Why are Plants Thriving in Woodlands on Stony Brook Campus Despite Acid Rain and Acid Soil?

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ABSTRACT

Long Island's woodland soils are naturally acidic. However, acid rain produced from sulfur dioxide and nitrogen oxides in emissions from smoke stacks and motorized vehicles have made the soil even more acidic. As soil becomes more acidic, poisonous Al replaces Ca, a plant nutrient. The pH of precipitation on Long Island was 5.6 before industrialization. By 1987 it had been reduced to 4.3. Since then it has continued to rise as a result of the Clean Air act. The pH of soil in wooded areas on Stony Brook campus is 2.8 to 3.2 at the contact of the organic and mineral layer and increases with depth. Since 1922 acid tolerant woodland plant species on Long Island have become more dominant. The Ca/Al ratio of leaves, rootlets and exchangeable cations in soil indicate the extent of adverse impacts on plants. Measurements of the Ca/Al ratios in leaves, rootlets and soil in wooded areas on Stony Campus indicate that the present acid tolerant plant life is not under stress. Available Ca in the soil is restricted to the topmost layer of soil. This indicates that the Ca available to the plants is from plant litter and airborne dust with little coming from the parent soil mineral matter. As the pH of precipitation continues to increase and more plant available Ca is added to the soil from airborne dust we may find acid intolerant plants returning to our woodlands.

INTRODUCTION

This report presents calcium and aluminum analyses of plant leaves and fine roots in an undeveloped wooded area on the Stony Brook University campus that may help explain why, while acid rain is acidifying the soil and discouraging the growth of acid-sensitive plants, the existing acid-resistant plants appear to be thriving.

Fig. 1 Location of Stony Brook

During the last 10 years, high school and college students have analyzed the pH of soil on Stony Brook University's campus (Fig. 1) to evaluate the effects of 70 or more years of acid rain on the plants and soil. We have found the soil pH in undeveloped wooded areas of the campus increases from 3.1± 0.3 to a pH of 4.2 ± 0.3 within the upper 30 cm. suggesting that 4.2 ±0.3 was probably the value of soil pH in the upper 30 cm before acid rain deposition. This is consistent with the results of Waka, 2013, and Donnelly, 2014, who studied soil under a house on Long Island in Hallockville, NY that was covered since 1765. They found a pH of 4.0.

The acid rain affecting Long Island is due to:

- sulfur dioxide from coal-powered industrial plants in Pennsylvania, Ohio and West Virginia
- nitrogen oxides from internal combustion engines in vehicular traffic in the Mid-Atlantic States

which were brought to Long Island by prevailing southwesterly winds (Mohnen, 1988). These oxides created nitric and sulfuric acid in precipitation, which lowered the pH of precipitation and subsequently, the pH of the soil.

The pH of rain was 5.6 before industrialization, by 1955-56 the pH was reduced to 4.8 (Mackenzie & Mackenzie, 1995) and by 1987 to 4.3 (NYDEC, 2005). As a result of the Clean Air Act and later amendments, the pH of rain on Long Island increased. By 2005 the pH was 4.6 (NYDEC, 2005). In 2005 the New York Department of Conservation stopped collecting the pH of precipitation on Long Island. The pH of rain in Washington Crossing, NJ on the path of southwesterly winds to Long Island also had a pH of 4.3 in 1987 and a pH of 4.5 in 2005. In 2013 the pH of rain had increased to 5.0 (New Jersey DEP, 2016) suggesting that there was a similar increase in the pH of precipitation on Long Island.

Acid rain enriches exchangeable hydrogen ions in the soil. More specifically, sulfuric acid dissociates in water and adds hydrogen ions to the system which react with the most common species of aluminum in the soil, gibbsite (Fig. 2).

$$Al(OH)_3 + H^+ \rightarrow Al(OH)_2 + H_2O$$
$$Al(OH)_2^+ + H^+ \rightarrow Al(OH)^{2+} + H_2O$$
$$Al(OH)^{2+} + H^+ \rightarrow Al^{3+} + H_2O$$

Fig. 2 Freeing of aluminum ions through addition of hydrogen ions.

