A Study of Soil pH in a Woodland at Stony Brook University

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Introduction

The Northeastern United States has been affected by acid rain for more than 50 years. Geography, prevailing winds, and soil composition have collectively subjected the Northeast to soil acidification by acid deposition. Long Island is especially vulnerable, both because it is underlain by quartz-rich, coarse, sandy glacial soils. In order to make an argument for the commencement of environmental monitoring programs, the author has sampled the soil in fifteen locations in Clara's Woods (see Fig. 1) on Stony Brook University campus to determine the effect of acid rain on soil pH. The purpose of this study is to establish a baseline for monitoring the pH of soil in a woodland on Long Island

Soil pH is affected by acid rain. The main sources of acid rain are electric power generation, automotive exhaust, and manufacturing plants, which add oxides of sulfur and nitrogen to the air. Acid precipitation occurs when atmospheric water reacts with these aerosols, forming nitric and sulfuric acids. The carbon dioxide thus emitted does not contribute to acidity as the water is at equilibrium with atmospheric CO_2 already. A large portion of these emissions, especially sulfur oxides come from the Ohio River Valley region as a result of burning sulfide rich coal (Driscoll et. al 2001). The emissions are carried east over the Island by prevailing winds

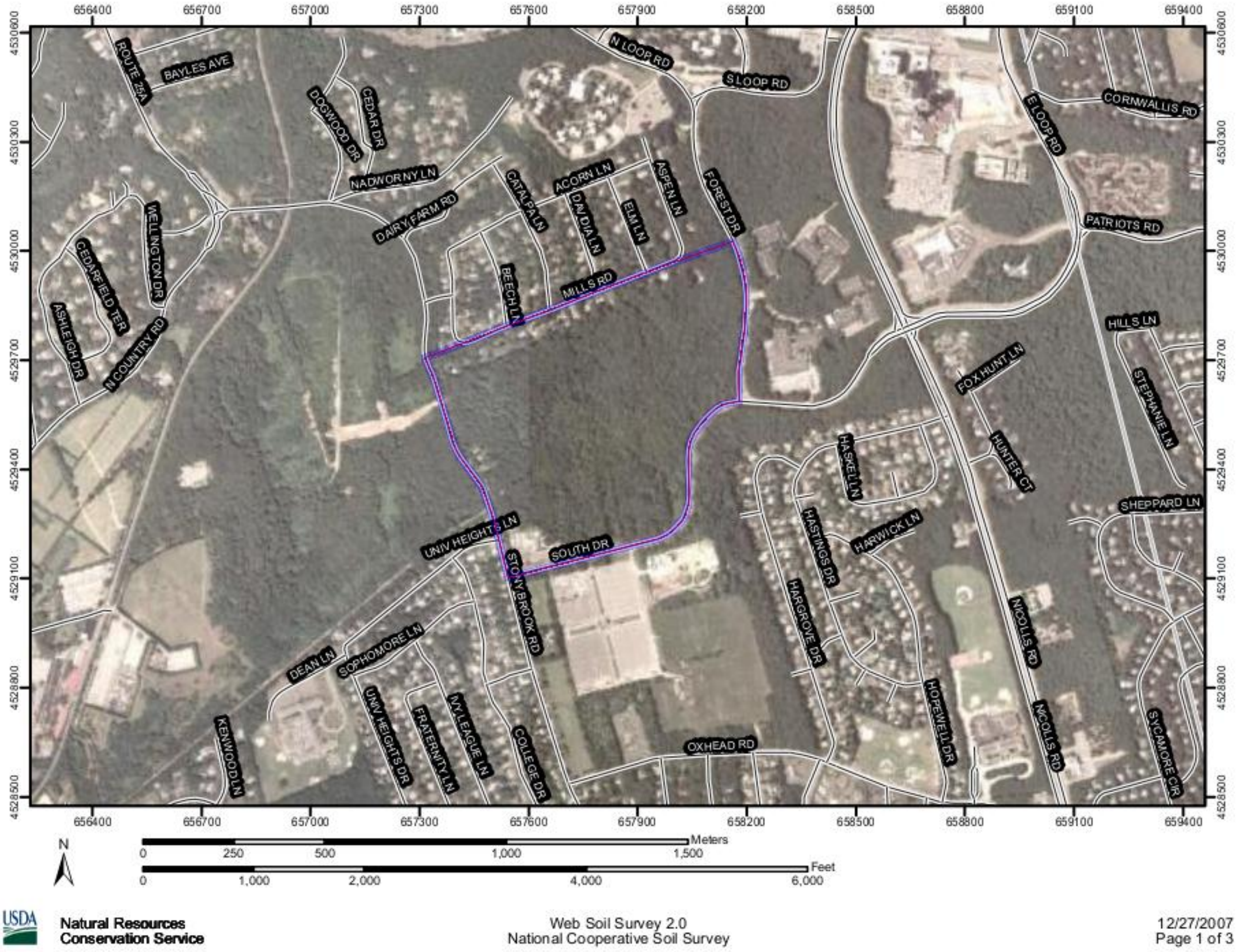

Figure 1 - Clara's Woods (highlighted in purple) on airphoto showing Stony Brook University campus and surrounding area.

