

Impact of Acid Rain and Fire on Soil pH  
in Dwarf Pine Plains, Long Island, New York

A Final Report Presented  
by Pushpa Jha

to

The Graduate School

In Partial fulfillment of the

Requirements

for the Degree of

Master of Science

in

Geosciences with concentration in Hydrogeology

Stony Brook University

December 2008

Stony Brook University

The Graduate School

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## **Abstract**

Soil pH has been determined on samples at 9 sites at depths up to 120 cm in the Dwarf Pine Plains, West Hampton, NY. Four sites were located in the area impacted by the fire of 1995 while the remaining sites were located in the unburned area. pH(CaCl<sub>2</sub>) of the soil for all sites increased to a depth of 40-50 cm (from pH 3.5 to 4.4) and was relatively constant below that (around pH 4.0 - 4.1). The lower pH at depths up to 40-50 cm is attributed to the persistent acid rain that this region has been subjected to for the past few decades. The pH at greater depths may reflect the soil pH prior to acid rain. In addition, the study also showed that the surface soil pH was greater in sites located in burned areas (3.48) compared that in unburned areas (3.23) suggesting that burning resulted in an increased soil pH near the surface.

## Acknowledgments

I would like to express my deep and sincere gratitude to my advisor Professor Gilbert N. Hanson. He constantly provided me guidance, wise suggestions, important resources and encouragement in completion of my research project. I am really grateful that he gave me support, confidence and untiring help during my difficult moments. I could not accomplish my research project without his generous help and encouragement. I am greatly thankful to Professor Richard Reeder for his detailed and constructive comments, and for his important support by providing me the lab instruments throughout this work. I would also like to thank Professor Troy Rasmury for her important suggestions. I am greatly thankful to Dr. Marilyn Jordan of The Nature Conservancy for providing me useful data. I like to thank my friends and lab colleagues for their help. I would like to thank Loretta Budd, the Department of Geosciences graduate program coordinator, for helping me in paper work. I would like to special thanks to my parents and my family living in India, for providing moral encouragement, support and love. Especially, I would like to give my thanks to my husband, Deepak Jha, whose inspiration and help enabled me to complete this work.

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## Introduction

This is a study of the effects of acid rain and fire on the pH of soil in the Dwarf Pine Plains on Long Island New York (see Figure 1). Long Island has been receiving acid rain since at least the 1950's. In 1955, the pH of rain was approximately 4.7 to 5 compared to the pH of natural rain of 5.6. By 1970's the pH of rain in Long Island had decreased further and was around 4.5 to 4.4 (Berner and Berner, 1996). The pH of rain has since increased to 4.6 - 4.7 according to the National Atmospheric Deposition Program Lab, after the Clean Air Act amendments in 1990. It is still below the pH of natural rain and continues to stress the forests in Northeast America according to the report "Acid Rain Visited" by Hubbard Brook Research Foundation released in March 2001. That report attributes the decline in tree populations in northeast America to acid rain and the resulting increase in the soil acidity.

There have been a number of studies on the relationship between acid rain and the increase in soil acidity in northeastern USA and this study builds on those results. In order to compare studies it is necessary to recognize which procedure was used for determining soil pH. Though some studies used pure water mixed with soil while others used dilute salt solutions mixed with soil to measure the soil pH, all the studies show that soil pH is affected by acid rain. In the following discussion the soil pH measured by water and a dilute salt solution such as .01 M  $\text{CaCl}_2$  are represented as  $\text{pH}(\text{H}_2\text{O})$  and  $\text{pH}(\text{CaCl}_2)$  respectively. Studies that have measured soil pH using both methods find a linear relation between them over the pH range that we are interested in. The values for  $\text{pH}(\text{H}_2\text{O})$  are approximately 0.6-0.8 pH units higher than values for  $\text{pH}(\text{CaCl}_2)$  (Kissel et al, 2004). Bauch (2007) studied soil pH in Clara's Woods on the Stony Brook University Campus and found that the mean difference between  $\text{pH}(\text{H}_2\text{O})$  and  $\text{pH}(\text{CaCl}_2)$  is  $0.73 \pm 0.08$  (one standard deviation) pH units.



Figure 1: The star shows the location of the Dwarf Pine Plains and insert shows location of Central Pine Barrens, (Source: Google Earth and Google map).



In 1922, Wherry (1923) recorded surface soil pH(H<sub>2</sub>O) and plant types in habitats with different elevations in the Hodenpyl Estate in Locust Valley. The elevation on this estate on the Harbor Hill Moraine ranges from 100 ft to 220 ft. Greller et al, (1990) repeated the study in 1985 and found that pH(H<sub>2</sub>O) had decreased significantly since 1922. The soil in the bottomland or bottoms of valleys showed the largest decrease of 2.4 pH units (Table 1).

*Table 1: pH(H<sub>2</sub>O) of soil in Locust Valley from Greller et al, 1990*

Habitat	1922	1985
Bottomland	6.5	4.1
Slopes	5.5	3.9
Ridge tops	4.5	3.8

Greller et al., found that the average surface soil pH(H<sub>2</sub>O) in the area varied from 3.8 to 4.1 and that the flora was dominated by acid tolerant species, whereas Wherry had found acid tolerant species only on ridge tops. As shown in Table 1, the average pH(H<sub>2</sub>O) of soil in ridge tops was 4.5 in 1922; however, by 1985, the soil pH of the entire area was less than that. It is not surprising then that acid tolerant species in 1985 were dominant throughout the estate regardless of habitat type. Greller speculated that the increase in soil acidity was associated with acid rain. Bauch (2007) also observed that soil at ridge tops has lower pH as compared to valleys in an area with 70 feet of relief in Clara's Woods on the Stony Brook Campus. According to his study, the average pH (CaCl<sub>2</sub>) of the surface soil of the hardwood forest in Clara's woods was 3.8 ± 0.08 and the average pH(H<sub>2</sub>O) was 4.4 ± 0.2.

Howard *et al*, 2003, analyzed soil samples from 21 separate sites in the Pine Barrens in Suffolk County and 22 sites from mixed hardwood forests in Suffolk and Westchester Counties in 1998. They found that the soil pH was consistent and averaged 3.38 ± 0.05 (one standard error) in the Pine Barrens and 3.53 ± 0.04 (one standard error) in mixed hardwood forests. They did not state whether these results are based on pH(CaCl<sub>2</sub>) or pH(H<sub>2</sub>O). In any case the study showed that pH of surface soil is similar in the entire metropolitan area regardless of habitat type.

Acid rain not only decreases the pH of the topsoil over time but also the lower layers as well (Bailey et al, 2005). Bailey et al, (2005) compared the soil pH, exchangeable base cations and exchangeable Al at various depths at forested sites on the Alleghany Plateau with the findings of a study that was conducted on the same sites in 1967. In 1967 this area had already been affected by acid rain for decades. So the study was able to show the continuing effect of acid rain on the soil. They found a significant decrease in soil pH at all depths sampled up to a depth of 150 cm compared to observations recorded in 1967 (Table 2). They suggested that acid deposition had continued to alter the entire soil profile. In fact rain pH had decreased from 4.5 to 4.2 in Alleghany Plateau area from 1955 to 1997. In Long Island rain pH was approximately 5.0 in 1955 and 4.4 in 1997 (Berner and Berner, 1996, and National Atmospheric Deposition Program).

Table 2: Average pH(CaCl<sub>2</sub>) of soil in Alleghany Plateau from Bailey et al, 2005

Depth	1967	1997
Oa/A horizon	3.8	2.9
Upper B horizon	3.7	3.5
50 cm	4.3	4
100 cm	4.2	4

While these studies establish the role of acid rain in determining the soil pH, there are other factors such as cation exchange capacity that play an equally important role. Cation exchange capacity of the soil determines its buffering capacity, which reduces the rate at which the soil turns acidic from acid rain. Boguslavsky (2000) conducted a study of cation exchange capacity (CEC) in Long Island glacial sediments, and found that in the top soil Al and Ca formed 75%-82% and 6%-8% of total cations respectively. Boguslavsky attributed the abundance of Al ions in the topsoil to acid rain. The exchangeable aluminum is the result of the acid reacting with gibbsite Al(OH)<sub>3</sub>. The aluminum in gibbsite is immobile but the aluminum released upon the reaction of acid with gibbsite is mobile.

Decomposing organic matter is acidic. It provides acid to the soil system by carbonic acid dissociation, and generation and protolysis of organic acid (Richardson, 2000). Thus organic matter decreases soil pH. However, fire oxidizes the organic matter including the organic acids and removes them from the soil system and eventually base cations are released from the ashes of the organic matter to the soil. As a result, the pH of the soil increases. Swan (1970) studied post fire response of four plant communities - northern hardwoods, oak woods, goldenrod poverty grass fields, and little bluestem fields in south-central New York State, which had been burned by wildfires in 1962, 1963, or 1964. He found that the average surface soil pH values in burned areas was significantly higher than that in unburned areas of both forests and fields – the difference being as high as 0.8 pH units. However, the difference in pH in the burned and unburned areas was slight at 6.0 cm depth.

To summarize, soil pH is a result of the interaction between the acid supplied to the soil system and the buffer capacity of the soil. Organic acids and acid rain provide acid to soil system and the gibbsite and the base cations present in the soil buffer the soil system against decrease in soil pH. Once, the acidity of the soil system is equilibrated at that depth, the excess acid leaches down through the soil. This acid continues to leach down through the soil system until at some depth there is no excess acid and the pH does not change. Nature replenishes the buffer capacity of the soil by dry deposition and weathering of rocks rich in cations. The situation is made more interesting by occurrence of fires, which has the effect of increasing the pH of the soil by removing the organic acid from the system and by adding base cations from the ashes of the organic matter. As a result, the immediate impact of the fire is expected to be most in the top layers of the soil because that is where the organic matter is burned.

Studies suggest that the surface soil pH on Long Island has declined in both hardwood and softwood forests because of acid rain. Hence, it would be interesting to study how deeper levels of soil have been affected by the persistent acid rain and the

degree to which fire has affected soil pH. These are the two objectives of this study: to determine the effect of acid rain on soil pH as a function of depth and to determine the effect of fire on soil pH.

