POTENTIAL EFFECTS OF ACID PRECIPITATION ON SOILS IN THE HUMID TEMPERATE ZONE

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INTRODUCTION

Acid precipitation is not a new phenomenon. As long as water has fallen on the surface of the earth it has probably contained varying amounts of oxides of carbons, nitrogen and sulfur that increase hydrogen ion activity. This was certainly true when volcanism prevailed. With the appearance of life spasmodic geologic expulsions of elements into the atmosphere were supplemented by more rhythmic biochemical cycles of organic matter production and decomposition. Since the Industrial Revolution consumption of fossil fuel has increased additions of atmospheric contaminants. In the first two and one-half centuries of industrialization combustion of coal caused large discharges of sulfur. In the latter half of the present century oxides of nitrogen have increased sharply because of the advent of the gasoline engine. According to Robinson and Robbins (1968) 73×10^6 tons of sulfur were emitted in the mid-1960's. They estimated that 70 percent of this came from combustion of coal and 16 percent from combustion of petroleum products. Other estimates of man's contamination of the environment based on pollution of river waters with sulfate range from 3.7×10^6 tons (Bertine and Goldberg 1961) to 33×10^6 tons (Berner 1971). Kellogg et al. (1972) consider that 50×10^6 tons of sulfur per year are contributed to the atmosphere by man. Annual discharges of NO and NO_2 into the atmosphere from man's activities are estimated to be about 50×10^6 tons. This is compared with estimated natural emissions of 500×10^6 tons NO_2, 5900×10^6 tons NH_3 and 1000×10^6 tons N_2O (Robinson and Robbins, 1968).

In the past few decades increasing evidence has linked atmospheric pollutants to undesirable plant responses but the influence of these pollutants on soil processes and characteristics has received little attention. The purpose of this paper is to examine potential effects of acid precipitation on soil and to relate these effects to acidification resulting from natural pedogenic processes or from

modification of these processes by agricultural practices. In this discussion we will emphasize the effects of sulfur and nitrogen on soils occurring in humid temperate zone forested regions.

SOIL FORMATION

From its inception soil formation is an acidifying process. The parent material may vary greatly in composition and state of subdivision but it is generally composed of silicate minerals containing different amounts of aluminum, iron, calcium, magnesium, potassium, sodium, manganese, and other elements. It may be igneous, metamorphic or sedimentary. It may have formed where it is exposed or it may have been transported varying distances by geologic agencies. Chemical equilibria established during the formation of the parent rocks and minerals from which the soil is ultimately formed have been disturbed and new equilibria are continually being established through the process of weathering.

Chemical weathering involves hydrolysis, hydration, oxidation-reduction reactions, carbonation and solution of the compounds and elements found in the parent material. Particle surfaces on which weathering begins are frequently not acidic. Abrasion pH values of many silicate rocks and minerals are commonly alkaline ranging as high as pH 8 or 9. As the more easily dissolved constituents such as calcium, potassium, magnesium and sodium are removed in solution the soil system becomes more and more dominated by hydrogen and aluminum ions.

The effects of chemical weathering are greatly accelerated as the quantity and variety of organic matter added to the soil increase. Consumer organisms, particularly bacteria and fungi, show corresponding changes in quantity and variety. Metabolic by-products from these organisms include carbon dioxide, organic acids and other compounds that not only increase acidity but also enhance solubility of mineral constituents by chelation. In many cases root systems of higher plants have specific organisms associated with them which promote availability of otherwise insoluble mineral constituents to the higher plant or which promote fixation of atmospheric nitrogen. Thus plant growth and production of more organic matter is enhanced.

With time the biogeologic system approaches the dynamic equilibrium imposed by climate and by the limits of the system itself and a characteristic soil evolves which reflects these combined influences. Nutrient cycling is essential in maintaining the progressive tendencies of vegetative systems and again, because of the dominance of microbial metabolism, the net effect is production of acidifying conditions. A brief discussion of the cycles of nitrogen and sulfur will serve to illustrate this process.

NITROGEN IN SOIL

The cycle of nitrogen in soil as an integral part of the overall cycle of nitrogen in nature has been reviewed by Stevenson (1965) and again by Wollum and Davey (1975). Over 97 percent of the earth's nitrogen is held in primary igneous rocks with substantially smaller amounts occurring in ancient sedimentary rocks. Most of this nitrogen does not circulate biologically, however, and the primary source of nitrogen in the soil is the atmosphere which contains only about two percent of the total nitrogen on earth. In the atmosphere, however, N_2 is the dominant gas, occupying about 80 percent of the gaseous volume. Combined forms of nitrogen including ammonia, nitrate, nitrite and organic nitrogen may also occur. These originate from soil or from oceans, from industrial sources or from fixation of atmospheric nitrogen by lightning, by photochemical oxidation or by the passage of meteorites.