Table 1 pH in Surface Soil -- Locust Valley Site in 1922 and 1985

Habitat	1922 Wherry, 1923	1985 Greller et al, 1990
Bottomland	6.5	4.1
Slopes	5.5	3.9
Ridgetops	4.5	3.8

Wherry (1923) studied the surface soil pH on the estate of Antonin Hodenpyl in Locust Valley in western Long Island. The same location was later resampled in 1985 by Greller et al, 1990 who found that the surface soil pH of samples collected in 1985 had decreased significantly since 1922 (Table 1). Wherry (1923) found that on average soil at ridge tops has a higher pH (pH=4.5) than the slopes (pH=5.5) than the bottoms of valleys (pH=6.5). Greller et al, 1990 found that the pH of the much lower the ridge tops had a pH or 3.8, the slopes 3.9 and valley bottoms 4.1. The reason for the soil acidification is the increasing acidity of rain on Long Island from a normal pH of about 5.6 to a pH of 4.2 in 1987 and a pH of 4.5 in 2009 (http://www.dec.ny.gov/chemical/24711.html)

Some plant species noted by Wherry (1923) at the Hodenpyl estate have disappeared or moved to different settings. This seems to be related directly to pH, as the species that flourished on the acidic ridgetops in 1923 are now confined to the bottomlands which were as of 1985 more acidic than the ridgetops were in 1922. Additionally, of the nine species noted in the bottomlands in 1923, five were missing in 1985. These are:

- Goosegrass, Galium aparine
- Spotted cranesbill or wild geranium, Geranium maculatum
- Licorice root or wild anise, Osmorhiza longistylis
- Bloodroot, Sanguinaria canadensis
- Lanceleaf figwort, Scrophularia lanceolata

Other species missing from the site in 1985 include:

- Flowering dogwood, Cornus florida
- Hay-scented fern, Dennstaedtia punctilobula
- Indian cucumber root, Medeola virginiana
- Cow wheat, Melampyrum lineare

Additionally, Maianthemum canadense (false lily of the valley), confined in 1923 to the acidic ridgetops, has spread to all three of the above-mentioned habitats. Species not noted in 1923 have appeared, such as Rhus radicans (better known as poison ivy). Viburnum acerifolium (maple leaf viburnum) found on the ridgetops in 1923 was found on the slopes and the bottomlands in 1985, and was missing from the ridgetops. There has been a similar migration of Gaylussacia baccata (black huckleberry) from the ridgetops to the slopes. The migrations and disappearances of plants are probably related to the acidification of the soil on the Hodenpyl estate

Soil acidification damages plants in several ways, though direct damage to tissues is not seen except in extreme cases. Instead, most damage is caused by the changes in soil chemistry that the higher concentration of hydronium ion brings about (http://en.wikipedia.org/wiki/Acid_rain#cite_note-19). Soils have a given *cation exchange capacity*, abbreviated CEC and defined as the concentration of cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+, Al^{3+}) the soil can sorb (Sposito, 1994). Cation exchange capacity "is a function of grain size, amount of organic matter, extent of coatings on the grains and composition of the sorbing material" (Boguslavsky 2000). Coatings with large cation exchange capacities are clays, organic matter and iron oxides. A soil with higher cation exchange capacity will have a slower response to acid input.

Adding acid to soil displaces Na^+, K^+, Ca^{2+}, and Mg^{2+} from the surfaces of the materials that sorb them and replaces them with hydronium and aluminum ions. The base cations Ca, Mg and K are major nutrients for plants; indeed, plants secrete small amounts of acid from their roots into the soil to free these for their own use. Acid precipitation allows them to migrate downward, out of the reach of plants. Haynes and Swift (1984) found that "with increasing soil acidification, increasing amounts of base the cations Ca^{2+}, Mg^{2+}, K^+, and Na^+ are leached from the soil and are

