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The acidification of a Long Island, New York forest

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City University of New York, 1994

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THE ACIDIFICATION OF A LONG ISLAND, NEW YORK FOREST

by

Joel Blickstein

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ABSTRACT

The Acidification of a Long Island, N.Y. Forest

by

Joel Blickstein

Advisor: Professor David Locke

Precipitation was collected at Queens College, N.Y., analyzed and compared with the results of similar studies. The average volume-weighted pH was 4.3. Rainfall acidity was primarily associated with sulfate and secondarily with nitrate.

An analysis was made of soil solutions collected with lysimeters from a site on the moraine on the north shore of Long Island, New York. The results indicate that long term acidification and nutrient depletion due to acid rain is ongoing in these sandy, quartz-rich soils. Nitrogen appears to play a substantial role through the process of nitrification or preferential uptake of NH_4^+ over NO_3^- which releases protons to the soil solutions. Soils and soil solutions are more acid than the ambient rainfall and are extremely depleted in nutrients. Disturbance of the forests on Long Island, N.Y. might have devastating effects on the ecosystem.

The suitability of ceramic cup lysimeters in acid soil studies was also considered in both laboratory experiments and a field test. The results indicate that leaching of aluminum from the lysimeters will occur if the pH of the soil solution is less than 5.0 even if the cups have been field "conditioned". These lysimeters are inappropriate for most studies in very acid soils.

Acknowledgements

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TABLE OF CONTENTS

Results and Discussion

Experimental Section

Appendix: The Suitability of Ceramic Cup Lysimeters for Acid Soil Studies

Tables

Tables (cont.)

Tables for Appendix

STUDY PURPOSE

Wherry (1923) originally sampled the study site in 1922 to determine the relationship between plant species and soil acidity. Greller et al (1990) resampled the site to determine any changes that had occurred. Tests of the topsoil showed that the pH changed in all areas. Ridgetops decreased in pH from 4.5 to 3.8 while bottomlands decreased from 6.5 to 4.1 with the slope change being intermediate. Given the logarithmic nature of the pH scale, this represents a drastic change over 68 years.

Changes in the understory herbs were also found. Geranium maculatum and Sanguinaria canadensis were previously dominant but are now rare or absent. They have been replaced by more acid tolerant species. This trend may represent a general pattern for much of Long Island.

Ideally to understand the chemistry of a forest ecosystem, a complete input-output budget should be established. This would include, in addition to the water flux (precipitation, throughfall, evapotranspiration and leaching), a complete knowledge of the chemical fluxes and reactions. Knowledge would be required of chemical interactions in the canopy (leaves, bark, epiphytes etc.), organic horizons (litter layer, rhizosphere) and precipitation and weathering reactions in the mineral soil. However attempts to quantify various element cycles based on incomplete knowledge can lead to spurious conclusions and is unnecessary for a qualitative understanding of the most important processes that effect the soils (DeVries and Breeuwsma 1987).

This study continues the previous studies of Wherry (1923) and Greller et al (1990). It assesses the current status of the soil and estimates and assesses the precipitation inputs to the forest system. Collection and analysis of soil solutions below the main rooting zones, as done in this study, permits a qualitative understanding of the chemical transformations and changes in the ecosystem.

INTRODUCTION

Long Island, N.Y. is the largest island of the continental United States. It is bounded on the north by Long Island Sound and the Atlantic Ocean on the south. It is 190 km long and 19 to 32 km wide. Its whale shape is caused by two long, narrow end moraines. These cross each other near the east end of the island producing a fluke-like appearance.

The moraines run along the center and north shore of the island. The island is therefore hilly and deeply indented along its northern shore. To the south, outwash plains form more gentle slopes to the Atlantic.

It has been estimated that the more northerly Harbor Hill moraine has been in place for at least 16,000 years (Gordon 1980). The final retreat of the ice may have been long after that however. During this period considerable fluctuations in climate probably occurred. In fact the climate of the last few centuries may have been cooler than that of the early Holocene (Fairbridge 1992).

Most of the Harbor Hill moraine, including the study site, is covered by hardwood forests as it probably has been for thousands of years. An important exception to this occurred during colonial time. The forest served the construction and especially ship building trades as well as for heating and cooking, and were apparently completely cleared by 1700 (Murphy 1964). The forests may not have been allowed to regrow for another century (Murphy 1964). The two periods without forests (after deglaciation and deforestation) may have had important effects on soil processes and raise the question of how forest succession occurs and its effects on soils.

SOILS

An enormous effort has been made in the last few decades to map and classify soils by the U.S. Dept of Agriculture soil scientists (Buol et al 1989). Some genetic considerations are implicit in this soil taxonomy system, but they are often unknown or very complex. An important purpose of the system is to provide information for specified uses, especially agriculture. It is not surprising that a common definition of soil is the top layer of the earth's surface suitable for plant growth (The American Heritage Dictionary 1979).

Buol et al (1989) point out that this definition requires something other than soil to define it, and that plants may grow almost anywhere. They consider soil the "natural body of mineral and organic matter that changes or has changed in response to climate and organisms". Unfortunately soils are not always natural and may respond to topography, time or unknown factors. Jenny (1980) is discontentedly unable to find a satisfactory definition, and I too will leave this rather obvious requirement unmet.

Other views on soils may be instructive. To an ecologist, soil is the mineral substance that mediates the complex interrelationships between soil microbes, soil fauna (ex. termites, worms) and larger animals (ex. moles, gophers) and vegetation. Soil supports and regulates and is in turn altered by organisms that depend upon it. Soil is an inseparable part of a larger system that must be viewed as a whole.

To a chemist, soil is a mix of organic and inorganic substances. The liquid, solid and gas phases must first be described. Energy inputs and outputs, activity coefficients and thermodynamic equilibrium calculations, regulated by pressure and temperature conditions, are used to determine the state of the system. Unreliable kinetics and the complexity of the reactions often make soils an enigma.

Botanists consider soil as only one factor affecting individual plants or plant communities. Although some soils with unusual chemistry (ex. serpentine) or texture (ex. vertisols) may greatly restrict the type of vegetation that can be supported, climate is usually considered the predominant factor. Botanists and soil scientists have in common the overriding consideration of the scale at which their subject is being examined (individual plant or soil profile to world view).

PATTERNS OF VEGETATION

Plants are subject to many great variations in conditions. Light intensity changes by a factor of 100 from the canopy to the forest floor, precipitation ranges from 10 to

5000 mm from deserts to tropical rain forest and available N 200 times from polar desert to tropical rain forest. Despite this range, plants are metabolically very similar in their requirements (Chapin et al 1987). There are about 250,000 known species of plants; 95% of them are angiosperms. Diversity falls logarithmically with decreasing temperature which usually correlates with increasing latitude.

Landscapes are environmental mosaics that can only be interpreted in terms of a defined scale. For example, oak seedling mortality decreases with increased precipitation but also shows a lower mortality on a regional scale in drier latitudes (Turner 1989). The distribution of plants is however not just regulated by the average availability of resources and climate, but also by temporal variations such as seasonal droughts or frosts (Osmond et al 1987).

Greller (1989) correlated the extremes of temperatures with average conditions and growing days for the forests of eastern North America. This seems to work well on the scale of half a continent. From a bird's eye view, a similar pattern can be seen as altitude increases.

In the southern Appalachian mountains, valley bottoms typically have mixed, broad-leaved forests which grade up slope into hemlock or oaks then becoming evergreen shrubs or pine forests (Whittaker 1967). In the forests of New England and New York, there is a transition from deciduous to boreal (conifer) forest to alpine tundra over a 1500 meter gradient (Bormann and Likens 1979). The Eastern forest complex is limited on the west by declining amounts of rainfall which creates a transition to grassland.

In greater detail, subdivisions naturally occur according to local conditions of moisture, climate and soil (Robichaud and Buell 1989). Balter and Loeb (1983) found distinct differences in arborescent taxa on soils developed on gneiss and limestone. The limestone stands showed higher means for pH, silt, clay, Ca and Mg. Gneissic soils had higher percentages of sand, organic matter, Fe and Al. It was not demonstrated which factor(s) was determinant for species preferences.

Forest growth should be considered a dynamic ongoing process. Webb (1987) elucidated the changes that have occurred in forest composition as the glacial ice retreated and the climate ameliorated. Lightning fires, wind storms, insect contagions and disease have produced a constant natural turnover that have accelerated the longer-term trend. The extensive interaction of humans with forest growth, even before colonization, makes the concept of a natural setting anywhere problematic. Such interaction must be considered in any study of a modern site (Robichaud and Buell 1989).

SOIL PROCESSES

Weathered and decomposed rocks are often considered the parent material for soils. They may also be formed from volcanic ash, wind-blown deposits (loess, dune sand) or previously eroded soil. Changes in the factors of formation may impose a new type of soil profile over an old one; the provenance of the mineral portion may be several times removed from the current soil type.

Climate is the combined effect of temperature and precipitation (Speidel and Agnew 1982). From a world view, it is probably the primary factor in soil formation (Brooks 1983). Since climate is also the primary factor in vegetation, it should not be surprising that there is a large degree of overlap in map areas of soil type and vegetation.

In hot, dry areas little organic matter is produced and that is rapidly decomposed leaving alkaline-rich and oxidized soils. In hot, wet zones, organic production may be high, but decomposition is faster still. The frequent percolation of water leaches the minerals leaving a soil rich in Fe and Al (laterite) (Brooks 1983).

In cold, wet climates organic production may be high, but the low temperatures prevent the complete decomposition of plant litter. Fulvic acids leach the surface soil of Al and Fe which are transferred lower in the soil profile. These podzolic soils often have a leached quartz-rich layer (A2 or E horizon) below the surface organic and mineral horizons (O and A respectively).

Besides climate and biota, topographic relief, parent material, time and other factors (especially human action) affect soil development. The classic method for assessing these factors is to find sequences of soils in which all but one remain essentially unchanged (Jenny 1980). If the function of time is being evaluated, the soils being compared are called chronosequences. Examples of these are materials left by glacial retreat, volcanic eruptions, dune and loess deposits, flood sequences, etc.

Toposequences show the changes along a slope. Downhill movement of soil particles and eroded particles is the primary mechanism of differentiation (Jenny 1980). Aspect, permeability, slope angle and configuration are important modifiers of the general process (Buol et al 1989).

Climosequences show variations based on climate. Jenny (1980) found it very convenient for study that a U.S. moisture gradient exists from east to west and is intersected at right angles by the south to north temperature gradient. Topo- and climosequences may be combined by studying mountainous areas. A transect up slope can often be expected to show an increase in organic matter, N, C/N ratio and decreases in pH, Ca, Mg and K (Buol et al 1989).

SOIL FORMATION

Obviously before there were plants, there must have been a substrate. Lichens can grow on rocks, where they accelerate rock weathering (Blatt 1982), Bryophytes (ex. mosses) are powerful ion exchangers that also excel at collecting ions from rain (Tyler 1990). This can provide nutrients and a base of organic matter essential for higher plants. A new substrate lacks available forms of N, so N_2-fixing as well as fast growing annuals are initially favored. Slower growing perennials take advantage of the newly introduced N and eventually shade out the more opportunistic species (Tilman 1988).

Carbonic acid produced during plant and microbial respiration aids in the dissolution of minerals. Organic acids are also metabolically exuded or produced by decomposition of litter. Dissolved ions move downward in the soil column or down slope as inputs to other areas, if they are not incorporated as part of the biota (Gorham et al 1979).

Glacier Bay National Park in Alaska is a well known area where soil forming processes have been frequently studied as ongoing glacial retreat has exposed the substrate (Bormann and Siddle 1990). A slowly initiated vegetation has achieved the average biomass for temperate, coniferous forests in 110 to 210 years. A succession of tree species is initially dominated by the N_2-fixing alder. Poplar and willow come afterward followed by domination by spruce with hemlock of minor importance.

Rapid organic production is associated at Glacier Bay with rapid soil weathering. Available N and P become immobilized in the biomass or are otherwise depleted and productivity begins to decline. Further progression may produce peat land and translocated iron produces an indurated subsurface and perched water tables. So far no evidence of this has been found. Turnover of soil by mechanisms such as windthrow and erosion may mobilize elements and sustain a dynamic equilibrium.