Nitrogen is transferred from the atmosphere to the soil by precipitation, by direct absorption of gaseous forms from the atmosphere and by biological fixation. Amounts added in rainfall vary greatly. Allison (1965) cites data showing additions of 1.7 to 22.3 kg/ha/year of inorganic nitrogen with an average of 8.7 kg. Over 2/3 of this is ammonia nitrogen. Eriksson (1952) gives values for Europe and the United States ranging from 0.74 to 21 kg per hectare per year. Values from the White Mountains in New Hampshire over an eleven year period average 19 kg/ha/year (personal communication from F. H. Bormann). While these amounts are generally insignificant for field crop production they are of considerable importance to natural ecosystems which in many instances tend to accumulate nitrogen. Because of increasing use of fossil fuel it is likely that amounts of nitrogen in precipitation will increase. Addition of nitrogen to the soil by absorption of gaseous nitrogen from the atmosphere has been reported to be of the same order of magnitude as additions in precipitation although there is not universal agreement on this subject (Allison, 1965).

The most efficient means for transferring gaseous nitrogen from the atmosphere to the soil is biological nitrogen fixation. This process may involve blue-green algae, free-living bacteria, bacteria associated with non-leguminous plants. Obviously the amounts of nitrogen added to the soil by these agencies will show much variation. Values given by Allison (1965), Jensen (1965) and Vincent (1965) for all of the nitrogen added may total as much as 100-200 kg/ha/year with most of this being added by leguminous crops. Additions in natural ecosystems are probably considerably less.

However nitrogen is provided it eventually becomes a constituent of plant protein or other nitrogen containing compounds in the plant. In natural forest ecosystems plant or animal tissues containing combined nitrogen are deposited on the forest floor where decomposition

begins. Details of this process vary with the type of tissue and the types of organisms involved but the broad outlines of decomposition in all cases are generally similar. Complex nitrogen-containing molecules are hydrolyzed to smaller and smaller polypeptides and peptides, to constituent amino acids and eventually to ammonia. Under favorable conditions variable amounts of ammonia are transformed to nitrate. This conversion which can be carried out by heterotrophic organisms as well as specific autotrophs is an acidifying process with two hydrogen ions being released for each nitrate ion produced according to the following highly simplified reaction:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+$$

Nitrogen can be absorbed by microbes or by higher plants either as ammonium or nitrate and recycled through another generation of plant tissues or nitrate may be reduced releasing nitrogen in gaseous form or it may be leached from the system. In managed agricultural soils the reactions are essentially the same except the amounts of nitrogen involved are much larger due to additions of nitrogenous fertilizers. Thus the potential for acidification is high and must be counter-balanced by periodic application of ground limestone.

SULFUR IN SOIL

The ultimate source of sulfur in soil is the rock material from which the soil is derived. The lithosphere contains about 0.06 percent sulfur (Jordan and Ensminger 1958). Unweathered igneous rocks may contain from 0.05 to 0.3 percent sulfur with basic igneous rocks generally containing more sulfur than acid igneous rocks (Whitehead, 1964). Sulfur in unweathered igneous rocks occurs primarily as sulfides of iron, copper, nickel and other metals. These same combinations may occur in somewhat higher concentrations in sedimentary rocks with values ranging from 0.03 percent sulfur in sandstones to 0.26 percent in shales. Limestones contain an average of about 0.11 percent sulfur (Rankama and Sahama, 1950).

In well-drained soils in the humid temperate zone sulfides released by rock weathering are oxidized by chemical and microbial reactions to sulfate which is either absorbed by plants or removed by leaching. The mechanisms of oxidation of sulfides are extremely complex and have not been fully resolved. The overall reaction stoichiometry for oxidation of pyrite can be represented by the following:

$$FeS_2 + \frac{15}{4} O_2 + \frac{7}{2} H_2O \longrightarrow Fe(OH)_3 + 2H_2SO_4$$

where four moles of hydrogen ions are produced, two from the oxidation of ferrous iron and two from the oxidation of sulfide (Stumm and Morgan, 1970). Presumably other metal sulfides are oxidized in a similar fashion. The rate of sulfur oxidation is of interest from the point of view of soil reaction, nutrient balance and soil formation. Wiklander (1958) indicated that when a silty subsoil high in iron sulfide was exposed to air for 120 days the pH value dropped from 6.3 to 2.9. Much of the sulfur in soil surface horizons is present in organic forms with only small amounts of sulfate. This relationship varies with soil type. Evans and Rost (1945) showed that organic sulfur constituted more than 70 percent of the total sulfur in the A horizon of chernozem and black prairie soils in western and southwestern Minnesota. The A horizons of podzol soils of northern Minnesota, however, contained less than 50 percent organic sulfur. These samples were of the mineral soil and did not include the humus layers in the podzol soils.

In subsoil horizons, however, appreciable amounts of sulfate may accumulate and constitute a major portion of the total sulfur (Neller, 1959). This is especially true in acid soils where sulfate adsorption by soils and clays reaches a maximum in the pH range from 2 to 4 (Williams and Steinbergs, 1962). Adsorption occurs on surfaces of mineral colloids particularly hydrated aluminum or iron hydroxide or on clay minerals particularly kaolinite. Several mechanisms of adsorption have been suggested (Schell and Jordan, 1959) including adsorption at exchange sites and occlusion between lattice sheets.

In addition to weathering sulfur is added to the soil by rainfall (Jordan et al. 1959, and other papers in this Symposium), by direct adsorption of SO_2 from the atmosphere by plants and by soil (Alway, Marsh and Methley, 1937; Fried, 1948; Ensminger, 1958 and Whitehead, 1964) or as a component of a fertilizer or soil amendment for agricultural or horticultural purposes. Crop responses to sulfur additions have been reported in Africa, Asia, Australia, Brazil, Canada, France, Japan, New Zealand, Norway, Spain, Sweden and West Germany (Freney, Barrow and Spencer, 1962; Nelson, 1965).