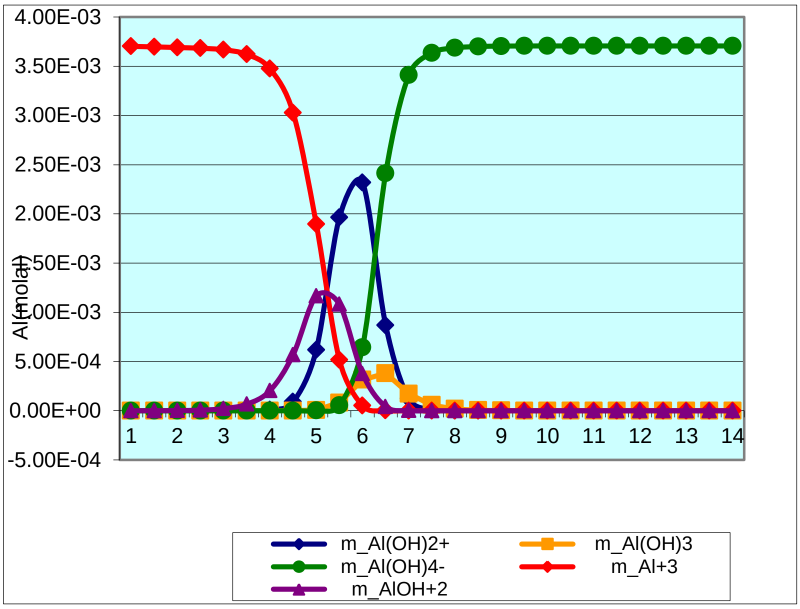

Figure 2: Aluminum speciation as a function of pH (Jha, 2008)

replaced by H^+ and Al^{3+}. Acidification limits the amount of nitrogen and sulfur available to the plants and acidification causes the formation of Al^{3+} and H^+ from the aluminum hydroxides in the soil (see Fig. 2). Al^{3+} is toxic to because it inhibits root growth (Delhaize and Ryan 1995), which makes the acidification process a destructive feedback loop; the plants, already nutrient-starved, cannot expand their root systems to compensate.

Methods

In his 1920 and 1923 papers, Wherry described a method for measuring soil pH in its "natural" state, which is the basis of modern soil pH analysis:

> "A sample of soil a gram or two in weight is shaken from the living roots into an empty vial, and 5 cc of the most nearly neutral and salt-free water available is added, the vial being shaken well to insure complete mixing. After the soil and water are thoroughly mixed, the solid matter may be compacted with a glass rod or a stick, and the vial then supported at an angle of 45 degrees and allowed to stand until the bulk of the suspended matter has settled. The more or less clear liquid is then decanted or pipetted off into another vial, a drop or two of bromothymol blue or one of the other indicators, the color changes of which occur near the neutral portion of the table, are added, and the color assumed is noted. If either of the extreme colors is shown, the process is repeated with the indicator whose color changes come next in the corresponding direction; and this is continued until either an intermediate color of one indicator, or opposing extremes of two overlapping ones, are obtained, whereupon the specific acidity or alkalinity can be read off from the chart."

Modern versions of this test use a pH meter instead of indicators for more precise measurements. The liquid has historically been distilled water, but in recent decades an 0.01-molar calcium chloride dihydrate solution has been used, e.g., as described by Robarge and Fernandez (1987). This solution is thought to give more accurate results, because the dissolved salts mimic those in rainwater. In this study the author has used 0.01-molar calcium chloride dihydrate and distilled water to compare the two approaches.

Sampling Protocol

Fifteen sites representing a variety of topographic settings in Clara's Woods were chosen. Based on the studies by Greller et al (1990) and Wherry (1923), the author hypothesizes that there will be a relationship between relative altitude and soil pH and has chosen sample points accordingly, including the highest and lowest points in the area.

At each site, a hole approximately a foot wide and six to eight inches deep was dug with a shovel. Soil from the sides of each hole ("sampling in place") in the A-horizon was removed with a trowel and transferred to a sealable plastic bag, which was squeezed to expel the air. Each bag was labeled with a number and the compass direction and number of steps from some landmark that were required to reach the site, usually the location of the last sampling point. The samples were air-dried at room temperature for 24 to 48 hours on paper and returned to their bags.

Preparation

Each sample was sieved through a 2-mm mesh sieve to remove any particles larger than sand. Any obvious pieces of organic matter such as roots and twigs were removed manually. 10 mL of each sample were placed into 50 mL plastic centrifuge tubes. Ten mL of either deionized water or 0.01-molar calcium chloride dihydrate solution was added to each tube. The tubes were shaken vigorously by hand for a minimum of 15 seconds and then placed upright in an ultrasonic water bath for five minutes, removed, and allowed to settle.

Analyses of Soil pH

Analyses were performed with an Accumet AB15 pH meter calibrated with buffers of pH 4 and 7. The electrode was lowered into the tube of soil solution and the holding tray was gently shaken in a circular motion for a few seconds. When the displayed value stabilized it was recorded, and the electrode was withdrawn from the solution. It was rinsed thoroughly with deionized water from a plastic wash bottle and blotted dry with task wipes after each measurement. The 15 samples were prepared with 0.01-molar calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) and analyzed one hour and one day after solution was added to the soil; and with distilled water analyzed at one day and two sets of samples at one hour after distilled water was added to the soil.

Results

Five sets of data were collected on the 15 surface soil samples: soil in calcium chloride dihydrate solution at one hour, soil in calcium chloride dihydrate solution at one day, soil in distilled water at one day, and two successive tests of soil in distilled water at one hour to verify reproducibility. The data are given in Table 2 and in graphic form in Fig. 3, 4 and 5.