These hydrogen ions replace exchangeable Mg and Ca and promote the production of exchangeable aluminum (Hedin and Likens, 1996). Exchangeable Ca and Mg ions are essential for healthy plant growth. Whereas, exchangeable Al3+ is deleterious to plants because it replaces the exchangeable Ca and Mg. The reduced availability of Ca and Mg impedes plant growth (Ericsson 1995). Cronan and Grigal (1996) reviewed research on correlations between adverse reaction on plant growth to decreases in Ca and increases in Al in soil solutions and plants. They found there is a greater than 50:50 risk of adverse impacts on plant growth if the Ca/Al molar ratio is:

- less than 12.5 in plant leaves
- less than 1 in soil solution and
- less than 0.2 for fine root tissue

This report reviews the research on the soil and plants on the Stony Brook University campus including pH and cation exchange capacity (CEC) of soil with depth and includes our more recent studies on the species distribution of plants, pH of soil and the chemical analysis of leaves and roots in a small area of the 27-acre forested Ashley Schiff Park Preserve on the Stony Brook University campus (Fig. 3).

Fig. 3 Location of study sites on Stony Brook campus. Yellow five-point star is location of pH of soil and leaf collection. Four-point star represents location of CEC analysis of soil.

Wherry (1923) studied the plant distributions and the pH of soil in a deciduous Long Island forest in Locust Valley on the same moraine, the Harbor Hill Moraine, as the Stony Brook campus is located. Greller et al (1990) restudied the pH of soil and plant distributions in the same forest in 1985. He found that a significant decrease in the pH of soil compared to what Wherry (1923) in 1922 (Table 4). Greller et al (1990) concluded that the decreased pH was a result of acid rain.

Greller et al (1990) found that there were fewer types of acid-sensitive plants within the forest and an increased dominance of acid-tolerant plants such as maple-leaved viburnum (Viburnum acerifolium), two-leaved Solomonseal (Maianthemum canadense) and white wood aster (Aster divaricatus) and a loss of less acid tolerant plants such as wild geranium (Geranium maculatum), bloodroot (Sanguinaria Canadensis) and Indian cucumber (Medeola virginiana).

These studies are important because they give historical data supporting that soil pH decreased and acid-tolerant plant abundances increased from 1922 to 1985 along with the increase in the acidity of rain from pH of 5.6 in 1922 to a pH of 4.3 by 1987 (Mackenzie & Mackenzie, 1995 and NYDEC, 2005).

METHODS

Leaves were collected on campus at three separate times by three different groups. In November 2015, newly fallen leaves were collected by Jovet Llanos, Bill Miller and Gilbert N. Hanson. In July 2016 leaves were collected on the plants by GeoPREP students under the direction of Gilbert N. Hanson and Megan Donnelly. In April 2017 leaves were collected by Karim Hanna and Gilbert N. Hanson during the budding period. Samples of soil for pH analysis were collected by Karim Hanna in Oct. 2017.

PREPARATION OF LEAVES FOR ANALYSIS

Leaf samples were first rinsed with deionized water, then placed in a 0.25% Palmolive detergent solution for 1 minute in an ultrasonic-bath. After the ultrasonic bath, the leaves were rinsed twice with deionized water, then immediately dried in a ventilated oven for 24 hours at 80˚C. Leaves were then ground into a homogenous powder in a coffee grinder twice for 2 minutes. Afterward, the samples were pulverized with tungsten carbide balls in the MixerMill three times for 10 minutes.

ACID DIGESTION OF LEAVES

ICP-AES metals analysis of leaves after hot plate acid digestion were done by the Cornell Nutrient lab at Cornell University.

PH ANALYSIS OF SOIL

Ten ml of soil were placed into a 50-ml centrifuge tube to which 10ml of 0.01 m CaCl2 solution was added and mixed vigorously by hand for one minute. The test tube was then placed in an ultrasonic bath for one minute. The pH was measured using a Vernier LabQuest 2 pH probe.

