NITROGEN CARRIER INDUCED CHANGES IN CHEMICAL, MINERALOGICAL AND MICROBIAL PROPERTIES OF A SANDY LOAM SOIL

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
JOHN W. SCHAFER, JR.
1968

This is to certify that the

thesis entitled

NITROGEN CARRIER INDUCED CHANGES
IN CHEMICAL, MINERALOGICAL AND
MICROBIAL PROPERTIES OF A
SANDY LOAM SOIL

presented by

JOHN W. SCHAFER, JR.

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in SOIL SCIENCE

H. D. Foth
Major professor

Date MAY 14, 1968

O-169

ABSTRACT

NITROGEN CARRIER INDUCED CHANGES IN CHEMICAL, MINERALOGICAL AND MICROBIAL PROPERTIES OF A SANDY LOAM SOIL

By John W. Schafer, Jr.

Residual effects of eight nitrogen carriers were studied after nine annual applications of 300 lb N per acre on a sandy loam soil. Carriers included $Ca(NO_3)_2$, $NaNO_3$, anhydrous NH_3, urea, ureaform, NH_4NO_3, NH_4Cl and $(NH_4)_2SO_4$. Adequate P and K for corn were supplied each year. Half of the plots were limed in the seventh and eighth years.

The rate of acidification of the soils was rapid and dramatic. By the third year soils receiving NH_4Cl and $(NH_4)_2SO_4$ were near pH 4.0 and Mn levels of plants exceeded toxic levels. In general, the extent of acidification was related to the residual acidity of the carrier. Two years after liming, the pH of soils receiving residually acidic carriers was less than expected. Soil receiving the two most acid carriers, had a pH near 5.0.

Nitrogen rates were in excess of plant needs. High concentrations of carrier ions increased mobility of cations replaced by protons released during nitrification. All soils

below pH 5.0 showed considerable inseason fluctuations of pH, potential acidity and nutrient levels. These fluctuations coincided with weather patterns conducive to movement of water and solutes between the surface and subsoil. Cationic iron hydronium complexes were probably the dominant mobile component of potential acidity. The failure of liming to correct this acidity or to increase exchangeable Ca to expected levels suggests that iron complexes are precipitating in the alkaline microenvironment of the lime particle, restricting its solubilization and neutralization value. Solubilization of Ca from lime was more retarded than the release of Mg.

Acidification depleted exchangeable Ca and Mg. Exchangeable K and P levels were only moderately affected, indicating weathering of K and P bearing minerals under acid conditions. The level of certain soil and plant nutrients seemed to be related uniquely to characteristics of certain carrier ions. Calcium suppressed Mg; sodium associated preferentially with leaching anions, reducing depletion of other cations; sodium and NH_3 displaced interlayer K from illitic minerals. The slow, concurrent release of HCO_3^- and NH_4^+ from ureaform dissipated the protons

released by nitrification and reduced residual acidity relative to urea or NH_3. With NH_4NO_3, retention of protons resulted in residual acidity in excess of expected values. Sulfate complexation by sesquioxides led to extreme soil acidification but promoted reversal with lime.

With acidification, foliar levels of Si, Fe, Al, Zn and Mn increased. The most striking nutritional imbalance was the high concentration of Mn in the tissue from all unlimed plots receiving residually acidic fertilizers. Liming reduced foliar Mn to below the 400 ppm toxic level. Levels of N, Mg, and P were deficient with certain treatments. It was impossible to pinpoint any specific cause for reduced yields on any single nutrient tested for in the plow soil or in foliar analyses. Subsoil nutrition influenced yields.

Nitrification rates and evolution of CO_2 in soils below pH 4.5 indicated little microbial activity.

Reduction in cation exchange capacity and alterations in mineralogy of the clay fraction of the soil were indicated. Increases in Fe, Al, Si, Mn, and Zn, and their slow reduction with liming, plus the failure of the lime to increase pH as expected, indicate drastic alteration of soil colloidal systems below pH 5.0.

Implications of this project include: (1) Simultaneous independent changes in soil systems below pH 5.0 are modified by interactions and equilibria in the complex and continuously changing chemical environment. (2) Specific ion effects are important in this environment. Mass action effects of each fertilizer species with increased application rates in modern agriculture further complicates the equilibrium. (3) High rates of application of fertilizers on lightly buffered soils without adequate leaching will eventually result in excessive soil acidity. There is no evidence yet that this is reversable. If it is, complete restoration of soil productivity will be a slow and expensive process.

NITROGEN CARRIER INDUCED CHANGES IN CHEMICAL, MINERALOGICAL AND MICROBIAL PROPERTIES OF A SANDY LOAM SOIL

By

John W. Schafer, Jr.

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science

1968

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. A. R. Wolcott for his guidance, support and encouragement during the course of this investigation. His allowance of freedom is conducting the research and his assistance in the preparation of this manuscript were an invaluable learning experience.

The author also wishes to express his appreciation to Dr. H. D. Foth for introducing the author to the need for this study and especially for his enthusiasm, interest and desire in promoting high quality undergraduate teaching. It was his example that encouraged the author to undertake this degree program.

He is thankful to Dr. E. P. Whiteside, and to Drs. M. M. Miller and J. K. Kinsinger for their assistance on his guidance committee.

The author also wishes to express appreciation to Dr. G. Benson Jones of the Ohio Agricultural Research and Development Center in Wooster, Ohio, for his assistance in the plant analysis; to Mrs. Nelly Galuzzi for assisting in the statistical analysis; and to Carl Kaechele and James McBride for their assistance with the first incubation study.

Many thanks are due to the professors and graduate students of the Soil Science Department for their advice, encouragement and friendship during the course of this study.

And finally, and especially, the author expresses thanks for the encouragement, assistance and patience of his wife, Grace.

TABLE OF CONTENTS

PAGE

RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The early civilizations of man in the Tigris and other river valleys recognized the value of the yearly flooding of the land in renewing the fertility of the soil. In contrast, depletion of soil fertility in medieval Europe, in the revolutionary war period of the United States, and today in much of the tropical regions of the world, cause man to move from one location to another. Natural processes will often gradually restore the soil to some basal fertility level, and then, man can move back for a few more years of cultivation before the soil is again depleted of its available nutrients.

As technology has advanced, particularly in the last 50 years, man has put higher and higher demands on the soil. He has depleted the natural fertility level of the soil much faster than natural processes can restore it. Some of man's activities, such as irrigating with poor water, have ruined the productivity of some soils. On the other hand, new techniques for maintaining high fertility and reclamation of unproductive soils have been developed.

Fertilizers are used to provide nutrients needed for intensive cropping and to maintain a proper nutrient balance in the soil. Today's high analysis fertilizers are often highly acidic. Some fertilizers are acidic because of the nature of the carrier. Other fertilizers may undergo chemical or biological transformations in the soil, resulting in an acidic residue. So that, while adding a beneficial inputs, nutrients we may also be adding something to our soils that is potentially very harmful, namely, acidity.

Thus, a fertility paradox results whereby man may destroy soil productivity by adding plant nutrients.

This project was undertaken to investigate several aspects of this paradox related to the acid nature of some nitrogen fertilizers:

1. How is soil pH affected by different fertilizer nitrogen sources applied at high rates and repeated annual applications over a period of time?
2. What effect will pH changes have on the fertility status of the soil as reflected by soil tests?

3. What effect will changes in soil pH have on crop nutrition as reflected in plant tissue tests?
4. How will these changes effect crop yields?
5. If extreme acid conditions result, are colloidal soil materials destroyed or their surface properties altered?

LITERATURE REVIEW

Historical Aspects

The fertility value of the silt deposited by annual floods was recognized by the early civilizations between the Tigris and the Euphrates rivers. It is not known when man first began to add amendments to improve soils, but the practice of adding manure to soils is mentioned in Homer's Odyssey which dates back to about 800 B.C. The early dwellers of Aegina dug marl and applied it to their fields. The use of marl was common among the Romans, the Greeks, and the Gauls before them. Pliny was one of several early writers to discuss the value of various types of marl. The use of limestone on sour soils was first investigated systematically in the United States. Early investigators included Edmund Ruffin and Benjamin Franklin (82).

The first long term field trials on nitrogen carriers were established in England in 1877 (70) and in Pennsylvania in 1882 (58). Each ran for more than 40 years. In both, $NaNO_3$ and $(NH_4)_2SO_4$ were used as two of the treatments. In England animal manure was used as a third treatment while in Pennsylvania, dried blood was used. In the former, wheat

and barley were grown while in the latter, a corn-oats-wheat-hay rotation was used. It took 16 years in Pennsylvania and 20 years in England before any marked treatment effects were observed at annual rates of 24 or 48 lbs N per acre per year . The effect of a given treatment depended on the crop grown. After 30 years in England, wheat yields on the $(NH_4)_2SO_4$ treated plots were significantly reduced relative to $NaNO_3$ while barley simply would not grow. After four decades, the group in Pennsylvania limed their plots and were able to bring yields of all treatments to the same level.

Early work in Alabama on cotton (81) showed similar differences between $NaNO_3$ and $(NH_4)_2SO_4$. The addition of lime eliminated differences in yield and soil pH between treatments.

The recognition that certain nitrogen carriers reduce soil pH has lead to attempts to predict the extent of this reduction. One of the first to attempt this was Pierre (62). From the calculated basicities and acidities of the cations and anions in the fertilizer and the effected biological alteration of ions by soil organisms, he predicted the amount of lime needed to maintain the soil pH. Twenty years later in 1954, using Pierre's data, Andrews (6) concluded that the predictions of Pierre were too low and that the effects of the various carriers were more acidic than Pierre estimated. In an earlier paper (7) Andrews and Cowart accurately predicted the effects of acid fertilizer on the soil, but to arrive at these values they measured and allowed for nitrogen uptake by cotton plants.

Hiltbold and Adams (35) have shown considerable variations in pH between soil samples receiving the same nitrogen source. By accurately accounting for all forms of nitrogen before and after an incubation period, they were able to relate these differences in pH to the amount of nitrogen volatilized.

It is generally held today that soil acidity that develops from a fertilizer is not a calculable constant for each fertilizer. It depends on: soil characteristics, the cropping system, the environment; whether nitrogen is removed by plants, or leached as an anion, cation or molecule, or lost by volatilization; as well as, on the nature of the fertilizer (3). Volk (94) compared urea and ammonium nitrate. These theoretically have the same potential acidity. He found that the resulting soil pH was higher for surface applied urea than for NH_4NO_3. This was attributed to higher volatilization rates of urea, and to its leaching and/or absorption by plants in molecular form. These processes could take place without altering soil pH.

It has also been shown that higher rates of fertilizer application usually result in more acidity per pound because of more leaching and less efficient use of the fertilizer by plants. Ammonium sulfate may be an exception to this (1).

Recent field trials in Ireland (11), Puerto Rico (72), the southern United States (2), Brazil (28) and Russia (105) have explored the acidic effects of fertilizers, particularly nitrogen. Wolcott, Foth and their associates at Michigan State University (100, 101, 102) have established experiments to investigate the acidic effects of certain nitrogen carriers. In one of these, heavy rates of nitrogen from several sources have been applied to a sandy loam soil annually since 1959. The yield of corn has been dramatically reduced by the more acidic carriers. The availability of several nutrients in the soil seems to be well correlated with fertilizer treatment (101).

Acid Properties of Nitrogen Fertilizers

The final acidic effect of any fertilizer depends on more than the nature of the carrier itself. But a relative

ranking of the carriers according to their chemical acidity is frequently useful. Table 1 (page27) lists the residual acidity for eight common nitrogen carriers. These values are average values calculated from several sources (6, 62, 82, 101). They represent the pounds of $CaCO_3$ needed to neutralize that amount of carrier which contains one pound of nitrogen.

Basic Carriers

Even though they leave a basic residue, calcium nitrate (residual acidity of -1.3) and sodium nitrate (-1.8) have an initial acidic effect on the soil due to direct displacement of exchangeable H^+ by Ca^{+2} or Na^+ to form HNO_3.The absorption of the nitrate by the plant, leaves an excess of calcium or sodium and the final effect on the soil is then basic.

Ammonia Carriers

Anhydrous ammonia (1.8), urea (1.9) and ureaform (1.9) all have an initial basic effect on the soil. Urea is quickly hydrolyzed by urease-synthesizing microorganisms to form NH_4OH. Anhydrous ammonia hydrolyzes to NH_4OH in the presence of soil moisture. Ureaform is a urea formaldehyde polymer which is more slowly hydrolized. The biological

oxidation of NH_4^+ to NO_3^- releases hydrogen ions to the soil system. The net effect of these fertilizers is acidic.

During the initial hydrolysis of anhydrous ammonia or urea, the soil pH in the micro-environment near the point of application may reach 9.5. At this high pH, nitrification is strongly inhibited. Oxidation begins at the periphery of this microenvironment where conditions are more favorable. High levels of nitrite may form temporarily that are toxic to nematodes, fungi and bacteria. The anhydrous ammonia can react with nitrous acid formed under these conditions giving the reaction:

$$NH_3 + HNO_2 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O.$$

This reaction, plus the direct loss of ammonia vapors, can result in considerable loss of applied nitrogen.