The Dwarf Pine Plains were chosen because they have been prone to acid rain for decades and part of the area was severely burned in the fire of 1995 (Jordan et al, 2003). We decided to study soil samples at various depths up to 100 cm from both burned and unburned areas. Based on past studies, we expected that the soil pH would be low on surface but the soil pH should be higher at deeper levels approaching the pre-acid rain era. However, if the acid rain continues to occur in future, then the deeper layers of soil will also be affected, thus reducing their soil pH as well. As a result, the system will find a new equilibrium point at lower soil pH value (Figure 2). Also, we expect that the surface soil samples from burned area should have a higher pH than those from the unburned area.

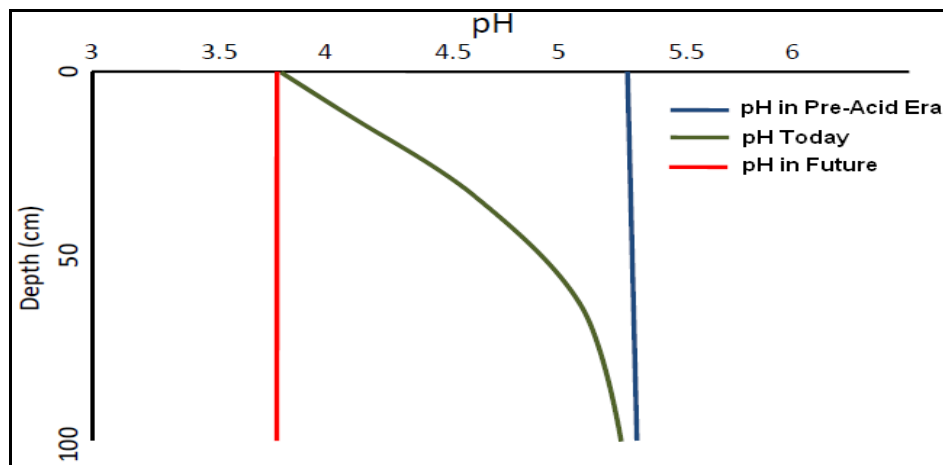


Figure 2: Prediction of Soil pH

Soil pH is an important factor for ecological monitoring. The quality of plant growth is directly affected by the pH of the soil that they grow in. This is because the pH of the soil has a direct bearing on the availability of plant toxins such as aluminum or plant nutrients such as calcium.

## Area of Study

The Long Island Pine Barrens is located in east-central Long Island about 100 kilometers (60 miles) east of New York City. The Long Island Dwarf Pine Plains are located on a sandy and gravelly glacial outwash plain that has some of the most rapidly draining, drought-prone soils in the Pine Barrens. The vegetation of the area is comprised of dwarf pitch pine and scrub oak with a low shrub layer of black huckleberry, hillside blueberry, golden heather, bearberry, and wintergreen growing beneath the pines and oaks. There are relatively few wetlands within the Dwarf Pine Plains that could serve as natural firebreaks. So the Dwarf Pine Plains represents a large "fireshed" superimposed upon coarse, rough soils and flammable vegetation (Jordan et al, 2003).

## Theory

Soil acidity is caused by acid rain and acid generated from the organic matter present in the soil. Acid rain adds hydrogen ions to the soil system, which produces aluminum ions that displace the base cations like calcium, magnesium, sodium and potassium, from soil particles. Acid rain is buffered in part by these base cations that are adsorbed onto organic and soil particles. As long as there is a sufficient amount of adsorbed base cations, the soil pH is not impacted by acid rain. Weathering of the minerals in the soil and dry deposition provide base cations to the soil system. Another source of soil acidity is organic acid associated with organic material derived from plant litter.

Figure 3 illustrates various sources and sinks of soil acidity as relevant to Long Island. In Long Island, most of the cations are from dry precipitation not weathering (Xin and Hanson, 1994) because the sandy soil is dominated by quartz, which has no base cations.

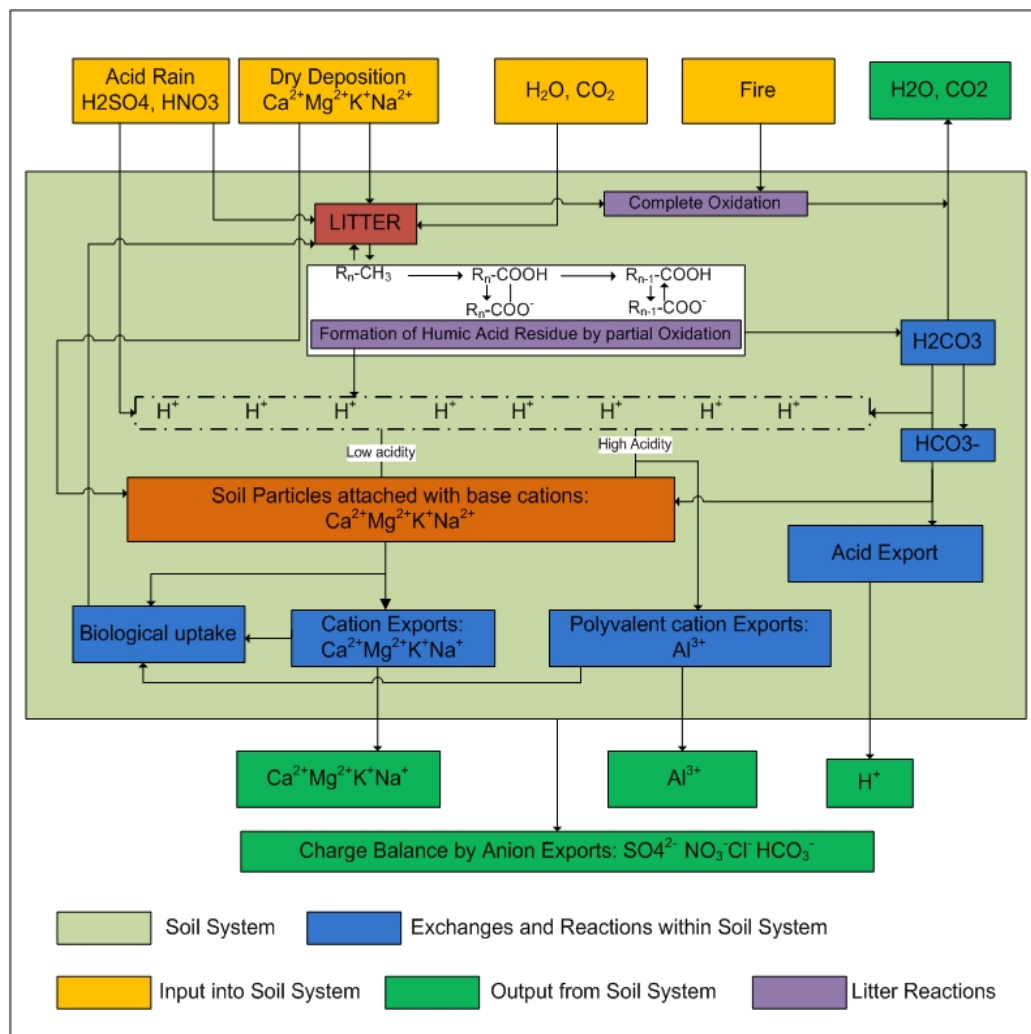


Figure 3: Major Sources and Sink of soil acidity, (Adopted from Krug and Frink and modified for Long Island).

Decrease in the soil pH leads to greater mobilization of the aluminum and increased leaching of the calcium leading to decline in Ca/Al ratio to less than one - which results in restricted plant growth and associated nutrient uptake (Cronan and Grigal, 1995). Aluminum is insoluble in the normal pH range occurring in natural waters. However, under acidic conditions, aluminum is soluble in the soil water system (Driscoll, 1985). A simple simulation in PhreeQC for gibbsite shows that below a pH of 4 Al<sup>3+</sup> becomes the dominant species in solution as shown in Figure 4.

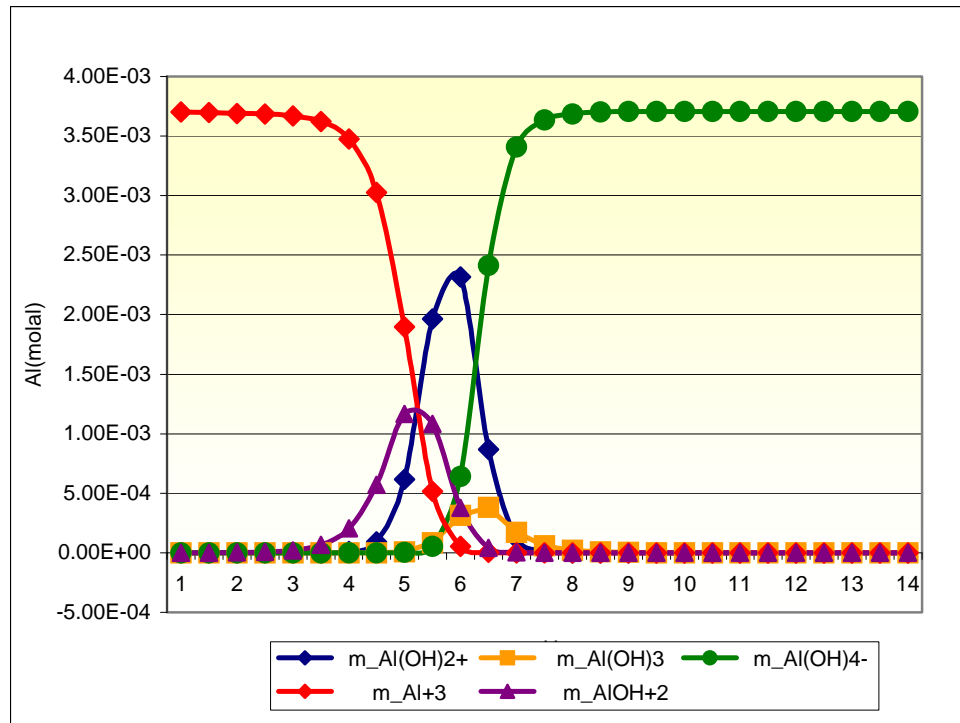
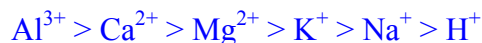


Figure 4: Aluminum speciation at different pH using phreeQC

This phenomenon where H<sup>+</sup> ions from the soil water react with gibbsite, Al(OH)<sub>3</sub>, produces soluble Al<sup>3+</sup> ions is represented by equation 1 (Langmuir, 1997):

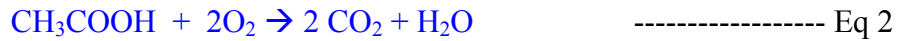


The soluble aluminum species displace the other base cations adsorbed on the soil particles and the base cations are then transported down the soil column. Also, multivalent cations are generally retained over monovalent cations. The order in which the cations replace other cations is (Gilbert and Laudelout, 1964 and Troeh et al, 2005):



Excessive Al<sup>3+</sup> ions released according to the series above replace the Ca<sup>2+</sup> ions and the soil becomes deficient in nutrients. In very acidic medium Al<sup>3+</sup> and H<sup>+</sup> will replace essentially all the other cations.