Table 2 – pH analyses with 0.01-m calcium chloride dihydride (CC) at on hour (1H) and one day (1D), the difference between them Δ(CC 1D –CC 1H), and the differences between 0.01-m calcium chloride dihydrate (CC) and distilled water (DW) Δ(CC - DW) at One Hour (1H) and One Day (1D). The average (AVE) and standard deviation (STDEV) exclude sample 6 and the lawn sample.

Sample	Habitat	CC 1H	CC 1D	DW 1H(A)	DW 1H(B)	DW 1D	Δ(CC 1D – CC) 1H	Δ(DW 1D – DW) 1H	Δ(CC - DW) 1H	Δ(CC - DW) 1D
1	RT	3.16	3.37	3.88	3.81	3.89	0.21	0.045	0.72	0.52
2	SL	3.52	3.77	4.20	4.20	4.26	0.25	0.06	0.68	0.49
3	RT	3.58	3.76	4.34	4.39	4.38	0.18	0.015	0.76	0.62
4	RT	3.58	3.76	4.37	4.37	4.42	0.18	0.05	0.79	0.66
5	SL	3.42	3.69	4.22	4.26	4.32	0.27	0.08	0.80	0.63
6	*BL*	*5.45*	*6.03*	*6.03*	*6.12*	*6.33*	*0.58*	*0.255*	*0.58*	*0.30*
7	BL	3.69	3.95	4.42	4.44	4.51	0.26	0.08	0.73	0.56
8	BL	3.92	4.16	4.70	4.75	4.78	0.24	0.055	0.78	0.62
9	SL	3.96	4.14	4.68	4.64	4.74	0.18	0.08	0.72	0.60
10	SL	3.64	3.88	4.40	4.38	4.47	0.24	0.08	0.76	0.59
11	RT	3.95	4.14	4.62	4.64	4.73	0.19	0.1	0.67	0.59
12	BL	3.85	4.00	4.57	4.58	4.67	0.15	0.095	0.72	0.67
13	SL	3.96	4.12	4.51	4.53	4.69	0.16	0.17	0.55	0.57
14	RT	3.59	3.85	4.36	4.31	4.38	0.26	0.045	0.77	0.53
15	SL	3.77	4.04	4.63	4.62	4.72	0.27	0.095	0.86	0.68
Lawn		(n/a)	(n/a)	6.20	(n/a)	(n/a)	(n/a)	(n/a)	(n/a)	(n/a)
AVE		3.69	3.90	4.42	4.42	4.50	0.22	0.08	0.74	0.60
STDEV		0.23	0.22	0.22	0.24	0.25	0.04	0.04	0.07	0.06

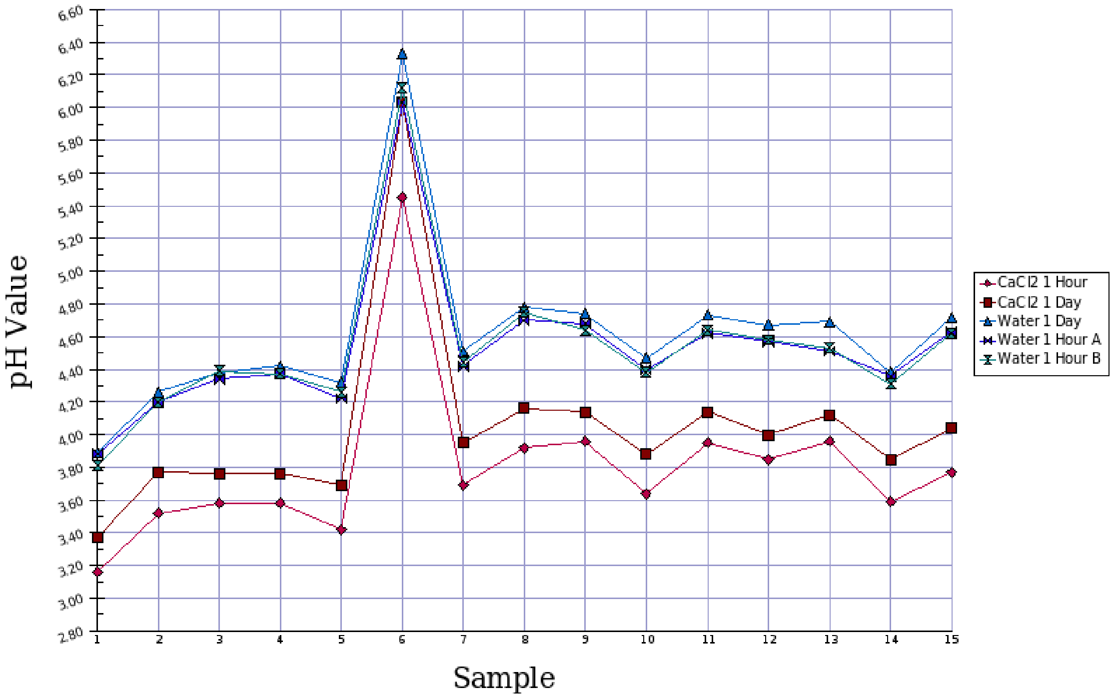

Figure 3 pH data for the 15 soil samples in 0.01 m calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) and in distilled water for one hour and one day.