Ammonium Carriers

Ammonium chloride (5.3) and ammonium sulfate (5.5) have an initial acidic effect on the soil due to hydrolysis and exchange reactions leading to the formation of hydrochloric or sulfuric acids. The low percentage of nitrogen in these compounds results in a high application of the anion per unit of nitrogen. This initial acidic environment is responsible for the slower oxidation of ammonium under acid soil conditions, when compared to anhydrous ammonia. Oxidation of ammonium is a further source of acidity. Thus these two carriers have the highest residual acidity of the common nitrogen fertilizers listed in Table 1. Monoammonium phosphate (5.9) tends to leave an even greater residue of acidity because of the lower solubility and greater retention of phosphate in soil, as compared with chloride or sulfate. The residual acidity of diammonium phosphate (3.6) is intermediate between these carriers and those which supply only nitrogen, as ammonia, urea or ammonium nitrate.

Ammonium nitrate (1.8) contains nitrogen in both the ammonium and nitrate forms. It is acidic both initially and residually but the total acidity is not as great as the other ammonium carriers (4, 5, 24, 25, 48, 71, 73, 82, 101).

Soil pH and Nutrient Availability

Soil pH

The pH test is probably the most common and most useful of all soil tests. Yet we do not really understand what is being measured when we measure soil pH. We define pH as the negative log of the hydrogen ion activity and it is

commonly measured with a glass electrode. For clear solutions the glass electrode probably does measure hydrogen ion activity in solution. But in a soil suspension the pH value obtained is influenced by several factors. Among them are the soil to water ratio, soluble salts and atmospheric CO_2 (21, 61). In addition, the pH value will vary depending on the position of the glass electrode and whether the suspension is in motion or has settled (18). This so-called suspension effect is not well understood, but two theories are suggested. It may be due to the charged nature of the clay particles in the suspension or to leakage across the fiber plug of the calomel electrode. Either of these theories should give the observed decrease in pH when a glass electrode is lowered from the solution into the soil (21).

Schofield and Taylor (76) found that pH was independent of electrolytic concentration if a weak $CaCl_2$ extractant was used. The suspension effect could be avoided if pH was measured in the clear supernatant. What they were actually measuring, however, was a function of (pH-1/2pCa) rather than pH. This corresponds to the activity of $Ca(OH)_2$ and was thus called the lime potential.

Turner and Nichol (87) showed that the amount of added $CaCl_2$ influenced (pH - 1/2pCa) but not the expression (pH - 1/2(Ca+Mg)). They suggested that lime potential should consider both calcium and magnesium. They further suggested that since this expression was a constant at a given pH, a more meaningful value for pH could be obtained by measuring (Ca + Mg) and the constant. Then the pH could be calculated from the expression K = pH - 1/2p(Ca + Mg).

Over the next seven years a series of papers came from the laboratory of Turner and his associates (83, 84, 85, 86, 88, 89, 90) as they studied various aspects of potential measurements. Their final conclusion was that lime potential is influenced by aluminum activity. As they and Linsey, Peach, and Clark (46) have shown, activity of aluminum in soils is extremely variable. So the potential concept has been abandoned as a practical way to determine soil pH.

Many studies have been conducted to investigate the effect of the hydrogen ion on plant growth. These have been rather unsuccessful. In soil systems it is impossible to drop the pH to 4.0 without influencing all other nutrients in the soil and usually the toxicity or deficiency of some nutrient becomes more important in controlling plant growth than the hydrogen ion concentration (42).

Jackson (42) has listed calcium, magnesium, molybdenum, manganese and aluminum as the inorganic elements which most often are responsible for reduced plant growth under strong acid conditions. In addition to these, other nutrients are known to play an important role in acid soil infertility under local conditions.

Calcium and Magnesium

Calcium, magnesium and hydrogen usually comprise more than 90 percent of the exchangeable cations in the soil. Thus a marked increase in acidity will be accompanied by a decrease in available calcium and magnesium. Neither of these ions seem to form compounds under acid conditions that render them unavailable to plants.

Calcium is involved in ion uptake from the soil by plants and seems to be important in protein synthesis. A deficiency of calcium results in failure of both terminal buds and apical root tips to develop properly.

Magnesium is an essential part of the chlorophyll molecule and seems to be important in phosphorus metabolism. It is mobile in plants and the deficiency shows up as a chlorosis of the lower leaves (42, 82).

Molybdenum

Molybdenum is usually found in the soil as the anion MoO_4^{-2}. Sometimes soils are low in native Mo, but usually a molybdenum deficiency is associated with low soil pH. Liming will usually correct the problem. Molybdenum is involved in nitrate reduction in the plant and is particularly important in plants that fix nitrogen. The plant will show nitrogen deficiency symptoms when Mo is deficient (42, 82).

Manganese

Divalent Mn is the form taken from the soil by plants. The ratio of divalent to Mn^{+4} increases as the pH is reduced. Toxicity usually occurs only in soils below pH 5.5. Aluminum does not give characteristic toxic symptoms in plants. Since Al and Mn toxicity often occur together, Mn toxicity symptoms may show up when Al toxicity is responsible for plant retardation. This may have led to some incorrect conclusions in earlier work. Toxicity of Mn can occur however at a slightly higher pH than aluminum toxicity.

The toxic level of Mn in the soil has not yet been determined. In solution culture the toxic level of Mn

depends on the concentration of the other salts in solution. The toxic level of Mn in dilute nutrient solutions is lower than the toxic level in more concentrated nutrient solutions. The determination of specific levels of toxicity is further hampered by the fact that drying a strongly acid soil at room temperature will increase the extractable Mn^{+2}. Thus, air dry soils may not reflect the true field situation.

The toxic effect of manganese on plants seems to be due in part to an induced iron deficiency and in part due to an amino acid imbalance (3, 42).

Aluminum

Jenny (43) has referred to the history of agronomic concepts concerning the role of aluminum in soil in the United States as the merry-go-round. Coleman and Thomas (21) in summarizing the state of our knowledge concerning aluminum and pH have stated that aluminum is involved in complex ion-exchange and hydrolysis reactions which have a definite influence on pH, but they have not been adequately evaluated.

Part of the problem has been the failure to understand soil systems. The role of aluminum in soil acidity was first postulated by Veitch in the early 1900's. In 1909 the concept of pH was defined and techniques perfected to measure it. For the next 40 years researchers generally ignored aluminum, and aluminum was given no importance in soil systems (43). It gradually became apparent, and today is universally accepted, that the H-clays studied during this period were actually (H,Al)-clays. The aluminum is believed to come from an acidic attack and breakdown of the crystal lattice of clay minerals. The resulting clay is primarily a (H,Al)-clay but contains some Mg, Fe, and other cations released upon degradation of clay (10, 20).

Soil pH measures the hydrogen ion activity in the system when the liquid and solid phases are in equilibrium. The hydrogen ion associated with the permanent charge of the clay is the most active form of soil acidity. But hydrogen associated with the hydrolysis of organic functional groups, hydroxyl-aluminum monomers, polymers and other acid-producing ions such as Fe and Mn are also important. The pH does not measure the activity of the metal ion itself, although these ions have a marked effect in buffering the soil system (50, 104).

The problem in studying aluminum is the almost infinite variety of aluminum compounds in the soil. It can occur in either tetrahedral or octahedral coordination in the crystal lattice. It can be crystalline, or form sols or gels. It is found in, between, or on the surface of the clay lattice. Aluminum forms compounds with many anions and forms complexes with both organic and inorganic constituents in the soil. It also polymerizes (39, 93).

Each of these forms has its own solubility equilibrium and the intermediates and complexes have corresponding intermediary pK values. This makes it almost impossible to define the system or to prepare an artificial system that is analogous to a soil system.

Soluble aluminum ions in the soil are octahedrally hydrated as $Al(H_2O)_6{}^{+3}$. The first step in the hydrolysis of this gives $AlOH(H_2O)_5{}^{+2}$. The pK value for the first stage of hydrolysis of aluminum is around 5.0. It is well established that there is an increase in soluble soil aluminum when the soil pH falls below 5.0. As the number of hydroxyls increases with further hydrolysis, there is a tendency for this to polymerize (21, 37, 39, 47, 51). Since this polymer is positively charged, it can react with the negative surface of soil colloids. This complexed Al can block exchange sites and it also serves as a cementing agent for clay and clay-organic matter complexes (15, 17, 30, 67).

Aluminum has been shown to both stimulate and reduce the growth of corn (21). Undoubtedly aluminum toxicity is a major factor of infertility in many acid soils. But soil conditions that result in aluminum toxicity have not yet been defined precisely enough for universal application. Aluminum level in soil has been reported as solution Al, exchangeable Al, or percentage Al saturation of the cation exchange. Experiments often show good relationships between measured aluminum and plant growth when the experiments are considered separately. When the experiments are considered collectively, inconsistencies between them are apparent. Toxicity has been reported for soils with as little as 1.2 ppm solution Al, 0.2 meq of exchangeable Al/ 100 g. of soil and at 4 percent Al saturation of the soil exchange (3, 33, 103).

Other Inorganic Nutrients

The nutrients zinc, copper and boron are often found to be deficient under alkaline soil conditions; however, they are usually very soluble under strongly acid conditions. The availability of sulfur increases with addition of lime. Phosphorus forms aluminum and iron phosphates under acid conditions. These are unavailable to plants (3. 82).

Iron, like aluminum, becomes soluble under acid conditions and forms various amorphous products that can react with clays and may eventually crystallize (80). Iron may be deficient at high pH, in the presence of high amounts of phosphorus, when high levels of metallic ions such as copper and manganese are present, and under conditions of high moisture or cool temperatures (82).

Mineral Nitrogen

In describing the effects on the soil of nitrification processes, Alexander has said "it is clear that nitrification is a mixed blessing and, possibly, a frequent evil." Nitrification can be considered a self-inhibiting reaction:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2\ ) - 2H^+.$$

The microorganisms (predominantly bacterial of the genera Nitrosomonas and Nitrobacter) that carry out these processes are acid sensitive. The reaction is acid producing and without lime to reverse this acidic drift, the products of reaction can inhibit the nitrifying autotrophs that carry it out. For reasons yet unclear, nitrogen oxidation stands out among biological processes in the soil for its sensitivity to pH. A pH of 5.0 is considered the minimum pH needed for significant activity of these organisms (4).

There is some evidence that other heterotrophs also produce nitrite at pH values below 5.0 and that a non-biological oxidation of nitrite to nitrate may take place below pH 5. But the importance of these in the soil has not yet been evaluated (91). Weber and Gainey (95), have shown nitrate production in soils as low as pH 4. They suggested either an acid tolerant strain was present, or some component in the soil protected organisms from acidity that is fatal in nutrient solutions.

As the soil becomes progressively more acid, the microbial population that mineralizes organic matter shifts from one dominated by bacteria and actinomycetes to one dominated by fungi. Mineralization of organic matter is less sensitive to pH, and thus, ammonium accumulates in a soil of low pH, while nitrate accumulates in soils above 6.0 (23, 42). Below pH 4.0, CO_2 production, hence release of ammonium by mineralization, is reduced, apparently because of increased solubility of aluminum. Organic matter-aluminum complexes are very slowly decomposed by microbes (57).

Clay Minerals And Amorphous Materials

Nutritional problems associated with the low soil pH can perhaps be alleviated by proper liming and fertilization practices. The question that does arise is: What happens to the colloidal properties of the soil under extremely acid conditions? Can strong acids destroy or alter clay minerals, amorphous materials, or their surface properties?

Cation Exchange

The cation exchange capacity of soils has been successfully correlated with the amount of organic matter and clay in the soil. More recent work has shown that amorphous material also makes a significant contribution to the exchange capacity (22, 32, 34, 55, 75, 99). As the pH of a soil decreases, the measurable cation exchange capacity also decreases. This decrease equals the amount of pH dependent exchange acidity (64, 98, 101). This appears to be a reversible phenomenon, but it may not be if at some point the exchange surface is altered or destroyed.

In the ordinary ranges of soil pH (5.0-7.0), exchange capacity due to clay is relatively unaffected by soil pH (34, 69). In this same range the bulk of the pH dependent sites have been traditionally ascribed to organic matter (64). But amorphous materials in the soil are also strongly pH dependent in their exchange properties and they are probably more important in the soil than previous believed (8, 40, 54).

At low soil pH, (5.0 and below) clay appears to exhibit pH dependency in its exchange properties (21, 34). Also in this region, alumino-hydronium ions exhibit properties of hydrogen exchange as a result of their hydrolysis (39).

Buffering Curves

The titration curves of clays and soils are one of the oldest tools in studying soil properties. Titration curves of solutions, resins and clays have been compared in an effort to understand some of the complexities of the soil system. Because of its complex nature, most work related to soil has dealt with pure clay systems. It was first believed that a hydrogen clay was like a weakly ionized acid. Later it was shown that a true hydrogen clay behaves like a strong acid. The weak acid character of clays is due to the presence of aluminum (21, 43).