Fires destroy organic acids and add base cations to soil. This is because fire combusts the litter and the undissociated organic acids (such as humic or acetic acid) and removes them from the ecosystem according to equation 2 (Fisher et al, 2000):



Base cations replace  $\text{H}^+$  from the soil, upon the release of base cations from the burned organic matter.

## Method and Procedure

Figure 5 shows the steps and methods in detail. The method used in this study to measure soil pH was adopted from the procedures described by Heckman (1994). For measuring pH, 0.01 M  $\text{CaCl}_2$ , referred to as  $\text{pH}(\text{CaCl}_2)$  was used as it is the best approximation for the pH used by plants because it better matches the soil solution (Schofield and Taylor, 1955). It is also useful in creating a baseline pH of an area that does not change with seasons (Kissel and Vendrell, 2006, <http://pubs.caes.uga.edu/caespubs/pubs/PDF/C875.pdf>). For comparison purposes, the soil pH was also measured using de-ionized water, referred to as  $\text{pH}(\text{H}_2\text{O})$ . The results revealed that  $\text{pH}(\text{H}_2\text{O})$  was always greater than  $\text{pH}(\text{CaCl}_2)$  by pH values of 0.5 to 0.9. The average difference I found between  $\text{pH}(\text{CaCl}_2)$  and  $\text{pH}(\text{H}_2\text{O})$  was 0.85 with a standard deviation of 0.27, which is similar that of Bauch (2007) who found an average of 0.73 with a standard deviation of 0.08).

### Site Selection:

The first step was to search for a sample site, where burned and unburned areas were adjacent to each other so that they had similar site conditions such as vegetation, soil type etc. The Dwarf Pine Plains were appropriate for conducting such a research. Fire data and aerial photos (provided by Dr. Marilyn Jordan of The Nature Conservancy) showed that the fire in 1995 had affected only certain areas of the Dwarf Pine Plains leaving the rest unburned. Soil type, vegetation type and elevation were then evaluated in ArcMap for choosing the sample sites.

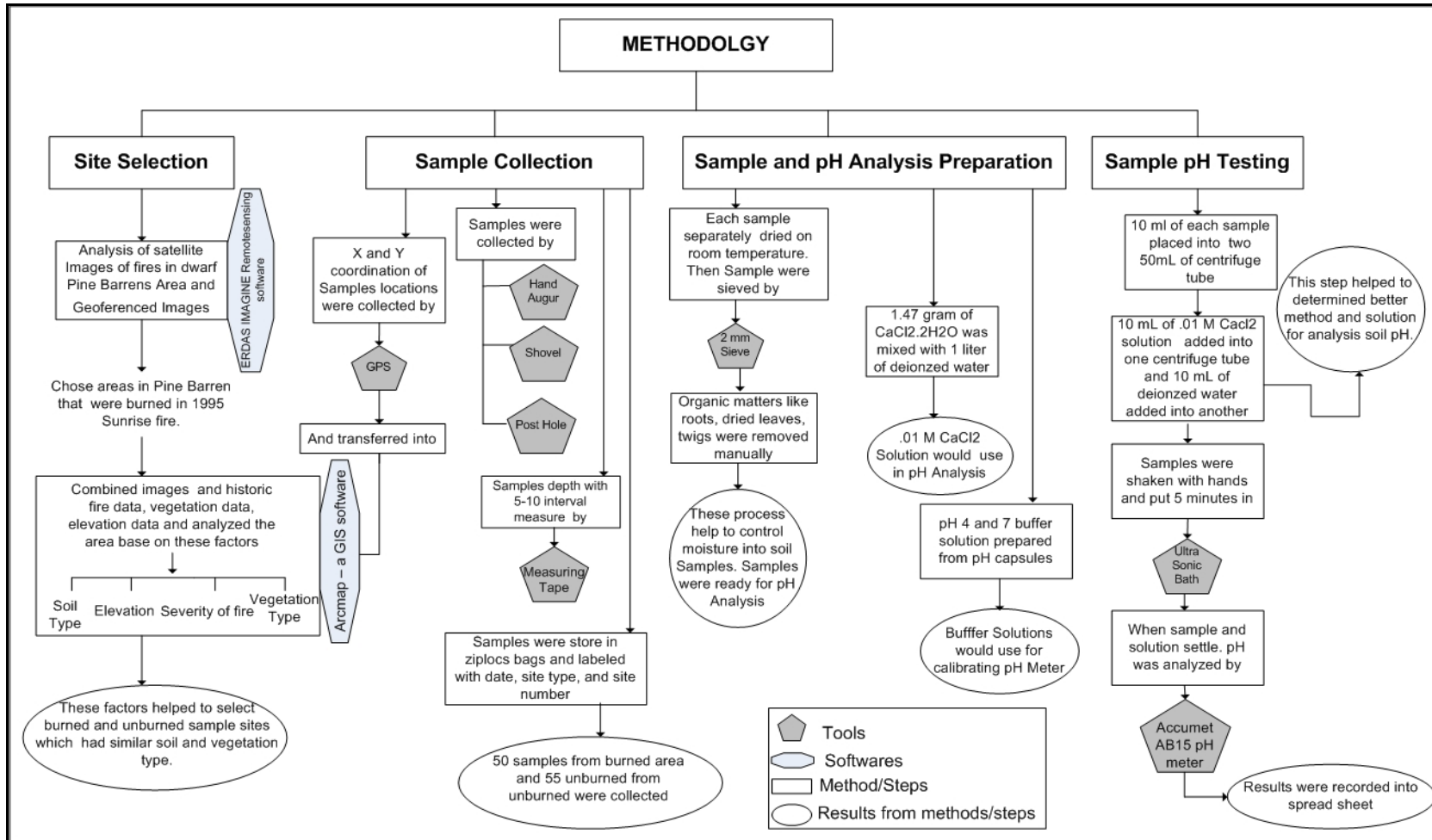
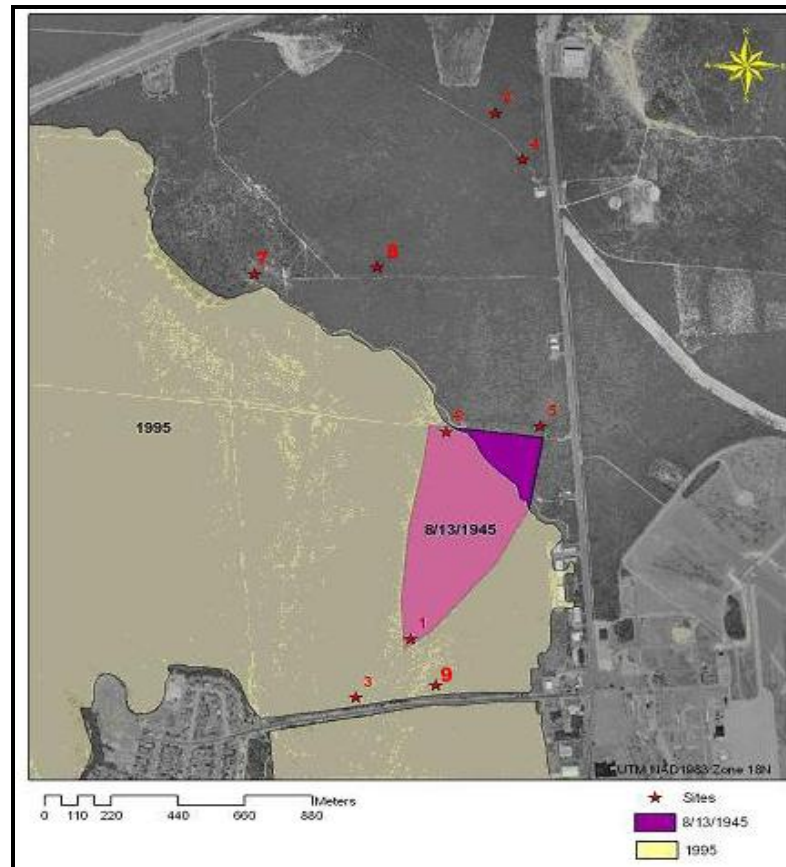


Figure 5: Steps and Methods involve in methodology

## Fire History:

Fire data provided by Dr. Marilyn Jordan of The Nature Conservancy shows that most recent fires were in 1945 and 1995, with no fires for a few decades before 1945. Sample sites 1, 3, 6, 7, 8 were in the burned area and site 2, 4, 5, 9 were in the unburned area.



*Figure 6: Fire History at sample site. The yellow area burned in 1995 the red area in 1945. The uncolored area had not burned for many decades before. (Data: The Nature Conservancy)*

## Vegetation:

The vegetation in the unburned area consists dominantly of dwarf pitch pine, whereas in the burned it was dominantly scrub oak with young pitch pine. Figure 7 shows the vegetation types in the area. The map was created in 1996 and shows scrub oak dominating in the burned area. During sampling in 2008, I observed that burned sites also had younger and shorter pitch pines than those in unburned area.