THE EFFECT OF PARENT MATERIAL ON SOIL FORMATION

Descriptions of soil development often refer to A,B,C and R horizons. A And B represent the "true" soil with the A horizon containing most of the organic material (humus). Fine particles are eluviated in water percolating through the A horizon. They are deposited mostly in the B horizon. Often clay layers form in the B horizon which may further enhance deposition of fines or precipitation of ionic or organically complexed substances from above. The C horizon is the zone of weathered parent material (usually shown as bedrock). The R horizon is the relatively unweathered bedrock. Organic debris (leaves, twigs etc.) which overlies the A horizon is known as the O horizon.

This idealized soil profile forms only in well-drained soil where precipitation is adequate to support vegetation and percolate through the soil. This differentiation into well defined horizons may take many tens or even thousands of years (Rose et al 1979). Of course this development may be interrupted by erosion by wind or water or mass wasting processes (soil creep, slumps).

Horizon development may also be altered by the turnover of soils due to the wind throw of trees or by burrowing animals. Additions to the soils may come by way of alluvium (flood deposits), colluvium (downslope deposition) or wind deposition. Glacial till and its outwash deposition may completely obscure any previous soil development.

Changes in soil formation due to different parent materials are called lithosequences. For example as glaciers retreat, till becomes exposed and subject to the soil-forming processes. If the new soil is rich in calcite, brown forest soils with thick A horizons may form, while podzols may form on calcite-poor soils. In warm, humid areas clayey, iron-rich, Al-poor soil may form from a weathered gabbro, while a quartz-rich, more acid and Al-rich soil may form from gneissic origins (Buol et al 1989).

Parent material is never an independent variable. Its effects on soil formation cannot be separated from the interrelated effects of climate, vegetation, relief and time (Buol et al 1989).

THE EFFECT OF TREE SPECIES

Poor soil conditions have often been associated with conifer species (Pinus, Picea). It might easily be assumed that degradation of the soil condition at Glacier Bay is caused by the forest succession to spruce (Picea), but this is probably not true. The production of organic acids from plants as well as proton production from the process of N_2-fixation by the alder (Alnus) may accelerate weathering of the soils (cf. Bolan et al 1991). The parent material at a new site is chemically more unstable than after succession; changes at Glacier Bay are especially rapid during alder succession (Gorham et al 1979).

Alban (1982) compared the effects of aspen (Populus), spruce (Picea) and pine (Pinus) litter. Aspen and spruce had a lower pH in the mineral soils but a higher pH in the organic soil horizons. pH was correlated with the amount of available Ca which in total was the same under all three species. Tree ages were correlated but not growth rates. Stone (1975) has observed that deciduous species are encouraged on the more fertile land which had reinforced stereotypical associations. Stone states that high macroporosity and infiltration rates characterize the surface layer of forests regardless of species or humus type.

THE EFFECT OF SINGLE TREES

Individual digger pines (Pinus subiniana) have no effect on grassland soils, but Kauri pines in New Zealand produce 'basket podzols' that thin going away from the trunk (Buol et al 1989). Gersper and Holowaychuk (1970) studied the effect of stemflow on soil around a beech tree (Fagus grandifolia). The concentrated flow down the trunk over many decades produced a large progressive increase in the cation exchange capacity (CEC) and exchangeable acidity inward toward the stem. These single-tree influences produce a mosaic of soil profiles that may be reflected in the ground cover and tree species that are present in the forest (Boettcher and Kalisz 1990).

THE IMPORTANCE OF LANDSCAPE POSITION

Stone et al (1985) observed difficulty in correlating the degree of soil erosion with crop yields. Crops grown on head and foot slopes almost always produced the highest yields. These areas receive additional subsurface water from higher elevations as well as direct precipitation. They concluded that landscape position was at least as important as any other factor.

Studies of productivity and erosion are confounded by a lack of understanding of the erosion process. Although it is generally believed that longer slopes produce greater erosion, Daniels et al (1985) found that all head slopes are both erosional and depositional settings depending on runoff intensity and position. Great differences in erosion may occur on linear slopes on any part of the slope. The seemingly random pattern might be related to slight perturbations in slope shape or to unknown thicknesses in the original uneroded surface horizons.

The distribution of elements is also affected by the slope position. Basic cations such as K, Mg and Ca will tend to be more concentrated in lower slope positions. Where conditions at the bottom of the slope are wet due to poor drainage, soils may be relatively rich in cations, while soils of the same parent material higher on the slope may be highly leached and relatively dry. A vegetative gradient may parallel the soil sequence (catena) (Marshall 1977).

HERBACEOUS UNDERSTORY PLANTS

As might be anticipated, the distribution of herbaceous plants changes along the major gradients of topography or elevation. However the distribution on the forest floor is very irregular. It may be that mineral nutrients become available at unpredictable times in unpredictable patches due to random decomposition or mineralization processes in the soil. The mosaic of organic matter and mineral soil of various depths may produce the clumping of the dominant herb species (Hutchings 1988, Bratton 1976). Seasonal shading of herb species might be considered to prevent growth of species produced later in the season, but Roger (1985) found this not to be true.

Muller (1990) notes that few studies have shown strong patterns of competition among deciduous forest herbs. Muller studied species at the Hubbard Brook Experimental Forest in New Hampshire where the oligotrophic conditions should have intensified competition. Instead no or very weak positive or negative spatial associations were found between species that might be considered potential competitors. It is suggested that the low light level at the forest floor is the primary limiting factor.

ACID RAIN

Robert Smith correlated the relationship between coal combustion, wind trajectories and precipitation chemistry over a century ago in England. He observed and wrote about damage to plants and corrosion to metals and fabrics. The term "acid rain" was originally proposed by Smith (in Cowling 1982).

Despite this early work, it is only since the 1950's that serious attention has been given to the potential problems of this kind of pollution. Since then damage to fisheries, soils and forests have been attributed to "acid rain". Almost no data are available on rainfall chemistry in the United States prior to 1950 (Cowling 1982, Galloway et at 1984).

The pH of water in equilibrium with the ambient pressure of CO_2 is 5.6. This is often taken as a starting point for the determination of the natural, pristine condition of rainfall (Solovyev 1989). Constituents of rainfall other than carbonic acid may also affect the pH.

NH_3 or $CaCO_3$ increase precipitation pH, while dissolved oxidation products of N and S emissions decrease it. The natural cycle of S (emissions from volcanos and S-containing gases from the ocean surface and coastal sediments) can produce rain with pH varying from 4.5 to 5.6. The NH_3/NH_4 cycle (mostly from decomposition of organic wastes) may cause as much variation as the S-cycle but is not necessarily in phase with it. These natural cycles can be expected to produce large variations in rainfall chemistry over both time and space (Charlson and Rodhe 1982).

Other constituents of rainfall, such as Ca, Mg and K, may be added by wind-blown soil and dust. Sea spray may add Na and Cl. However of greatest concern are the anthropogenic sources of rainfall acidification which dominate in some areas.

The burning of fossil fuels produces emissions of SO_2 and oxides of N (NO_x). Dissolved in rainwater, SO_2 evolves to sulfuric acid (Munger and Eisenreich 1983, Chang et al 1987). NO_x may oxidize to nitric acid, although unlike SO_2 this apparently occurs in the gas phase (Farmer 1987). Smil (1985) and Bubenick (1984) emphasize that the conversion chemistry is complex and still not fully understood.

Local sources of NH_4 may come from waste incineration, fossil fuel combustion, manure spreading, industrial processes and animal feedlots. Although not acidifying in rainfall, these point sources may be indirectly acidifying to soils as NH_4 oxidizes or is taken up by plants (Abrahamsen and Stuanes 1983, equation (1) below).

Since rainfall is naturally acid, and the gas and solid phases may be important components, it is more accurate to speak of atmospheric deposition than "acid rain" (Tabatabai 1985). The relative importance of the constituents is often determined by geography. The mean volume-weighted average pH for croplands in the Plains states for 1983-1985 was 5.1. In the Mid-Atlantic area (De, Md, NJ, NY, Pa), the mean was only 4.1 for the same time period (NADP/NTN 1989).

Very limited data indicate that in areas not prone to dustfall, such as coastal and forest areas, mean concentrations of Na, Cl and H are not significantly affected by dry deposition (Munger and Eisenreich 1983). In forested areas, however, leaf surfaces may be effective scavengers of fine particulate matter. This dry deposition may be very important to nutrient cycling and soil chemistry (Norden 1991, Mollitor and Raynal 1983, Skeffington 1983).

Although still considered controversial (Tabatabai 1985), it is generally agreed that increased anthropogenic emissions since industrialization have increased precipitation acidity due to an increase load of sulfuric and nitric acids (Hileman 1983). This increased load has been confirmed by ice cores (Solovyev 1989, Pearman et al 1989) and ionic correlations of precipitation chemistry (egs. in U.S.: Verry and Harris 1988, Galloway et al 1984, Gorham et al 1984). Rainfall chemistry data are still relatively scarce however.

ACID SOILS

The acidification of soils due to increased atmospheric acid load from fossil fuel emissions is far more controversial and difficult to quantify than rainfall chemistry. Acidification of soils is often a natural process (eg. Ford 1990). Krug (1991) emphasizes that the effects of climate and land use (especially forest cutting and regrowth) are often overlooked in evaluating acidification processes. A strong correlation also may also exist between plant ecosystems and soil development.

The diversity of soils and soil-related processes may appear to make discussion of this controversial topic of soil acidification nearly impossible. However relatively simple arguments are used to evaluate the effect of anthropogenic acids. Krug and Frink (1983) state that the equivalent of thousands of years of rainfall acidity are stored in the organic anions in soils. An increase in strong acids decreases the solubility of these buffering organic anions with little change in pH. The organic acids that accumulate will be oxidized to CO_2 and H_2O. Tabatabai (1985) states that "no in situ detrimental effect of acid rain on soils or plants, attributed to increased anthropogenic deposition, have been documented except for point sources...."

Van Breeman et al (1985) summarize the opposing arguments as follows. Soil acidification may be defined as a decrease in the acid neutralizing capacity (ANC)(Van Breeman et al 1984). This occurs by removal of cations (mostly K, Ca, Mg, Al) from the mineral soil or by addition of acidic components (base neutralizers such as SO_3). The total acidity of a soil is its base neutralizing capacity. The total acidity is irrelevant, because only a small fraction of the acid organic matter is able to donate protons under acid conditions ($<$pH 4.5). Net fluxes due to organic acids are negligible. Cations exist in three phases in soils: soil solution, adsorbed to soil particles or in soil minerals (Abrahamsen and Stuanes 1983). Adsorbed cations may be replaced by H^+. Removal of these cations through leaching permanently reduces the ANC of the soil. Weathering of soil minerals replaces the lost adsorbed cations. If the weathering rate is less than the rate of removal of leached cations, soil solutions will be acidified. Abrahamsen (1985) cites a number of studies in Europe which appear to confirm the relationship between soil acidification and acid pollution.

SITE DESCRIPTION

The site coordinates are 40^0 52'00"N latitude and 73^0 34' 10" W longitude. Greller et al (1990) studied the area in 1985. Using an aerial photograph, they had a two foot contour topographic map drawn (the map on page 25 is a simplified version). The three E-W trending ridges and valleys range in elevation from 27 to 71 m. The largely undisturbed area is considered an "Oak, Beech, Mixed Dicot" type of deciduous forest. Average rainfall is 114.2 cm/year (Greller et al 1990).

In a recent soil survey, the soils are considered part of the Montauk series common to much of the northern part of the island. They are considered extremely to moderately acid (pH <4.5 to 6.0, Wulforst 1987). Although modern soil surveys are competent for their purposes (mainly land use), the soil survey of Bonsteel and "Party" (1904) gives a much better description for understanding the nature of the area. Soils east of Hempstead Harbor are dominated by the "Alton stony loam" on the moraines and plateaus. Medium to fine brown or reddish yellow sandy loam and gravel are underlain by gray or yellow cross-bedded sand and gravel. Numerous boulders of many different types of rock are found in the soil and subsoil.