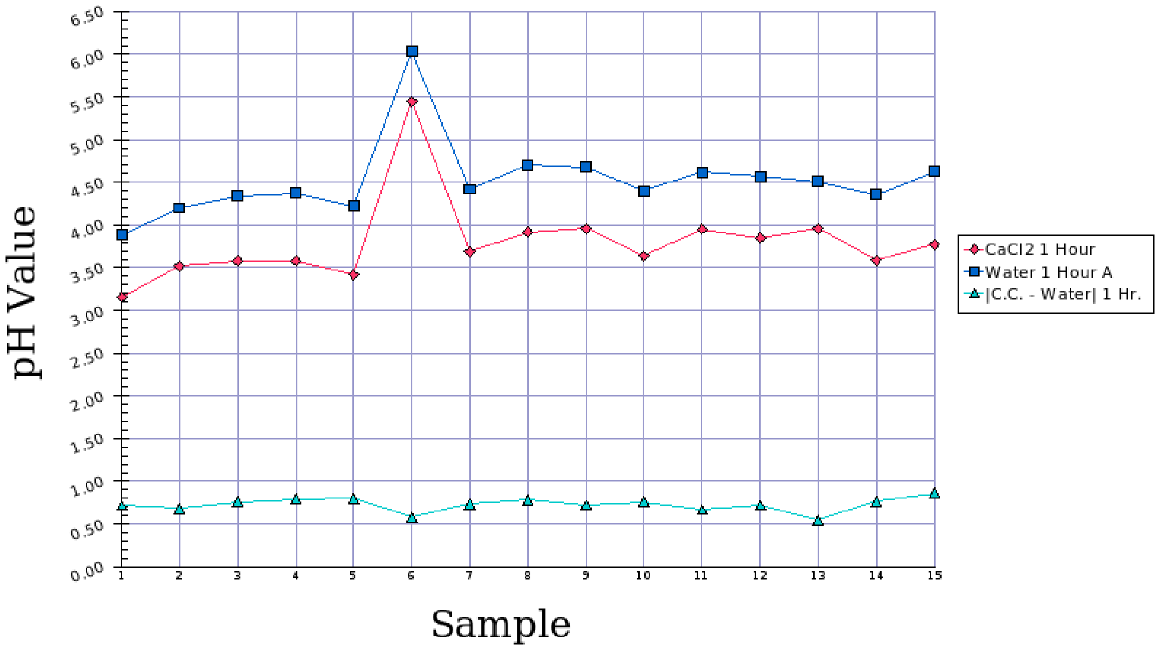

Figure 4 – 0.01 m Calcium chloride dihydride ($CaCl_2{\cdot}2H_2O$) solution compared to distilled water (A) at one Hour