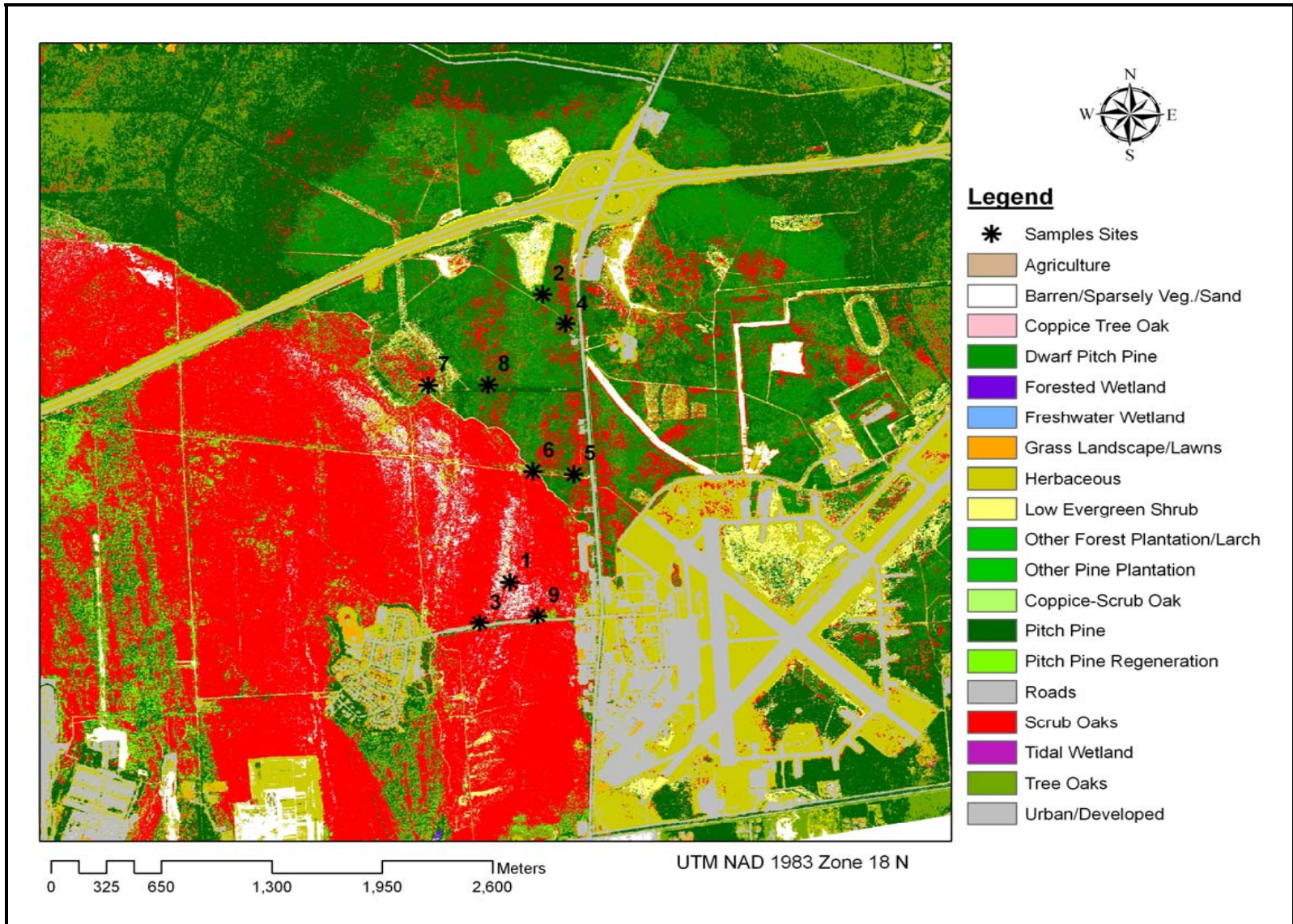


Figure 7: Vegetation at sample sites. (Data: The Nature Conservancy)

## Soil Type:

All the sites have similar soil type – CpA (Carver and Plymouth sands association). This association is comprised of Plymouth loamy sands (approximately 50 percent), Carver sands (25 percent) and minor soils. Plymouth and Carver soils are deep, excessively drained, poor in nutrients and prone to fires (Kurczewski and Boyle, 2000).

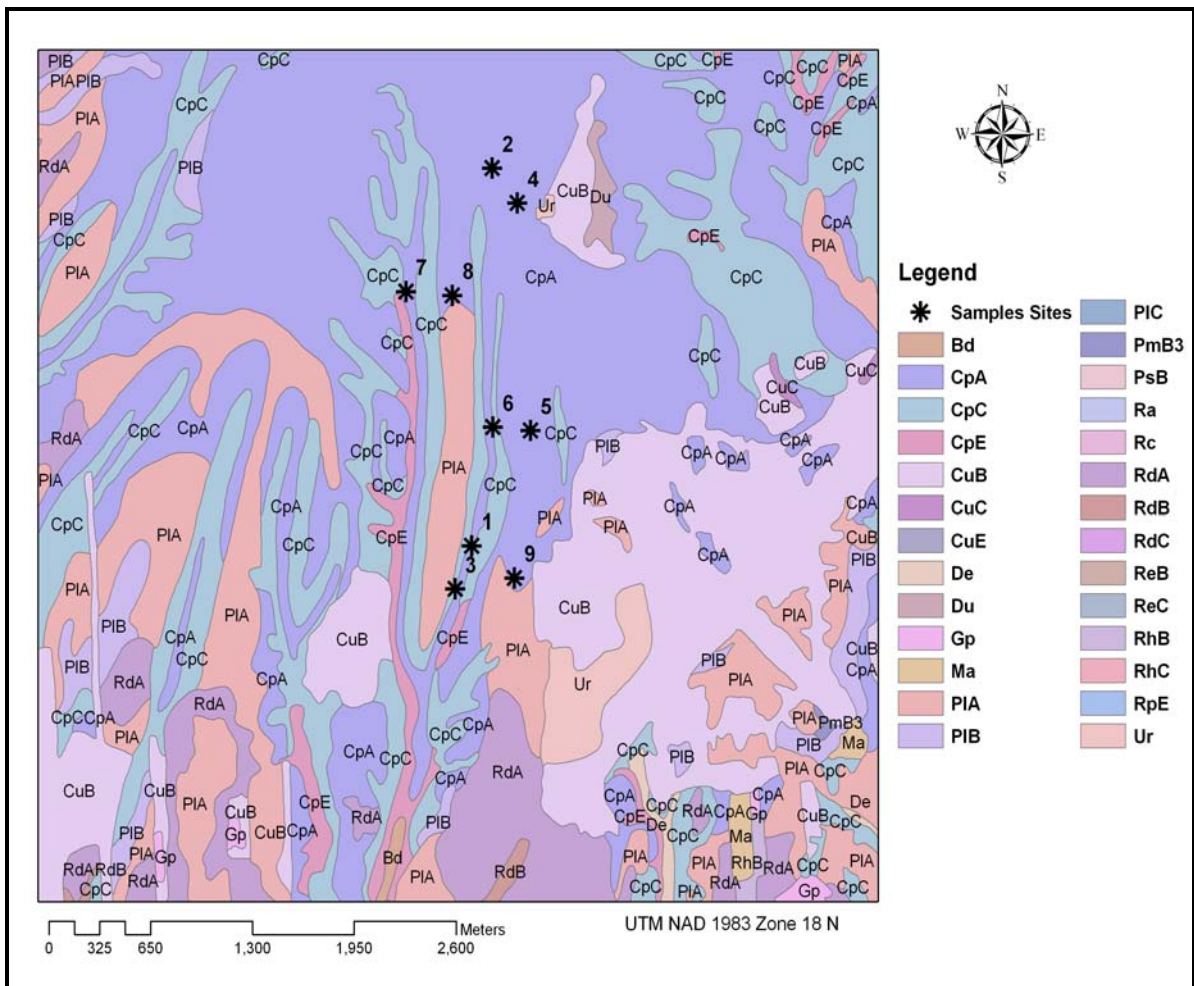
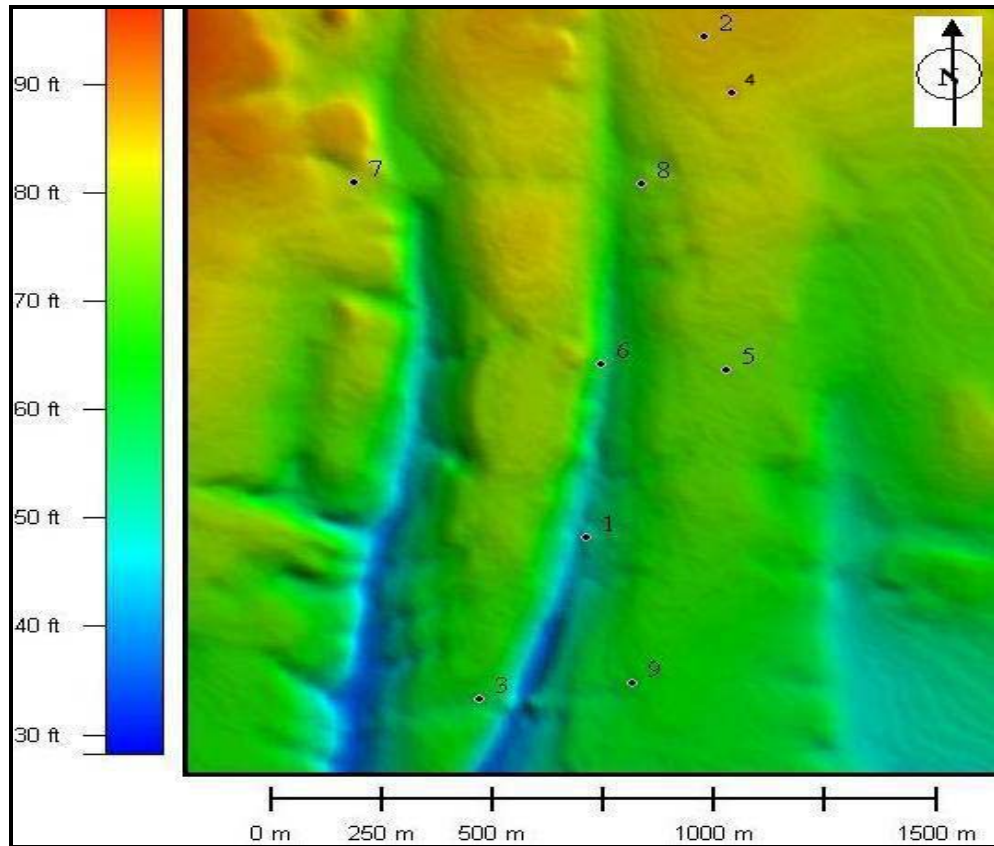


Figure 8: Soil type at sample site. (Geospatial Data Gateway, USDA Natural Resources Conservation Service)

## Elevation:

Site 1 and 6 are in a dry valley and are at lower elevations than rest of sites. The elevation of sites varied from 50 – 80 ft above sea level (DEM, Figure 9).