The coarse nature of the soil gives a good natural underdrainage except in kettle holes of moraine areas where finer sediment from adjoining slopes has accumulated. Older sedimentary beds, overridden by the glaciers, have imparted an unusual amount of quartz to the glacial material. Some local beds of Cretaceous clay have been worked into the mass.

Typically at the study site, a blanket of leaf litter is underlain by a mass of fine roots (<1mm diameter) in the top 10 cm of soil. This is typical of forest soils where 90% of fine to large roots (1 to 10 mm in diameter) are found in the top 30 cm of soil (Harris et al 1980). Accumulation in and seasonal turnover of these roots may be a major factor in retaining and recycling plant nutrients. It has been estimated that fine root turnover ranges from 40 to 92% annually in forests and may be more important than litterfall in returning organic matter to the soil (Ross 1989).

The soils at the study site have an unusually uniform texture and chemistry (vertically and horizontally). No strong horizonization has formed, although a fragipan was found at site E at a depth of about three and one half feet. The depth of the fragipan, the sloping nature of the site and uniform textural coarseness makes the area one of excessive drainage in all seasons.

Site Map

(from Greller et al 1990)

____S Stream --- pH transects Sample sites are labelled A, B, C, D, E
Elevations are in feet

RESULTS AND DISCUSSION

RAINFALL CHEMISTRY

Three studies of rainfall chemistry were conducted at the Brookhaven National Laboratories located in the central part of Long Island, New York. This is approximately 32 miles ESE of the study site. Lee et al (1986) compared the results of the three studies and concluded that most of the total acidity (H^+ + NH_4^+) could be accounted for by H_2SO_4 and HNO_3 based on their average concentrations. Their volume weighted averages and those of two previous studies at Brookhaven and this one (1992) are shown in Table One below:

Table One

	1977	1981	1986	1992
H^+	53.5	50.2	51.2	42
NH_4^+	16.9	19.6	17.9	14
SO_4^{+2}	124.2	100.8	49.4	65
NO_3^-	24.7	28.0	27.9	18
Ca	NM	NM	NM	14
Na	44.3	22.9	32.4	19
Cl^-	51.5	33.3	37.2	26
Mg	NM	NM	NM	7
K	NM	NM	NM	1

NM = not measured Units are in uM

Raynor and Hayes (the 1981 study cited in Lee et al, 1986) found precipitation acidity best correlated with the sulfate ion alone. Their correlation of H^+ with nitrate + nitrite was significantly lower. The correlation was lower still with ammonia and appeared uncorrelated with sodium and chloride concentrations. They and Wolff et al (1979) found that pH values were the lowest in the warm months when cold fronts and air mass thunderstorms are most common. They are highest with lows formed in the Gulf of Mexico or over the Atlantic Ocean.

This study found the following volume-weighted averages for pH (based on H^+ concentrations): May 3.96, June 4.27, July 3.94, August 4.23, Sept. 4.44, Oct. 4.15, Nov. 4.17, Dec 4.07. The two most acidic rain events occurred on 7/26/92 and 8/19/92 with the pH of the precipitations 3.40 and 3.35 respectively. The highest pH precipitation was 5.00 on 9/22/92 (from Table Three).

Table Two below shows that in this study the highest linear correlation ($r^2 = .35$) of H^+ is with sulfate (except Fe which was found in relatively very small quantities [not in table]). It was also found that this is a better correlation than H^+ with SO_4 + NO_3 ($r^2 = .21$, not shown). Lee et al (1986) state that the total free acidity should include NH_4, since ammonia normally is a neutralizer of free acid. The correlation is still best with sulfate alone ($r^2 = .58$) while that of sulfate + nitrate is improved ($r^2 = .46$) but is still less than with sulfate alone. For total free acidity with nitrate alone $r^2 = .28$). These correlations indicate that precipitation acidity is most closely associated with sulfate and secondarily with nitrate. In agreement with Raynor and

Hayes (1981), there appears to be no correlation of H^+ with sodium or chloride concentrations. In addition there appears to be no correlation of H^+ with K, Ca or Mg concentrations.

Table Two

	H^+	Cl	NO_3	SO_4	NH_4	Na	K	Ca	Mg
H^+	--	.01	.08	.35	.17	.02	.03	.00	.00
Cl	--	--	.28	.21	.07	.86	.26	.53	.62
NO_3	--	--	--	.73	.54	.28	.32	.83	.79
SO_4	--	--	--	--	.56	.21	.17	.57	.56
NH_4	--	--	--	--	--	.11	.25	.31	.29
Na	--	--	--	--	--	--	.29	.48	.61
K	--	--	--	--	--	--	--	.39	.41
Ca	--	--	--	--	--	--	--	--	.95

Table Two shows linear correlations (r^2) of rainfall chemistry (from Table Three).

The ratio of Na to Cl for the 1977 and 1986 studies were .87 and .86 respectively (Table One). Since the ratio in seawater is .86, it is reasonable to assume that almost all of the Na and Cl had a seawater origin (Raynor and Hayes 1981). The ratio for this study and that of 1981 is .73 and .68 respectively (Table Three and Table One respectively) indicating a nonmarine source of Cl, since seawater is virtually the sole source of Na in precipitation. Normalizing to Na, the marine salt spray content of the rainwater can be approximated and removed from the data (Norden 1991). Sulfate then shows a slightly higher correlation with H^+ ($r^2 = .37$). Nitrate has higher correlations with Ca and Mg ($r^2 = .84$ and .86 respectively, not shown) indicating that the cations had marine and nonmarine sources, since nitrate is negligible in seawater (Schreiber 1986).

Caution should be taken in the comparison of studies, because the Brookhaven data were taken in a different location, at a different time and with different methods (wet only vs. bulk precipitation in this study). Wolff et al (1979) found that the average pH of rainfall (20 events) in Queens was 4.64 which was the highest in the metropolitan area. The overall average for the N.Y. City area was 4.28. This indicates that the results of all of these studies are substantially the same. Calculations of inputs to the forest site are based on this study only.

Winchester (1989) reports that free H_2SO_4 in aerosols can have a pH <0. Dissolution of soil dust aerosols may occur as H_2SO_4 forms liquid films on their surfaces. This process may account for the small concentrations of Fe and Al found in the precipitation as a result of acid dissolution of Al silicates in these fine particles (Table Three).

SOIL SOLUTION CHEMISTRY

Results in this section are taken from Tables 4-27.

Nitrogen

Unlike other major nutrients, nitrogen does not originate from soil minerals and does not accumulate significantly on exchange sites. In unpolluted forests N-deficiency is common and widespread (Ross 1989, Johnson 1992). While under low-pH conditions autotrophic nitrifiers are inhibited, there is competition for nitrogen among plants, heterotrophs and nitrifiers. Ammonia released in N-deficient soils is readily recycled biologically (DeVreis and Breeuwsma 1987).

The N soil reactions that may affect acidity are mineralization of organic matter, nitrification, NH_4^+ fixation, NH_3 volatility and denitrification. In sandy soils, only mineralization and nitrification may be relevant (Ross 1989). Both of these processes are acidifying.

Ammonification of organic compounds followed by nitrification should generate one net mole of protons for each mole of N transformed. Nitrification of ammonia (equation 1) generates two net moles of protons for each mole of N transformed (Bolan et al 1991).

Nitrification: $NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$ (1)

Preferential uptake by plants can also affect acidity. Uptake of NH_4^+ requires the release of a proton because of the requirement for electrical charge balance. For the same reason nitrate uptake reduces acidity by requiring release of a hydroxide ion (Barber 1985).

Nitrogen deposited in excess of biological requirements is mostly lost through nitrate leaching. This process may be enhanced by the small frequent inputs of nitrogen supplied by air pollution, because it seems to favor nitrification (Johnson 1992). The nitrification of ammonia (equation 2) occurs even in low-pH conditions (DeVries and Breeuwsma 1987). The volume-weighted ratio of $NH_4^+$to NO_3^- in rainfall is .78 (Table one). Site B 18", D 18", E 18", B 24", E 24" had soil solution ratios of .20, .06, .03, .49 and .07 respectively (Tables 18-27) indicating substantial nitrification occurred.

Soil column experiments have shown that nitrate may be leached preferentially over sulfate and therefore may be more effective in removing nutrient cations in low-base, sandy soils (Harris and Stone 1992). This appears to be borne out by the data in this study. The ratio of $NH_4^+ + NO_3^-$ to SO_4^{-2} in the rainfall data is .49. In the soil solution the ratios are 1.47, 3.84, 2.69, 2.43, and .42 for sites B 18", D 18", E 18", B 24" and E 24" respectively (Tables 18-27).

It is probable that the N influx is higher than indicated by the rainfall data alone. The synergistic effect of exposure to SO_2 may greatly enhance deposition of NH_4 to foliage (McLeod 1990). It is known that bulk precipitation substantially underestimates N deposition (Johnson 1992).

McLeod et al (1990) estimates that the "critical load" for N deposition in forests is 10-20 kg per ha year. Beyond this amount the forests may be damaged. Data in this study indicate that almost 5.1 kg per ha year of N is being added in rainfall. The previous studies at Brookhaven (Lee et al 1986) indicate as much as 7.5 kg per ha year of N are being added in wet only precipitation (from Table one, based on 114.2 cm of rain/year (from Greller et al, 1990)).

Sulfate

In unpolluted areas S-cycling does not produce acidification in forests (DeVries and Breeuwsma 1987). However unlike N, sulfur has a very small requirement in the biological cycle which is easily exceeded in polluted areas. Because of this, and sulfate's predominance in "acid rain", it is often the leading suspect in temperate acidification studies.

The anthropogenic increase in sulfate has increased the total ionic charge in precipitation as well as its acidity. H^+ reacts with soil minerals to displace Ca (or other nutrient cations) by mineral dissolution and cation exchange. The exchangeable H^+ is replaced by Al species (Ruess and Johnson 1986). In the soils at the study site, this process is demonstrated by the predominance of exchangeable Al over H^+.

Even without additional acidity, the increased ionic concentration due to sulfate addition will always depress the soil pH in highly acidic soil if the soil has a net negative charge. This is because additional electrolytes displace Al^{+++} and H^+ from cation exchange sites. The displaced Al^{+++} may hydrolyze and liberate H^+:

$$Al^{+++} + H_2O = Al(OH)^{2+} + H^+ \quad (2)$$

Concentrations may also be increased by evapotranspiration and reduced by leaching from precipitation. This concentration effect is most likely to be evidenced in acid soils with low ionic strength soil solutions (Richter et al 1988). Sulfate is being added to the soils by precipitation at a rate of 36 kg per ha year (from Table Three).

Aluminum and Iron

Concern about Al toxicity to plants in acid soils is well known, although the specific causes and effects are poorly understood. Toxicity is usually determined by models of Al speciation rather than direct evidence. The main concern is damage to fine roots (Marschner 1991). Aluminum toxicity will probably not be a problem at the study site in the near future, because it apparently requires a Ca/Al ratio less than .10 (Murach 1988), but this subject has little documentation in the literature (Tables 18-22).

Al may enter soil solutions by either direct exchange with other solution cations or by dissolution of some solid Al phase. Exchangeable Al is acidifying as shown in equation (2). Dissolution of gibbsite or an amorphous $Al(OH)_3$ can have a buffering effect:

$$Al(OH)_3 + 3H^+ = Al^{+++} + 3OH^- \quad (3)$$

Reaction (3) can be expected to become increasingly important as the soil pH decreases below 5.

Various Al sulfate minerals may also precipitate and dissolve (Evans 1991). These reactions are extremely difficult to assess, because it is impossible at this point to know all the chemical species that might be in solution or whether a particular solid phase is in equilibrium with the soil solution. Under very acid conditions, and especially at low Eh, Fe^{++} may become soluble.

Hydrolyzed Fe and Al oxides may also be chelated by soluble organic molecules in a process known as cheluviation. These molecules may be precipitated further down in the soil column as the organic molecules become saturated and/or the solution chemistry changes. Where trivalent cations of Fe and Al are available from weathering, the association of soluble organic molecules with the lower valent nutrient cations (Na, K, Ca, Mg) should be low. A mechanical sieving effect on small particles is also possible and may be responsible for the development of iron-rich fragipans.