Schwertmann and Jackson (77) have shown three buffer ranges in a H-vermiculite. The first is below pH 4 and is the result of the presence of hydronium (H_3O^+). A second buffer range in the region of pH 4.0-5.6 is due to exchangeable alumino-hexahydronium ions. A third buffer range (pH 5.6-7.6) results from the neutralization of non-exchangeable hydroxy aluminum produced by hydrolysis and polymerization of aluminum. This aluminum results from

an acidic attack on the vermiculite structure at low pH. This third range is weakly exhibited in a freshly prepared H-vermiculite, but as the H-vermiculite ages, it becomes stronger. These aluminum polymers exist as coatings in the interlayers and on the surface of clays. They account for most of the pH-dependent buffer capacity (exchange sites) that has been attributed to clay. This source, plus organic exchange sites, provide most of the buffering capacity of soils between pH 5.5 and 8.0 (21).

Clay

A variety of laboratory tests on clay minerals, involving various solutions, temperatures and pressures, indicate in general, that clays are somewhat soluble in acids and unaffected by bases (31). The acidic breakdown of clays has been previously discussed. There appears to be no work with regard to the importance of this degradation under field conditions. Will the aluminum recrystallize to form fresh clay if an acid soil is limed? If so, how long will it take? If the clay contains large amounts of magnesium which can be leached or absorbed by plants, will the new clay be the same type as the original? Wolcott and others (101) have presented indirect evidence that clays in a soil will be destroyed under highly acid conditions. But they did not investigate the effect of liming on these soils.

Amorphous Material

Allophane is rigidly defined to include only amorphous colloidal alumino-silicates, but more generally the term refers to all amorphous silica, aluminum, iron and alumino-silicates in the colloidal fractions of the soil. This general connotation includes the aluminum polymers discussed above that are found as coatings on the clay particals. The important consequences of the properties of allophane in the soil are not emphasized in the literature, because methods for accurate characterization have not yet been developed (49). The general properties of allophane are rather broadly and vaguely defined. Procedures for isolating and estimating allophane have been established. These procedures generally give good results. However, no one really knows just what is being measured (8, 29, 40, 68). It is generally held that crystalline materials are acid soluble and amorphous materials are alkali soluble. Amorphous material is readily subject to alteration by treatment, and any attempt to isolate or study it may in part alter or destroy it (54).

EXPERIMENTAL PROCEDURES AND METHODS OF ANALYSIS

History Of The Field Trial

In 1959 an experiment was established on the Soil Science Experimental Farm at Michigan State University to study the effects of nitrogen carriers on the soil and on plant growth. Ten treatments were replicated four times in a randomized complete block design. Each plot was 14 by 25 feet. Corn (*Zea mays*) has been grown continuously year after year. Michigan 480 and in recent years Michigan 300 hybrids, have been used. In the early years of the experiment, corn was planted in 42 inch rows. In 1967, 28 inch rows were planted. An initial plant population of 25,000 plants per acre was established. This was thinned to 16,000 plants per acre when the plants were two feet high. Simazine was used for weed control.

The soil was first described as a Hillsdale Sandy Loam (Typic Hapludalf) (101). In a recent reclassification, it has been tentatively called a Hodunk Sandy Loam (Ochreptic Fragudalf) (See appendix for description) (74, 96).

The treatments are shown in Table 1. The basal fertilizer treatment was applied before plowing. Some years the plots were plowed in the fall, and in other years, they were plowed in the spring. The supplemental nitrogen fertilizer was applied just before planting each year at the

rate of 300 pounds of nitrogen per acre and disked in. In 1961, the anhydrous ammonia was not applied.

In the spring of 1965, the center two replications were uniformly limed with the equivalent of two tons of dolomitic limestone per acre. In the spring of 1966, additional dolomitic limestone was applied to the same two replications, so that total limestone applied on each treatment was equal to twice the lime requirement test for that treatment. The totals used in 1966 are indicated in Table 1.

In 1967, the urea fertilizer intended for plot #7 in one unlimed replication was accidentally placed on the adjacent plot #6. This plot also received 300 pounds of nitrogen as anhydrous ammonia five weeks later. The urea plot (#7) received no nitrogen other than that in the basal fertilizer in 1967.

Macronutrient Soil Tests

Soil samples from the plow layer have been taken each fall since the initiation of the experiment. Samples were taken periodically throughout the 1967 growing season.

Table 1. Fertilizer and lime treatments in the field experiment

Treatment number	Base fertilizer treatment	Supplemental nitrogen source	%N	Relative residual acidity	Limestone applied in 1966
	*	#		**	tons per acre ##
1	None	None	--	--	2
2	5-20-20 200 lbs	None	--	--	4
3	"	Sodium nitrate	16.0	-1.8	2
4	"	Calcium nitrate	15.5	-1.3	2
5	"	Anhydrous ammonia	82.2	1.8	4
6	"	Urea	46.0	1.9	6
7	"	Ureaform	38.0	1.9	6
8	"	Ammonium nitrate	32.5	1.8	6
9	"	Ammonium chloride	28.0	5.3	8
10	"	Ammonium sulfate	20.5	5.5	10

*Total N+P+K = 10+18+33 per acre per year beginning in 1959.

#Annually, 300 lbs. N per acre per year beginning in 1959.

**Lbs. of $CaCO_3$ to neutralize a weight of carrier containing one pound of nitrogen.

##This is in addition to the 2 tons of lime applied to each of these plots in 1965.

Soil pH (glass electrode, 1:1 water suspension), available P (0.025 N HCl in 0.03 N NH_4F, 1:8 soil-to-extract ratio), and K, Ca, and Mg exchangeable with 1N NH_4OAc were determined by routine procedures of the soil testing laboratory at East Lansing. Lime requirement was estimated using p-nitrophenol, triethanolamine buffer of Shoemaker et al. (78).

Micronutrient Soil Tests

Soil samples were taken from the plow layer for micronutrient analysis on October 25, 1967, using plastic and stainless steel equipment.

Zinc was extracted using a procedure developed for Michigan soils by Melton (52). Forty grams of dry soil were placed on Whatman No. 3 filter paper that had been previously rinsed with deionized water. The soil was leached with 25 ml. of deionized water. When the first 25 ml. had drained through, a second 25 ml. was added in small aliquots, allowing the soil to drain between aliquots. The leachate was analyzed for zinc on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer.

Manganese was extracted using the method of Hoff and Mederski (36), which Pailoor (60) found best suited for

Michigan soils. Five grams of soil, with 50 ml. of 0.1 N H_3PO_4, 7 drops of 0.1 N silver nitrate, and a quarter teaspoon of activated carbon was placed on a shaker for 10 minutes. The solution was filtered through Whatman No. 40 filter paper. The filtrate was analyzed for manganese on a Perkin-Elmer 303.

Iron was extracted from the soil using the method suggested by Olson (59) as an availability index for iron. A flask with 12.5 g. of soil and 50 ml. of 1.0 N ammonium acetate was shaken for 30 minutes. The suspension was filtered and the filtrate analyzed for iron on a Perkin-Elmer 303.

Aluminum was determined according to the method of Laflamme (45). Ten grams of soil was shaken for 30 minutes in 100 ml. of 1.0 N KCl. The mixture was filtered and 50 ml. was placed in a centrifuge tube. Two ml. of 1000 ppm iron solution and two drops of phenol red indicator were added. Ammonium hydroxide was added drop-wise until the color changed from yellow to red. The solution was centrifuged for 20 minutes at 3000 rpm, decanted, and the precipitate dissolved in 5 ml. of 4 N HCl. The solution was diluted to 100 ml. and aluminum determined on the Perkin-Elmer 303.

Copper was determined using the method suggested by Fiskell (27) for available copper. Fifty grams of air dry soil was shaken for one hour in 100 ml. of 0.1 N ammonium nitrate. The suspension was filtered through Whatman No. 3 filter paper and copper determined on the leachate using the Perkin-Elmer 303.

Sulfate was determined using the method of Bardsley and Lancaster (9). Ten grams of soil was shaken with 25 ml. of ammonium acetate extracting solution for 30 minutes. Then, 0.25 g. of charcoal was added. The mixture was shaken for 3 minutes and filtered through Whatman No. 42 filter paper. To 10 ml. of filtrate was added 1 ml. of 20 ppm K_2SO_4. It was swirled and 0.5 g. of $BaCl_2$ added. After one minute it was swirled till crystals dissolved. Within 2 to 8 minutes after the crystals dissolved, turbidity was read on a spectophotometer at 420 mu.

The method of Pratt (66) was used to determine soil sodium. Ten grams of soil and 25 ml. of 1.0 N, pH 7.0, NH_4OAc were placed in a centrifuge tube. After 10 minutes of shaking, it was centrifuged until clear. Sodium was determined on the supernatant on a Coleman Model 21 flame photometer.

Plant Analysis

On July 31, 1967, when the corn was in the tasseling stage, leaf samples were collected. The leaf below the ear leaf was removed. Ten leaves per plot were taken and dried at 150° F. One sample was lost in the drying process. The samples were then ground in a Wiley Mill with stainless steel screens. The samples were sent to Ohio State University where they were analyzed for potassium, phosphorus, calcium, magnesium, manganese, iron, boron, copper, zinc, aluminum, strontium, molybdenum, cobalt, sodium, silicon, barium and nitrogen.

Soil Mineralization Studies

Two soil mineralization rate studies were conducted. The first was conducted on duplicate samples from the plow layer of all 40 plots. Samples were brought moist from the field on August 1, 1967. Each sample was analyzed for ammonium and nitrate nitrogen using the microkjeldahl techniques of Bremner (13). Two grams of moist soil plus 10 ml. of 2 N KCl and approximately 0.1 g. of MgO were placed in the distillation flask. A 50 ml. graduated Erlenmeyer flask containing 5 ml. of two percent boric acid plus indicator was placed under the condensing tube,

and 25 ml. of condensate was collected. Following the distillation, the condensate was titrated with standard 0.005 N H_2SO_4 to determine ammonium-nitrogen. At the completion of the first distillation, about 0.2 g. of ball-milled Devarda's alloy was added to the distillation flask and 25 ml. of condensate was collected in a second Erlenmeyer flask containing 5 ml. of boric acid plus indicator. This was titrated with the standard acid to determine nitrate-nitrogen which had been reduced to ammonium. A sample of the soil was dried to determine soil moisture.

The mineralization study was a modification of the method suggested by Bremner (14). A weight of moist soil, equivalent to ten grams of dry soil, along with 30 grams of clean 30- to 60-mesh quartz sand were placed in a bottle. Sufficient $(NH_4)_2CO_3$ solution (0.1 mg. N per ml.) was added to bring all the soils to the same ammonium level (0.2 mg. ammonia-N per g. soil). Sufficient distilled water was added so that the total liquid (moisture in the soil + ammonium carbonate solution + water) equalled 6.0 ml. The bottles were capped with a piece of plastic held in place with a rubber band. The bottle was placed in a 30 C constant temperature room for 14 days. After incubation, 100 ml. of

2 N KCl was added to each bottle, they were stoppered, shaken for one hour and allowed to settle for 30 minutes. Then 20 ml. of supernatant was distilled to determine ammonia and nitrate using the procedure outlined above.

The second incubation was carried out on samples taken on September 28, 1967. This time four replications of only six of the ten treatments were used. The procedure was the same as outlined above with the following changes. The total amount of liquid, soil, sand and ammonium level was increased by a factor of ten. A small vial of 0.5 N NaOH was placed in the jar to absorb CO_2. The jars were sealed with an airtight cover and periodically the vials of NaOH were removed and fresh ones inserted. Barium chloride was added to the base and titration carried to the phenolphthalein end point with 0.25 N HCl under CO_2-free conditions, using the apparatus depicted in Figure 1. At the end of the 14-day incubation period, the soil samples were shaken for one hour with 300 ml. of 4 N KCl. Ammonium and nitrate was determined as described above.

Seasonal Changes In Mineral Nitrogen

In order to study the effect of carriers on the ammonium and nitrate nitrogen level in the soil at different times

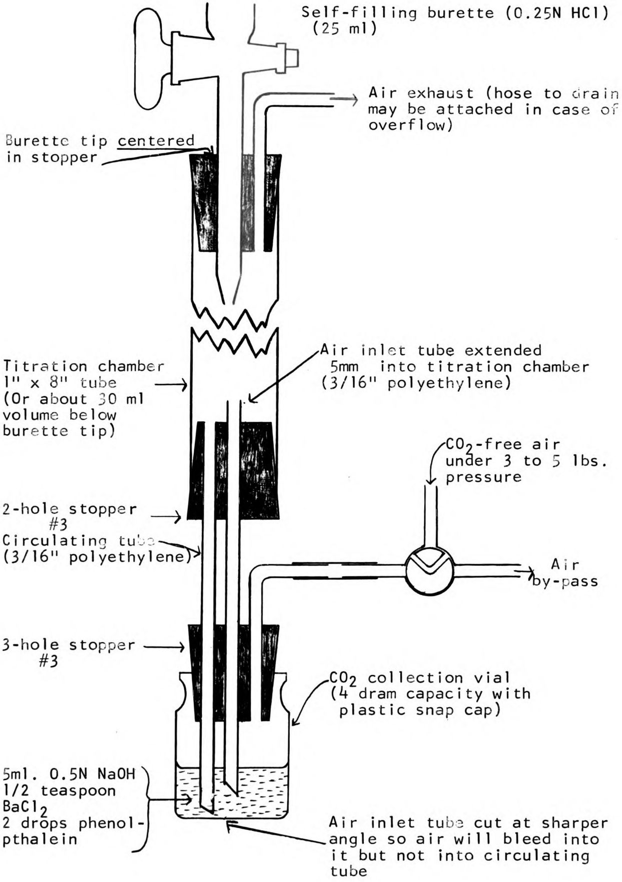


Figure 1. Apparatus for titration under CO_2 free conditions

during the season, plow layer soil samples were taken periodically during the 1967 growing season. Only the four replications of treatments 2, 4, 8, and 10 were used in this study. Ammonium and nitrate nitrogen were determined on moist samples by the microkjeldahl method of Bremner (13) as described above. Air dried soil samples were sieved through a 20-mesh screen and sent to the soil testing lab. Lime requirement, pH, Ca, Mg, K, and P were determined by the methods previously described. In addition, on October 25, 1967, these plots were sampled at 0-10, 10-15, and 15-20 inch depths and the above analyses were made.