*Figure 9: DEM of Sample Site Area, red and orange shows higher elevation and green and blue shows lower elevation (Plate HH57 west Hampton). The blue does not indicate water.*

## Sites Description:

**Site 1 (Burned): UTM Coordinates: Zone 18 N; Easting: 697948; Northing: 4524263 (+/- 5 meters) Date – 7th July 2007, Temp 25 C, Sunny**

This site was located north of Stewart Avenue. This site was the bottom of first dry valley west of old Riverhead Road near Sunrise highway. Though there was no vegetation at the exact sampling site, the surrounding area just a few feet away was completely covered with dead and burned pine trees, dwarf pine tree, scrub oak, huckleberry, bearberry and lichen.

*Table 3: Physical characteristics of sample from Site 1*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Black	Lot of litter, very fluffy, some sand
2	5	Dry	Black-Gray	Decomposed organic material with medium sand
3	9	Dry	Black-Gray	Fine to medium sand
4	22	Dry	Dark brown	Fine to medium sand
5	32	Moist	Dark brown	Medium Sand
6	42	Moist	Brown	Medium Sand
7	60	Moist	Brown	Medium Sand
8	70	Moist	Brown	Medium Sand
9	83	Moist	Tan	Medium Sand with few pebbles
10	100	Moist	Tan	Medium Sand with more pebbles
11	112	Moist	Tan	Medium Sand with pebbles
12	127	Moist	Tan	Medium Sand with pebbles

**Site 3 (Burned): UTM Coordinates: Zone 18 N; Easting: 697769; Northing: 4524000 (+/- 5 meters); Date – 4th August 2007, 32 C, Sunny**

This site was also located north of Stewart Avenue. This site was on the highest elevation of first dry valley wall near Stewart Avenue. Sample location had lots of dead, burned trees, dwarf pines, scrub oak.

*Table 4: Physical characteristics of sample from Site 3*

<b>Sample No.</b>	<b>Depth (cm)</b>	<b>Moisture State</b>	<b>Soil Color</b>	<b>Soil Texture</b>
1	0	Dry	Black	Black with decomposed litter and organic material
2	2	Dry	Black-Grayish	Decomposed organic material with medium sand
3	5	Dry	Black-Grayish	Fine to medium sand
4	14	Dry	Dark brown	Fine to medium sand
5	22	Dry	Dark brown	Medium Sand
6	30	Moist	Brown	Medium Sand
7	40	Moist	Brown	Medium Sand
8	55	Moist	Brown	Medium Sand with few small size pebbles
9	75	Moist	Tan	Medium Sand with more small to medium pebbles
10	95	Moist	Tan	Medium Sand with few small size pebbles
11	110	Moist	Tan	Medium Sand with pebbles
12	120	Moist	Tan	Medium Sand with pebbles

**Site 6 (Burned): UTM Coordinates: Zone 18 N; Easting: 698042; Northing: 4524967 (+/- 5 meters) Date – 31<sup>st</sup> August 2007, 28 C, Partial Cloudy**

This site was located at the beginning of western edge of dry valley near sunrise highway. The vegetation at this site was comprised of huckleberry, bearberry, scrub oak, dwarf pine and few scattered old pine.

*Table 5: Physical characteristics of sample from Site 6*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Black	Black with decomposed litter and organic material
2	2	Dry	Black	Decomposed organic material with medium sand
3	10	Dry	Gray- Black	Fine to medium sand
4	15	Dry	Dark brown	Fine to medium sand
5	20	Moist	Dark brown	Medium Sand
6	25	Moist	Dark brown	Medium Sand
7	30	Moist	Brown	Medium Sand
8	40	Moist	Brown	Medium Sand with few small size pebbles
9	45	Moist	Brown	Medium Sand with more small to medium pebbles
10	50	Moist	Tan	Medium Sand with few small size pebbles
11	60	Moist	Tan	Medium Sand with small pebbles
12	65	Moist	Tan	Medium Sand with small pebbles
13	70	Moist	Tan	Medium Sand with small pebbles
14	80	Moist	Light Tan	Medium Sand with small to medium pebbles
15	90	Moist	Light Tan	Medium Sand with small to medium pebbles
16	100	Moist	Light Tan	Medium Sand with small to medium pebbles

**Site 9 (Burned): UTM Coordinates: Zone 18 N; Easting: 698116; Northing: 4524049 (+/- 6 meters); Date - 7th June 2008, 27 C, Sunny**

This site was located at western site of Old Riverhead Road and north side of Stewart Avenue. The vegetation at this site was same as at other burned sites.

*Table 6: Physical characteristics of sample from Site 9*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Black	Thin layer of litter with dried leaves
2	4	Dry	Black	Decomposed organic material with medium sand
3	6	Dry	Black-Gray	Fine to medium sand
4	11	Moist	Dark brown	Fine to medium sand
5	19	Moist	Dark brown	Medium Sand
6	27	Moist	Dark brown	Medium Sand
7	33	Moist	Brown	Medium Sand with small size pebbles
8	43	Moist	Brown	Medium Sand with few small pebbles

**Site 2 (Unburned): UTM Coordinates: Zone 18 N; Easting: 698185; Northing: 4524263 (+/-5 meters) July 7th 2007, Temp 25 C, Sunny**

This site was located west side of Old Riverhead Road and in the Dwarf Pine Plain County Preserve. Old dwarf pitch pines were the main vegetation at this site mixed with lesser scrub oaks. Sampling was only to 38 cm at this site because we hit gravel at a depth of 39 cm.

*Table 7: Physical characteristics of sample from Site 2*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Dark Brown	Litter with dried leaves and medium sand
2	3	Dry	Gray- brown	Decomposed organic material with medium sand
3	5	Dry	Brown	Medium sand
4	25	Moist	Brown	Fine to medium sand with small size pebbles
5	38	Moist	Brown	Medium Sand with medium size pebbles.

**Site 4 (Unburned): UTM Coordinates: Zone 18 N; Easting: 698277; Northing: 4525908 (+/-5 meters) Date – 4th August 2007, 32 C, Sunny.**

This site was located in Dwarf Pine Plains County Nature Preserve at first trail west site of Old Riverhead Road. Dominant vegetation was old dwarf pitch pine with scrub oak.

*Table 8: Physical characteristics of sample from Site 4*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Grayish-Black	Decomposed organic material with medium sand
2	2	Dry	Black-Grayish	Fine to medium sand
3	5	Dry	Dark brown	Fine to medium sand
4	10	Dry	Dark brown	Medium Sand
5	15	Dry	Dark brown	Medium Sand
6	25	Moist	Brown	Medium Sand with small size pebbles
7	40	Moist	Brown	Medium Sand with few small size pebbles

**Site 5 (Unburned): UTM Coordinates: Zone 18 N; Easting: 698324; Northing: 4524950 (+/-5 meters) Date – 31st August 2007, 28 C, Partly Cloudy**

This site was located at 25 steps west of first north-south intersecting trail on western side of Old Rive rhead Road. Scrub oak, dwarf pi ne, huckleberry, and bearberry were m ain vegetation at this site.

*Table 9: Physical characteristics of sample from Site 5*

<b>Sample No.</b>	<b>Depth (cm)</b>	<b>Moisture State</b>	<b>Soil Color</b>	<b>Soil Texture</b>
1	1	Dry	Black	Black with decomposed litter and organic material
2	4	Dry	Black-Grayish	Decomposed organic material with medium sand
3	6	Dry	Black-Grayish	Fine to medium sand
4	10	Dry	Dark brown	Fine to medium sand
5	15	Dry	Dark brown	Medium Sand
6	30	Moist	Brown	Medium Sand
7	40	Moist	Brown	Medium Sand
8	50	Moist	Brown	Medium Sand with few small size pebbles
9	55	Moist	Tan	Medium Sand with small to medium pebbles
10	60	Moist	Tan	Medium Sand with few small size pebbles
11	65	Moist	Tan	Medium Sand with pebbles
12	72	Moist	Tan	Medium Sand with pebbles
13	80	Moist	Light Tan	Medium Sand with pebbles
14	85	Moist	Light Tan	Medium Sand with pebbles
15	90	Moist	Brown	Medium Sand with pebbles
16	100	Moist	Brown	Medium Sand with pebbles
17	105	Moist	Brown	Medium Sand with pebbles
18	115	Moist	Brown	Medium Sand with pebbles
19	130	Moist	Brown	Medium Sand with pebbles



**Site 7 (Unburned): UTM Coordinates: Zone 18 N; Easting: 697489; Northing: 4525488 (+/-6 meters); Date - 7th June 2008, 27 C, Sunny.**

This site was located south site of Dwarf Pine Plains County Nature Preserve and west site of Old Riverhead Road. The vegetation at this site was same as at other unburned sites.

*Table 10: Physical characteristics of sample from Site 7*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Black	Black with decomposed litter and organic material
2	2	Dry	Black-Grayish	Decomposed organic material with medium sand.
3	4	Dry	Black-Grayish	Fine to medium sand
4	7.5	Dry	Dark brown	Fine to medium sand
5	11	Dry	Dark brown	Medium Sand
6	13	Dry	Brown	Medium Sand
7	18	Dry	Brown	Medium Sand
8	19	Dry	Brown	Medium Sand
9	19-20	Moist	Tan	Medium Sand with more small to medium pebbles, may be mix 19 cm soil.
10	26	Moist	Tan	Medium Sand with few small size pebbles
11	30	Moist	Tan	Medium Sand with pebbles
12	32	Moist	Tan	Medium Sand with medium size pebbles

**Site 8 (Unburned): UTM Coordinates: Zone 18 N; Easting: 698136; Northing: 4525484 (+/-6 meters); Date - 7th June 2008, 27 C, Sunny**

This site was also located south site of Dwarf Pine Plains County Nature Preserve and west site of Old Riverhead Road. The vegetation at this site was same as at other unburned sites.

