83° 59' 44.8"	RB-M5-S
RB-M7	2460	55.7	539	35° 21' 98.8"	83° 59' 44.5"	RB-M5-S
RB-M8	1700	60.6	418	35° 21' 96.9"	83° 59' 49.3"	RB-A6-S
RB-M9	1800	67.6	276	35° 21' 97.4"	83° 59' 49.3"	RB-E3-S
RB-M10	2720	78.1	476	35° 21' 97.5"	83° 59' 49.2"	RB-E4-S
RB-A1	2370	34.6	475	35° 22' 01.4"	83° 59' 44.6"	RB-A1-S
RB-A2	1750	42.6	451	35° 22' 01.9"	83° 59' 44.6"	RB-A1-S
RB-A3	2810	53.4	629	35° 22' 01.4"	83° 59' 45.2"	RB-A3-S
RB-A4	2610	64.1	569	35° 22' 20.4"	83° 59' 45.0"	RB-A4-S
RB-A5	2390	59.5	648	35° 22' 04.0"	83° 59' 45.6"	RB-A5-S
RB-A6	3320	54.3	763	35° 21' 96.8"	83° 59' 49.2"	RB-A6-S
RB-A7	4830	68.7	676	35° 21' 97.3"	83° 59' 49.1"	RB-A6-S
RB-A8	1830	70.8	599	35° 22' 91.2"	83° 59' 44.8"	RB-A8-S
RB-A9	1710	51.7	647	35° 22' 91.4"	83° 59' 45.8"	RB-A8-S
RB-A10	3250	73.1	384	35° 22' 91.6"	83° 59' 45.8"	RB-A10-S
RB-E1	2250	49.6	516	35° 22' 01.7"	83° 59' 45.0"	RB-A3-S
RB-E2	2460	61.8	539	35° 22' 04.0"	83° 59' 45.6"	RB-A5-S
RB-E3	3270	54.6	663	35° 21' 97.4"	83° 59' 49.3"	RB-E3-S
RB-E4	3320	68.2	481	35° 21' 97.4"	83° 59' 49.2"	RB-E4-S
RB-E5	3020	63.8	575	35° 22' 01.5"	83° 59' 44.8"	RB-E5-S
RB-E6	2830	55.1	455	35° 22' 01.4"	83° 59' 44.8"	RB-E5-S
RB-E7	1610	76.1	382	35° 22' 01.7"	83° 59' 44.7"	RB-E5-S
RB-E8	2950	51.9	749	35° 22' 02.6"	83° 59' 44.9"	RB-E8-S
RB-E9	2770	54.0	748	35° 22' 02.6"	83° 59' 44.9"	RB-E8-S
RB-E10	1160	52.6	567	35° 22' 91.6"	83° 59' 45.8"	RB-A10-S
Std. Dev.	878	16.0	129			
Mean	2630	63.0	568			
Mean E	2570	58.8	567			
Mean A	2690	57.3	584			
Mean M	2630	72.8	552			

Table 14
Ca, Mg, and Al Concentrations, Coordinates and Corresponding Soil Sample for Foliar Samples Taken at Spruce Mountain

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)	Latitude	Longitude	Soil Sample
SM-M1	1210	84.3	449	35.61297	83.17538	SM-M1-S
SM-M2	3140	45.0	828	35.61301	83.17545	SM-A1-S
SM-M3	1980	53.5	551	35.61280	83.17532	SM-M3-S
SM-M4	2060	157	466	35.61299	83.17553	SM-M4-S
SM-M5	1990	148	485	35.61230	83.17564	SM-P6-S
SM-M6	2520	66.8	620	35.61300	83.17568	SM-A8-S
SM-M7	2660	109	844	35.61299	83.17565	SM-A8-S
SM-M8	1760	85.8	503	35.61299	83.17567	SM-E7-S
SM-M9	2200	64.4	539	35.61290	83.17510	SM-E9-S
SM-M10	3670	89.4	652	35.61287	83.17561	SM-A9-S
SM-A1	1660	67.4	456	35.61304	83.17548	SM-M1-S
SM-A2	2430	109	684	35.61296	83.17548	SM-A1-S
SM-A3	871	94.3	383	35.61298	83.17552	SM-E3-S
SM-A4	1780	46.9	456	35.61300	83.17553	SM-M4-S
SM-A5	3030	83.6	637	35.61300	83.17550	SM-M4-S
SM-A6	1790	67.4	637	35.61298	83.17564	SM-A6-S
SM-A7	2370	82.1	701	35.61297	83.17557	SM-P6-S
SM-A8	2800	78.1	673	35.61294	83.17570	SM-A8-S
SM-A9	2660	60.7	524	35.61284	83.17566	SM-A9-S
SM-A10	2880	99.4	594	35.61287	83.17555	SM-A9-S
SM-E1	1630	76.5	601	35.61302	83.17542	SM-M1-S
SM-E2	2200	59.4	625	35.61301	83.17547	SM-A1-S
SM-E3	2010	65.8	717	35.61298	83.17549	SM-E3-S
SM-E4	1620	98.7	590	35.61299	83.17551	SM-E3-S
SM-E5	2710	42.1	559	35.61283	83.17531	SM-M3-S
SM-E6	4130	33.7	904	35.61283	83.17531	SM-M3-S
SM-E7	2260	64.2	656	35.61297	83.17569	SM-E7-S
SM-E8	2910	106	591	35.61297	83.17567	SM-E7-S
SM-E9	3120	53.7	648	35.61292	83.17567	SM-E9-S
SM-E10	2100	62.1	519	35.61290	83.17567	SM-E9-S
Std. Dev.	702	28.6	121			
Mean	2340	78.5	603			
Mean E	2470	66.2	641			
Mean A	2220	78.9	574			
Mean M	2320	90.4	594			