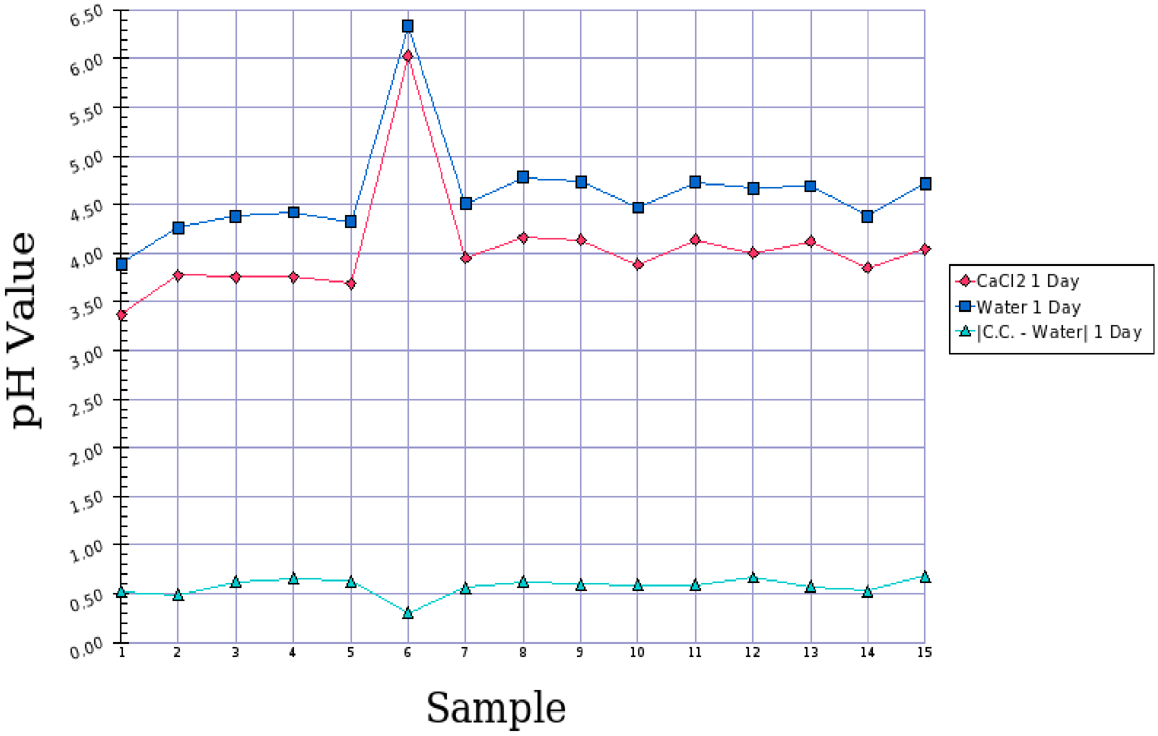

Figure 5 - 0.01 m Calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$) solution compared to distilled Water at one day

The results of these analyses show that letting the soil interact with distilled water and 0.01 m calcium chloride dihydrate give different values. Time that the solution is in contact with the soil increases the pH (one hour and one day), although the difference is smaller for distilled water, average of 0.08 pH units compared to an average of 0.22 pH units for 0.01 m calcium chloride dihydrate. The mean difference between using 0.01 m calcium chloride dihydrate and distilled water for one hour is 0.74 pH units, and for one day is 0.60 pH units. Since there is precedent for testing with distilled water at one day, the Fig 6 shows the pH values of the surface soil using the distilled water for one day data digital elevation model.

Because the 0.01 m calcium chloride dihydrate solution is more similar to rainwater, the author recommends its use in future testing in Clara's Woods. However, because there is such precedent for using distilled water, it would be wise to perform tests with distilled water as well.