*Table 11: Physical characteristics of sample from Site 8*

Sample No.	Depth (cm)	Moisture State	Soil Color	Soil Texture
1	0	Dry	Black	Decomposed litter and organic matter
2	1	Dry	Black-Gray	Decomposed organic matter with medium sand.
3	3	Dry	Black-Gray	Fine to medium sand.
4	5	Dry	Brown	Fine to medium sand
5	10	Dry	Brown	Medium Sand
6	13	Dry	Brown	Medium Sand
7	17	Moist	Brown	Medium Sand
8	21	Moist	Brown	Medium Sand

## **Sample Collection:**

Soil samples from the burned and unburned sites of Dwarf Pine Plains were collected at various depths from 0 to 100 cm below the surface. The O horizon was from approximately 0.5 to 1.0 cm consisting dominantly of litter. Burned areas had thicker litter layer than unburned area. The samples were collected using a hand augur, shovel and post hole digger. The O horizon samples were collected using a small shovel. The soil samples contained sediment that varied in grain size from pebbles to silt and in color from black to light tan. The depths at which the samples were collected was measured using a measuring tape. The soil samples were stored in zip-locked bags labeled with site number, site type, depth and date. Each sample site was located with GPS.

## **Sample Preparation:**

The samples were dried at room temperature for 24 to 48 hours on clean paper so that any moisture in the sample could be attributed to either deionized water or 0.01 M  $\text{CaCl}_2$  that would be added to the sample for measuring pH. After the samples had dried, large particles of organic matter such as roots and twigs were removed manually. Samples of the O horizon were crushed. The samples were sifted with a 2-mm sieve, to remove any pebbles.

## **Sample pH analysis:**

There are two main laboratory methods for measuring soil pH –using deionized water or using a 0.01 M calcium chloride solution mixed with soil. The method using calcium chloride solution is considered to be more appropriate because it includes dissolved salts in the soil solutions – a good approximation for what plants experience. Moreover, it has been found that the results are not as dependent on the soil to solution ratio as is the pH measured with deionized water. It also gives the same pH for air-dried soil stored for as long as one year. Usually  $\text{pH}(\text{H}_2\text{O})$  is greater than  $\text{pH}(\text{CaCl}_2)$  by 0.5 to 0.9 (Hendershot et al, 1993, Kissel and Vendrell, 2004, Bauch, 2007). In order to ensure that this behavior was consistent with the samples used in this study, initial samples (sites 1 to 6) were analyzed using both de-ionized water and 0.01 M  $\text{CaCl}_2$  solution and the results are shown in Figure 10. Once the results were consistent, the remaining samples (sites 7 to 9) were measured using 0.01 M  $\text{CaCl}_2$  solution alone.

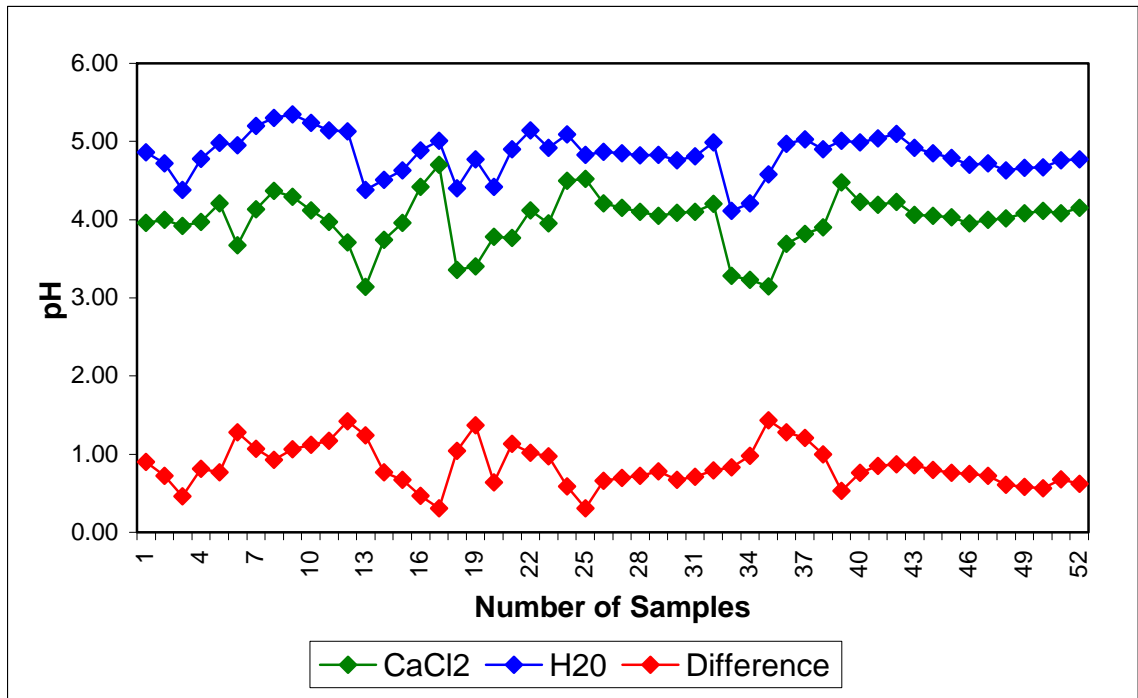


Figure 10: Comparison of  $pH(H_2O)$  and  $pH(CaCl_2)$  Average Difference 0.85 and Standard Deviation 0.27

To measure the pH, 10 mL of air-dried soil was added to a 50 mL plastic centrifuge tube. 10 mL of deionized water or 10 mL of 0.01-molar calcium chloride solution was then added to the tube containing the sample. The tubes were shaken vigorously for a few seconds to mix the samples. The tubes were then placed into an ultrasonic bath for five minutes. They were then removed, and allowed to settle until the solution became clear, approximately 3-5 minutes. The soil pH was measured using an Accumet AB15 pH meter, which was calibrated with buffers of pH 4 and 7. Slopes for the pH Meter calibration (the pH meter reading versus the buffer pH) varied from 98 to 99 percent. Usually a slope greater than 90% between two buffer points (4 and 7) indicates proper calibration. To measure the pH of the soil solution, the electrode of the pH Meter was lowered into the tube of soil solution and the first stabilized display value was recorded. The electrode was rinsed thoroughly with de-ionized water after each measurement.

The procedure was repeated for each of the samples including litter samples and the readings were plotted for each of the samples. I reanalyzed pH for samples from site 1, site 4, site 5 and site 9. The duplicate measurements were made on new sample solutions, which were placed in the ultrasonic bath for 10 minutes instead of 5 minutes. The average difference between the duplicate analyses was 0.05 pH units with a standard deviation of 0.04.

## Results

The pH(CaCl<sub>2</sub>) values for the samples collected from the 9 sites are in Table 12. The pH(H<sub>2</sub>O) data for the sites 1 to 6 are in Table 13. A plot of pH(CaCl<sub>2</sub>) versus depth is in Figure 11. The samples were collected at various depths up to 120 cm. For sites – 9 (in burned) and 2, 4, 8 (unburned), samples could not be collected at depths greater than 50 cm because of the presence of gravel. The tabulated data and their plots reveal that the pH of the soil for all the sites (in both burned and unburned areas) followed a similar trend. The pH of the soil in both burned and unburned locations increases rapidly with depth to 40 cm below which it may decline slightly, although that may be a function of the smaller number of samples with depth.

*Table 12: pH (CaCl<sub>2</sub>)*

Depth	Burned Area				Unburned Area				
	Site 1	Site 3	Site 6	Site 9	Site 2	Site 4	Site 5	Site 7	Site 8
0	3.39	3.60	3.36	5.64	3.13	3.25	3.28	3.14	3.33
1-3	3.96	3.42	3.40		3.74		3.23		3.31
3-5	4	3.44		4.32	3.96	3.38	3.69	3	3.64
5-10	3.92		3.78	5.5		3.70	3.82	3.22	
10-15		3.48	3.77	4.43		3.93	3.90		3.95
15-20				4.64				3.6	
20-25	3.97	3.92	4.12		4.42	4.15			
25-30		3.89	3.95	4.6			4.48	4.18	
30-35	4.21			4.73				4.34	4.45
35-40		4.09	4.50		4.7		4.23		
40-50			4.21	4.43		4.10	4.19	4.42	4.52
50-60	4.13	3.99	4.15				4.23	4.28	4.59
60-70	4.37		4.10				4.06	4.25	
70-80		3.95	4.05				4.05	4.22	
80-90	4.29	3.90	4.09				3.95	4.47	
90-100	3.97	4.07	4.10				4.00		
100-120	3.71	3.92	4.20				4.08		

Table 13: pH(H<sub>2</sub>O)

Depth	Burned Area			Unburned Area		
	Site 1	Site 3	Site 6	Site 2	Site 4	Site 5
0	4.68	4.55	4.40	4.38	4.12	4.11
1-3	4.86	4.61	4.77	4.51		4.58
3-5	4.72	4.89		4.63	4.08	4.97
5-10	4.38		4.42		4.39	5.03
10-15		4.53	4.90		4.48	4.90
20-25	4.98	4.72	5.14	4.89	4.65	
25-30		4.89	4.92		5.00	5.01
30-35	4.95					
35-40		4.95	5.09	5.01		4.99
40-50			4.83		4.80	5.04
50-60	5.20	4.73	4.87			5.10
60-70	5.30		4.82			4.92
70-80		4.70	4.83			4.85
80-90	5.24	4.68	4.76			4.79
90-100	5.14	4.79	4.81			4.76
100-120	5.13	4.82	4.99			4.77