SOIL DATA

Table 15
Soil Ca, Al, and Mg Concentrations at Balsam High Top

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)
BT-E1-S	478	6870	263
BT-E4-S	775	3650	222
BT-E6-S	328	7380	233
BT-E8-S	306	9040	288
BT-E9-S	227	8160	225
BT-E10-S	458	6090	249
BT-A1-S	674	5230	146
BT-A8-S	469	19100	912
BT-M4-S	472	4930	217
BT-M6-S	575	3380	128
BT-M8-S	476	5070	196
BT-M9-S	271	10300	613
Std. Dev.	162	4220	226
Mean	459	7430	308

Table 16
Soil Ca, Al, and Mg Concentrations at Clingman's Dome

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)
CD-E1-S	482	8790	989
CD-E2-S	1080	2350	545
CD-E4-S	808	6780	1270
CD-E5-S	232	14900	3100
CD-E6-S	329	12500	1380
CD-E8-S	1970	3640	245
CD-E10-S	302	5950	1010
CD-A1-S	432	18600	2620
CD-A2-S	689	15000	3910
CD-A3-S	953	5510	993
CD-A4-S	413	14100	3620
CD-A8-S	255	6720	1080
CD-M1-S	327	16700	2730
CD-M3-S	415	15500	2620
CD-M7-S	277	10900	1340
CD-M8-S	262	3740	493
CD-M9-S	469	13700	2210
Std. Dev.	440	5180	1140
Mean	570	10300	1770

Table 17
Soil Ca, Al, and Mg Concentrations Near Double Spring Gap

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)
DS-D1-S	1860	5170	575
DS-E2-S	807	7180	815
DS-E5-S	282	15300	2700
DS-E6-S	279	19300	3150
DS-E7-S	370	16900	2790
DS-E10-S	335	18900	3140
DS-A2-S	263	17500	3020
DS-A3-S	464	13800	2450
DS-A4-S	413	14500	2840
DS-M1-S	306	18200	3170
DS-M10-S	360	15000	2550
Std. Dev.	469	4610	913
Mean	522	14700	2470

Table 18
Soil Ca, Al, and Mg Concentrations at Mt. LeConte

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)
LC-A1-S	202	3320	425
LC-A5-S	1100	2110	292
LC-A6-S	798	2340	170
LC-M1-S	727	3220	1200
LC-M2-S	2790	1650	892
LC-M3-S	699	2320	380
LC-M4-S	120	938	560
LC-M11-S	46	2900	131
LC-E5-S	853	1500	216
LC-E7-S	392	3330	607
LC-E8-S	903	1610	220
LC-E10-S	1260	1420	258
Std. Dev.	729	823	323
Mean	824	2220	446

Table 19
Soil Ca, Al, and Mg Concentrations at Mt. Sterling

Sample ID	Ca ppm (μg/g)	Al ppm (μg/g)	Mg ppm (μg/g)
MS-E8-S	377	11900	1090
MS-E10-S	351	10300	813
MS-A1-S	550	14400	1960
MS-A2-S	285	18000	1910
MS-A6-S	305	15300	1720
MS-M1-S	364	15100	1280
MS-M2-S	319	16100	1320
MS-M3-S	296	13500	1130
MS-M5-S	773	5680	578
MS-M8-S	364	19500	2960
Std. Dev.	151	3960	689
Mean	398	14000	1480

Table 20
Soil Ca, Al, and Mg Concentrations at Richland Balsam

Sample ID	Ca ppm (μg/g)	Al ppm (μg/g)	Mg ppm (μg/g)
RB-E3-S	476	8180	1290
RB-E4-S	362	10100	2140
RB-E5-S	464	3020	186
RB-E8-S	374	12600	2290
RB-A1-S	397	4460	418
RB-A3-S	440	8890	850
RB-A4-S	610	10300	895
RB-A5-S	964	9870	785
RB-A6-S	366	12700	2970
RB-A8-S	362	16200	4700
RB-M5-S	444	12000	3200
RB-A10-S	296	11500	2450
Std. Dev.	177	3600	1350
Mean	463	9980	1850

Table 21
Soil Ca, Al, and Mg Concentrations at Spruce Mountain

Sample ID	Ca ppm (µg/g)	Al ppm (µg/g)	Mg ppm (µg/g)
SM-E3-S	601	6550	681
SM-E7-S	526	10500	900
SM-E9-S	638	7070	368
SM-A1-S	535	8280	571
SM-A6-S	642	13000	1160
SM-A8-S	793	8590	481
SM-A9-S	837	9210	460
SM-M1-S	504	12000	819
SM-M3-S	1140	9590	405
SM-M4-S	741	10000	1360
Std. Dev.	237	2920	341
Mean	741	8810	757