CEC METHODS

One gram of soil was placed into a 15ml centrifuge tube to which 4ml of 2M NH4Cl was added. It was then agitated with vortex mixer for 1 minute, placed in an ultrasonic bath for 30 minutes and centrifuged for 38 minutes to separate the solution from the soil. Supernatant liquid was passed through a 0.45 µm-pore-size filter into test tube to which 0.5 ml of 6m nitric acid was added. The tube was then placed on a vortex machine for 30 seconds. The procedure was repeated on the same sample three times and each replicate was added to the same tube for ICP analysis.

SPECIES DISTRIBUTION PLANTS

Species distribution of plants was determined using quadrats in the Stony Brook's Ashley Schiff Park Preserve. A study area of 12x12x13.6x15.2 meters was chosen to estimate the percent coverage of plant species in the area (Table 3).

RESULTS

All plants in the study area (Table 1 and Fig. 3) are considered acid resistant (Gawler and Sneddon 2015). The most common plant species seen, maple-leaf viburnum, makes up 67% of the plants covering the forest floor. The elemental abundance of the leaves is shown in Table 1. While leaves were collected at three separate times, there are not enough samples to show a pattern in chemical abundance for species with seasons. Maple-leaf viburnum, the most abundant plant, has the highest concentrations of Al, Ca, Mg and K but the lowest Ca/Al ratio. There is a fairly large variability in the chemistry among the samples as indicated by the relatively large average deviation which is 30% to 40% for Ca, Mg, and K and 95% for Na and Al. The Ca/Al molar ratios have a larger average deviation of 60%. This is true not only for all samples, but also for the replicates of black birch and sassafras which were collected at different seasons. It is not clear if the variations are related to changes in leaves' chemistry associated with the season that they were collected or to other factors. For both the sassafras and the black birch the fallen leaves collected in November have a higher aluminum concentration and a lower Ca/Al ratio than those collected in the spring or summer.

The cation exchange capacity (CEC) and exchangeable cations expressed as milliequivalents (mEq) per 100 grams of soil collected in a small wooded area near the Earth and Space Sciences building (Fig. 3) were determined by Jovet Llanos in 2015 at 0, 15, 30 and 45 cm depth (Table 4 and Fig. 4). The Ca/Al molar ratio at the boundary of the organic and mineral layer, 0 cm depth, is 12.8. At 15cm depth, the ratio is 0.06, at 30 cm it is 0.04 and at 45 cm it is 0.03.

The pH values of soil with depth were determined at the kettle hole site where the leaves were collected. The soil samples for pH analysis were collected at the ridge top, along the slope and on the valley floor of the kettle (Fig. 5). For each site the pH value of the organic matter in the O-horizon has a significantly higher value than that at the O-A-horizon boundary. These data suggest that as the rain passes through the O-horizon it releases organic acids from the plant litter. Below the O-Horizon the pH of the soil for each site then increases

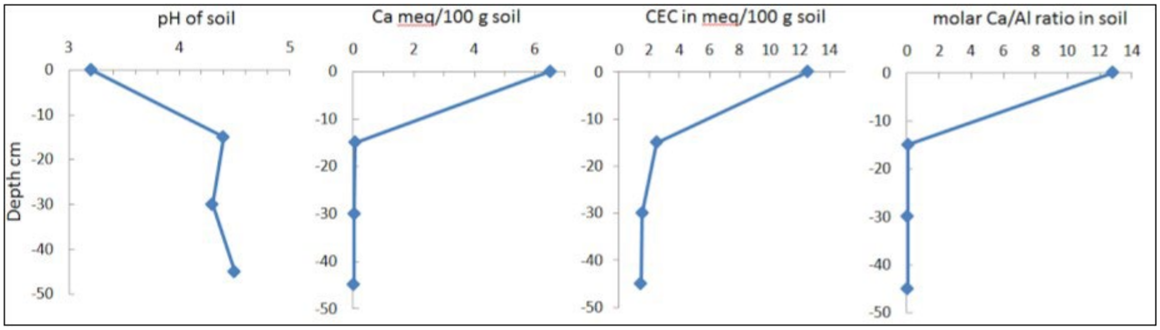

Fig. 4: Soil pH, cation exchange capacity and molar Ca/Al ratio at a site in undeveloped woods near the Earth and Space Sciences Building on Stony Brook University campus.