Na and Cl

There is little nutritional requirement for either Na or Cl and both can be easily leached through soils where precipitation exceeds evaporation. However their movements through soils do not necessarily coincide with each other (Fitter and Hay 1981). The volume-weighted average of equivalents of Na to Cl in rainwater had a ratio of .73 during this study. The average ratios in soil solutions are .73, 2.12, .70, 1.01, 1.37 for sites B 18", D 18", E 18", B 24" and E 24" respectively (Tables 18-27). Especially in coastal areas Na and Cl may be deposited on leaves and increase their concentrations in throughfall compared to open areas (eg. McColl 1978). This increases the ionic concentrations of soil solutions and may decrease the pH as described for sulfate.

K

K is usually the dominant monovalent cation in soils except for H^+ in acid soils (Barber 1985). Supply of K in soil is usually less variable than other ions. Organic matter such as leaf litter is the primary source (Fitter and Hay 1981). Foliar leaching of K is greater than that of Ca or Mg, and it is more easily displaced from cation exchange sites (Reuss and Johnson 1986). The results shown in Tables 18-22 of soil solutions collected by lysimeters appear to confirm this process. The relative proportion of K in the soil solutions is much higher than in precipitation as compared to Na, Ca or Mg (Tables 18-22).

It is possible that in a mature forest such as at the study site, large quantities of K may have been stored in excess of nutritional requirements. A four-fold range in K concentrations can be found in the dry leaf weight (Fitter and Hay 1981). The apparent loss of this vital nutrient to leaching may foretell a future deficiency.

Ca and Mg

There is a two to one ratio of Ca to Mg in the rainfall (Table one), but the soil solutions had approximately equal concentrations of each (Tables 18-22). The acid leaching test showed that there is a greater reserve of Mg in the soils than Ca (Table 17). The cation exchange sites are dominated by Ca over Mg (Table 15).

The original composition of these soils is obviously unknown, but it is apparently not unusual for Mg to exceed Ca as a percentage of composition in either orthoquartzites or other sandstones (Pettijohn et al 1987). It is the reactions at the cation exchange sites that should greatly predominate in soil solutions, since weathering is a relatively slow process. Ca probably predominates here because it is less easily dissociated than either K or Mg (Barber 1985).

Reuss and Johnson (1986) state that soil solutions will be dominated by Ca + Mg if they occupy more than about 20% of the cation exchange sites (Tables 15 and 16). The tables of soil solutions collected by lysimeters show this is predominantly true in this study also (Tables 18-23). Some caution should be maintained in considering base saturation in determining the extent of leaching, since the cation exchange capacity may well be reduced as soil acidity increases (Gilman 1991).

Unlike most other nutrients (especially K), Ca cannot be translocated within plants once it has been used for plant growth but must be supplied by uptake (Barber 1985). Ca deficiency restricts root growth to the point where roots will not grow in soil that is devoid of it (Barber 1985, van Riij 1991). Plant root membranes may also select Ca in favor of Mg in uptake of soil solutions (Fitter and Hay 1981). Ca at this site is to some degree apparently being conserved in the ecosystem. This may be a similar result to that of Johnson et al (1988) where incorporation of Ca into woody tissue has conserved Ca in the system despite decreases in Ca in the forest floor and soils.

H^+

Although pH varied considerably from sample to sample, the average pH (based on H^+ concentrations) was very similar for each site. The averages were 4.11, 4.17, 4.00, 4.09 and 4.08 for B 18", D 18". E 18", B 24" and E 24" respectively (Tables 18-22). This is considerably more acid than the precipitation, but some of this may be due to evaporative concentration (i.e. increased ionic strength and the salt effect). Many reactions that would have increased or decreased the concentration of H^+ could have occurred. DeVries and Breeuwsma (1987) describe the H-cycle as the most complex of all. However it is the uncoupling of the other cycles that permits leaching of the cation nutrients and acidification of the soils. The European beech can be damaged by a Ca/H^+ ratio below one (Ulrich 1989). Some of the soil solutions are near or below this ratio (Tables 18-22).

This acidification process can be considered to have had four phases. The first was the stage prior to European settlement. Although Indians are known to have exploited the forest and may have deliberately set fires (Wacker 1979), it is probable that the site was lightly used and natural processes predominated. Fires occur naturally and wind throw, disease and insect infestations create a natural turnover in forests.

The second phase was extensive cutting of the forests by European settlers during colonial times. Removal of trees decreases the total base cation pool of the ecosystem (Joslin et al 1992). In addition removal probably subjects the soils to increased leaching of cations due to the increased flux of water through the soils (McColl 1978).

Phase three is the regrowth of the forest which removes large quantities of nutrients from the soil. This apparently occurred during the nineteenth century. It is very likely that soils at the site never had a very large cation reserve pool due to their siliceous nature. Bicarbonate and organic ions would have removed some portion of this pool by leaching under natural conditions.

Soils in the midrange pH 4.5 to 6 are the most sensitive to the acidification process. Soils of higher base saturation are well buffered, while more acidic soils are buffered by Al dissolution (Joslin et al 1992). Under very acidic conditions some H^+ is leached from the system (Bolan et al 1991).

Under pristine conditions, the bicarbonate ion is protonated and not a factor below a pH of about 5. At this point Al solubility buffers the soils and acidification should slow. Dissociation of strong organic acids is unlikely to occur, except in Histosols, in the pH range <4.5 (Buol et al 1989). The organic acids should have a low affinity for base cations if Fe and Al are available (Ross 1989).

The last phase of the acidification process is ongoing. Studies of tree ring chemistry in North America show a general trend to higher concentrations of cations in the mid-1900's followed by a general decline. This may coincide with an increased level of anthropogenic acidity in rainfall. If this is so, initially cations would have been made more abundant by displacement from exchange sites followed by decreased availability (Joslin et al 1992).

The soil solution data clearly show an excess of N and S is being added to the ecosystem beyond its ability to use them. The primary acidification processes are:

1. increased ionic concentrations which lower the soil solution pH
2. nitrification of NH_4^+ to NO_3^- which adds two moles of protons to the soil solution for each mole of NH_4^+ (equation 1) or preferential uptake of NH_4^+ which requires release of a proton
3. decoupling of the sulfate and nitrate ions from sulfuric and nitric acids which results in leaching of the base cations (especially K)
4. direct addition of protons from the acidified precipitation.

Soil Nutritional and Moisture Status

The bulk of the fine roots at the study site are found in the top 10 cm of soil. Based on the acid extraction of soils (Table 17), 8.0 kg/ha of Ca and 2.7 kg/ha of K are potentially available in this soil zone. Rainfall adds about 6.4 kg/ha/year of Ca and 0.4 kg/ha/year of K. Clearly these soils have a very limited nutritional status.

A comparison with the Lakewood soil of the New Jersey pine barrens may be made (Tedrow 1979, Markley 1979). These spodic soils are composed predominantly of quartz sand in all horizons. They are considered highly acid, excessively drained and exceedingly deficient in both major and trace nutrients:

Horizon	Depth (cm)	CEC	pH
A2 (E)	0-20	<1	4.7
B	20-50	2-3	4.6
C	50-100	1.1	5.0

Soils at the study site are more acid and have approximately the same CEC. Unlike the Lakewood soils, they do not have a low base saturation. This can probably be explained by the small quantity of aluminous clay minerals in the Lakewood soils.

Comparison can also be made to other Long Island, New York soils. Olsvig et al (1979) show a transition from oak-pine forests to pine barrens to a transitional zone and finally pine plains vegetational communities. This transition shows a linear decrease in the major nutrients P, K, Ca and Mg in the organic horizons which hold most of these nutrients. A similar linear decrease in the percentage of fines (clay + silt) is found in the mineral soils. Oak-pine forests had 18.8% fines, barrens 17.6 %, transition 13.2%, plains 6.4% and heath 9.0%.

Whittaker (1979) also ascribes a transition of Oak forest to Dwarf Pine to a soil texture gradient. The coarser soils are the more xeric and are associated with the Dwarf Pines. The percentage of fines at the study site was found to average 13%. However the clay fraction, which has the greater moisture-retaining capacity was <<1%. The sand fraction averaged 80%. The fraction >2 mm averaged 7%.

CONCLUSIONS

The rainfall data confirm the anthropogenic acidification of precipitation in this region. Wolff et al (1979) found an average rainfall pH for a site in Queens, N.Y. of 4.64 based on twenty samples. This was the highest for the metropolitan area which averaged a pH of 4.28 overall. Generally the components which are scavenged by precipitation show a homogeneous regional distribution (Berdtsson 1993). Comparison with the previous Brookhaven studies (Table One) shows the rainfall data in this study may be reasonably used for estimates of the inputs at the forest study site.

Greller et al (1990) found that pH values ranged at the study site from an average of 3.8 on the ridgetops to 4.1 on the bottomlands. This compares to 4.5 and 6.5 respectively in Wherry's (1923) study of the same area. Greller et al (1990) also showed that plant distribution changes correlate with the higher acidity. The acidity of the soil samples listed in this report correspond to the values in the latter study (Tables 4-8,13,14).

Soils and soil solutions are now more acid than the ambient rainfall. This is also the case for highly acid, low base soils of the southeast Coastal Plain of the United States. Studies there indicate that soils even under these conditions are subject to still further acidification (Gilliam 1991).

Ulrich (1989) studied beech and spruce forest in central Europe. He found severe nutrient cation losses from the soils. Standing trees are surviving due to the nutrient deposition associated with the air pollution. However the future appears dim, because aggrading stands with their higher nutrient requirements may show increasing nutrient deficiencies.

In the southern outwash plains occupied by the Pine Barrens on Long Island, where the root systems of the canopy dominants Pinus rigida and Quercus ilicifolis were destroyed by bulldozing, a heath community has become established. The sensitive nature of the soils (acid, xeric and nutrient deficient) has not allowed the natural system to recover, and the prospects for recovery appear dubious (Olsvig et al 1979).

Disturbance, whether natural or not, and damage to the root systems at the study site could have a further devastating effect on the ecosystem. Similar forests cover much of the morainal area of northern Long Island as people who live or have driven through the area are aware. They are one of the major attractions of the region. Unfortunately soils of a sensitive nature are also common throughout these same areas (Water Resources Program 1981). Further study of this potential problem seems warranted.

Experimental Section

LABORATORY PROCEDURES

Organic Matter

(Palmer and Troeh 1977)

1. Weigh accurately a soil sample between 1 and 4 grams. A sample test will allow an estimate of the amount of soil that can be used. If the sample contains too much OM, the proper color changes will not occur.

2. Place the soil sample in a 250 ml erlenmeyer flask.

3. Add exactly 10 ml of 1N, accurately determined, $K_2Cr_2O_7$ solution.

4. While gently swirling add 20 ml of concentrated H_2SO_4 from a burette.
(Caution: make sure mouth of flask is pointing away from you)

5. After 10 minutes add 150 ml of distilled water (I used 150 ml of water, rather than the 100 ml recommended, because this made the color changes more obvious). Mix the suspension by swirling.

6. Filter the suspension.
(Note: the filtrate must be absolutely free of sediment)

7. Run a blank determination by following steps 3 to 6. No soil is used. This is the blank for standardizing the 0.5N $FeSO_4.7H_20$.

8. Add 3 or 4 drops of o-phenanthroline indicator for the filtrate and to the blank.

9. Titrate the filtrate and blank containing the indicator with 0.5N $FeSO_4.7H_2O$. (Note: The final end point is a change from blue to a deep red or maroon. Just before this point is reached, the solution becomes greenish then dark green.)

10. Calculate the percent organic matter using the following formula:

$$\%OM = \frac{(\text{meq. } K_2Cr_2O_7 - \text{meq. } FeSO_4.7H_2O) \times 0.76}{\text{dry weight of soil sample in grams}} \times 100$$

Notes:

1. Normality (N) of $FeSO_4.7H_20$ is calculated from the blank determination by the following relationship:

$$\frac{\text{meq. } K_2Cr_2O_7}{\text{ml } FeSO_4 \cdot 7H_20} = \text{N of } FeSO_4.7H_2O$$

2. The factor, 0.76 is based on about 75% recovery of the organic carbon and equivalent weight of 5.7 for converting meq. of C to mg of organic matter.