In the United States considerable attention has been given to sulfur in relation to crop needs (Hart and Peterson, 1911; Shedd, 1914; Ames and Boltz, 1916; Stewart, 1920; Greaves and Gardner, 1929; Alway, 1940; Kelley and Midgley, 1950). According to Nelson (1965) 40 percent of the sulfur consumed in the United States finds its way into the manufacture of fertilizers and consumption for this purpose was, at that time, increasing at an annual rate of five percent. Whitehead (1964) indicated that where the atmosphere supplies more than about 10 kg of sulfur per hectare per year, sulfur deficiency is unlikely to occur. Tisdale and Rucker (1964) ascribe increasing occurrence of sulfur deficiency to an absolute decrease in the amount of sulfur being added to the atmosphere as the result of the shift from coal to natural gas and petroleum fuels that contain less sulfur

than coal, to increasing use of high analysis fertilizers that do not contain sulfur as a by-product, to the production of higher yielding crop varieties that place greater demands on the sulfur supplying ability of the soil and to losses of sulfur through leaching. While these observations might apply to situations where highly specialized agronomic crops are being grown, it seems highly unlikely that sulfur deficiency will occur where forest vegetation is growing on unmanaged soil.

The relatively small amounts of sulfate usually found in the upper horizon suggests that this form of sulfur is quickly leached. Lysimeter studies (McKell and Williams, 1960) have corroborated this and estimates on a global basis indicate that the rivers of the world carry considerable amounts of sulfate to the ocean each year. Eriksson (1963) estimated that for the period around 1960 the total annual amount of sulfate carried to the sea was 240×10^6 tons which included 45×10^6 tons from rock weathering, 30×10^6 tons applied to the soil as fertilizer and 165×10^6 tons from precipitation or dry deposition. Berner's (1971) calculations for flux of sulfate to the oceans via the world's rivers showed a total of 368×10^6 tons which included 268×10^6 tons coming from natural sources and 100×10^6 tons coming from pollution from various sources. Berner considered his estimate of the quantity contributed by pollution to be conservative.

Plants take up most of their sulfur from soil as sulfate. Simple organic sulfur compounds may also be utilized but the intense microbial activity in the immediate vicinity of plant roots suggests that this is not a significant source. In unmanaged soils then, sulfur available for plant growth will come either from the atmosphere or from conversion of organic sulfur compounds to sulfate by microbial decomposition. From this point on sulfur mineralization and immobilization bears a close resemblance to mineralization and immobilization of nitrogen (Walker 1957; Barrow 1960). According to Walker the amount of sulfate formed from organic matter is affected by total sulfur in the organic matter and by the carbon/sulfur ratio, and pH in much the same way as the formation of mineral nitrogen is influenced by corresponding factors. Whitehead (1964) found the ratio of nitrogen to sulfur in soils to vary from about 6:1 to 9:1 and Williams, Williams and Scott (1960) observed a close relationship between the contents of soil sulfur and soil nitrogen in Scottish soils with correlation coefficients as high as 0.984.

Transformations of sulfur in soil are primarily microbial and while there are organisms specifically associated with oxidation of elemental sulfur and simple sulfur compounds it is likely that many different types of heterotrophic bacteria and fungi are involved in the sulfur cycle.

Microbial transformations of sulfur have been described in detail by Alexander (1961) and Freney (1967). Sulfate absorbed by growing plants is transformed into a large number of organic compounds in various parts of the plant. Numbers and characteristics of these compounds vary with the plant species. In the forest these tissues are eventually deposited on the forest floor and here further transformations associated with decomposition take place. Decomposition end products vary depending upon climate, microclimate, soil type, the nature of the material being decomposed and the nature of the decomposing organisms. The simple inorganic sulfur compounds resulting from decomposition are then reassimilated into the tissues of microbes or higher plants or are leached from the soil profile or lost in gaseous form to the atmosphere. Many details of the decomposition process are not known but generally speaking under anaerobic conditions mercaptans and hydrogen sulfide will accumulate while in the presence of atmospheric oxygen sulfate is commonly the end-product (Stevenson, 1964).

As in the case of weathering reactions that release sulfur from parent rocks many reactions associated with organic matter decomposition are potentially acidifying although oxidation to sulfuric acid or intermediate acids may be buffered to a far greater extent by the organic system than is the case in rock weathering. In poorly drained anaerobic situations sulfide may accumulate and when such soils are allowed to oxidize pronounced increases in acidity may occur. Hill and Shearin (1970) observed decreases of as much as three pH units when soils from tidal marshes of Connecticut and Rhode Island were dried for 18 days. Initial pH values in these soils ranged from about 5 to 7. In marsh soils that had been exposed for clay mining pH values ranged from 3.6 at the surface to 2.2 at a depth of about four meters.