Clay Studies

Composite samples of both replications of the unlimed starter, ammonium nitrate, and ammonium sulfate plots, and the limed ammonium sulfate plots were prepared for x-ray analysis using standard methods. Salts, organic matter, and free iron were removed and the clay fraction separated, using sedimentation techniques (44, 97). The samples were x-rayed after magnesium saturation, potassium saturation, heating to 300 C and heating to 550 C.

The method suggested by Pratt (65) was used to determine total potassium in order to estimate the amount of illite in the clay fraction of the soil. A 0.1 g. sample of clay was placed in a platinum crucible. Perchloric acid (1 ml.) and hydrofluoric acid (5 ml.) were added and the sample evaporated to dryness on a sandbath. The residue was dissolved by heating in 5 ml. of 6 N HCl and 20 ml. of water. The sample was diluted to 100 ml. and potassium determined on a Coleman Flame Spectrophotometer Model 21.

Amorphous Material

Allophane was estimated using the method described by Jackson (41). A 0.1 g. sample of clay was wetted in a nickel beaker with a small amount of 0.5 N Na OH. Then 200 ml. of boiling 0.5 N NaOH was added and the suspension boiled for 2.5 minutes. After rapid cooling and centrifugation, the supernatant was decanted and stored in a plastic bottle. Silicon was determined by placing 10 ml. of 15 percent ammonium molybdate solution, 30 ml. of distilled water, 5 ml. of 6 N HCl and 5 ml. of extract into a 50 ml. volumetric. The solution was made up to volume and the absorbance determined 30 minutes later on a Bausch & Lomb Spectronic 20 colorimeter at 420 mu. Aluminum was determined by placing 10 ml. of pH 4.2 ammonium acetate buffer solution, 30 ml. of water, 10 ml. of 0.04% aluminon reagent and 5 ml. of extract in a 50 ml. volumetric. The

solution was made to volume and the absorbance at 520 mu. was determined after 30 minutes on a Bausch & Lomb Spectronic 20 (38).

The percent allophane in the soil was estimated to be 1.21 times the sum of the percentage of SiO_2 plus the percentage of Al_2O_3 in the sample.

Cation Exchange Capacity

The cation exchange capacity of the soil was determined using the conductometric technique adapted for estimating pH dependency by Chodan (16) from the method developed by Mortland and Mellor (56). Ten grams of soil was placed in a 250 ml. beaker. To this was added 100 ml. of 1 N BaOAc buffered to the desired pH with acetic acid. The suspension was stirred on magnetic stirrer for two hours while nitrogen gas was bubbled through the system. The pH of the suspension was then adjusted with $Ba(OH)_2$ to the original buffer pH and stirred for another two hours. This was continued until the pH of the suspension was equal to the original buffer pH of the BaOAc. The suspension was then filtered through a Buchner funnel (Whatman No. 42 filter paper) and washed with 50 ml. of 1 N $BaCl_2$. The soil was washed with 30 ml. increments of deionized H_2O until the leachate was chloride free using the silver nitrate test. The soil was

washed from the filter paper into a 250 ml. beaker with exactly 100 ml. of deionized water. This was stirred for one hour and allowed to set overnight with nitrogen bubbling through the system. Then 50 ml. of absolute ethyl alcohol was added and the suspension stirred for one-half hour. The suspension was titrated with 0.4 ml. increments of 0.2 N $MgSO_4$. After each addition the system was allowed 10 minutes to equilibrate before the conductivity of the suspension was measured. If the suspension was not at equilibrium after ten minutes it was stirred for an additional five minutes and the conductivity again determined.

The cation exchange capacity was determined on eight composite samples. The two replications of the starter, calcium nitrate, ammonium nitrate and ammonium sulfate treatments were each mixed. This was done for both the limed and unlimed plots. To measure the pH dependency of the exchange capacity, it was determined at pH 4.0, 5.0, 6.0, 7.0 and 8.0 by appropriate adjustment of the BaOAc buffer.

Other Investigations

During the summer of 1966, soil samples were taken by increments to a depth of 66 inches on several plots. It was originally planned to determine ammonium and nitrate on these samples. However, the samples sat, moist and at room temperature, for several weeks, so these determinations were not made. The samples were subsequently dried and sent to the soil testing lab for routine analysis.

Samples taken from the 40 plots at a 10-15 inch depth in the fall of 1966, were analyzed for percent sand, silt and clay using the method of Bouyoucous (12). One hundred grams of soil, with 60 ml. of Calgon solution (50 g./l.) were placed in a dispersion cup along with sufficient distilled water to fill the cup half way. The suspension was stirred on a mechanical stirrer for 15 minutes and then transfered to a sedimentation cylinder. The cylinder was filled with water, shaken, and hydrometer and temperature readings taken at 40 seconds and 2 hours.

Statistical Analysis

Where appropriate, analysis of variance was performed on the results, using facilities of Michigan State University's Computer Center. The experimental design was a randomized complete block design, biased slightly so that all four anhydrous ammonia treatments were in line for ease of application. In 1965 and 1966, the two center replications were limed. Although this resulted in systematic disposition of the main plot factor, lime, the data were treated as in a split plot design. The original four replications were treated as two replications of two lime treatments: unlimed and limed. The carrier treatments were treated as sub-effects.

One of the plant samples was lost during drying. Values for this plot were estimated using standard procedures for calculating missing plot values.

If the F test from the analysis of variance indicated signficance at the 5 percent level, an LSD .05 was determined. Where appropriate, the results were arrayed and grouped into ranges of equivalence, using Duncan's multiple range procedures (19, 26, 79).

In the split plot analysis of two replications, two lime levels and ten carriers, degrees of freedom were distributed as follows:

Source	Degrees of Freedom
Replication	1
Lime	1
Error A	1
Carrier	9
Carrier-lime interaction	9
Error B	18
Total	39

Because there was only one degree of freedom for lime and one for replication, the basis for statistical inferences regarding lime effects was very weak. It must be emphasized that real effects of lime may have been statistically significant if an experimental design with more replication had been used. An attempt is made in the discussion to put the lime effect in proper perspective.

RESULTS AND DISCUSSION

I. SOIL AND PLANT ANALYSIS

Changes in Soil pH and Lime Requirement Since 1959

Table 2 shows the history of the changes in soil pH of the various fertilizer treatments. The initial pH for the experimental area was 6.2. No soil samples were taken after the 1959 or 1960 growing seasons. By 1961, the ammonium chloride and ammonium sulfate treated soils were already below pH 5.0 -- a surprisingly rapid change.

After 1961, there was a general decline in soil pH on the unlimed plots. The 1964 pH values were consistently higher on unlimed plots than in either 1963 or 1965. There is no apparent explanation for this. Liming increased soil pH, but not to the extent expected for the double lime requirement rates used. The urea, ammonium chloride, ammonium sulfate, and ammonium nitrate treated soils, after liming, still had a pH below 6.0 in 1967. Theoretically, a pH near 7.0 could have been expected on all limed plots by this time. (Lime requirements are calculated to raise soil pH to 6.5 to 6.8 in a traditional 7-inch plow layer. A double lime requirement with a 10-inch plow layer should raise the soil pH to above 7.0.

Table 2. Changes in soil pH since 1959[1] as influenced by nitrogen carriers[2] and lime[3]

Fertilizer treatment	Lime treatment	Soil pH by years 1961	1962	1963	1964	1965	1966	1967
No fertilizer	No lime	5.9	5.7	5.7	6.0	5.2	6.0	5.5
	Lime					5.8	6.4	6.6
Basal fertilizer	No lime	5.7	5.9	5.9	6.1	5.6	5.9	5.4
	Lime					6.3	6.8	6.7
$NaNO_3$	No lime	5.9	6.0	6.2	6.5	6.2	6.4	6.4
	Lime					6.2	7.0	7.0
$Ca(NO_3)_2$	No lime	5.7	5.8	5.8	6.1	5.6	5.7	5.4
	Lime					6.2	6.6	6.1
NH_3	No lime	5.2	5.4	5.1	5.6	5.6	5.1	4.5
	Lime					5.1	5.7	5.8
Urea	No lime	5.1	4.9	4.9	5.2	4.8	4.6	4.6
	Lime					4.6	5.6	5.8
Ureaform	No lime	5.4	5.3	5.0	5.2	5.0	4.8	4.4
	Lime					5.0	5.6	6.0
NH_4NO_3	No lime	5.4	4.8	4.8	5.1	4.4	4.4	4.0
	Lime					5.0	5.5	5.8
NH_4Cl	No lime	4.9	4.6	4.4	4.6	4.3	4.0	3.7
	Lime					4.5	4.5	4.8
$(NH_4)_2SO_4$	No lime	4.5	4.2	4.0	4.4	4.1	3.9	3.5
	Lime					4.2	4.4	5.4

[1] Initial lime requirement not reported

[2] Supplemental nitrogen carriers applied at the rate of 300 lbs. N per acre each year, beginning 1959

[3] Two tons per acre dolomite in 1965. Additional dolomite in 1966 to total twice the lime requirement by soil buffer test for each fertilizer treatment

Lime requirement was not determined on these soils until 1961. The lime requirement increased in 1962 and 1963, as shown in Table 3. In 1964 the lime requirement of all treatments decreased nearly 50 percent. This paralleled the pH increase between 1963 and 1964 and also cannot be explained. It does not appear to have been a systematic error in measurement. Soil pH values in 1965 were again in line with earlier and later years; whereas, it took two or three years before the lime requirement of most of the soils returned to the 1963 level. And even in 1967, the lime requirement of most unlimed soils were still lower than the 1963 values.

Annual rainfall since 1960 is given in Table 4. It is reported on an October to September basis, rather than a January to December basis. This better corresponds to the sampling dates.

Rainfall data alone does not explain the change in lime requirement and pH noted. If the number of rains over 0.40 inches can be taken as an index of the number of leaching rains, there is an increase in 1964 over the two previous years. This may help to explain the changes noted. Soluble acids may accumulate during dry periods and be leached in wet periods. This would be reflected in soil pH and lime requirement measurements. A study of natural runoff and

Table 3. Changes in lime requirement[1] since 1959 as influenced by nitrogen carriers[2] and lime[3]

Fertilizer treatment	Lime treatment	Lime requirement ($ppt\ CaCO_3$) by years						
		1961	1962	1963	1964[4]	1965[4]	1966[5]	1967
No fertilizer	No lime	1.6	2.1	3.1	1.5	1.5	1.5	2.2
	Lime					1.8	.5	0
Basal fertilizer	No lime	1.8	2.0	2.3	1.3	1.8	1.5	1.8
	Lime					.8	0	.8
$NaNO_3$	No lime	2.3	1.6	1.5	.8	.8	1.5	1.0
	Lime					1.2	0	0
$Ca(NO_2)_2$	No lime	1.8	1.4	1.8	1.3	1.5	2.2	2.2
	Lime					.8	.5	1.0
NH_3	No lime	3.1	3.2	4.8	2.4	1.8	3.5	4.5
	Lime					1.8	1.8	1.5
Urea	No lime	2.8	2.2	5.0	2.6	3.8	4.0	3.8
	Lime					3.2	1.8	1.5
Ureaform	No lime	2.3	2.6	4.3	2.5	3.5	5.0	4.5
	Lime					3.0	1.5	1.5
NH_4NO_3	No lime	2.3	3.0	5.0	3.0	4.2	4.5	5.0
	Lime					2.2	2.5	1.5
NH_4Cl	No lime	3.0	3.8	6.0	3.8	3.5	5.0	4.5
	Lime					3.8	3.2	2.8
$(NH_4)_2SO_4$	No lime	4.6	6.2	7.6	4.0	5.5	5.0	7.0
	Lime					5.2	4.0	1.5

---

[1] Initial lime requirement not reported

[2] Supplemental nitrogen carriers applied at the rate of 300 lbs. N per acre each year, beginning 1959

[3] Two tons per acre dolomite in 1965. Additional dolomite in 1966 to total twice the lime requirement by soil buffer test for each fertilizer treatment

[4] Maximum value reported by Soil Test Lab: 5.5 ppt

[5] Maximum value reported by Soil Test Lab: 5.0 ppt

Table 4. Annual rainfall for the 1960-1967 sampling years *#

Year	Total rainfall	Number of rains over 0.40 inches
	inches	
1960	31.02	15
1961	23.21	17
1962	21.45	8
1963	22.30	10
1964	23.44	14
1965	23.84	10
1966	28.28	11
1967	26.19	16

* Sampling year defined as October 1, of previous year to September 30, of year listed in table.