Test for Aluminum

Aluminon Method

(Hsu 1963)

Reagents

Aluminon-acetate buffer

1. Dilute 120 ml of glacial acetic acid to approximately 900 ml with distilled and deionized water.
2. Add 24g of NaOH and mix.
3. Add 0.35g of aluminon. Dilute to 1L and mix.

Standards were prepared from $Al_2(SO_4)_3 \cdot 18H2O$.

Procedure

1. Transfer aliquot (approx. 5 ml) of sample to 25 ml volumetric flask containing 2 ml of 1M HCl.
2. Heat @80-90 degrees C for about 30 minutes.
3. Dilute to 15 ml, add 5 ml aluminon-acetate buffer, dilute to volume and mix.
4. Measure color intensity @530nm after waiting at least one hour.

Note: All soil solutions were filtered through a 0.2um filter. Rain samples were tested with and without filtering.

Hsu (1963) found the variation in color intensity due to the addition of acid to be less than 1% if the final solution is within a range of pH from 3.7 to 4.0. This is also the range of maximum color intensity.

Exchangeable Acidity and Exchangeable Aluminum

KCl Method

(Rhoades 1982)

Materials

1. 1N KCl (74.56g KCl/L)
2. Aluminum complexing solution: 1N KF (58.1g KF/L titrated to a phenolphthalein endpoint with NaOH).
3. Approximately 0.1N HCl, standardized.
4. Approximately 0.1N NaOH, standardized.
5. Phenolphthalein solution (1g phenolphthalein per 100 ml ethanol).

Procedure

1. To a 10g sample of soil, add 25 ml of 1N KCl. Mix and let stand for 30 minutes.
2. Transfer to a Buchner funnel fitted with filter paper and mounted on to a 250ml vacuum flask.
3. Add 125 ml of 1N KCl in 25 ml increments (total 150 ml-exact volume is not critical).
4. Add 4 or 5 drops of phenolphthalein solution and titrate with 0.1N NaOH to first permanent pink endpoint (deep pink is too far).

$$\text{meq KCl acidity} = \frac{\text{ml NaOH sample - NaOH blank}}{\text{g sample}} \times 100\text{N}$$

5. Record titer for NaOH, add 10 ml of 1N KF, titrate with 0.1N HCl until pink color disappears. Wait 30 minutes, then add additional HCl to a clear endpoint.

$$\text{meq KCl exchangeable Al} = \frac{\text{ml HCl} \times \text{N} \times 100}{\text{g sample}}$$

meq H = KCl acidity - KCl exchangeable Al

Exchangeable Cations

(Knudsen et al 1982)

Materials:

1. Reagent grade 1N NH_4OAc
2. 3N acetic acid
3. 3N NH_4OH
4. Glacial acetic acid (99.5%) and concentrated NH_4OH (for optional method)
5. 50 ml Erlenmeyer flasks
6. Whatman #2 or similar grade filter paper

Procedure for extracting solution:

1. Dissolve 77.1g of reagent grade 1N NH_4OAc in about 90 ml of distilled/deionized water. Mix thoroughly.
2. Adjust pH to 7.0 with 3N acetic acid or 3N NH_4OH.
3. Dilute to 1L.

OR

1. Dilute 57 ml of glacial acetic acid (99.5%) with distilled/deionized water to 500 ml.
2. Add 69 ml of concentrated NH_4OH.

   Caution: Use Hood

3. Dilute to 900 ml. Mix thoroughly.
4. Adjust pH as above. Dilute to 1L.

Extraction Procedure:

1. Weigh 1g of soil into a 50 ml Erlenmeyer flask.
2. Add 10.0 ml of extracting solution to each flask.
3. Shake vigorously by hand with an up and down motion for one minute.
4. Filter extract. Refilter if it is not clear.

$$\frac{\text{meq } M^+}{\text{100g soil}} = \frac{100}{\text{soil wgt (g)}} \times \frac{\text{extract vol (ml)}}{1000} \times \text{meq } M^+/L$$

Acid Extraction of Soils

1. Place a dried, weighed soil sample (approximately 30 g) into a 250 ml flask.
2. Add 3 times the sample weight of 0.5N HCl (measured by volume).
3. Cover the flask tightly and place it in a mechanical wrist-action shaker for one hour.
4. Let the flask sit for 48 hours, decant and filter.

Soil pH

(Greller et al 1990)

1. To a tared beaker add about 25 ml of soil (stones, leaves, sticks and roots removed).
2. Weigh beaker and add a volume of distilled water equal numerically to the weight of the soil.
3. Stir and measure pH after one hour.

A Fisher #107 pH meter (precision +/- .05 pH units) was used after a daily calibration at pH 4.00.

Rainfall pH

The pH of the rainfall was usually measured within a few hours of its collection. The rain was stored in Wheaton bottles at room temperature. The pH was remeasured occasionally and was found to remain stable for at least six months.

Particle Size Analysis

Pipette Method

(McRae 1988)

Materials:

1. Soil separator
2. 2 mm and 63 um sieves
3. Plastic container (larger than sieve size)
4. 1 liter glass cylinder
5. 20 ml pipette

Procedure:

1. Plastic bags containing air-dried soil samples were completely emptied into a separator for division and the process repeated until a suitable sample size was obtained (typically about 20g).
2. Place sample into a tared beaker and weigh.
3. Sift sample through both sieves into a plastic container.
4. Wash any remaining fine particles from the beaker through the sieves with distilled water. Carefully wash the sand particles.
5. Wash the sand particles into pre-weighed filter paper. The sand and pebble size fractions can be weighed after oven drying (about 105 degrees C).

6. Wash the <sand-sized fraction into the 1L glass cylinder. Make the volume up to exactly 1L. Record the temperature of the suspension.

7. Seal the cylinder and mix thoroughly by inversion (several times if necessary).

8. Place the cylinder on a bench and immediately take a 20 ml sample of the suspension at about 15-20 cm depth (depth is not critical).

9. Transfer the 20 ml pipette sample to a pre-weighed beaker. Rinse the pipette and add the rinsings to the beaker.

10. Evaporate the sample to dryness overnight in an oven (about 105 degrees C).

11. Mix contents of cylinder again.

12. Place cylinder on a bench away from direct sunlight or heat source and carefully note the time.

Note: the cylinder must not be disturbed during settling.

13. The settling time can be determined from the table:

Temperature (degrees C)	Time (h:min)	Temperature (degrees C)	Time (h:min)
14	10:23	20	8:00
15	9:05	21	7:48
16	8:51	22	7:37
17	8:37	23	7:26
18	8:24	24	7:16
19	8:12	25	7:06

14. Make a mark on the 20 ml pipette 10 cm from the tip. One minute before the end of the settling time insert the pipette very gently into the suspension up to the mark.

15. At the set time gently withdraw a 20 ml sample from the suspension to represent the <2 um fraction.

16. Transfer the sample to a pre-weighed beaker and determine the weight as in step 9.

$$\frac{(\text{silt} + \text{clay}) - \text{clay}}{\text{sample}} \text{ X } 50 \text{ X } 100\% = \text{percentage silt}$$

$$\frac{(\text{silt} + \text{clay}) - \text{silt}}{\text{sample}} \text{ X } 50 \text{ X } 100\% = \text{percentage clay}$$

Notes:

1. A pinch of dish washing detergent was added to several of the topsoil samples to prevent flocculation of the particles.

2. The time for settling of the clay particles can be varied by also changing the depth of sampling proportionately. For example at 20 degrees C and four hours the sample may be taken at 5 cm depth instead of 10 cm.

FIELD METHODS

Rainfall Collection

A corrugated polyethylene sheet 2 feet 2 inches by 3 feet collected precipitation which ran into a curved plexiglass plate which then directed the flow into a polyethylene funnel and six gallon polyethylene container (0.25 inches per gallon). This apparatus was set up on the third floor roof of the chemistry building at Queens College in Flushing, New York (approximately 16 miles southwest of the study site). The container was emptied after each precipitation event or more frequently if rainfall was longer than one day or unusually heavy. A total of 31 inches was collected in the period from 5/10/92 to 1/5/93 (Table 3). Samples were collected and stored at room temperature in Wheaton bottles.

Soil Samples

Soil samples on the pH transects were taken from the first mineral soil beneath the litter layer using a trowel as in Greller et al (1990, see tables 13 and 14). Some samples were placed in sealed plastic bags and kept on ice until the pH could be measured (within 24 hours). Soil samples from sites A, B, C, D, and E were taken from trenches that had been dug approximately perpendicular to the slope gradient. Most of these samples were not kept on ice, because the results of lab tests showed that the pH of the soils were stable for at least 48 hours at room temperature.

Soil Solutions

Plastic lysimeters with dimensions 5" x 5" x 2" deep (capacity 1.3 pints) were placed in upslope positions in the sides of the trenches from which the soil samples were taken. Tygon tubing was placed in the top of the plastic containers and buried in the soil with a tightly clamped end exposed to the surface. To remove the soil solutions a capillary tube was inserted into the Tygon tubes and the solution withdrawn using a syringe.

Analytical Methods

Although all soil solution data are shown in the Laboratory Results, the analysis of data only includes those samples from which complete data sets were obtained. Complete data sets are given for all rain samples. Ca, Mg and Fe were analyzed by atomic absorption on a Perkin Elmer 3030b spectrophotometer. K and Na were analyzed by emission on the spectrophotometer or with a Dionex 2020i chromatograph. Sulfate, nitrate and chloride were analyzed with the Dionex 2010i. Al was analyzed colorimetrically by the method of Hsu (1963). Measurements of pH were made with a Fisher #107 pH meter (precision of .05 pH units).

The reproducibility of the chromatograph unit is about 2%. According to the manufacturer the spectrophotometer has the following analytic capability for atomic absorption:

	Sensitivity	Detection Limit (mg/l)
Ca	0.09	0.002
Mg	0.008	0.0001
Fe	0.10	0.004
K	0.043	0.002
Na	0.012	0.0002

Flame emission has better detection limits than atomic absorption for K and Na.

Sensitivity is defined as the concentration of an element (expressed as mg/l) required to produce a signal of 1% absorption (0.0044 absorbance units). The detection limit is defined as the concentration of the element which will produce a signal/noise ratio of 2.

Table 3
Rainfall Analyses
Values in microequivilants/liter

Date	H^+	Cl	NO_3	SO_4	NH_4	Na	K	Ca	Mg	Fe	Al	Rain in	Tot (-)	Tot (+)
05/10/92	178	17	66	119	50	13	0	10	8	0	0	1.75	202	259
05/15/92	141	11	47	108	50	9	0	15	8	0	0	0.5	166	223
05/24/92	50	54	142	173	133	57	20	135	49	0	44	0.25	368	489
05/31/92	32	59	18	37	11	57	3	15	16	0	0	1.5	114	133
06/05/92	14	20	13	27	17	17	0	15	8	0	0	1.5	60	71
06/08/92	282	20	194	241	139	13	3	40	16	7	11	0.1	455	511
06/19/92	22	31	50	56	17	30	3	55	25	0	0	0.6	137	152
06/24/92	126	17	52	135	78	22	3	25	8	0	0	0.5	204	261
06/25/92	141	25	79	144	100	39	3	25	8	4	0	0.15	248	319
06/26/92	316	34	202	302	177	30	5	85	25	11	0	0.1	537	649
07/04/92	56	45	44	98	61	52	28	35	16	0	0	0.8	187	249
07/05/92	89	59	32	81	6	22	3	30	8	0	0	0.3	173	157
07/09/92	112	28	45	108	28	30	0	20	8	0	0	0.7	182	199