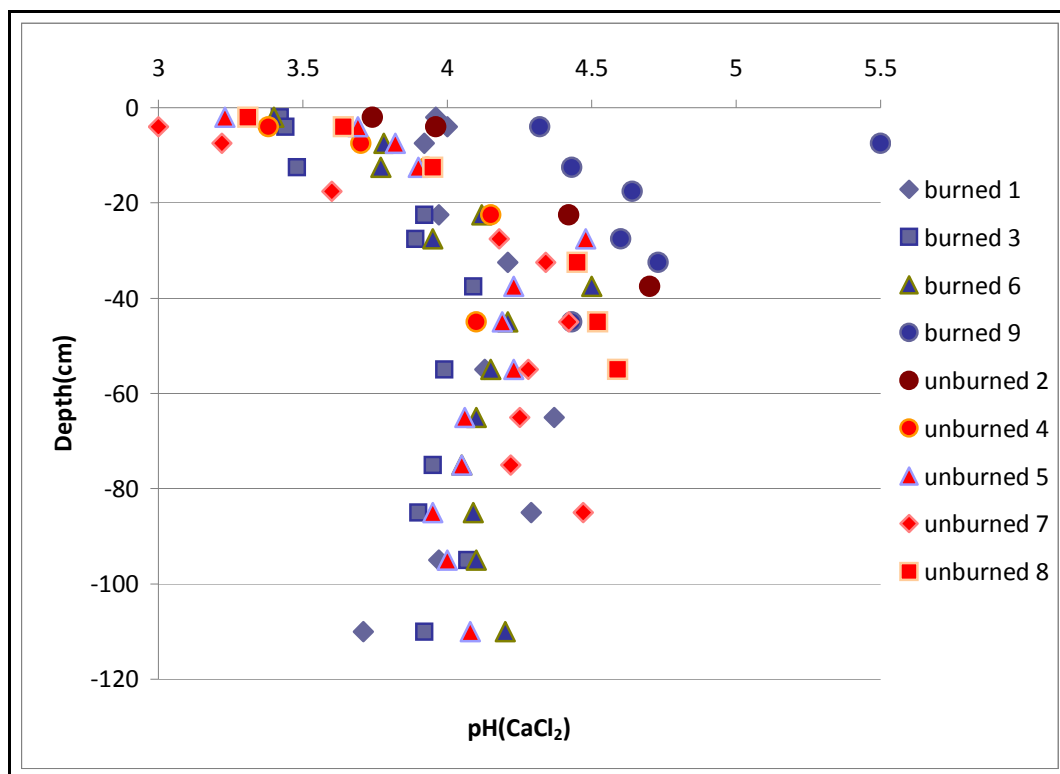


Figure 11: Individual pH Value of burned and unburned area of Dwarf Pine Plains.

Figure 12 shows a plot of pH (CaCl<sub>2</sub>) versus depth for each of the sites along with the trend lines. All the plots show a similar trend. For site 9, there is much higher pH for the surface soil. Apart from site 9 and site 3, all other sites had low values of pH at surface soil. Sites 3 and 9 are both located near a road, it could be that the surface pH at these sites were influenced by other factors. Figure 13 shows the plot of average pH (CaCl<sub>2</sub>) for burned and unburned areas along with polynomial trend lines. The trend-lines have a high R<sup>2</sup> value indicating that they represent true trends of pH data with depth. The pH values for burned areas were slightly higher than that in unburned areas up to depth of 40 cm. The largest difference occurred at depths from 5 to 25 cm, where the average soil pH in the burned area is 4.00 while the average pH in the unburned area is 3.45. However, at depths greater than 50 cm, the average values of soil pH in both burned and unburned areas are similar.

Each of the sites had an O horizon consisting of dark, fluffy organic matter that was 1 to 1.5 cm thick. At site 1 the O horizon was 2-3 cm thick. The O horizon in the burned area consisted of decomposing organic matter and burned plant remains. The O horizon in the unburned area consisted only of dead plant material. The O horizon samples did not include larger branches and leaves. The pH (CaCl<sub>2</sub>) of the O horizon at site 9 was 5.64. Ignoring pH data from site 9, the pH values ranged from 3.1 to 3.3 in unburned area and 3.4 to 3.6 in burned area.

*Table 14: pH(CaCl<sub>2</sub>) of O horizon material*

Site number	Site Status	pH(CaCl <sub>2</sub> )
4	Unburned	3.25
5	Unburned	3.28
7	Unburned	3.14
8	Unburned	3.33
Average		3.25
9	Burned	5.64
6	Burned	3.36
1	Burned	3.39
3	Burned	3.60
Average (excluding site 9)		4:00 (3.45)

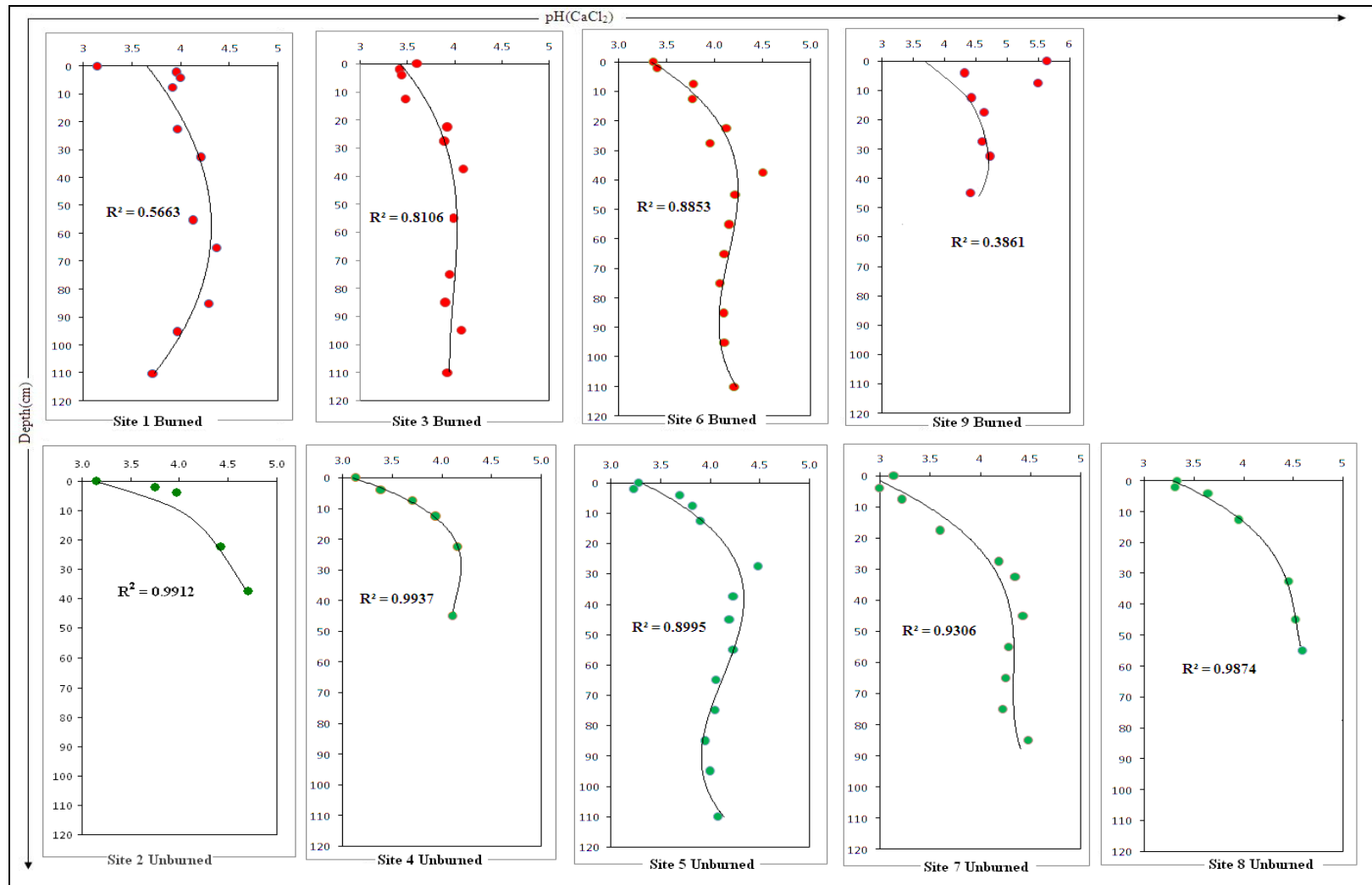


Figure 12: pH as function of depth in burned area and unburned area with polynomial trend lines.

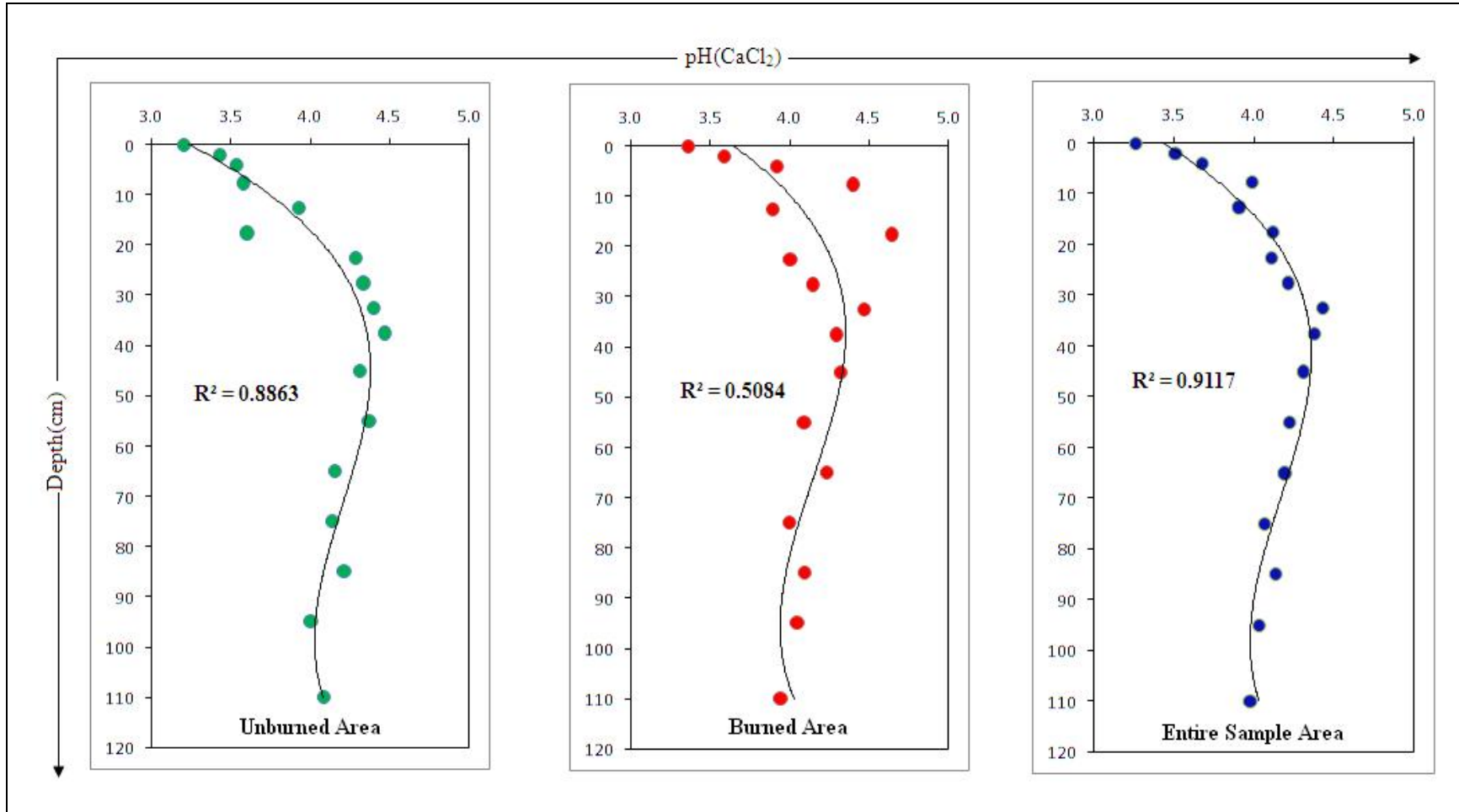


Figure 13: Average pH as function of depth in burned area, unburned and in both sample area with polynomial trend lines.