\# Rainfall data through December 31, 1966 from East Lansing Horticulture Farm Weather Bureau Station. Located about one-third mile east of plots. Rainfall data for 1967, from East Lansing 3SE Weather Bureau Station. Located about one mile south of plots.

infiltration on this site might be helpful but these data are not available.

Lime requirements tabulated in Table 3 were subject to policy changes in the soil testing laboratory. Beginning in 1964, maximum lime recommendation reported was 5.5 tons per acre, regardless of how low the value of buffer pH. In 1966, a maximum of 5.0 tons per acre was established. In the fall of 1967, this restriction was removed for research samples.

Only a few of the values in Table 3 were restricted by these policy changes. These were the unlimed plots of $(NH_4)_2SO_4$ in 1965 and unlimed ureaform, NH_4Cl and $(NH_4)_2SO_4$ in 1966.

Substantial fluctuations in lime requirement can be expected because soils are highly responsive to their environment. The organic component of soil buffering systems varies in quantity and exchange activity with rates of return of crop residues and their rate of decomposition. In soils below 5.0, soluble aluminum compounds contribute significantly to active and potential acidity, hence lime requirement. These compounds will tend to accumulate in dry periods and can be rapidly leached in a wet period.

For these and other reasons not yet fully understood, the lime requirement of a soil changes considerably in response to climatic changes and management between and within seasons.

Macronutrient Soil Tests

Tables 5-7 show the values for soil pH, Ca, Mg, K, P, and lime requirement of samples taken on July 31, 1967, for the various treatments.

pH

Table 5 shows the soil pH values. Lime effect was significant only at the 7.5 percent level, although there was a full pH unit difference between the means for unlimed and limed plots. Carrier effects were highly significant. The interaction was not significant. Sodium nitrate resulted in the highest pH. The two controls, and NH_3 treatments formed a second group not significantly different from sodium nitrate. The last three were also not different from the calcium nitrate or ureaform treatments. The ammonium chloride and sulfate treatments resulted in the greatest soil acidity. The pH associated with use of ammonium nitrate was between these and that for urea and ureaform, and was not significantly different from either group.

These results fall in line with the known acidic nature of the fertilizers, except for anhydrous ammonia. Plot #6, an unlimed anhydrous ammonia plot, accidentally received

Table 5. Effects of nitrogen carriers and lime on pH and lime requirement in the plow layer

Carrier	Soil pH			Lime requirement**		
	Unlimed	Limed	Average	Unlimed	Limed	Average
				ppt##	ppt	ppt
No fertilizer	5.8	6.7	6.2	1.5	0	.8
Basal fertilizer	5.8	6.8	6.3	2.0	0	1.0
$NaNO_3$	6.2	6.9	6.6	1.5	0	.8
$Ca(NO_3)_2$	5.4	6.4	5.9	1.8	0	.9
NH_3	5.9	6.1	6.0	1.5	1.2	1.4
Urea	4.8	5.7	5.2	3.5	1.5	2.5
Ureaform	4.6	6.2	5.4	4.2	1.5	2.9
NH_4NO_3	4.1	5.6	4.9	4.2	1.5	2.9
NH_4Cl	4.0	5.0	4.5	5.0	1.8	3.4
$(NH_4)_2SO_4$	3.8	5.1	4.4	5.0	2.0	3.5
Means	5.0	6.0*	5.5	3.0	1.0#	2.0
$LSD_{.05}$ for carriers	.73	.73	.52	1.36	1.36	.96

*Significantly different from unlimed at 7.5 percent level

#Significantly different from unlimed at 20.0 percent level

**Maximum value of 5.0 ppt reported

##ppt = parts per thousand

600 lbs. of nitrogen in 1967 as previously noted (p. 26). Both this plot and the adjacent urea plot (#7), which received no nitrogen in 1967, often gave results other than expected for each treatment. In this case, the average pH value for the two unlimed NH_3 plots was 5.9. This is an average of 6.6 (plot #6) and 5.2 (its replicate in block 2). If the 5.2 is truly representative of the effects of this carrier, than the overall carrier average (ignoring lime) would be 5.5. This is approximately the same as the pH of the ureaform plot, and is what would be expected considering the residually acid nature of anhydrous ammonia. It will be shown later (p. 127) that the urea and anhydrous ammonia applied to plot #6 resulted in a soil exchange with a high percentage of ammonium ions. This fact helps to explain the high pH value, as well as some of the other discrepancies that show up for this treatment.

Lime Requirement

As was true for pH, there was no statistical significance to the effect of lime on lime requirement (Table 5). In both cases, this must be attributed to the inadequate design of the experiment. The consistent direction and magnitude of changes in both of these measurements provide reasonable quantitative estimates for real effects of lime.

The effect of carriers was significant, and the plots were separated into two groups. The anhydrous ammonia treatment is grouped with the no fertilizer, basal, and the sodium and calcium nitrate plots. The low lime requirement for the basic, basal and no fertilizer treatments was expected since they did not contain acid forming materials. The lime requirement of plot #6 was zero. The anhydrous ammonia treated soil in block two had a lime requirement of 3.0. This would group anhydrous ammonia with the other acid forming fertilizers that form the second statistical group.

As was true for pH, there was no significant carrier x lime interaction. Each limed carrier treatment received twice the amount of lime needed, as indicated by the buffer test, to raise pH into the 6.5 to 6.8 range.

It would be expected that dolomite would react quicker in more acid soils. Actually, the change in pH and lime requirement was less than expected for all acidifying carriers. The greatest discrepancy occured with the two most acidic carriers, NH_4Cl and $(NH_4)_2SO_4$. Ten and twelve tons per acre of dolomite, respectively, had raised soil pH to only 5.0 or 5.1 after two years. It must be concluded that residual acidity from these materials has drastically altered the character of buffering systems in the soil.

Calcium

Exchangeable calcium (Table 6) was influenced by lime. The lime plots contained more exchangeable calcium than the unlimed plots. The calcium nitrate plot contained the most exchangeable calcium. It had received calcium with the carrier through the nine years of the experiment, as well as the lime applied in 1965 and 1966. The two no-nitrogen treatments and the sodium nitrate treatment resulted in less exchangeable calcium than the calcium nitrate plots. The three ammonium carriers and ureaform resulted in the least soil calcium. The anhydrous ammonia and urea plots had an intermediate level of calcium, significantly different only from the calcium nitrate plot.

There was no statistically significant carrier×lime interaction. However, the exchangeable calcium on the limed plots, as shown in Table 6, is inversely related to the quantities of limestone applied (Table 1). The release of calcium from dolomite, or its exchangeability after release, was suppressed by soil conditions associated with strongly acidic carriers. Whether this may have been an artifact due to inadequate buffering of the exchange extractant was not investigated.

Table 6. *Effects of nitrogen carriers and lime on exchangeable calcium and magnesium in the plow layer*

Carrier	Exchangeable Ca			Exchangeable Mg		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	pp2m	pp2m	pp2m	pp2m	pp2m	pp2m
No fertilizer	1040	1128	1084	134	234	184
Basal fertilizer	863	1391*	1127	92	241*	167
$NaNO_3$	1040	1128	1084	128	206	167
$Ca(NO_3)_2$	1128	1913*	1520	42	148	96
NH_3	597	1128*	862	64	256*	160
Urea	508	1215*	862	56	292*	174
Ureaform	508	952*	730	42	242*	142
NH_4NO_3	329	952*	640	28	256*	142
NH_4Cl	329	952*	640	35	284*	160
$(NH_4)_2SO_4$	240	952*	596	14	328*	171
Means	658	1170*	914	64	249#	156
$LSD_{.05}$ for carriers	391	391	276	63	63	45

*Significantly different from unlimed at 5 percent level

#Significantly different from unlimed at 1 percent level

Magnesium

The effect of treatment on magnesium in the soil is shown in Table 6. The effects of lime, carrier and their interaction were all significant. The limed plots had considerably more exchangeable magnesium than the unlimed plots. This is to be expected since the limestone added was dolomitic. The overall carrier effect separated the calcium nitrate plot from all the others. The low level of magnesium for this treatment suggests that the exchangeability of magnesium was suppressed by the calcium added with the carrier and lime. This suppression was expressed in limed and unlimed plots. The mechanism is not apparent.

The effect of lime within carriers was not significant for the unfertilized check, sodium nitrate or calcium nitrate treatments. These plots received two tons of lime in 1966; all other plots received more than two tons.

Ranking carriers within limed plots gives an order generally reflecting the amount of lime added. When they are ranked within unlimed plots, the order is essentially reversed. As pH was depressed by carrier, the magnesium level dropped. Low pH resulted in low magnesium level and high lime requirements. When dolomitic limestone was applied, those with the lowest level of soil magnesium received the highest amount of dolomitic limestone. So carriers with lime show a trend opposite to that exhibited by carriers without lime. The calcium nitrate treated plots are an exception to this, containing less magnesium than would be expected if only the acidic properties of the fertilizer were considered. This is true whether or not lime effects are considered.

It is apparent that the magnesium released from the dolomite, particularly in very acid soils, appears in the soil in forms having very different exchange properties than calcium released under the same conditions.

Potassium

Table 7 shows the potassium levels for the various plots. Only the carrier effect was significant at the 5 percent level. The lowest K level was in the check plot which received no potassium fertilizer. All other plots have received potassium each year. The acid forming carriers, in general, have similar K levels which are significantly higher than the check in the unlimed series.

The exchangeability of K in plots receiving the basic fertilizers or the two control treatments were unaffected by lime. The addition of lime consistently reduced exchangeable K in plots receiving acidifying N carriers, and this effect was more pronouned with the ammonium carriers. With the

Table 7. Effects of nitrogen carriers and lime on exchangeable potassium and Bray extractable phosphorus in the plow layer

Carrier	Exchangeable K			Bray P		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	pp2m	pp2m	pp2m	pp2m	pp2m	pp2m
No fertilizer	86	98	92	60	42	51
Basal fertilizer	174	197	186	124	141	134
$NaNO_3$	252	247	249	143	112	127
$Ca(NO_3)_2$	151	155	153	151	126	138
NH_3	220	182	201	164	130	148
Urea	155	128	142	153	145	149
Ureaform	155	128	142	157	133	145
NH_4NO_3	174	128	151	159	160	159
NH_4Cl	174	120	147	160	159	159
$(NH_4)_2SO_4$	147	102	124	184	153	168
Means*	169	148	159	146	130	138
$LSD_{.05}$ for carriers	52	52	37	40	40	28

*Lime effects not significant

most acid treatment (ammonium sulfate), exchangeable K after liming was the same as in the unfertilized check.

Two treatments, anhydrous ammonia and sodium nitrate, seemed to behave anomalously. They contained more exchangeable K than would be expected. Potassium is a common impurity in sodium compounds and this may have contributed to higher soil K with $NaNO_3$ fertilization. However, both sodium and ammonia can replace interlayer potassium in illite. It will be shown later (p. 139) that illite is present in the clay fraction of this soil. One ammonia treated plot (#6) received an exceptionally high application of ammonium in 1967. The K level of plot #6 was 282 lbs. while the correctly treated duplicate plot had 159 lbs. This in itself suggests displacement of K by ammonia. Assuming the 159 value to be a more accurate reflection of the effect of anhydrous ammonia, the average K level (ignoring lime) would be 170 pounds. This is still higher than would be expected from its acidic tendencies alone. In nine growing seasons, both $NaNO_3$ and NH_3 could have replaced considerable interlayer K from illite.

Phosphorus

Table 7 shows the effects of treatment on phosphorus extractable with 0.025 N HCl in 0.03 N NH_4F. A very significant carrier effect was expressed. This was due mainly to the 2- to 3-fold increase in phosphorus in all fertilized plots over the unfertilized check. This was true whether the plots were limed or not.

Extractable phosphorus was consistently higher in all unlimed plots receiving supplemental nitrogen treatments than in those receiving basal fertilizer alone. This increase was statistically significant with NH_3 and $(NH_4)_2SO_4$. These two carriers, ureaform and the two basic materials, showed a tendency for phosphate to be depressed with the addition of lime.

Although this effect of lime was pronounced, neither the main effect of lime nor the carrierxlime interaction was statistically significant.

The tendency for phosphate extractability to increase with decreasing pH and to be decreased by the addition of lime in this acid pH range (Table 5), are contrary to what one might expect. Phosphorus availability generally decreases in acid soils. Below pH 5.5, phosphorus often becomes deficient due to the formation of iron and aluminum phosphates.

If the apparent anomalies in this experiment are, in fact, real phenomena, it could be due to accelerated weathering of certain phosphate minerals at low soil pH;

and also, to the associated anion exchange and mass action effects of the sulfate, nitrate, chloride, hydroxyl and bicarbonate ions introduced with the various nitrogen carriers. If the products of such reactions at low pH could be identified, the apparent depression effect of lime might well be explained by pH-solubility product relationships.