However, the ridge and slope samples have significantly lower pH's than the valley floor even though the differences in elevation are only a few meters (Fig. 3). The changes in pH with depth for the four sites change with essentially the same pH differences.

DISCUSSION

With the exception of poison ivy (Toxicodendron radicans), all recorded species were seen in historical data (Greller et al. 1990, Wherry 1923). Maple-leafed viburnum (Viburnum acerifolium) is the most prominent species by groundcover percentage present in the undeveloped area of Stony Brook campus. This is consistent with data collected by Greller et al. and suggests the trend of acid-tolerant species becoming more dominant is continuing.

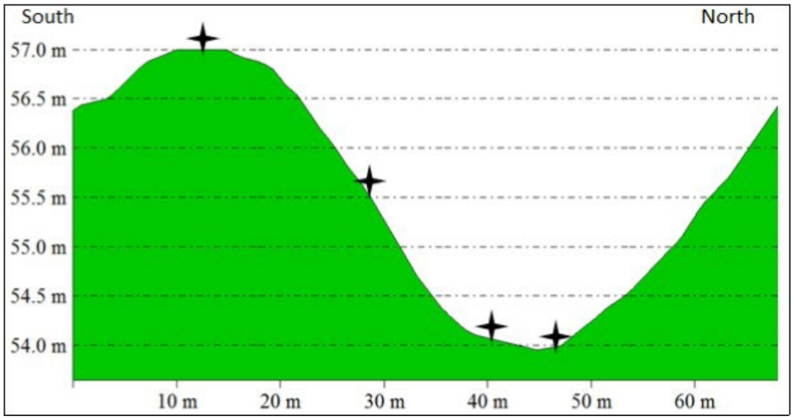

Fig. 5: Cross-section across kettle hole in Ashley Schiff Park Preserve showing location of samples selected for pH analysis from south to north at ridge top, ridge slope and two samples in the valley.

Though our data was collected in an area farther east, forest compositions are similar based on taxa comparison from the Greller and Wherry studies and are typical of temperate deciduous forests. To explain this shift from acid-sensitive to acid-tolerant species Greller et al, 1990 stated: "We offer the explanation that the present range of average soil pH, 3.8-4.1, is so low that only more acid tolerant taxa can dominate, regardless of habitat."

The lowest value for Ca/Al molar found in foliar tissues is 17.2 for Maple-leafed viburnum (Viburnum acerifolium). The mixed fine root tissue shows a Ca/Al molar ratio of 0.92. Both values are above the 50% risk ratio determined by Cronan and Grigal (1990) and show that the plants are in favorable conditions for growth. While the uppermost soil has a high Ca/Al molar ratio (12.8) the fine roots, which uptake nutrients around this depth, exhibit a much lower Ca/Al ratio of 0.92. We offer two explanations for why this may be: 1) The Ca/Al molar ratio drops dramatically from 0 cm depth to 15 cm depth. The fine roots may be exposed to both calcium rich and calcium poor soil depending on what depth they are deriving nutrition from. 2) Cronan and Grigal identified a similar trend and attributed the ratio difference to the aging of fine roots, suggesting that overtime aluminum accumulates in the root tissue but, does not enter the rest of the plant unless through a breakage in a section of the epidermal layer of the roots.

In summary, the Ca/Al molar ratios throughout the system are as follows:

- An average of 107 in plant leaves (all species included).
- 0.92 for mixed fine root tissue.
- 12.8-0.06 in soil solution from 0-15 cm depth.

The woody portions of the plant were not used as a metric as Ca/Al ratios in this area are misleading. Elemental movement in woody tissues is unpredictable and not reflective of the external environment (Brownridge 1984).

The high levels of Ca/Al ratios seen in the foliar tissue is expected as Ca2+ is found throughout the cell wall and membrane of plant cells (Hepler 2005). These structures comprise a sizable portion of the total mass of foliar tissue.