All burned areas occur at lower elevations than unburned areas. Average elevation is 60 ft in burned area and 80 ft in unburned area. Site 1 is at the lowest elevation (pH of 3.4) and Sites 2 and 4 (pH of 3.1) are at the highest elevation in the sampled area (Figure 15)

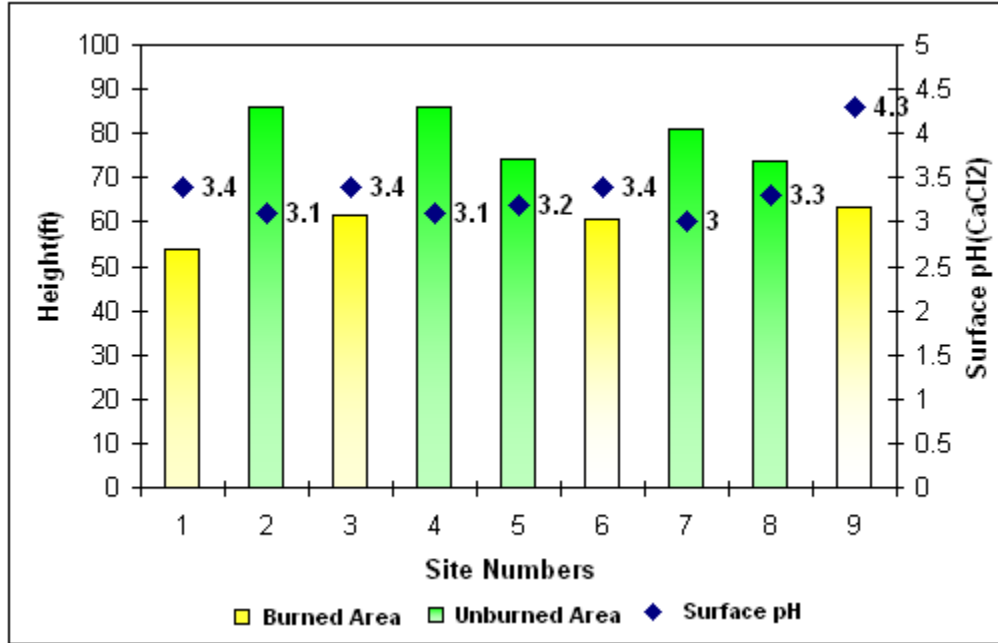


Figure 14: Comparison of Surface Soil pH(CaCl<sub>2</sub>) and Elevation at Samples Sites.

## Discussion

All sites showed remarkable similarity in their pattern for variation with depth. Site 9 has an extraordinarily high value of pH at surface level. This may be attributed to its proximity to roads and buildings.

In addition to comparing the average pH values for unburned and burned sites, it is interesting to compare a couple of individual sites – one in burned area and the other in unburned area. In this respect, Site 5 (unburned) and Site 6 (burned) are appropriate because of their proximity to each other; the samples being available for depth up to 100 cm for both the sites and trend lines for the plots of soil pH at both the sites have high R<sup>2</sup> values. Both trend lines reveal a similar pattern – except at depths in the range of 1 to 10 cm where the soil at site 6 in the burned area has higher pH values than that at site 5.

Average pH data at the same depths in the burned and unburned areas show that H<sup>+</sup> concentration is approximately 45% higher in unburned area as compared to burned area on surface up to 5.0 cm. At the soil surface, the difference in pH between the burned and unburned areas is 0.25, which is less than difference of 0.6 units observed by Swan's results (Table 15). The smaller difference for my sample may be because my study was conducted 13 years after the fire, whereas Swan carried out his study only 6 years after the fire. The pH values start to decrease after the fire incident because the extra base cations released by fire were released by cation exchange with the acid from rain and

organic matter. Moreover, Swan sampled at seventeen sites whereas I only sampled nine sites.

*Table 15: Comparison of surface soil pH with Swan 1970*

Depth	Average pH (Unburned)	Average pH (Burned)
My data	3.49	3.76
Swan's Data	5	5.6

The average pH of the O horizon material in the burned area (3.45) is 0.2 units higher than pH values in the unburned area (3.25). It may be because some ash particles from fire of 1995 were still present in the O horizon or the younger organic matter may have had more base cations.

The results in this study also showed that pH increases with depth, which is consistent with the findings of Bailey (2005). The pH recorded by Bailey was lower than results of this study, which is understandable because the rain in his study area has a lower pH than that on Long Island and the his study area had been subjected to acid rain for a longer period of time. However, his data shows a similar trend with depth as observed in this study. Bailey's results also showed that there was large difference in soil pH in 1997 between Oa/A horizon and upper B horizon (2.9 in Oa/A horizon and 3.5 in upper B horizon), but there were no changes in soil pH below 50 cm. Similarly, this study showed that the pH(CaCl<sub>2</sub>) varied rapidly until a depth of 40 cm (from 3.3 to 4.4) but became constant at depths below 60 cm with a pH of 4.1. This leads me to believe that the soil pH of 4.1 at deeper levels represents the pH of the soil not affected by acid rain. If there had been no acid rain, the soil should have had a pH of 4.1 from the surface down.

The result also shows that the O horizon has a lower pH than the mineral-rich soil just below (at a depth of 1 cm) and the pH increases with depth. This may be because the soil surface consists of organic matter and organic acids derived from them. Without acid rain, organic acid is the main contributor of acidity to the soil system, in which case the pH of 4.1 would be the equilibrium value between the organic acids and the buffering capacity of the soil. With acid rain soil pH is combination of organic acid and acid rain. When acid rain enters this soil system, the H<sup>+</sup> ions in the infiltrating rain-water interacts with the base cations in the surface soil and cation exchange occurs until equilibrium is reached. This resulting soil solution has an intermediate pH between acid rain and organic acid. As this solution travels deeper it continually interchanges H<sup>+</sup> ions reaching new equilibrium points, which have a higher pH than the layers above it.

PhreeQC simulation shows that Al<sup>+3</sup> is the dominant species, if pH is less than 4. My soil samples have a pH less than 4. Hence, the surface layer should have a high exchangeable Al<sup>+3</sup> concentration. This aluminum will displace other cations. As the solution travels down, the H<sup>+</sup> ions will react with gibbsite and by replace other cations. The lower part of soil profile will have the higher remnant pH. The results of this study show this pattern. However, with continuous infiltration of acid rain a lower soil pH will be found at greater and greater depths until the whole soil column has the same lower pH

at all depths. This soil pH will be in equilibrium with the pH of the acid rain plus organic acids at all soil depths.

The comparison of soil pH values in burned and unburned areas reveal that the sample sites in burned area had a higher pH than those in the unburned area though the difference was marked only at depths of 5- 25 cm. The soil pH at the surface level for both burned and unburned had comparable values. The reason for this might be that thirteen years have passed since the fire and the soil in both areas have equilibrated with acid rain. Because acid rain lowers the pH of upper layers of soil before affecting the deeper layers, it is quite possible that acid rain has equally affected the upper 5 cm of soil in both the burned and unburned areas as a result of thirteen years of acid rain deposition. As a result the increased soil pH due to burning has migrated to greater depths. The plots for both types of sites show marked convergence at depths below 50 cm. However, it is difficult to conclusively state this because of lack of sufficient number of samples at greater depths.

The pH values recorded in this study are compatible with the soil pH data recorded by Boguslavsky (2000) (pH = 5.12 to 5.27, up to depth 480 cm). Although her pH (H<sub>2</sub>O) values are greater than those in this study, it could be because she used a water to soil ratio of 10:1 whereas I used a ratio of 1:1. An increased water to soil ratio results in an increased pH (Krug and Frink, 1983).

The results did not show much variation between various samples based on elevation. Probably because there is little elevation difference between sample sites.

In conclusion, the results support the prediction shown in Figure 3. In Figure 3 the equilibrium value before acid rain was considered to be 5.2 but I found a value of 4.1. However, the predicted variation with depth is essentially correct. Acid rain has disturbed the dynamic equilibrium between the organic acid and buffering capacity of the soil in Dwarf Pine Plains. Acid rain has led to a decrease in the pH of the upper levels of the soil and undoubtedly caused an increase in aluminum content and leaching of base cations from the upper levels of the soil. This is because as the acid rain comes into contact with surface soil, which reacts with gibbsite and the base cations this solution, seeps down where it continues to react with gibbsite and interact with the adsorbed base cations. As a result the soil at the surface has lower pH than the soil at greater depths. However, the soil pH shows an interesting trend of increasing rapidly in Oa/A horizon before decreasing slightly and finally becoming almost constant. The reason behind this increase in pH and the slight decline with depth is not clear. Analyses of more sites would be needed to see if it is statistically significant. Further studies could include a comparison of pH in the soil profiles and the cation compositions. In addition, this study shows that the near surface soil in burned areas has a slightly higher pH than in unburned areas. However, this difference diminishes at depths greater than 40 cm.

It is noteworthy that acid rain has altered soil chemistry especially in upper few centimeters in just 60 years. It remains to be seen if acid rain will continue to change soil pH at deeper levels. Therefore, a proper monitoring mechanism needs to be established for tracking the soil pH. If the acidity keeps increasing, more acid tolerant plants will replace the plants in the Dwarf Pine Plains. Fire can help check the increase in soil acidity but an effort needs to be made to eliminate acid rain.

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