Micronutrient Soil Tests

Zinc

Liming the plots significantly decreased the level of zinc in the soil as shown in Table 8. The effect of carriers was also significant. In general, the more acid carriers resulted in a higher level of zinc in the soil. The unlimed ammonium carriers promoted a significantly higher zinc level than the others. Soil pH with these carriers was 4.1 or less (cf. Table 5). Since zinc becomes soluble in the soil at low pH, these results are as expected.

Manganese

Table 9 shows the effect of treatment on soil manganese. Only the effect of carrier was significant. Ammonium chloride and sulfate had significantly less manganese in the soil than the other unlimed plots. Liming tended to increase

Table 8. Effects of nitrogen carriers and lime on extractable zinc in the plow layer

Carrier	Extractable Zn		
	Unlimed	Limed	Average
	ppm	ppm	ppm
No fertilizer	.03	.06	.04
Basal fertilizer	.06	.04	.05
$NaNO_3$	.08	.05	.06
$Ca(NO_3)_2$	.07	.04	.06
NH_3	.10	.06	.08
Urea	.16	.06	.11
Ureaform	.10	.05	.07
NH_4NO_3	.68	.05*	.36
NH_4Cl	.60	.12*	.36
$(NH_4)_2SO_4$	.50	.07*	.28
Means	.24	.06*	.15
$LSD_{.05}$ for carriers	.35	.35	.24

*Significantly different from unlimed at 5 percent level

Table 9. Effects of nitrogen carriers and lime on extractable manganese and iron in the plow layer

Carrier	Extractable Mn			Extractable Fe		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	ppm	ppm	ppm	ppm	ppm	ppm
No fertilizer	128	124	126	10	6	8
Basal fertilizer	112	117	114	10	5*	7
$NaNO_3$	110	118	114	8	4	6
$Ca(NO_3)_2$	142	112	128	12	4*	8
NH_3	117	126	122	17	8*	13
Urea	114	106	110	16	10*	13
Ureaform	132	108	120	17	6*	12
NH_4NO_3	122	124	123	33	10*	21
NH_4Cl	80	102	91	44	21*	32
$(NH_4)_2SO_4$	77	92	85	67	22*	45
Means	114	113	113	23	10*	16
$LSD_{.05}$ for carriers	26	26	19	5	5	4

*Significantly different from unlimed at 5 percent level

the Mn level with these two treatments. The solubility of Mn compounds and the ratio of Mn^{-2} to other valence forms increases rapdily below pH 5.0. This often results in toxic effects of Mn in the plant. Abnormally high Mn in the corn tissue was the first nutritional imbalance to appear in this experiment, as the soil pH declined with treatment since 1959.

Toxic levels of Mn (400 ppm or more) were already present in the third season on plants receiving NH_4Cl and $(NH_4)_2SO_4$. The extraction procedure used here failed to show this relationship to pH in the soil. Hoff and Mederski (36) have shown good relationships between Mn extracted with this method and plant response. They, too, were unable to show any relationship between pH and extractable Mn in the soil. Perhaps the form of manganese extracted with phosphoric acid is not the form responsible for the toxic effects noted.

On the other hand, it may be that these results are accurate. Mn toxicity may not be due simply to high levels of soluble Mn in the soil. It is possible that the total manganese in the soil has been extensively depleted over the 7 or 8 years in which soil pH in the unlimed NH_4Cl and $(NH_4)_2SO_4$ plots have been below 5.0. The lime applied in the seventh growing season may have reduced this rate of depletion during the last two years. Or it may have promoted release from some, as yet unrecognized, complexes which may form at low soil pH.

Iron

Table 9 shows that lime, carriers and their interaction significantly affected extractable iron. Lime decreased extractable soil iron. The effect of lime within carriers was significant for all fertilizer treatments except the unfertilized check and sodium nitrate treatments. Except for calcium nitrate, all plots showing a significant decrease in iron received more than two tons of lime.

Unlimed plots receiving no nitrogen or those which received nitrogen from basic carriers showed the lowest level of iron. All acidifying carriers showed a significantly higher level than the basal fertilizer treatment. In the case of ammonium nitrate, chloride, and sulfate, there was a highly significant stepwise increase related directly to increasing acidity over the range from pH 4.6 to 3.8 (Table 5). When the plots were limed, extractability of iron was reduced for all treatments; although in the ammonium chloride and sulfate treated plots, it remained significantly higher than for the other treatments.

Ten to twelve tons per acre of lime have been applied to the plots receiving these strongly acidifying carriers (Table 1). The failure to reduce iron extractability to levels comparable to the other treatments supports the inference made earlier that buffering systems have been altered by long exposure to low pH in these soils.

Copper and Aluminum

All plots contained less than 0.03 ppm copper. This is too low a level to detect differences between plots. Like zinc, copper becomes soluble at low pH but usually at lower values. Either the pH was not low enough to affect solubility of copper compounds, or the soil was too low in copper minerals to bring about an increase in extractable copper.

The aluminum analysis also gave extremely low results. The unlimed ammonium sulfate, chloride and nitrate plots averaged about 1.25 ppm Al. The unlimed urea and ureaform plots averaged about 0.90 ppm Al. All other plots contained no detectable aluminum. This was similar to the results for iron except the amounts present were less. Although the differences were small and hard to detect, they were probably real. This adds further evidence to the contention that soil buffering systems have been materially altered by prolonged use of acidifying carriers. The effects of ammonium carriers on extractable zinc (Table 8), iron and manganese (Table 9) serve as further evidence of such changes.

Sulfur and Sodium

The level of sulfate S in the soil varied somewhat throughout the season in the ammonium sulfate treated plots. This variation will be discussed in a later section (p. 117). All other plots showed sulfate levels of less than 2 ppm S. Sulfur in the ammonium sulfate treated plots ranged from 5 to 25 ppm during the season. The limed ammonium sulfate plots showed a slight, but consistent, reduction in sulfur than the unlimed plots (Table 25).

All treatments except the sodium nitrate treatment showed less than 20 ppm of sodium in the soil. The sodium nitrate treated plots averaged about 130 ppm of sodium and showed no effect of lime.

Foliar Analyses

Nitrogen

The level of nitrogen in plants, as shown in Table 10, was affected only by carrier. The NH_3 plot which received 600 lbs. of nitrogen by mistake in 1967, had a foliar nitrogen content equal to the plot receiving 300 lbs. of nitrogen.

Phosphorus

Table 10 also shows the phosphorus content of corn leaves for the various treatments. Differences in phosphorus were small, but the carrier effect was significant. The plots that received no supplemental nitrogen and those that received ammonium sulfate resulted in the lowest phosphorus content and the differences between these treamtnets were not significant. The anhydrous ammonia treated plots had the most plant phosphorus, but it was significantly different only from the above three treatments. The differences in foliar P did not closely reflect differences in soil P. In general, the three ammonium carriers resulted in less plant P, but higher soil P, relative to the other treatments (cf. Table 7).

Table 10. Effects of nitrogen carriers and lime on foliar nitrogen and phosphorus

Carrier	Foliar N			Foliar P		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	%	%	%	%	%	%
No fertilizer	1.50	1.55	1.52	.21	.24	.22
Basal fertilizer	1.32	1.35	1.34	.20	.20	.20
$NaNO_3$	2.40	2.62	2.51	.30	.29	.30
$Ca(NO_3)_2$	2.65	2.52	2.59	.28	.35	.32
NH_3	2.62	2.40	2.51	.34	.32	.33
Urea	2.32	2.46	2.40	.30	.28	.29
Ureaform	2.65	2.65	2.65	.30	.32	.32
NH_4NO_3	2.60	2.50	2.55	.28	.28	.28
NH_4Cl	2.62	2.40	2.51	.28	.26	.27
$(NH_4)_2SO_4$	2.52	2.35	2.44	.26	.26	.26
Means*	2.32	2.28	2.30	.28	.28	.28
$LSD_{.05}$ for carriers	.44	.44	.31	.08	.08	.06

*Lime effects not significant

Potassium

The unfertilized check and the ammonium sulfate treated plants contained the lowest amount of K (Table 11). The basal fertilizer, and the base forming nitrate carriers, resulted in the highest levels of plant K. There was a highly significant difference for lime treatment. The plants receiving lime were lower in potassium. The largest reduction was for the urea treatment. This was due primarily to the high K level in the plants which mistakenly received no nitrogen fertilizer in 1967. The array of treatments according to contents of soil K and plant K gave a similar order of treatments.

Calcium

The data in Table 12 show no significant average effect of lime on calcium content of corn leaves. There was however, a very highly significant (P = 0.1 percent) carrier lime interaction. The average effects of carriers were also very highly significant.

Without lime, calcium content was significantly increased by $Ca(NO_3)_2$ relative to the basal fertilizer. It was significantly reduced by NH_4Cl. The reduction by $NaNO_3$ and $(NH_4)_2SO_4$ approached significance at 5 percent.

Table 11. Effects of nitrogen carriers and lime on foliar potassium

Carrier	Foliar K		
	Unlimed	Limed	Average
	%	%	%
No fertilizer	2.37	2.04	2.20
Basal fertilizer	3.24	3.10	3.17
$NaNO_3$	3.49	3.19	3.34
$Ca(NO_3)_2$	3.08	2.98	3.03
NH_3	2.84	2.75	2.79
Urea	3.98	2.85*	2.91
Ureaform	2.74	2.58	2.66
NH_4NO_3	2.56	2.71	2.64
NH_4Cl	3.08	2.61*	2.84
$(NH_4)_2SO_4$	2.62	2.47	2.54
Means	2.90	2.73#	2.81
$LSD_{.05}$ for carriers	.43	.43	.37

*Significantly different from unlimed at 5 percent level

#Significantly different from unlimed at 1 percent level

Table 12. Effects of nitrogen carriers and lime on foliar calcium and magnesium

Carrier	Foliar Ca			Foliar Mg		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	%	%	%	%	%	%
No fertilizer	.50	.64	.60	.32	.58*	.41
Basal fertilizer	.63	.62	.62	.24	.32	.28
$NaNO_3$	.48	.48	.48	.32	.34	.33
$Ca(NO_3)_2$	.86	1.12*	.99	.21	.43*	.32
NH_3	.73	.58*	.66	.21	.36*	.29
Urea	.71	.74	.72	.22	.54*	.38
Ureaform	.66	.78*	.72	.22	.56*	.39
NH_4NO_3	.60	.59*	.65	.22	.45*	.33
NH_4Cl	.44	.83*	.64	.15	.42*	.29
$(NH_4)_2SO_4$	.51	.76*	.63	.16	.56*	.36
Means	.62	.72#	.67	.23	.45*	.34
$LSD_{.05}$ for carriers	.14	.14	.10	.13	.13	**

*Significantly different from unlimed at 5 percent level

#Significantly different from unlimed at 15.1 percent level

**Average carrier effects significant only at 7 percent level

The addition of lime increased foliar calcium with most carriers, notably with $Ca(NO_3)_2$ and the two most acid carriers. Lime significantly reduced leaf calcium when combined with the NH_3 treatment. This was not due to the mistaken application of fertilizer as the two plots had similar leaf calcium levels.

Calcium levels in the plants with $NaNO_3$ were significantly lower than with basal fertilizer, regardless of lime treatment. One suspects that the high levels of soil and plant K associated with this treatment, plus high concentrations of Na available to the plant from the carrier itself, may have promoted an imbalance leading to reduced uptake of Ca.

Magnesium

The magnesium content of corn leaves is shown in Table 12. Average effects of carriers were significant at the 7 percent level of probability. The average effect of lime was significant at the 4 percent level. The significance level for the interaction of these two effects approached 1 percent.

Lime increased plant Mg as it had soil Mg. Plant magnesium levels showed non-significant responses to lime only for the sodium nitrate and basal fertilizer treatments.

Soil magnesium showed no significant differences for lime in the sodium nitrate, calcium nitrate and the unfertilized check treatments.

The foliar magnesium levels were lowest for the unlimed ammonium chloride and sulfate treatments. This is similar to the results for plant calcium. Sodium nitrate, unlimed, gave the highest magnesium content. This is in contrast to the fact that this treatment gave the lowest foliar calcium content when compared to other treatments. But it reflects the high soil Mg level. The low level of plant Mg, from unlimed ammonium carrier plots, reflects the low soil Mg test for these treatments.

Manganese

The effects of treatment on plant manganese shown in Table 13 are very striking and distinct. The average lime effect approached significance ($P = 0.55$) at the 5 percent level. The average effect of carriers and the carrier lime interaction were both very highly significant ($P < .0005$).

The toxicly high Mn content of corn growin in acid soils without lime was directly related to increasing acidity below pH 5.0 (cf. Table 5). This result is in contrast to soil Mn (cf. Table 9). The lowest soil tests for available

Table 13. Effects of nitrogen carriers and lime on foliar manganese and zinc

Carrier	Foliar Mn			Foliar Zn		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	ppm	ppm	ppm	ppm	ppm	ppm
No fertilizer	50	34	42	24	24	24
Basal fertilizer	70	33	51	24	18	21
$NaNO_3$	63	55	59	26	21	23
$Ca(NO_3)_2$	87	78	82	30	22	26
NH_3	482	73*	278	51	26*	39
Urea	740	174*	457	46	34*	40
Ureaform	519	82*	300	48	27*	37
NH_4NO_3	729	122*	426	60	26*	43
NH_4Cl	678	400*	539	44	56*	50
$(NH_4)_2SO_4$	776	317*	546	43	42	42
Means	419	137#	278	39	30**	35
$LSD_{.05}$ carriers	134	134	95	12	12	8

*Significantly different from unlimed at 5 percent level

#Significantly different from unlimed at 5.5 percent level

**Significantly different from unlimed at 6.1 percent level

Mn were in the most acid soils where ammonium chloride and sulfate had been used.