THE NATURE OF SOIL ACIDITY

In addition to soil acidity generated by microbiological energy transfers the contribution of inorganic components must be considered. The role of hydrogen and aluminum in soil acidity has perhaps been studied more intensively than any other single soil property, yet many questions remain unanswered. Jenny (1961), in reflecting on the "soil acidity merry-go-round", noted that during a half century of work many investigators had gone full circle from early theories that acid soils were Al-saturated, through the period when soils were considered to be H-saturated polybasic acids, and back to the present notion that the properties of acid soils are largely determined by aluminum. Given this history of differing interpretations of what in essence were identical experimental findings, it is clear that experts on the nature of soil acidity expound their ideas at their own risk.

We will not attempt a comprehensive review of soil acidity here since a recent monograph edited by Pearson and Adams (1967) presents an excellent summary of current views. The chemistry of soils receiving external sources of strong acids from rainfall or from the oxidation of reduced nitrogen compounds should resemble in many respects the chemistry of acid sulphate soils which were the subject of a recent international symposium (Dost, 1973). The chemistry of aluminum in these soils was reviewed by Frink (1973) and provides the basis for much of the following discussion.

Acidity of soils in the pH range of present concern is believed to be controlled by the hydrolysis of aluminum according to the first-stage hydrolysis reaction:

$$Al^{+3} + H_2O = AlOH^{+2} + H^{+}$$

where water of hydration of aluminum ions has been omitted for convenience. The thermodynamic equilibrium constant for this reaction has the familiar form:

$$K = \frac{(AlOH^{+2})\ (H^{+})}{(Al^{+3})}$$

where parentheses indicate ion activities. If these ion activities are expressed as negative logarithms, and the equation rearranged, we have:

$$pH = pK - pAlOH + pAl.$$

Since the pK for this reaction is approximately 5.0, soils containing aluminum ions would be expected to be well buffered at pH = 5.0, i.e. when pAlOH = pAl.

This buffering is indeed observed in soils, although the pH of maximum buffering capacity has been shown to decrease with increasing concentration of aluminum (Frink and Sawhney, 1967). The source of aluminum in acid soils is the soil itself. A fully H-saturated soil clay may have a pH as low as 2.5 but it rapidly increases to about pH 3.5 as aluminum and other ions are released by decomposition of the clay. Thus, this decomposition serves to set some lower limit on soil pH unless large amounts of free acidity are produced more rapidly than can be neutralized by the clay as is the case in some acid sulphate soils (Dost, 1973). Forested soils in Connecticut (Lunt, 1948) rarely have pH values as low as 3.5. Hence it appears unlikely that modest amounts of acidity in rainfall, when compared with the potential acidity from nitrification of litter, will lower the pH of unmanaged soils below pH 3.5.

Organic acids from decomposing organic matter also provide an important source of acidity in forest soils, but less is known of their reaction. Most organic acids are weakly dissociated and would not be expected to contribute to soil acidity at low pH values. Organic acids are known to form complexes with aluminum, however, which makes interpretation of their role more difficult.

The relative importance of these various sources of acidity, i.e. organic acids, aluminum hydrolysis and hydrogen ions from strong acids has also been examined by titration curves of soils and soil clays. As Jenny (1961) pointed out, however, interpretation of data has lagged far behind their collection. Titration curves of acid soils show a number of buffer ranges which still defy complete analysis. In general, when base is added to an acid soil, free acid, if present, is neutralized first, followed by the neutralization of aluminum with a pronounced buffer range. A third and final neutralization range is observed which may include neutralization of clay lattice hydroxyl groups and both free and complexed organic ligands.

When acid is added to a neutral soil, this process is presumably reversed, but very few detailed studies are available. Agronomic practices have been developed more or less empirically for predicting the amount of aluminum or elemental S required to lower soil pH for crops requiring an acid environment. Titration curves of neutral soils with acid, however, show a pronounced hysterisis which has not been examined in any detail. It is likely that much of the discrepancy between the shapes of titration curves of acid soils with a base and the reverse, or back-titration curves, reflects lack of equilibrium rather than irreversible changes in the soil.

The foregoing discussion has largely neglected cation and anion exchange properties of soils since these properties complicate interpretations of soil acidity considerably. One complication is the changes in cation exchange capacity brought about by changes in soil acidity; the second is measurement of soil acidity itself.

Considering the first problem, cation exchange capacity (CEC) of acid soils is generally observed to increase substantially with increasing soil pH. The nature of this pH dependent charge is uncertain but is thought to be associated with the third, or final, buffer range observed in titration curves. The magnitude can be quite large: a soil with pH 4.2 was found to have a neutral-salt CEC of 1.4 meq/100g and an additional pH dependent CEC of 5.7 meq/100g determined at pH 8.2 (Sawhney, Frink and Hill, 1970). Acidifying a neutral soil will likely decrease its CEC, but again some hysterisis is observed. In a recent study of acid soils Gebhardt (1973) found little change in pH-dependent CEC in the range pH 3.5-4.0. Hence, the CEC of acid forest soils is not likely to be altered by acid rainfall.

So far we have assumed that soil acidity is easily measured and therefore is well defined. This assumption is particularly important if we are to examine trends with time. Thus, how valid is it?. First, we have the usual problem of analytical methods changing with time. Prior to about 1930, soil pH was measured with indicator dyes, interference from colored or turbid soil extracts, and the ability of the eye to compare colors. Experience suggests that measurements with dyes generally indicate a higher pH than that measured with the glass electrode and that relative errors of 0.5 pH units would not be unlikely. Electrometric methods were developed and the first measurements in the 1930's were made with the quinhydrone electrode since it could be used with a simple potentiometer. The quinhydrone electrode was a vast improvement over dyes, but is sensitive to the presence of oxidizing or reducing agents as well as to the hydrogen ion. Use of the glass electrode began with the development of the vacuum tube potentiometer and continued to the highly sophisticated digital instruments common in today's soils laboratories.