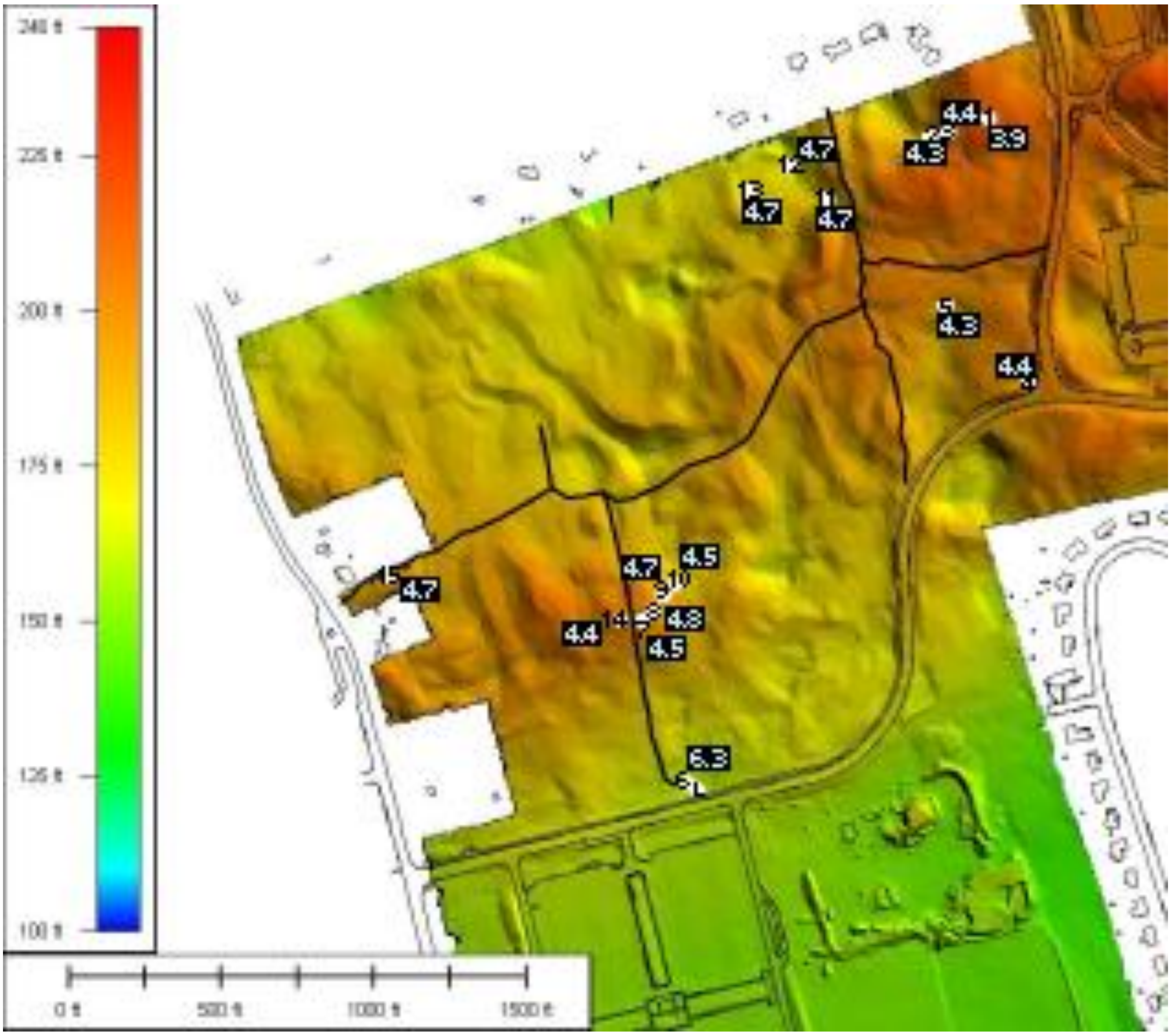

Figure 6 - pH of surface soil using distilled water in contact with the soil for one day on a digital elevation model of Clara's woods

Interpretation

There is an inverse relationship between the elevation of the terrain and soil pH; that is, the pH decreases with altitude. This is a trend shown by Wherry (1923). He divided the terrain in a similar moraine setting with hills and valleys into three types: the bottoms of the valleys he called bottomlands, slopes, and ridgetops. with the bottomlands showing the highest pH and the ridgetops the lowest. In this study, samples 1, 3, 4, 11, and 14 are ridgetops with an average pH of 4.36. Samples, 2, 5, 9, 10, 13, and 15 are from slopes and have an average pH of 4.53, and 6, 7, 8, and 12 are in the bottomlands and have an average pH of 4.65. The data for Clara's woods are compared to the data from Valley Stream in Table 3.

Table 3. Comparison of the surface soil pH for Locust Valley in 1922 and 1985 with the pH surface soil in contact with distilled water for one day for Clara's woods in 2007

Habitat	1922 Wherry, 1923	1985 Greller et al, 1990	2007 Clara's Woods
Bottomland	6.5	4.1	4.7
Slopes	5.5	3.9	4.5
Ridgetops	4.5	3.8	4.4

There are also several distinct soil units in Clara's woods. Most of Clara's woods is underlain by Riverhead sandy loam of varying steepness, from 0 to 15%, with a few small regions of Haven loam and a patch of the Carver and Plymouth sands in the northwest quadrant (see Fig. 7). Most of the samples are from the RdB and RdC soil types (Riverhead Sandy Loam of 3-8% and 8-15% slopes), though samples 6, 15, and the Lawn sample are from an area of

HaB (Haven Loam, 2-6% slopes).

In Fig. 8 we see that there is no discernable relationship between soil type and pH for Clara's Woods. Sample 15 is in a unit of Haven Loam, while sample 11, which has the same pH and is at roughly the same elevation, was taken from Riverhead sandy loam.