continuation
of
Table 3

Date	H^+	Cl	NO_3	SO_4	NH_4	Na	K	Ca	Mg	Fe	Al	Rain in	Tot (-)	Tot (+)
07/12/92	251	39	90	398	0	48	0	170	49	14	44	0.03	527	577
07/13/92	45	14	11	83	0	17	0	45	16	0	0	0.05	109	123
07/15/92	158	42	60	83	22	30	0	20	8	0	0	0.8	185	239
07/23/92	71	17	39	69	50	17	0	25	8	0	0	0.6	124	171
07/26/92	398	118	145	406	183	78	3	35	33	7	0	0.15	670	737
07/31/92	126	45	53	119	83	35	3	30	16	0	0	0.7	217	293
08/04/92	89	23	97	127	122	26	5	65	25	4	0	0.1	246	335
08/09/92	71	17	34	77	67	17	3	25	8	0	0	0.8	128	190
08/11/92	141	14	65	121	67	9	0	25	8	0	0	0.6	199	250
08/14/92	18	20	19	21	11	17	0	15	8	0	0	0.4	60	69
08/17/92	63	20	21	33	17	13	0	5	0	0	0	1	74	98
08/18/92	14	6	5	10	0	4	0	5	0	0	0	1.5	21	23
08/19/92	447	28	147	443	133	13	0	85	25	11	22	0.05	618	735
09/03/92	32	56	71	100	44	52	5	95	41	0	0	0.3	227	269
09/07/92	28	262	92	185	0	148	5	230	82	0	0	0.03	539	493
09/10/92	45	290	119	200	0	100	10	324	74	0	0	0.03	610	553

continuation
of
Table 3

Date	H^+	Cl	NO_3	SO_4	NH_4	Na	K	Ca	Mg	Fe	Al	Rain in	Tot (-)	Tot (+)
09/11/92	35	17	15	33	0	9	0	25	8	0	11	0.7	65	88
09/19/92	28	124	481	402	211	100	20	579	148	4	11	0.03	1006	1101
09/22/92	28	322	92	156	144	235	10	259	74	0	0	0.05	570	751
09/22/92	10	65	21	54	61	26	10	60	16	0	11	0.05	140	195
09/24/92	35	11	15	33	17	4	0	15	8	0	0	0.5	59	80
09/27/92	45	118	18	44	17	96	5	30	25	0	22	0.6	180	239
09/28/92	32	17	21	31	33	4	10	15	8	0	0	0.3	69	103
10/09/92	40	51	23	35	17	30	3	55	25	4	22	0.6	109	195
10/10/92	22	124	15	35	17	104	8	25	25	0	0	0.3	174	201
10/12/92	126	121	11	33	39	9	5	30	8	4	0	0.3	166	220
10/14/92	71	34	73	104	83	13	3	90	25	0	0	0.03	211	284
10/18/92	89	446	714	668	227	318	23	933	230	18	78	0.02	1828	1916
10/26/92	112	31	105	156	78	13	3	110	33	4	22	0.25	292	374
10/31/92	112	34	102	112	33	13	3	105	25	4	11	0.1	248	305
11/03/92	40	34	6	23	0	17	0	10	8	0	0	1.5	63	75
11/06/92	141	20	53	73	22	9	0	35	8	4	0	1	146	219

continuation
of
Table 3

Date	H^+	Cl	NO_3	SO_4	NH_4	Na	K	Ca	Mg	Fe	Al	Rain in	Tot (-)	Tot (+)
11/12/92	316	116	295	289	39	52	8	254	91	18	56	0.03	700	833
11/13/92	40	206	13	50	0	183	8	35	41	0	22	0.4	269	328
11/22/92	50	42	10	25	0	26	0	15	8	0	0	1.5	77	99
11/25/92	79	37	29	46	17	17	3	25	16	0	11	0.2	111	169
11/27/92	56	37	11	29	11	4	0	10	0	0	0	0.7	77	82
12/02/92	200	56	160	112	50	35	3	90	25	4	11	0.1	328	416
12/11/92	56	116	16	40	0	96	0	20	25	0	0	1.5	171	197
12/12/92	71	121	11	46	0	109	3	15	25	0	0	1.5	178	222
12/17/92	126	23	24	52	11	13	0	20	8	0	0	0.9	99	178
12/23/92	158	62	103	112	28	57	0	80	33	4	11	0.08	278	370
12/30/92	112	175	34	102	28	148	5	50	41	0	0	0.3	311	384
01/04/93	178	102	52	117	33	17	3	25	8	4	0	0.6	270	268
01/05/93	56	25	8	23	0	22	3	5	8	0	0	1	56	94
total												31		

LABORATORY RESULTS

Table 4

Site A

(ridge top)

Sample #	soil depth	pH	OM%	Color**
1	topsoil	3.75	2.7	10Yr2/1black
2	"	3.65	6.0*	"
3	"	3.30	3.2	"
4	"	3.60	3.2	"
5	12 in.	4.35	0.7	10Yr4/3 dk br
6	"	4.50	0.8	"
7	"	4.35	0.8	"
8	"	4.35	0.7	"
9	24 in.	4.45	0.8	10YR6/4ly/br
10	"	4.45	0.3	"
11	"	4.40	0.6	"
12	"	4.45	0.5	"
13	36 in.	4.40	0.6	"
14	"	4.50	0.1	"
15	"	4.50	0.2	"
16	"	4.50	0.1	"

*contained charcoal fragments **Munsell Color Chart

Table 5

Site B

Sample #	Soil Depth	pH	OM%
1	topsoil	3.75	---
2	"	4.05	2.4
3	"	4.25	1.6
4	"	4.05	2.1
5	6 in.	4.25	0.8
6	"	5.55*	1.0
7	"	4.35	0.9
8	"	4.35	0.6
9	18 in.	4.35	0.5
10	"	4.35	0.3
11	"	4.30	---

Table 6

Site C

Sample #	Soil Depth	pH	OM%	Color
1	topsoil	3.95	2.7	10YR3/2 v dk gy/br
2	"	3.95	3.8	"
3	"	3.95	3.3	"
4	"	4.05	2.9	"
5	10 in.	4.15	---	10YR4/2 dk gy/br
6	"	4.30	---	"
7	"	4.30	0.9	"
8	"	4.35	---	"
9	18 in.	4.30	0.5	10YR4/3 br-dk br
10	"	4.30	0.4	"
11	"	4.35	0.4	10YR4/4 dk y-br
12	"	4.35	0.4	"

Table 7

Site D

Sample #	Soil Depth	pH	Color
1	topsoil	3.90	10YR3/2 v dk gy-br
2	"	4.05	"
3	"	4.05	"
4	12 in.	4.25	10YR4/6 dk y-br
5	"	4.35	"
6	"	4.30	10YR3/4 dk y-br
7	24 in.	4.25	7.5YR5/4 br
8	"	4.25	"
9	"	4.35	"
10	36 in.	4.35	10YR5/4 y-br
11	"	4.35	10YR5/6 y-br
12	"	4.30	10YR5/4 y-br
13	48 in.	4.55	10YR6/6 br-y
14	"	4.50	"
15	~6 ft. (auger)	4.75	

Table 8

Site E

Sample #	Soil Depth	pH	Color
1	topsoil	3.90	10YR3/2 v dk gy-br
2	"	4.05	"
3	"	4.05	10YR2/2 v dk br
4	12 in.	4.25	10YR5/4 y-br
5	"	4.30	10YR5/3 br
6	"	4.35	10YR5/4 y-br
7	30 in.	4.30	2.5Y5/6 lt ol-br
8	"	4.25	"
9	"	4.30	2.5 6/4 lt y-br
10	42 in.	4.50	"

Table 9

Site A		Site B	
Sample #	% Moisture (air dried)	Sample #	% Moisture (air dried)
1	5.0	1	22.4
2	9.0	2	11.4
3	9.5	3	8.3
4	4.6	4	7.9
5	5.2	5	12.8
6	3.6	6	10.9
7	3.7	7	7.8
8	3.8	8	5.6
9	1.8	9	8.9
10	1.4	10	6.6
11	2.4	11	5.4
12	0.8		
13	1.1		
14	0.6		
15	0.9		
16	0.8		

Table 10

Site C		**Site D**	
Sample #	% Moisture (air dried)	Sample #	% Moisture (air dried)
1	7.4	1	15
2	8.7	2	18
3	8.9	3	23
4	7.5	4	10
5	7.0	5	11
6	7.0	6	16
7	6.8	7	15
8	7.7	8	14
9	6.0	9	10
10	6.0	10	11
11	4.4	11	12
12	6.2	12	11
		13	10
		14	11

Table 11

Site E

Sample #	%Moisture (air dried)
1	7.4
2	8.7
3	8.9
4	7.5
5	7.0
6	7.0
7	6.8
8	7.7
9	6.0
10	6.0
11	4.4
12	6.2

Table 12

Site B

	(Weight %)		
Sample #	>2mm	Sand	Silt
1	2	88	10
2	5	83	11
3	3	85	12
4	12	79	10
5	12	80	8
6	5	81	14
7	3	81	16
8	5	81	14
9	8	83	9
10	12	75	13
11	5	65	30
12	5	84	10

Site C

	(Weight %)		
Sample #	>2mm	Sand	Silt
1	16	71	14
2	8	75	15
3	2	82	16
4	10	76	14
5	4	82	13
6	8	82	9
7	4	88	8
8	9	83	8
9	6	88	6
10	4	87	9
11	12	80	8

Table 13

Soil pH Transects

South to North just east of the ridges

	Location	pH
1	southeast corner of site	3.80
2	"	3.60
3	"	3.80
4	"	4.25
5	"	4.45
6	south ridge top	3.85
7	near valley bottom	4.00
8	valley axis	4.10
9	nose of middle ridge	4.20
10	valley bottom	3.90
11	nose of north ridge	3.85
12	valley bottom	4.55

Table 14

North to South Soil pH transect across ridge noses

Location	pH
1 valley bottom	4.90
2 north ridge top	4.05
3 valley axis	4.35
4 middle ridge top	4.05
5 valley axis	5.25
6 nose of middle ridge	4.15
7 valley axis	3.95
8 valley axis 100 ft. south	4.10
9 south ridge top	4.05
10 south mid-ridge (south side)	4.25

Additional pH values for samples along the axis of the second valley from the south: 4.20, 4.45, 4.25, 4.40, 3.95.

Table 15

Cation Exchange Capacity

(values in meq per 100g soil)

Sample #	Na	K	Ca	Mg	Tot ex. M
B1	.08	.19	.78	.28	1.33
B2	.09	.20	.57	.25	1.10
B3	.04	.08	.35	.13	0.60
B4	.09	>500	.83	.15	>500
B5	.02	.05	.10	.03	0.20
B6	.03	.05	.10	.03	0.36
B7	.03	.04	.17	.05	0.30
B8	.04	.04	.18	.06	0.32
B9	.03	.07	.11	.04	0.25
B10	.03	.04	.09	.02	0.17
B11	.05	.05	.23	.07	0.39
C1	.05	.30	.52	.16	1.07
C2	.06	.21	.49	.19	0.95
C3	.04	.11	.35	.13	0.61
C4	.04	.12	.26	.16	0.56
C5	.06	.06	.24	.09	0.45
C6	.04	.04	.23	.08	0.41
C7	.04	.06	.23	.08	0.41
C8	.05	.05	.25	.12	0.47
C9	.05	.03	.22	.07	0.37
C10	.05	.06	.37	.12	0.60
C11	.04	.03	.22	.07	0.37
C12	.07	.08	.43	.14	0.72

Table 16

Base Saturation

(values in meq per 100g soil)

Sample #	Ex. Al	Ex. H	Tot. Ex. Acidity	Base Sat.%
B1	1.8	0.7	2.5	35
B2	1.5	0.2	1.7	39
B3	1.2	0.2	1.4	30
B4	1.4	0.2	1.6	>99
B5	1.3	0.1	1.4	13
B6	0.75	0.01	0.76	32
B7	1.2	0.6	1.8	14
B8	0.79	0.07	0.86	27
B9	1.25	0.06	1.31	16
B10	1.04	0.02	1.06	14
B11	1.05	0.05	1.10	26
C1	1.49	0.29	1.78	38
C2	1.89	0.39	2.28	29
C3	1.82	0.26	2.08	23
C4	1.33	0.55	1.88	23
C5	1.19	0.04	1.23	27
C6	0.52	0.46	0.98	30
C7	0.97	0.07	1.04	28
C8	0.95	0.03	0.98	33
C9	1.06	0.03	1.09	26
C10	0.49	0.04	0.53	53
C11	0.75	0.03	0.78	32
C12	0.65	0.06	0.71	50

Table 17

Acid Extraction of Soils

(values in meq per 100g soil)