What is measured when we blithely insert the glass and calomel electrodes in a soil suspension and report the pH, sometimes to three significant figures? A simple experiment of placing both electrodes first in the clear liquid and then in the soil paste reveals differences of as much as 0.5 pH units with the paste usually appearing more acid. This so-called "suspension effect" has plagued soil scientists since its discovery and the issue is not yet resolved. Other factors affecting the measured pH are the soil water ratio and the salt content of the suspension.

The suspension effect arises because there is no known method for measuring individual ion activities; i.e. one cannot measure the potential of a single reversible electrode but must use a pair. The glass electrode is commonly used to measure the hydrogen ion activity (pH) by comparing its potential with that of a nonspecific calomel electrode making electrical contact with the solution via a salt bridge. However, at the liquid junction between the salt bridge and the solution, a diffusion potential arises which is a function of the mobilities of the cations and anions in the bridge and the activities of ions on either side of the junction. The use of saturated KCl in the calomel electrode and salt bridge is thought to minimize the junction potential, since the mobilities of K and Cl are nearly equal. This assumption is reasonably satisfactory for dilute aqueous solutions and enables one to measure the activity of hydrogen ions in such systems with some confidence.

In a sol or suspension of charged particles, however, the junction potential may be large, apparently due to a reduced mobility of the counter ions near charged surfaces. Other explanations have been suggested but regardless of the cause, the effect is real and can result in substantial differences in apparent pH depending on where the electrodes are placed. Other factors such as the effect of the

soil water ratio are also attributed to the suspension effect: as the suspension concentration increases the suspension effect also increases and the measured pH decreases.

Increasing the salt concentration has several effects: first, it alters the junction potential, although the direction and magnitude of the change is different with different salts. Second, increasing the salt concentration decreases the potential difference between the clay surface and the equilibrium bulk solution and decreases the measured pH. This is often attributed to displacement of H and Al ions from exchange sites but may be equally well described by changes in electrical potential across the double layer. However, salt also has some specific effects which are better described in terms of exchange reactions. At low salt concentrations where diffusion between clay platelets is restricted, or in the presence of ions causing lattice closure, the hydrolysis of adsorbed aluminum is enhanced. This increase in hydrolysis, which is presumed due to the specific sorption of some hydrolyzed species of aluminum, results in a lower pH of the clay suspension that would be predicted from simple electrostatic considerations.

Various investigators have proposed ways of minimizing these errors in measurement of soil pH. The most common method is the addition of a 1 N salt solution (frequently KCl) to swamp effects produced by varying salt concentrations among different soil samples. This has at least one drawback: the ionic strength is so high that calculations of ion activity coefficients are impossible and hence thermodynamic constants based on pH measurements in 1 N salt solutions are unsatisfactory. An alternative is the measurement of pH in 0.01 N $CaCl_2$, a concentration considered near that of natural soil solutions, yet with an acceptably low ionic strength. No method is considered completely acceptable and hence Van Olphen (1963) cautions against direct comparisons of the pH of soil suspensions with those of true solutions.

LYSIMETER STUDIES IN CONNECTICUT

In the same way that man has altered the composition of the atmosphere by industrial activities the composition and nature of soils have been altered wherever man has practiced agriculture. This experience provides guidelines for evaluating potential soil changes caused by atmospheric contaminants.

Agriculturists have known for at least two centuries that rainfall contains plant nutrients such as nitrogen and other dissolved constituents. The earliest chemical analyses were apparently reported by Marggraf (in Miller, 1905) who found "nitric acid, chlorine and

lime in rain-water collected during the winter of 1749-1750".

Analyses continued until the major constituents in rainfall were identified. Thus rain contains the anions nitrate, sulfate, chloride and their accompanying cations ammonium, calcium, magnesium, potassium, sodium and hydrogen.

Since the amount of nitrogen in rainfall represents a significant portion of the total nitrogen budget for many crops, several long term studies of the composition of rainfall are available. Measurements of ammonia and nitrate nitrogen were begun at Rothamsted Experimental Station in the 1850's and these early results were summarized by Miller (1905). Chlorine and sulfuric acid were also determined during some of this 50 year period. Not all analyses were conducted at any one time, but analyses during 1881-1887 for sulfate and chloride and during 1888-1894 for ammonia and nitrate are shown in Table 1.

Table 1. Chemical composition of rain-water at Rothamsted, England 1881-1894 (Miller, 1905).

Constituent	Rainfall, cm	kg/ha
N_2O_5	72	1.1
NH_3	72	3.1
SO_3	76	19.5
Cl	76	16.4

Several items need be considered in the interpretation of such data. First, agriculturists generally report analyses of this sort in lbs/acre or kg/ha, since these are units of importance in agriculture. Where records of rainfall are available, it is possible to calculate the apparent concentration in the rain in ueq/liter, a unit common in studies of precipitation. However, since the samples were generally composited and stored for some time before analysis, the apparent distribution of nitrogen between nitrate and ammonia forms should be viewed with caution. Other changes in chemical composition may also occur during storage, but are probably less serious.