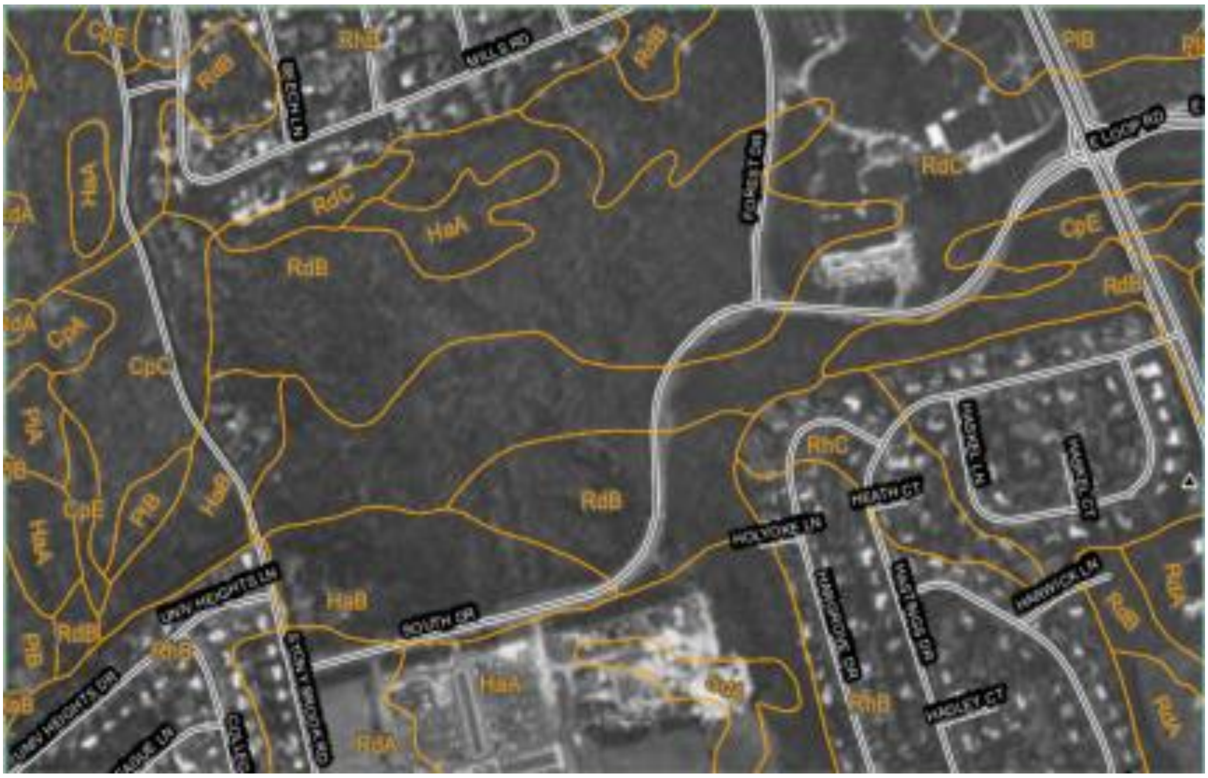

Figure 7 - Soil Types on air photo of Clara's Woods

Figure 8 – pH of surface soil using distilled water in contact with the soil for one day on a soil map with overlay of the digital elevation model in Fig. 6

Discussion

Howard et. al (2002) reported on a 1998 study conducted at 24 sites in Westchester and Long Island which measured the pH of soil in pine barrens and mixed hardwood communities. They found values for pH of 3.38 ± 0.05 for the barrens and 3.53 ± 0.04 for the mixed hardwood areas. However, they do not report whether they used distilled water or 0.01 m calcium chloride dihydrate for the soil solution. The average pH for the Clara's woods samples in 0.01 m calcium chloride dihydrate solution for one hour is 3.69 + 0.23 and for one day is 3.90 + 0.22 and in distilled water soil solution for one hour is 4.42 + 0.23 and for one day is 4.50 + 0.25. Jha (2008) in a study of surface soils from the Dwarf Pine Plains in Westhampton, Long Island found an average pH of 3.31 for eight samples in 0.01 m calcium chloride dihydrate for one hour. The results for soils analyzed for pH after one hour in 0.01 m calcium chloride dihydrate in Clara's woods and in the Dwarf Pine Plains (see Table 4) give results similar to those of Howard et. al (2002).

Table 4. Comparison of pH in surface soils in solutions of 0.01 m calcium hydrite solution for one hour. It is not known if Howard et al (2002) used this analytical technique but their data are consistent if they did.

Habitat	Hardwood Forest Howard et. al (2002)	Pine Barrens Howard et. al (2002)	Clara's woods This study	Dwarf Pine Plains Jha (2008)
pH	3.53	3.38	3.69	3.31

Boguslavsky (2000) and Bailey et al (2005) analyzed samples collected at various depths below the surface. This allows the researcher to build up a vertical profile of the soil pH. The upper layers (O-horizon, A-horizon) tend to be more acidic, with the pH rising steadily into the B- and C-horizons. With time and continuous infiltration of acidic rain, the hydronium ions are exchanged for base cations on the soil to greater depths . Boguslavsky (2000) showed that this leads to an increased concentration of exchangeable aluminum species in the upper layers of the soil, as well as depletion of calcium, etc., in those layers.

What can we expect for the future in terms of acid precipitation and its effects on Long Island? We will likely see continued acidification of the soil. Because leaching proceeds from the O-horizon downwards, we should see more change in the upper layers of the soil than the lower layers. However, given enough time and acid, the pH of the lower layers will begin to be affected as well (Bailey et al, 2005). We may expect to see continued loss of exchangeable base cations from the top down and an increase in exchangeable aluminum species such as Al^{3+}.

As a result of pollution controls the pH of rain in the Northeast has *increased* in the last decade according the National Atmospheric Deposition Program. Rain with higher pH may slow further acidification but it will not reverse the damage that has already been done, because it will be necessary to replace the phytotoxic Al^{3+} in exchangeable sites on the soil surfaces with base cations which are plant nutrients. Xin and Hanson (1994) showed that the base cations on Long Island are added to the soil by dry precipitation (dust). Soil recovery after the pH of rain approaches natural values can only occur once enough base cations have been added to the soil by dry precipitation to replace Al^{3+} in exchangeable sites on the soil.

The author believes the best course of action is to establish monitoring protocols for Clara's Woods. It is a natural laboratory in which to study the effects of acid rain in a deciduous temperate forest in an increasingly densely-populated area.

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