This relationship between soil pH and plant Mn is consistent with the expected effect of pH on Mn availability. The low soil tests for Mn under acid conditions must be ascribed to Mn depletion of the soil, to formation of Mn complexes in the soil or to laboratory artifacts, which were not detectable by the analytical procedure used.

Where lime was applied, plant Mn was reduced. The reduction with all acidifying carriers was large and very highly significant statistically. The reduced levels in limed plots were, however, more closely related to soil pH (cf. Table 5) than to the soil tests of Mn (cf. Table 9).

Zinc

Average effects of lime were significant at six percent and highly significant carrier and interaction effects were evident in foliar Zn contents presented in Table 13.

Without lime, Zn in leaves of corn grown with acidifying carriers was significantly higher than for $Ca(NO_3)_2$, $NaNO_3$ or the two control treatments.

The addition of lime reduced plant Zn significantly with four of the acidifying carriers. With NH_4Cl there was a significant increase in leaf Zn with addition of lime; with $(NH_4)_2SO_4$ there was no lime effect.

The high levels of Zn found in the unlimed soil with the use of the three most acidifying nitrogen carriers would have led to the prediction of high plant Zn. However, the high plant Zn content associated with the other acid carriers was not anticipated. Liming significantly reduced the level of Zn in the soil where the three ammonium carriers were used. But of these three, only the use of lime with ammonium nitrate significantly reduced foliar Zn. Foliar Zn actually increased by liming the NH_4Cl plots and was unaffected by lime on the ammonium sulfate treated soils. As in the case of Mn, foliar Zn was more closely related to soil pH (cf. Table 5) than to the soil test for available Zn.

Frequently Zn uptake has been found to be closely and inversely related to soil P. There was no evidence of such a relationship here (cf. Tables 7 and 10).

Aluminum

Aluminum content of corn leaves was influenced significantly by carrier and carrier lime interaction (Table 14).

The array of foliar Al values for unlimed carriers reflected increasing residual acidities of the carriers.

Table 14. Effects of nitrogen carriers and lime on foliar aluminum and iron

Carrier	Foliar Al			Foliar Fe		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	ppm	ppm	ppm	ppm	ppm	ppm
No fertilizer	92	82	88	136	130	133
Basal fertilizer	116	88	102	138	121	130
$NaNO_3$	96	80	88	190	140	166
$Ca(NO_3)_2$	93	85	89	166	190	178
NH_3	126	172	149	223	204	214
Urea	130	80	104	218	167	192
Ureaform	112	85	99	186	187	186
NH_4NO_3	178	78*	128	227	138	182
NH_4Cl	240	102*	172	233	180	206
$(NH_4)_2SO_4$	342	95*	218	304	172	238
Means	152	95#	124	202	163##	182
$LSD_{.05}$ for carrier	108	108	76	80	80	56

*Significantly different from unlimed at 5 percent level
#Significantly different from unlimed at 8.8 percent level
##Significantly different from unlimed at 20.5 percent level

Although, only with NH_4Cl and $(NH_4)_2SO_4$ were Al contents significantly higher than the basal treatment.

The addition of lime significantly reduced plant Al, with the three ammonium carriers, to levels statistically the same as for all other limed carriers.

Iron

Iron content of corn foliage is shown in Table 14. Only the carrier effect was signficant. Iron in plants without lime increased with the acid nature of the carrier in an array very similar to that for aluminum. The increase over the basal fertilizer was significant for NH_3, urea, and the three ammonium carriers. As was true for aluminum, plant iron was generally reduced by lime. Although for Fe, these reductions were statistically significant only at the 20 percent level.

In the limed series, foliar iron was significantly higher with NH_3 treatment than with the basal fertilizer treatment. A similar effect of NH_3 was expressed in limed plots on foliar Al. There the effect on Al was large but not significant statistically.

Silicon

Table 15 shows the silicon content of the plants. Carrier effects were highly significant ($P < .005$) and the interaction with lime approached significance ($P = 0.067$ percent). Liming of soils receiving acid nitrogen carriers, or the use of basic carriers, suppressed plant silicon levels compared to the unlimed controls. Liming the ammonium chloride treated soil was an exception to this. The unlimed ammonium chloride and sulfate treatments resulted in the highest foliar silicon. The use of ureaform (without lime) gave results more like the basic carriers than the ammonia carriers.

Ureaform has the same theoretical residual acidity as urea. Foliar silicon, aluminum and iron (cf. Table 14) in plants receiving ureaform were consistently, although not always significantly, less than in plants receiving urea. Perhaps the slow release of nitrogen from ureaform is associated with a slow release of acidity and the soil buffering system is better able to handle this acidity when it is introduced over a longer period of time. This difference between ureaform and urea was not found in soil extractable iron (cf. Table 9). The lime requirement was higher and the pH lower (not significantly) for the soils receiving ureaform when compared to those receiving urea (cf. Table 5).

Table 15. Effect of nitrogen carriers and lime on foliar silicon

Carrier	Foliar Si		
	Unlimed	Limed	Average
	%	%	%
No fertilizer	.34	.22*	.28
Basal fertilizer	.36	.26*	.31
$NaNO_3$	.20	.18	.19
$Ca(NO_3)_2$	.22	.22	.22
NH_3	.34	.20*	.27
Urea	.40	.23*	.32
Ureaform	.26	.20*	.23
NH_4NO_3	.36	.18*	.27
NH_4Cl	.44	.42	.43
$(NH_4)_2SO_4$	.50	.31*	.40
Means	.34	.24#	.29
$LSD_{.05}$ for carriers	.07	.07	.10

*Significantly different from unlimed at 5 percent level

#Significantly different from unlimed at 16.1 percent level

This would tend to weaken the argument that ureaform acidity is more easily handled by the soil buffering system.

These apparent differences between urea and ureaform may reflect mass action effects or rate of carbonate release on dissipation of hydrogen ions through hydrolysis of carbonic acid to CO_2 and water. Ammonium carbonate is released rapidly by the hydrolysis of urea, much more slowly by hydrolysis of ureaform. The transiently high concentrations of ammonium and carbonate which accompany urea hydrolysis would promote more extensive displacement of H^+ released during nitrification and its dissipation as H_2O through hydrolysis of carbonic acid.

The increased solubility of iron and aluminum with increased soil acidity is clearly indicated by soil tests. This is reinforced by the observed influence of nitrogen carriers, hence soil pH, on foliar Al, Fe, and Si. Foliar iron, aluminum, and silicon were reduced by the application of lime. Foliar Al and Si were reduced with the use of basic carriers. Ammonium chloride and sulfate fertilizers, when unlimed, resulted in the highest levels of foliar Si, Al, and Fe, and the highest amounts of soil extractable iron and aluminum.

At low pH, Jackson (39) refers to the decomposition of primary and secondary crystalline minerals as the "ultimate" buffering mechanism in the soil. It is accompanied by the release of cationic species of Al and Fe. The hydrated hydronium complexes of Al and Fe formed are themselves potent pH buffers. The ability of sesquioxides to neutralize bases is well recognized and is the basis for the use of various buffering systems to estimate lime requirement of soils.

The influence of nitrogen carriers on soil and foliar Al, Fe, and Si contributes more evidence to the conclusions drawn from other soil and plant parameters (pp. 51 and 65) that the nature of the soil buffering system, as well as, capacity has changed with declining soil pH.

The reduction in plant Si, Al and Fe, when the soil is limed, indicates that polymers or other insoluble complexes have been formed. Perhaps Ca is coordinated with, or trapped by, these polymeric or complexed species and this may explain the "disappearance" of the Ca (cf. Table 6) applied as lime to the acidic ammonium sulfate plots and the failure of the pH and lime requirement (cf. Table 5) to give the expected response.

Table 16. Effects of nitrogen carriers and lime on foliar copper and barium

Carrier	Foliar Cu			Foliar Ba		
	Unlimed	Limed	Average	Unlimed	Limed	Average
	ppm	ppm	ppm	ppm	ppm	ppm
No fertilizer	11.0	10.5	10.8	9.0	6.5	7.8
Basal fertilizer	10.5	12.0	11.2	10.5	7.0	8.8
$NaNO_3$	12.0	13.5	12.8	8.0	7.0	7.5
$Ca(NO_3)_2$	13.5	12.5	13.0	8.5	7.0	7.8
NH_3	13.0	13.0	13.0	11.0	7.5	9.2
Urea	12.5	12.5	12.5	14.0	7.0	10.5
Ureaform	13.0	14.0	13.5	14.5	7.5	11.0
NH_4NO_3	11.5	11.5	11.5	15.0	7.0	11.0
NH_4Cl	10.0	9.5	9.8	11.0	9.5	10.2
$(NH_4)_2SO_4$	11.0	12.0	11.5	7.5	5.0	6.2
Means	11.8	12.1#	12.0	10.9	7.1##	9.0
$LSD_{.05}$ for carriers	2.7	2.7	1.9	4.1	4.1	2.9

#Lime effect not significant at 20 percent
##Significantly different from unlimed at 13.2 percent level

Copper

The solubility of copper in the soil is expected to increase at very low pH values. Table 16 indicates that liming did not appreciably alter foliar copper. There was a general increase in foliar copper over the checks with the application of either basic or slightly acidic nitrogen carriers. The highly acidic carriers (NH_4Cl and $(NH_4)_2SO_4$) resulted in a plant copper content similar to the checks. Whether this was a result of carrier affect on soil copper or due to the contribution of the supplemental nitrogen in basic or moderately acidic forms, on the general health of the plant, is not known.

Barium

In unlimed soils, the use of basic or highly acidic carriers tended to depress foliar barium. Moderately acidic carriers (urea, ureaform and NH_4NO_3) significantly increased foliar barium over both controls and $(NH_4)_2SO_4$.

When limed, foliar Ba was reduced with all carriers. The resulting level with $(NH_4)_2SO_4$ was significantly lower than for NH_4Cl.

This differential response to liming for the two most acidifying carriers again indicates that more than just the acidifying effect of the carrier was involved. At these high rates of application, it appears that the non-nitrogenous cation or anion is also influencing the soil system. If only the direct contribution by carriers to soil acidity were of importance, then liming these soils with appropriate amounts of lime should result in soils with similar chemical and nutritional characteristics. In this particular case it is probably simply due to solubility products of the salts involved.

Carrier Anion x Lime Interactions

It was noted during earlier years of this experiment, that decreases in soil pH and exchangeable bases, and increases in lime requirement occurred most rapidly with ammonium sulfate (101). It is known that divalent anions are sorbed more extensively by soils than are monovalent anions. The sorbed anions themselves contribute to titratable acidity.

Anion sorption mechanisms include replacement of hydroxyl in hydrous sesquioxides ("anion penetration"). The complexes formed with Fe and Al at low pH are polymeric cations. Those formed by divalent anions are more basic (weaker in acidic character) than are those formed by monovalent anions (39). Thus charged sesquioxide-SO_4 species would be more effective in displacing metal cations from exchange sites than are cationic sesquioxide-Cl and sesquioxide-NO_3 species.

The acidifying carriers (NH_3, urea, ureaform, NH_4NO_3, NH_4Cl and $(NH_4)_2SO_4$) have in common the fact that none supply a stable cation to neutralize the nitric acid produced when ammonium is nitrified.

The first four of these differ in the chemistry of their reactions in the soil by reason of the anions which are associated with ammonium after solution or hydrolysis (hydroxyl, carbonate or nitrate). Urea and ureaform both form ammonium carbonate on hydrolysis, but the rate of hydrolysis and the associated concentrations of ammonium and carbonate are much lower with ureaform. Some of the observed differences in residual effect of these four carriers must be ascribed to mass action effects of specific anion concentrations associated with solution or hydrolysis.