More troublesome are the changes in analytical methods that have occurred over the years. Few generalizations as to the effects of such changes are possible, since comparative studies of analytical methods are not very rewarding and few are available. However, it is likely that both the precision and the accuracy of early methods were low. Moreover, rain-water is quite dilute and even present day methods may lack the necessary sensitivity; hence an error of a factor

of 2 would not be unlikely in the analyses shown in Table 1.

A more subtle problem but potentially the largest source of error in interpretation of early data is the chemical form reported by the analyst. For example, the study at Rothamsted speaks of nitrate, nitric nitrogen and nitric acid in the text but the tabular data identifies this form of nitrogen as N_2O_5. This is understandable, since chemical terminology had not reached its present level of standardization. However, the most serious problem is knowing whether the 1.1 kg/ha is reported as N_2O_5 or as N. The history of analytical chemistry suggests that analyses during this era are likely to be reported as the oxide. However, the NH_3 and N_2O_5 are subsequently added together and called "nitrogen." If this be the case, the N_2O_5 should have been reported as N. Thus, we are left with a considerable uncertainty in any attempt to determine changes with time.

Taking the data at face value, however, rainfall at Rothamsted during 1881-1894 apparently contained 4.2 kg/ha of ammonia and nitrate nitrogen. Miller (1905) notes that about 1.5 kg/ha of organic nitrogen was also found, for a total of about 5.7 kg/ha. The amounts of sulfur are also difficult to interpret, since they are reported as SO_3, but in any event are somewhat lower than in rainfall in Connecticut. In this connection Miller (1905) notes: "Compared with London rain the amount of sulphuric acid found at Rothamsted is small." Unfortunately, the data for London are not given. The amount of chloride in the rain appears similar to amounts found today in areas of similar proximity to the ocean.

Data from lysimeter studies in Connecticut from 1929-1948 provide valuable information on inputs of various cations and anions in rainfall and amounts of these constituents removed by crops and by leaching. Chemical composition of precipitation during that period is shown in Table 2. and is taken from Windsor Lysimeter Series A (Morgan,

Table 2. Chemical composition of precipitation at Windsor, Connecticut, 1929-1948, in kg/ha.

	1929-34	1935-39	1939-44	1944-48
$N(NO_3 + NH_4)$	5.0	3.1	6.6	7.4
SO_4-S	19.0	30.9	34.4	22.8
Cl	12.2	21.5	36.3	24.0
K	6.2	11.2	8.5	4.2
Ca	13.7	27.8	13.1	17.3
Mg	3.0	6.5	8.1	4.1
Na	11.9	12.1	5.3	7.1
Rainfall, cm.	91	118	98	102
Lysimeter series	A	D	E	H

1936), D (Morgan, Jacobson and Street, 1942), E (Jacobson, Swanson and Smith, 1948) and H (unpublished).

Unfortunately the separate analyses of nitrate and ammonia were combined as N in the published reports. Unpublished data for NO_3 in rain for 1937-1948 show a mean input of 3.8 kg/ha during that period with no apparent trends with time. The mean for the data shown as N in Table 2. is 5.5 kg/ha; hence we assume that 5.5-3.8 or 1.7 kg/ha must have been ammonia.

Thus, the rain is assumed to have had the following average composition for the period 1929-1948 with 102 cm of precipitation.

Mean 1929-48

	kg/ha	μeq/liter
Anions		
NO_3-N	3.8	27
SO_4-S	26.8	164
Cl	23.5	65
		256
Cations		
NH_4-N	1.7	12
K	7.5	19
Ca	18.0	88
Mg	5.4	43
Na	7.3	31
		193

Assuming that the excess of anions over cations is balanced by hydrogen ions, the calculated acidity is 63 ueq/liter of H or pH - 4.2. Given the uncertainty of analyses of samples composited and stored for various periods of time, it appears that the rainfall during that period was perhaps nearly as acid as that presently being reported for the Northeastern United States (Cogbill and Likens, 1975). However, it is not our present purpose to examine trends with time but rather to examine the effects of this rain on soil.

First, what are some possible effects? The acidity in rainfall at pH 4.2 corresponds to 63 ueq/liter of hydrogen ions. Under 114 cm of rainfall, the yearly average in Connecticut, this would require the equivalent in neutralizing power of about 36 kg/ha of $CaCO_3$. Since agronomic practice frequently dictates the application of several thousand kg/ha of limestone, the acidity in rainfall does not seem a direct threat to agricultural soils. Changes in unmanaged soils might be expected and we will examine experimental data for both managed and unmanaged soils shortly.