Sample #	Na	K	Mg	Ca	Fe	Al
B2	.08	.18	.57	.60	1.9	18.0
B4	.05	.12	.49	.40	1.6	18.3
B5	.07	.10	.54	.04	3.1	25.0
B6	.09	.15	.47	.09	2.8	25.4
B10	.20	.11	1.04	.06	3.1	22.3
B11	.32	.12	.77	.04	2.7	22.3
D2	.13	.10	1.03	.40	2.9	21.3
D6	.07	.05	.79	.19	2.9	24.0
D8	.07	.07	1.18	.93	5.5	24.4
D10	.07	.05	1.23	.54	4.5	21.7
D13	.08	.07	1.33	.54	4.2	17.0
E1	.09	.28	1.20	.88	4.0	27.6
E2	.04	.25	1.11	.69	4.1	19.7
E4	.12	.03	.52	.27	3.4	22.7
E5	.08	.06	.20	ND	2.8	24.4
E7	.05	.07	.39	ND	4.0	17.6
E8	.05	.06	.77	.45	4.9	15.0

Table 18
Soil Solutions Collected by Lysimeters

(values in microequivilants/liter)
Site B
(Cations)
18" depth

Date	pH	H^+	NH_4	Na	K	Ca	Mg	Fe	Al	Tot
6/8/92	5.60	3	161	48	105	25	25	4	nm	
7/6/92	4.25	56	177	39	148	75	49	nd	33	577
7/16/92	4.65	22	67	48	205	180	115	nd	nm	
8/5/92	4.35	45	33	30	148	110	82	nd	78	526
8/11/92	nm	nm	39	109	151	125	82	nd	nm	
8/13/92	4.15	71	55	35	176	140	107	18	178	780
8/20/92	4.15	71	nd	13	51	30	25	nd	67	257
9/12/92	4.15	71	nd	22	92	40	33	50	78	386
10/12/92	nm	nm	nm	nm	nm	140	90	11	nm	
11/24/92	3.95	111	nd	48	102	65	58	7	122	513
12/14/92	3.95	111	nd	483	87	60	90	11	111	953
1/6/93	4.00	99	nd	126	49	15	25	11	nm	

nm = not measured (generally due to insufficient quantity)

Table 19

Soil Solutions

SITE B

(Cations)

24" Depth

Date	pH	H^+	NH_4	Na	K	Ca	Mg	Fe	Al	Tot
7/6/92	4.60	25	416	65	215	90	90	104	44	1049
8/5/92	nm	nm	nm	nm	nm	130	132	nm	nm	
8/13/92	3.95	111	161	174	192	120	132	nd	234	1124
8/20/92	4.15	72	94	87	102	95	82	nd	156	688
9/12/92	3.80	157	22	65	46	30	49	nd	367	736
11/24/92	4.50	31	416	78	215	70	66	7	156	1043
12/14/92	4.05	88	194	213	61	90	99	14	178	937
1/6/93	4.15	74	477	244	51	30	33	14	nm	

Table 20

Soil Solutions

SITE D
(Cations)
18" Depth

Date	pH	H^+	NH_4	Na	K	Ca	Mg	Fe	Al	Tot
7/6/92	5.85	1	96	39	115	65	74	nd	nm	
7/16/92	nm	nm	96	nm	nm	60	66	nm	nm	
8/5/92	nm	nm	183	333	199	55	74	nm	nm	
8/13/92	4.45	35	39	22	125	105	82	nd	133	541
8/17/92	5.10	8	57	39	102	55	41	nm	nm	
8/20/92	4.70	20	26	22	82	75	58	nd	22	305
9/12/92	4.40	39	35	44	148	85	66	nd	33	450
9/27/92	nm	nm	65	nd	120	65	58	32	nm	
10/12/92	4.15	70	52	nd	136	125	99	32	67	581
11/4/92	4.05	88	30	155	128	235	181	39	156	1012
11/24/92	4.05	93	39	333	161	225	148	7	122	1128
12/14/92	3.90	125	57	771	235	494	527	7	656	2872
1/6/93	nm	nm	nm	nm	nm	190	nm	nm	nm	

Table 21

Soil Solutions

SITE E

(Cations)

18" Depth

Date	pH	H^+	NH_4	Na	K	Ca	Mg	Fe	Al	Tot
7/6/92	4.75	18	183	87	151	215	132	18	nm	
7/16/92	nm	nm	nm	204	nm	nm	nm	nm	nm	
8/5/92	4.65	22	17	48	166	185	123	11	nm	
8/13/92	4.45	35	44	35	138	75	74	nd	145	546
8/20/92	4.45	35	nd	135	100	70	66	nd	100	506
9/12/92	4.15	71	11	30	133	70	82	14	122	533
10/12/92	nm	nm	nm	52	159	125	115	47	>500	
11/4/92	3.85	140	83	104	309	594	551	14	589	2384
11/24/92	3.70	198	28	87	256	484	428	11	423	1915
12/14/92	3.95	112	nd	104	133	414	535	14	411	1723

Table 22

Soil Solutions

SITE E

(Cations)

24" Depth

Date	pH	H^+	NH_4	Na	K	Ca	Mg	Fe	Al	Tot
8/13/92	4.10	79	50	96	90	100	156	nd	256	827
8/20/92	4.15	71	nd	87	92	100	156	nd	267	773
9/12/92	3.95	112	39	65	115	70	140	nm	nm	
12/14/92	4.00	99	nd	113	59	150	255	nd	400	1076

Table 23

Soil Solutions

SITE B

(Anions)

18" Depth

	Cl	NO_3	SO_4	TOTAL (-)
6/8/92	20	76	144	240
7/6/92	25	224	192	441
7/16/92	34	418	237	689
8/5/92	20	285	177	482
8/11/92	39	369	183	591
8/13/92	25	318	217	560
8/20/92	14	63	96	173
9/12/92	20	118	131	269
10/12/92	NM	NM	NM	
11/24/92	96	242	108	446
12/14/92	722	52	142	916
1/6/93	40	45	92	177

Table 24

Soil Solutions

SITE B

(Anions)

24" Depth

	Cl	NO_3	SO_4	Tot -
7/6/92	51	323	416	790
8/5/92	42	460	331	833
8/13/92	96	768	269	1133
8/20/92	39	460	239	738
9/12/92	42	463	246	751
11/24/92	124	406	227	757
12/14/92	324	226	229	779
1/6/93	161	158	231	550

Table 25

Soil Solutions

SITE D

(Anions)

18" Depth

	Cl	NO_3	SO_4	Tot -
7/6/92	39	ND	264	303
7/16/92	NM	NM	NM	
8/5/92	62	53	273	388
8/13/92	23	97	312	432
8/17/92	28	34	187	249
8/20/92	11	45	227	283
9/12/92	51	126	217	394
9/27/92	133	287	148	568
10/12/92	116	415	187	718
11/4/92	130	729	167	1026
11/24/92	130	823	112	1065
12/14/92	175	2744	146	3065
1/6/93	73	>600	181	

Table 26

Soil Solutions

SITE E

(Anions)

18" Depth

	Cl	NO_3	SO_4	Tot-
7/6/92	59	484	391	934
7/16/92	NM	NM	NM	
8/5/92	56	390	319	765
8/13/92	28	165	239	432
8/20/92	20	68	287	375
9/12/92	34	177	252	463
10/12/92	76	415	287	778
11/4/92	195	2216	477	2888
11/24/92	181	1563	377	2121
12/14/92	257	1574	575	2406

Table 27

Soil Solutions

SITE E

(Anions)

24" Depth

	Cl	NO_3	SO_4	Tot -
8/13/92	45	202	648	895
8/20/92	39	147	662	848
9/12/92	34	208	548	790
12/14/92	133	434	695	1262

Table 28

Stream Samples

(values in microequivilants/liter)

	pH	H^+	Ca	Mg	K
11/12/91	5.70	2	115	33	56
11/19/91	5.90	1	125	33	41

APPENDIX

The Suitability of Ceramic Cup Lysimeters for Acid Soil Studies

Introduction

Consideration was given to the use of ceramic cup lysimeters for the collection of soil solutions at the study site. The use of these lysimeters (or any other approach) for this purpose has special problems and remains controversial. Some believe that only soils with less than pH 4.0 will cause leaching of ceramic cup material that will obscure the soil solution chemistry. It is also believed that the problem decreases over time as the ceramic cup equilibrates with the soil. This has never been fully tested (c.f. Grossman and Udluft 1991).

Experimental work was performed to determine the effect of the pH of an initial solution on the concentration of aluminum in the sample solution. The ceramic cups used in this study are model #1905L06 from Soilmoisture Equipment Corp., P.O. Box 30025, Santa Barbara, Ca. 93105. Aluminum determinations were made using the aluminon method of Hsu (1963). The 8-hydroxyquinoline method of James et al (1983) was considered and rejected due to inconsistent results during trials.

Initially only nonreagent grade aluminon was available. Using this, standards were analyzed to calibrate the absorbance at different concentrations of aluminum in solution (A1). The linear correlation coefficient (r) is .994 (N = 7). Least squares analysis shows the slope equal to 5.7 x 10^{-4}. The intercept (b) is .269 (Table A1). Hsu (1963) found the quality of the aluminon can greatly affect the sensitivity, the intensity of the blank and the slope of the calibration curve.

Calibration of the absorbance made using reagent grade aluminon showed a correlation coefficient (r) of .9991 (N = 11). Least squares analysis found the slope to be 7.4 x 10^{-4}. The intercept is .430 (Table A2). The absorbance using the reagent grade aluminon was therefore 30% more sensitive to increases in concentrations of aluminum when reagent grade aluminon was used. All data reported here are based on the use of reagent grade aluminon unless otherwise stated.

All 24 ceramic cups used in these experiments were first cleaned by drawing through each (using a vacuum) one liter of 1M HCl and then one liter of distilled and deionized water as recommended by Deble et al (1988) and Creasey and Dreiss (1988). No other cleaning procedures were used. All glassware was cleaned by rinsing with hot, dilute HCl and then thorough rinsing with distilled and deionized water. A Fisher #107 pH meter (precision to .05 pH units) and a Perkin Elmer Lambda 3B spectrophotometer were used.

Methods

.1M sodium acetate buffered solutions were prepared. Cup samplers were placed in flasks and the buffered solution was drawn through each sampler using a vacuum. The solution drawn into each sampler was then tested for aluminum using the method of Hsu (1963).

Hsu (1963) recommends waiting one hour after sample preparation before spectrophotometer readings. I found that a minimum of two hours or more were required to achieve stable readings. This method uses an aluminon-acetate buffer to maintain a narrow pH range. The pH was occasionally checked and was always found to be in the proper range. Buffered solutions were never used more than once.

Results

Data reported are an average of two or more readings. All samples were eventually diluted to 25 ml prior to spectrophotometer readings. Initial measurements were made by drawing solutions buffered at pH 5.0 (.1M Na acetate buffer) into the cup samplers. Results (Tables A3, A4) of measurements (excepts sampler #6) were with the range of absorption measured for the blanks. The slight aluminum contamination of #6 decreased in the next extraction.

Similar results were obtained using the nonreagent grade aluminon (data not shown).

Using a buffered solution of pH 4.0, an initial extraction showed only slight or undetectable amounts of aluminum in most cases (Table A5). The blank did however give the lowest of the 25 absorbance readings. Subsequent extractions (Tables A6-A10) had increasing absorbance readings for almost all of the samples with each trial. It is obvious that aluminum was being leached into the sample solution from every sampler.

Samplers were left standing in flasks with buffered solution (pH 4.0) from 8/2/91 to 9/9/91 (Table A11). During this period the pH of the buffered solution in the flasks containing the samplers increased by .15 to .20 pH units. On 9/12/91 six samplers were placed in a flask with a buffered solution (.1M) of pH 4.2 (Table A12). Several tens of milliliters of solution were drawn through each sampler and discarded to eliminate pore fluids from previous procedures. Samples were then drawn out and measured for aluminum. Significant amounts of aluminum had continued to leach into the sample solutions from the cup samplers.

Unused buffer from 9/12/91 was diluted 1:100. The pH was remeasured and found to be 4.15. Cup samplers (#9,15,16,17,20 and 22) were placed in a flask with the diluted buffered solution. The samplers were partially filled and left to stand overnight. The combined solution from the samplers was found to have a pH of 4.35. The pH of the buffered solution that remained in the flask with the samplers was 4.20.