The paucity of exchangeable soil calcium at 15 cm and greater depths suggests that plants are absorbing essentially all the calcium within the upper 15 cm of soil (Fig. 4). Boguslavsky (2000) analyzed the CEC of forest soil in Cathedral Pines State Park on Long Island. She used a 0.1 M BaCl2 solution for CEC analysis because it has a higher exchange affinity than does NH4Cl. She did not sample at a small scale for the upper 30 cm of soil, but rather selected bulk samples. She found the Ca/Al molar ratios for bulk samples representing 0 to 30 cm, 30 to 60 cm and 60 to 90 cm depths to be 0.16, 0.05 and 0.12 respectively. These data are consistent with our results in suggesting that the molar Ca/Al ratios in soil water at depths greater than 15 cm are much less than 1, the value that Cronan and Grigal (1996) found has a greater than 50:50 risk of adverse impacts on plant growth.

The most likely reason that the Ca is restricted to the uppermost layer of the soil column is that the quartz-rich and calcium poor soils on Long Island are not an important source of base cations to the soil (Kundic, 2005 and Xin and Hanson, 1994). This would suggest that calcium is added to the soil dominantly from decaying plant litter and dry precipitation (Fig. 6). Munster (2008) collected dry plus wet precipitation monthly at five sites on Long Island monthly between December 1, 2005 and July 5, 2007. She found that the average of total dry plus wet precipitation has a Ca concentration of 0.60 mg per liter. Long Island has an average of about 120 cm of rain per year. For each square meter, 1.2 cubic meters or 1,200 liters of precipitation are added to the soil each year. This amounts to 2.5 grams of Na, 0.31 gm of Mg, 0.68 gm of K and 0.60 gm of Ca of these base cations added to each square meter each year.

If one could follow a calcium cation throughout the system (Fig. 6), we would see it enter the soil through either organic leachate from the dead leaf litter or from atmospheric dust. Both mechanisms would need to be in aqueous solution and therefore rely on rain to enter the structure. From here the calcium cation would be absorbed through the fine roots of the surrounding plants. It is at this time where the aluminum would most likely be trapped by the epidermal layer of the fine roots and the calcium would continue to travel through plant tissue. This is most likely a form of active transport. From here the calcium cation will pass through the xylem until reaching the foliar tissue where it will be incorporated into cell walls, membranes as well as be used for basic cell functions. If the calcium in a leaf or woody matter falls to the ground, it may be recycled in the system.