One might also expect that the alkalinity of lake waters might be affected. The State Board of Fisheries and Game (1942), surveyed 47 Connecticut lakes during 1937-1939 and found that the alkalinity of the softest lakes was about 150 ueq/liter HCO_3^-. Recently, Norvell and Frink (unpublished data) have reexamined 23 of these lakes to determine if changes in fertility and productivity had occurred. An extensive sampling study during 1973-1974 revealed that although many other changes had occurred, the softest lakes still contained about 150 ueq/liter of HCO_3^-. Acid rain at pH 3.8 would contain 150 ueq/liter of hydrogen ions capable of neutralizing this bicarbonate alkalinity but apparently this has not occurred during the 35 years between these two lake surveys in Connecticut. Beeton (1965) found that concentrations of sulfate and chloride have nearly doubled in Lake Erie and Lake Ontario in the last 50 years and Winkler (1970) attributes much of this to the polluted atmospheres around the lake. Unfortunately, the State Board of Fisheries and Game report (1942) did not include SO_4 or Cl so we do not know if similar changes occurred in Connecticut lakes.

Returning to the effects of rain on soil, numerous lysimeter experiments were conducted in Connecticut during the period when rainfall analyses are also available (Table 2.). Looking first at managed soils, considerable information is available on the effect of various cropping practices and fertilizer formulations on the composition of water draining through the soil. Drainage in lysimeters only occurs by saturated flow (owing to the lack of capillary suction below as in a normal soil) and hence the results are not identical with those expected in undisturbed soils. However, they should be adequate for our present purpose.

Table 3 shows the amounts of various constituents removed by leaching when tobacco is grown with conventional fertilization techniques. The amounts added to the crop include contributions from both fertilizer and rainfall. Amounts removed by the crop are shown, as well as the net change in the soil during the 9-year period.

Table 3. Effects of rainfall on Merrimac sandy loam planted with tobacco, 1931-1940 (Morgan, Jacobson and Le Compte, 1942).

Constituent	Added kg/ha	Removed		Net change kg/ha
		Crop kg/ha	Leaching kg/ha	
N	228	94	50	+84
SO_4	69	9	59	+ 1
Cl	31	9	17	+ 5
K	197	110	65	+22
Ca	31	49	60	-78
Mg	40	21	17	+ 2
Na	85	6	67	+11

The fertilizer used supplied about 80% of the nitrogen in organic forms (cottonseed meal and castor pomace) with 20% as inorganic sodium nitrate. However, organic meals readily nitrify during the growing season and of 50 kg/ha of nitrogen in the leachate, 49.7 kg/ha was NO_3 with the remaining 0.3 kg/ha as NH_4.

Since the contributions of rainfall to the nitrogen budget of a heavily fertilized crop such as tobacco are almost negligible, little can be said of the fate of the approximately 5.5 kg/ha of N contributed by rain. As with other sources of nitrogen, however, once past the root zone of crops NO_3 continues to move downward unless it is lost by dentrification. Small amounts of SO_4 and Cl were removed by the crop and the remainder was leached as might be expected since anions are generally not retained in large quantities by soils.

The fate of the cations is more complex. Sodium is not tightly held and leaches almost completely through these sandy soils. Magnesium, in this case, was about evenly distributed in the crop and leachate and no significant net change was observed. The most pronounced changes are evident in the budget for K and Ca. Potassium is readily fixed by clay minerals (for a recent review of these fixation reactions see Sawhney, 1972) and accumulated at the annual rate of 22 kg/ha. Thus, one would expect that most of the 7.5 kg/ha of K in rain would be fixed in soils of the northeast whether they are cropped or not. Calcium, on the other hand, was significantly depleted in the soil by leaching during the nine-year period.

The pH of the soil decreased from 5.5 at the start of the experiment to pH 5.0 at its conclusion. The effect of the acidity of the rain, however, is small in comparison with the acidity of the various soil amendments. For example, about 270 kg/ha of $CaCO_3$ would be required to neutralize the acidity generated by the nitrification of

the 180 kg/ha of meals used in this experiment (De Roo, 1958). Hence, acid rain seems of little importance in tobacco culture.

The leaching of various fertilizer cations and anions was also examined in uncropped soil at Windsor (Jacobson, Swanson and Smith, 1948). Although the amounts added are far greater than those in rainfall, the results illustrate the effects of the additions of large amounts of basic and acidic constituents to soils. In one portion of the study, urea was added to Merrimac sandy loam in 20 cm-deep lysimeter tanks at the rate of 224 kg/ha of N annually for 5 years. The cations Ca, Mg, K or Na were added annually in amounts calculated to be chemically equivalent to the amount of nitrate produced by complete nitrification of urea. (For example, this would require 320 kg/ha of Ca.) The various cations were added as the salts of sulfate, chloride or carbonate and the leachate analyzed for the 5 year period 1939-1944. Table 4 indicates the effects of these treatments on leaching and soil acidity. Not shown are the nitrogen losses, but these can be summarized by saying that all the added nitrogen was leached completely from the soil as NO_3, the average annual loss being 253 kg/ha or about 30 kg/ha more than was added.

Table 4. Effects of various cations and anions on leaching losses in uncropped Merrimac sandy loam (Jacobson, Swanson and Smith, 1948).