Field Tests

Many papers suggest "conditioning" by field placement improves the leaching or CEC characteristics of ceramic cups (c.f. Grossman and Udluft 1991). To test this, four samplers (#3,4,7 and 19) were placed in top soils at various locations according to the manufacturers instructions on 9/12/91. Augured soils, removed for the cup emplacements, were placed in separate plastic bags and later measured for pH (4.45, 4.55, 4.00, 4.05 respectively).

Sampler numbers 3 and 7 were removed on 12/19/92; numbers 4 and 19 were removed on 1/6/93. Soils from just above the ceramic part of the cups were removed and test for pH. The soil pH's were 4.35, 4.30, 4.05 and 4.15 for sampler numbers 3, 4, 7 and 19 respectively.

The samplers were placed in a flask with a 0.1M Na acetate buffer with a pH of 4.25. Several tens of milliliters were drawn through each and discarded. After five days samples from each cup sampler and from the flask were tested for pH and aluminum.

The pH of each sample was 4.30 or 4.35. The aluminum concentrations were 0.6, 1.2, 1.7, 3.1 and 0.8 PPM for sampler numbers 3,4,7,19 and the flask solution respectively. The procedure was repeated using the same buffered solution. The pH results were 4.35, 4.35-40, 4.30, 4.35-40 and 4.40 respectively. Results of the aluminum test were 1.5, 1.0, 1.1, 1.3 and 1.1 PPM respectively.

Discussion and Conclusions

Hughes and Reynolds (1990) tested ceramic cup lysimeters for aluminum contamination of sample solutions. Their cups were from Soilmoisture Equipment Corp. also, although a different model was used. Their cups had been used in field studies for approximately six years in soil with a pH of about 4.5. They found in lab studies that sequential extractions of solutions of pH 4.0 showed an initial increase and then substantial decreases in Al concentrations after two extractions.

Hughes and Reynolds (1990) concluded that the initial increase was due to the slight cation exchange capacity of the ceramic cups. They believe that Al leached into solutions from the cups gradually decreases with time and is inhibited from leaching by Al in the soil solutions. They therefore believe that the ceramic cups may be used where soil solutions are higher the pH 4.0.

Raulund-Rasmussen (1991) also investigated the characteristics and determined the composition of Soilmoisture Equipment Corp. ceramic cups by using the powdered material. It was concluded that cup dissolution and not the CEC are responsible for the release of aluminum. Raulund-Rasmussen (1991) concluded that Al activity would eventually reach equilibrium with gibbsite solubility.

It is clear from the results of my experiments that a CEC of the cup material can not explain the increasing concentration of Al in solution with each additional extraction. Varying rates of dissolution of the cup materials due to slight differences in composition and manufacture is a more reasonable explanation. The idea that Al in the soil solution would inhibit leaching of Al from the cups in not useful, since it would be impossible to distinguish the two sources.

Gibbsite becomes increasingly soluble below a pH of 5.0 (Garrels and Christ 1990, p.354). Aluminum also forms complexes with organic matter, silicates and sulfate which could greatly increase the solubility of other aluminum phases (Johnson and McBride 1991, Xu et al 1991). Assuming a relationship of the ceramic cups to gibbsite solubility, this type of ceramic lysimeter should not be used below a soil pH of 5.0.

LABORATORY RESULTS

Table A1

Calibration of Absorbance

Aluminon Method (Hsu 1963)

(nonreagent grade aluminon)

Parts per billion	Absorbance
blank (dis./deion. H_2O)	.276
24	.303
108	.336
216	.411
240	.415
320	.461
400	.509

Using the least squares method, the slope is 5.7×10^{-4}. The intercept is .269. The correlation coefficient (r) is .994.

Table A2

Calibration of Absorbance

Aluminon Method (Hsu 1963)
(reagent grade aluminon)

Parts per billion	Absorbance
blank (dis./deion. H_2O)	.427
8	.435
16	.437
24	.448
32	.451
40	.456
80	.488
160	.562
240	.614
320	.673
400	.714

Using the least squares method, the slope is 7.4×10^{-4}. The intercept is .430. The correlation coefficient (r) is .9991.

The following standards included 5 ml of Na acetate buffer (.1M with pH 5.0).

blank	.449
80	.523
160	.585

Above data from 7/15/91

Table A3

7/15/91 0.1M Na Acetate Buffer (pH 5.0)

Cup sampler#	ml of sample	Absorbance
3	5	.441
5	5	.461
10	4	.467
14	5	.452
18	5	.444
23	5	.430
7/18/91		
2	7.5	.459
3	7.5	.449
6	7.5	.484
10	7.5	.465
14	7.5	.450
18	7.5	.433
unused buffer	7.5	.445

Table A4

7/20/91 0.1M Na Acetate Buffer (pH 5.0)

Cup sampler #	ml of sample	Absorbance
1	7.5	.463
9	7.5	.454
10	7.5	.464
12	6.0	.472
13	5.5	.460
15	7.0	.458
17	7.5	.453
18	7.5	.454
19	6.0	.447
20	5.5	.454
21	7.5	.452
22	6.0	.452
23	6.5	.460
24	7.5	.471
unused buffer	7.5	.458-.472

Table A5

7/24/91 0.1M Na Acetate Buffer (pH 4.0)

Cup sampler #	ml of sample	Absorbance	PPB (undil.)
1	7.5	.598	670
2	7.5	.500	230
3	7.5	.467	170
4	7.5	.472	80
5	7.5	.569	540
6	7.5	.662	950
7	7.5	.482	140
8	7.5	.487	170
9	7.5	.478	130
10	7.5	.553	460
11	7.5	.534	380
12	7.5	.617	750
13	6.0	.474	140
14	7.5	.488	170
15	7.5	.498	220
16	7.5	.472	100
17	7.5	.488	170
18	7.5	.473	100
19	7.5	.479	130
20	6.0	.458	50
21	---	----	---
22	7.5	.468	80
23	7.5	.480	140
24	7.5	.493	190
unused buffer	7.5	.450	---

Table A6

7/25/91 0.1M Na Acetate Buffer (pH 4.0)

Cup sampler #	ml of sample	Absorbance	PPB (undil)
1	7.5	.579	580
2	7.5	.514	290
3	7.5	.491	190
4	7.5	.485	160
5	7.5	.694	860
6	7.5	.845	>1750
7	7.5	.515	290
8	7.5	.510	270
9	7.5	.508	260
10	7.5	.712	1180
11	7.5	.616	750
12	7.5	.754	1350
13	7.5	.528	350
14	7.5	.516	300
15	7.5	.523	100
16	7.5	.502	230
17	7.5	.516	300
18	7.5	.511	280
19	7.5	.487	170
20	6.0	.474	140
21	7.5	.505	250
22	7.5	.482	140
23	7.5	.523	330
24	7.5	.531	370
unused buffer	7.5	.449	---

Table A7

7/26/91 0.1M Na Acetate Buffer (pH 4.0)

Cup sampler #	ml of sample	Absorbance	PPB (undil.)
1	7.5	.579	580
2	7.5	.536	390
3	7.5	.501	230
4	7.5	.497	210
5	7.5	.857	>1800
6	7.5	.995	>2400
7	7.5	.537	390
8	7.5	.525	340
9	7.5	.521	320
10	7.5	.816	>1640
11	7.5	.683	1050
12	7.5	.819	>1660
13	7.0	.549	480
14	7.5	.552	460
15	7.5	.538	400
17	7.5	.523	330
18	7.5	.532	370
19	7.5	.505	250
20	7.5	.511	280
21	7.5	.552	460
22	7.5	.508	260
23	7.5	.534	380
24	7.5	.545	430
unused buffer	7.5	.452	---

Table A8

7/27/91 0.1 Na Acetate Buffer (pH 4.0)
(new aluminon solution, slope (m) = 7.2 x 10^{-4}, intercept (b) = .445)

Cup sampler #	ml of sample	Absorbance	PPB (undil)
1	5.0	.561	810
2	7.5	.579	620
3	7.5	.533	410
4	7.5	.539	440
5	5.0	1.035	>4000
6	5.0	1.068	>4000
7	7.5	.541	440
8	7.5	.564	550
9	7.5	.558	520
10	5.0	.937	>3400
11	5.0	.785	>2300
12	5.0	.871	>2900
13	7.5	.579	620
14	7.5	.600	720
15	7.5	.561	540
16	7.5	.542	450
17	7.5	.557	520
18	7.0	.582	680
19	7.5	.534	410
20	6.0	.519	430
21	7.5	.579	620
22	7.5	.543	450
23	7.5	.614	780
24	7.5	.620	800
unused buffer	7.5	.445	---

Table A9

7/30/91 0.1M Na Acetate Buffer (pH 4.0)

Cup sampler #	ml of sample	Absorbance	PPB (undil.)
1	5.0	.582	950
2	7.5	.610	760
3	7.5	.578	620
4	7.5	.548	480
5	5.0	1.105	>4500
6	5.0	1.085	>4400
7	7.5	.558	520
8	7.5	.579	620
9	7.5	.573	590
10	5.0	.980	>3700
11	5.0	.834	>2700
12	5.0	.914	>3200
13	7.5	.615	790
14	7.5	.599	710
15	7.5	.577	610
16	7.5	.560	530
17	7.5	.559	530
18	7.5	.596	700
19	7.5	.530	390
20	7.5	.554	500
21	7.5	.585	650
22	7.5	.549	480
23	7.5	.600	720
24	7.5	.614	780
unused buffer	7.5	.429	---

Table A10

8/2/91	0.1M Na Acetate Buffer (pH 4.0)		
Cup sampler	ml of sample	Absorbance	PPB (undil.)
1	5.0	.604	1100
2	7.5	.616	790
3	7.5	.564	550
4	7.5	.556	510
5	5.0	1.412	>6700
6	5.0	1.274	>5700
7	7.5	.577	610
8	7.5	.601	720
9	7.5	.587	660
10	5.0	1.004	>3800
11	5.0	.885	>3000
12	5.0	.932	>3300
13	7.5	.629	850
14	7.5	.629	850
15	7.5	.590	670
16	7.5	.583	640
17	7.5	.589	670
18	7.5	.625	830
19	7.5	.567	560
20	7.0	.568	610
21	7.5	.623	820
22	7.5	.589	670
23	7.5	.634	870
24	7.5	.646	930
unused buffer	insuff. qty.	---	---

Table A11

9/9/91 0.1M Na Acetate Buffer (pH 4.0)

Samplers were left standing in this buffered solution from 8/2/91 until 9/9/91.

Cup sampler #	ml of sampler	Absorbance	PPB (undil.)
1	5.0	.955	>3500
2	5.0	.622	1130
3	5.0	.584	965
4	5.0	.561	806
5	5.0	1.188	>5100
6	5.0	1.170	>5000
7	5.0	.601	1080
8	5.0	.614	1170
9	5.0	.591	1010
13	5.0	.662	1510
14	5.0	.605	1110
16	5.0	.583	960
18	5.0	.608	1130

The buffered solution increased in pH by .15 to .20 units over the period of this experiment.

Table A12

9/12/91 0.1M Na Acetate Buffer (pH 4.2)

Samplers were allowed to evacuate several tens of milliliters of buffered solution each to eliminate any remaining pore fluids from the previous experiments with buffered solutions.

Cup sampler #	ml of sample	Absorbance	PPB (undil.)
9	7.5	.588	660
15	7.5	.579	620
16	7.5	.583	640
17	7.5	.587	660
20	7.0	.577	660
22	7.5	.592	680
used buffer	7.5	.563	550

The original unused buffered solution was retested and found to have a pH of 4.15. At the same time, the used buffered solution was measured at a pH of 4.20. The pH meter used is precise only to within .05 pH units.

Four milliliters of the buffered solution were diluted to 400 ml with distilled and deionized water. The pH was remeasured and found to be 4.15. Cup samplers numbered 9, 15, 16, 17, 20 and 22 were placed in a flask filled with the diluted buffered solution. The samplers were then partially filled using a vacuum and left to stand overnight in the flask. The combined pH of the solution in the samplers after 23 hours was 4.35. The pH of the buffered solution that remained in the flask with the samplers was 4.30.

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