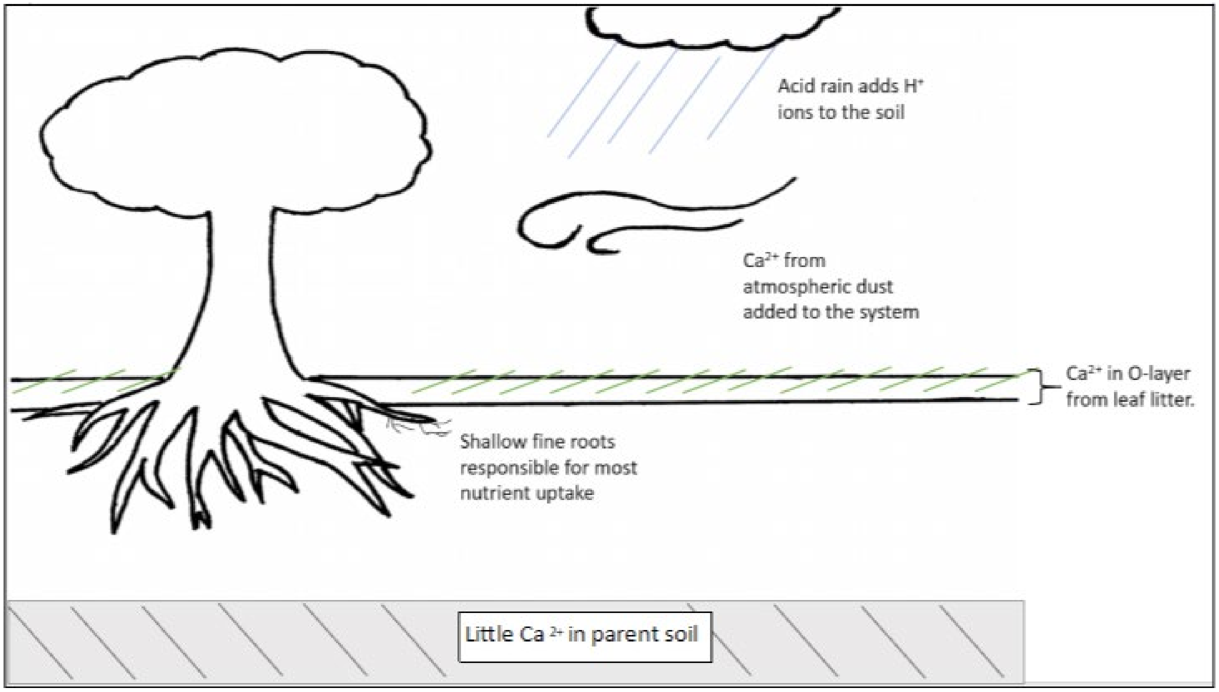

Fig. 6: Movement of calcium and hydrogen throughout the system.

TABLES

Table 1: Chemical analysis of leaves

	Date	Al	Ca/Al	Ca	Mg	K	Na	P	Fe	Mn
	collected	mg/kg	molar	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Beech	April 2017	23.6	56.2	1970	840	5330	484	234	40.0	1150
Black Birch	April 2017	6.1	220	2000	1240	14400	115	2440	44.1	995
Black Birch	July 2016	21.0	121	3800	2700	11900	135	806	71.6	5550
Black Birch	Nov. 2015	32.0	78.5	3730	2090	4790	1580	287	69.4	5790
Maple	July 2016	6.7	195	1950	1710	15600	188	5290	41.1	2020
Maple-leaf Viburnum	July 2016	245	17.2	6260	4700	16100	175	836	110	1680
Red Maple	July 2016	15.7	193	4510	1770	9660	94.2	803	41.0	6160
Sassafras	July 2016	36.9	62.6	3430	2090	16000	163	1130	57.8	1110
Sassafras	Nov. 2015	90.2	22.6	3030	1760	5730	1561	242	60.1	907
Average		53	107	3409	2100	11057	499	1341	59	2818
Average Dev.		51	67	1041	711	4159	476	1122	16	2010

Table 2. Chemical Analysis of rootlets

Al	Ca/Al	Ca	Mg	K	Na
mg/L	molar	mg/kg	mg/kg	mg/kg	mg/k
1320	0.92	1800	639	1340	273

Table 3: O-Horizon and Soil pH in Ashley Schiff Park Preserve in cm below the O-Horizon A horizon boundary

Depth cm	Ridge	Slope	Valley	Valley
O-Hzn	3.22	3.13	3.35	3.32
0	3.05	2.85	3.21	3.11
5	3.22	3.17	3.7	3.67
10	3.36	3.33	3.81	3.79
20	3.58	3.56	3.88	3.86
30	3.62	3.63	3.94	3.92

Table 4: Quadrat information for plant distribution in basal percent coverage in Ashley Schiff Park Preserve

Quadrat	New York Fern	Maple-leaf Viburnum	Red Maple	American Beech	Sassafras	White Oak	Poison Ivy	Winter green
1	35	17	3	1	7	3	10	0
2	0	60	0	2	1	3	0	10
3	0	60	1	0	5	7	5	0
4	0	40	0	2	7	0	3	0
Average	3	44.25	1.30	1.25	5	3	6	2.50

TABLES

Table 5 Aluminum, base cations and pH in soil solutions in undeveloped woods near ESS building on Stony Brook University campus.

Depth cm	Al^{+3} meq/100 gm	Ca/Al molar	Ca^{+2} meq/100 gm	Mg^{+2} meq/100 gm	K^{+1} meq/100 gm	Na^{+1} meq/100 gm	pH
0.00	0.76	12.8	6.50	3.07	0.55	0.11	3.2
-15.00	1.74	0.06	0.07	0.21	0.16	0.04	4.4
-30.00	1.19	0.04	0.04	0.13	0.08	0.01	4.3
-45.00	0.93	0.03	0.03	0.18	0.11	0.01	4.5

Table 6 Soil pH using distilled water in a forested area in Valley Stream

	Ridgetop	Slope	bottomland
Wherry (1923)	4.5	5.5	6.5
Greller et al (1990)	3.8	3.9	4.1

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