Salt Added	pH	Cation Budget		
		Added kg/ha	Leached kg/ha	Difference kg/ha
As Carbonate				
Ca	5.0	320	380	- 60
Mg	5.3	195	142	+ 53
K	5.0	626	320	+306
Na	5.1	368	301	+ 67
As Chloride				
Ca	4.5	320	576	-256
Mg	4.4	195	207	- 12
K	4.6	626	379	+247
Na	4.6	368	328	+ 40
As Sulphate				
Ca	4.2	320	554	-234
Mg	4.2	195	213	- 18
K	4.5	626	366	+260
Na	4.3	368	335	+ 33

Since the acidity of the added urea corresponds to about 400 kg/ha of $CaCO_3$, we might expect some substantial decreases in soil pH from its original value of pH 5.6. Table 4 shows that indeed soil pH decreased in all treatments. The decline was least where carbonates were added, with the mean for all four cation treatments being pH 5.1. In this series of treatments, the calculated basicity from the added carbonates always exceeded the calculated acidity expected from the nitrification of urea; hence the reason for this decline in soil pH is not clear. The most likely explanation is that soils are slow in equilibrating with any added base or acid and that the observed pH is a function of the rates of the various reactions rather than a true equilibrium value. In the absence of any added base, urea alone lowered the pH of the soil to 4.3, so the carbonates obviously prevented some of this increase in acidity.

Differences in soil pH in the other cation/anion combinations are evident, but probably are not significant within the anion groups. The mean pH for the chloride group was 4.5 and for the sulfate group 4.3. It is likely that the pH of the sulfate group is significantly lower than the chloride group but the data are not adequate for statistical analysis. Moreover, it is noteworthy that this leaching did not lower the pH below that of the control treated with urea alone.

Leaching losses of cations follow the pattern observed earlier in soils cropped to tobacco (Table 3). Sodium is not readily retained and is leached almost completely. Magnesium also appears to leach readily, with a slight release from soil minerals possible. Calcium, however, was leached in amounts much greater than those added, and soil minerals were obviously decomposed. From 40 to 50% of the added potassium was fixed in these soils and was not lost by leaching.

In summary, these data suggest that changes in soil or nutrient status due to the small amounts of cations and anions in rainfall will be modest in most agricultural soils. In unmanaged soils, however, we might expect more substantial changes and we next examine some data from studies of forest soils in Connecticut.

Lunt (1948) summarized the results of both pan and tank lysimeter studies under red pine and hardwood stands during the period 1934 to 1936 and 1938 to 1940. The rainfall analyses in Table 1. while not at the same site, are considered representative for Connecticut during that period. The pan lysimeters which were undisturbed and contained active tree roots show an interesting comparison with data from the tank lysimeters containing disturbed soil and no roots (Table 5).

The data reveal that in the absence of roots, large amounts of nitrogen and other elements are lost by leaching from forest soils. In the presence of roots, however, the amounts lost are very low, and are indeed less than the amounts added in rain (Table 2). Hence,

Table 5. Leaching losses of several elements from the surface horizon of forested soils (Lunt, 1948).

Element	Lysimeter Type*	Annual loss, kg/ha	
		Red Pine	Mixed Hardwoods
N	Tank	48.9	93.2
	Pan	1.2	1.6
S	Tank	37.0	42.2
	Pan	2.2	6.2
K	Tank	26.4	49.3
	Pan	1.1	4.1
Ca	Tank	53.9	27.7
	Pan	3.4	2.5
Mg	Tank	-	7.9
	Pan	-	1.6

*Installed 10 cm below the ground line. Tanks are disturbed soil with no roots, pans are undisturbed with roots present.

plant nutrients in rain are apparently taken up at least in part by vegetation and are an important part of the nutrient budget of forest stands.

Lunt (1951) also examined the changes in pH and nutrient status under red pine during the period 1929-1944. He compared the pH of the control plot with the pH of a plot receiving about 4500 kg/ha of limestone in 1929 and 2250 kg/ha in 1930. The pH value in the control plot declined to 3.8 in the litter layer from an initial pH of about 4.3-4.4, but changes in the 0-2.5 cm layer of mineral soil were not significant. Limestone of course initially increased the pH of the litter layer to over 7 but this value gradually declined to the level of the control plot.

During the 15-year period for which records of soil acidity are available, about 3980 kg/ha of litter was returned annually to the forest floor. The litter raked from other plots contained about 0.5% N; thus we estimate that about 20 kg/ha of N were added annually to these limed and unlimed plots. Nitrification of this protein N and the general course of litter decomposition undoubtedly contributes to the acidity.

SUMMARY AND CONCLUSIONS

Acid precipitation is not a new phenomenon. Nitrate, sulfate and chloride along with substantial quantities of hydrogen ions were found in rain by analysis during the late 18th and early 19th centuries. Recently, man's activities have increased emissions of oxides of nitrogen and sulfur and the acidity of rain has increased accordingly.

We have examined some possible effects of this acid precipitation on soils in the humid temperate zone of the northeastern United States. Additions of acid in rainfall to agricultural soils are insignificant in comparison with acidity produced by agricultural soil amendments. Moreover, this acidity is readily neutralized by additions of limestone in the normal course of agricultural practice.

In unmanaged soils, acid rainfall might be expected to have more pronounced effects. However, acidity produced by biological cycling of nitrogen and sulfur compounds in forested stands exceeds that found in rainfall at present. Moreover, the pronounced buffering exerted by soil minerals and organic matter tends to minimize changes in soil pH when acids are added.

If acidity in precipitation should increase substantially or if the buffering capacity of the soil ecosystem is seriously reduced, we would expect detrimental changes in soil productivity. At present, however, acid precipitation does not appear to pose a serious threat to soils in the Northeast.

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