With these four carriers, as well as with NH_4Cl and $(NH_4)_2SO_4$, all of the nitrogen applied either as ammonium or nitrate appears as HNO_3 as soon as the ammonium is nitrified:

$$NH_4^+ + NO_3^- \xrightarrow{2O_2} 2\ NO_3^- + 2\ H^+ + H_2O$$

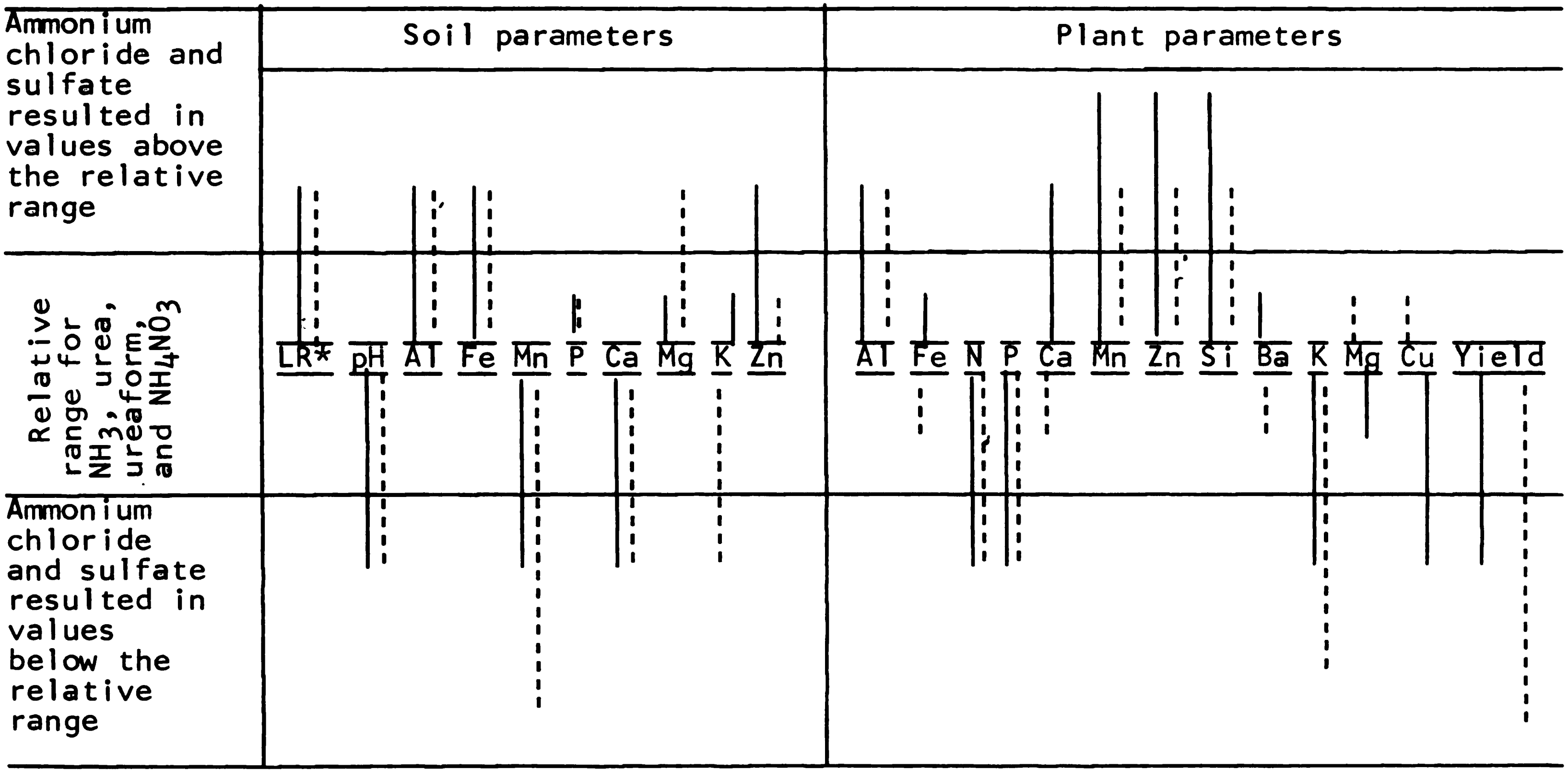
The major difference, then, between the four moderately acidifying carriers and NH_4Cl and $(NH_4)_2SO_4$ is that, in addition to nitric acid, equivalent amounts of hydrochloric or sulfuric acid are released when the ammonium in the latter two carriers is nitrified.

Figure 2 is an attempt to summarize, graphically, residual effects in limed soils which could be ascribed uniquely to chloride (solid line) or sulfate (dashed line). The various soil and plant parameters measured are identified along the center line of the diagram which represents the relative range for these parameters for the lined ammonium nitrate, urea, ureaform and anhydrous ammonia plots. Deviations from this mean for NH_4Cl or $(NH_4)_2SO_4$ are shown as vertical lines whose length is relative to the range of deviations from the other four acidifying carriers.

Both the sulfate and the chloride produced values out of the range for other carriers for numerous measurements: for soil pH and lime requirement, for soil Al, Fe, Mn, and Ca, for foliar Al, N, P, Mn, Zn, Si and K, and for corn yield.

Unique effects of NH_4Cl were expressed on soil Zn and on foliar Ca and Cu. Foliar Zn, Si and Ba were significantly higher with NH_4Cl than with $(NH_4)_2SO_4$, whereas foliar Mg

Figure 2. Residual effects on soil and plant parameters for ammonium chloride (solid line) and sulfate (dashed line) relative to other acidifying carriers two years after liming



*LR = Lime requirement

was significantly lower. Foliar Fe and Mn also tended to be higher with the chloride than with the sulfate.

Exchangeable Mg was uniquely higher with ammonium sulfate, exchangeable K was uniquely lower. Soil Mn, foliar K and final yield were depressed to a greater extent by the sulfate than the chloride.

The complexity of soil solution chemistry precludes any simple explanation for these data. A number of possible mechanisms may be operating in these systems.

Jackson (39) has noted that divalent sulfate promotes the polymerization of monomeric aluminum. Hydrolytic polymerization of monomers and low polymers of Fe and Al is also promoted by increasing pH from below 5.0.

Exchangeable Ca after liming was much lower with all acidifying carriers than in the fertilized or unfertilized controls, whereas exchangeable Mg was higher, notably with ammonium sulfate. This would suggest that Ca is trapped in forming polymers of hydrated iron and aluminum. A steric effect might be involved, since the hydrated calcium ion is larger than the hydrated magnesium ion. However, the marked differential effect of sulfate on the exchangeability of these two cations could as readily be understood in terms of the different solubilities of their respective sulfate salts.

Plant Al, Mn, Zn and Si were higher with the two most acid carriers than with the four moderately acid carriers. The latter three elements were higher in ammonium chloride treated plants than in ammonium sulfate treated plants. These differences may be partially explained in terms of solubility product relationships among the sulfate and chloride salts of the cations. With reference to Si, a higher activity of Cl^- than of SO_4^{--} in the soil solution can be inferred, leading to greater displacement of silicic acid by mass action equilibria. The higher activity of Cl^- would derive partly from the greater solubility of many of its salts and partly from its lesser tendency to form complexes with hydrated iron and aluminum.

These data clearly illustrate the important role of fertilizer anions in soil acidification. The processes involved are obviously complex and it is not possible to pin-point specific mechanisms for each of the phenomena observed. The solubilities of compounds, the activities of ions, their tendencies to complex and polymerize, and mass action equilibria among diverse species present are certainly involved.

Below pH 5.0, qulitative changes occur which greatly accelerate the retention of titratable acidity and the associated decline in soil fertility. It is probable that some of these changes can be reversed by liming. However, it is apparent from the data that unusual amounts of lime are required and that recovery will, at best, be slow. There is no evidence, as yet, that there may not be residual effects which lime alone cannot correct. This is both a warning for practical soil management and a challenge for further research.

Other Micro-elements

With three exceptions, the foliar sodium level from all treatments was less than 0.01 percent. The unlimed check in block two had a sodium level of 0.01 percent while the two unlimed sodium nitrate plots resulted in foliar sodium levels of 0.01 and 0.02 percent.

Boron, strontium, molybedenum and cobalt were also measured in the plant tissue. None of these elements were affected by nitrogen carrier or lime treatment. Table 17 shows the probabilities for treatment effects, the mean values and the range for each of these elements in the tissue.

Table 17. Effect of nitrogen carriers and lime on several micro-elements in corn tissue

Element	Significance level of F test			Mean	Range
	Lime	Carrier	Interaction		
				ppm	ppm
Cobalt	.627	.599	.651	2.86	1.6-4.66
Boron	.500	.124	.600	10.2	6.5-15.0
Molybdenum	.313	.299	.356	1.81	1.00-3.12
Strontium	.304	.404	.120	27.8	23-32

Plant Performance

Yields of corn in Table 18 are expressed in two ways -- as the weight of the dried ear in metric tons per hectare and in bushels of grain per acre, adjusted to 15.5 percent moisture.

Lime, carrier and their interaction effects were all significant. Lime, ignoring carrier, resulted in an average yield increase of 15 bushel. A comparison of lime within carrier treatments showed that lime was significant in increasing yield in only three treatments, the three most acid nitrogen carriers.

Corn on unlimed plots of these three treatments was severely reduced in stand and vigor by nutritional imbalances which could not be identified by visible symptoms with any particular nutrient. With $(NH_4)_2SO_4$ treatment only a few scattered, chlorotic, severaly stunted plants survived after the plants reached about three inches. Survival was only slightly better with NH_4Cl. With NH_4NO_3 treatment, the plants were distinctly more vigorous but stands were spotty, ranging from 40 to 80 percent of a perfect stand. A uniform stand was achieved on all other plots (including limed plots of these three treatments) by thinning to 16,000 stalks per acre.

Table 18. Effects of nitrogen carriers and lime on corn yields

Carrier	Yields of corn					
	Grain, 15.5% moisture Bushels per acre			Ear corn, oven dry Metric tons per hectare		
	Unlimed	Limed	Average	Unlimed	Limed	Average
No fertilizer	26.0	38.8	32.4	1.77	2.63	2.20
Basal fertilizer	53.6	46.2	49.8	3.64	3.13	3.38
$NaNO_3$	64.2	77.6	70.9	4.35	5.27	4.81
$Ca(NO_3)_2$	85.3	83.8	84.6	5.79	5.69	5.74
NH_3	70.4	94.7	82.5	4.78	6.43	5.60
Urea	69.0	50.2	59.6	4.68	3.41	4.05
Ureaform	72.0	62.8	67.4	4.89	4.26	4.58
NH_4NO_3	26.4	77.2*	51.8	1.79	5.24*	3.52
NH_4Cl	14.3	59.4*	36.8	.97	4.03*	2.50
$(NH_4)_2SO_4$	1.0	44.0*	22.5	.07	2.99*	1.53
Means	48.2	63.4*	55.8	3.27	4.31*	3.79
$LSD_{.05}$ for carriers	25.6	25.6	22.7	1.73	1.73	1.54

*Significantly different from unlimed at 5 percent level

On limed plots, the fullness of leaves and diameter of stalks were reduced, but not plant height, with $(NH_4)_2SO_4$ and NH_4Cl. A mild chlorosis was maintained through the growing season. These plants looked more vigorous all season than the limed checks which were also chlorotic but showed severe midrib firing characteristic of nitrogen deficiency. Final yields on the limed plots were not significantly different between the checks and the ammonium chloride and sulfate treatments.

The large reduction in the stand and yield with the unlimed plots for the three most acidic carriers was responsible for the significant limexcarrier interaction.

In unlimed plots, the only significant yield increase for carrier over basal fertilizer at the 5 percent level was with $Ca(NO_3)_2$. In limed plots, increases for $Ca(NO_3)_2$, NH_4NO_3 and NH_3 were significant.

Plant Performance in Relation to Soil and Plant Analyses

Relationships among the various soil and plant parameters presented in previous sections are being investigated by extensive correlation and regression analyses. These are byond the scope of this report.

Table 19 summarizes the ranges observed for eleven nutrients in the plants of this investigation. Levels of these elements associated with deficiency, toxicity or normal conditions are also presented. These critical levels have been drawn from several sources which are summarized in a recent review edited by Pierre et al. (63).

Major Nutrients

Availability of nitrogen was the major deterrent to yield in plots which received no supplemental nitrogen. The optimal range for maximum plant growth is 2.38 to 3.30 percent. All plants that received no supplemental nitrogen fell below this range. All other plants fell within this range.

Nearly twice the amount of P was applied to the soil as would have been recommended based on the soil test for extractable P (53). This recommendation is based on a yield goal of 95 bushels of corn which is an acceptable goal for this sandy loam soil. This goal was obtained on the limed anhydrous ammonia plot (cf. Table 18).

Foliar P on the other hand, was near or below the critical minimal level of .295 percent phosphorus. The purpling of the leaves typical of P deficiency was occasionally

Table 19. Comparison of observed ranges and deficient, normal and toxic levels of nutrients in corn leaves.[1]

Element	Reference table	Units	Critical levels			Ranges from experiment
			Deficiency	Normal	Toxic	
Nitrogen	10	%	< 2.38-3.30			1.32-2.65[2]
Phosphorus	10	%	< .295			.20-.35[3]
Potassium	11	%	< 1.6			2.04-3.98
Calcium	12	%	< .2			.48-1.12
Magnesium	12	%	< .25			.15-.56[4]
Manganese	13	ppm	< 25	50-300	> 400	33-776[5]
Zinc	13	ppm	< 15	40-100	> 300	18-60
Iron	14	ppm	< 30	75-500		130-304
Copper	16	ppm	< 6	8-20	> 50	9.5-13.5
Boron	17	ppm	< 2			6.5-15.0
Molybdenum	17	ppm	< .3	.8-5	10	1.00-3.12

[1] See Pierre et al. (39).

[2] Checks 1.32-1.55. All others 2.32-2.65.

[3] Only NH_3 and limed $Ca(NO_3)_2$ above .30

[4] All unlimed plots except $NaNO_3$ and no fertilizer below .25. All limed plots above .25

[5] All unlimed plots receiving acidic nitrogen carriers above 400. All others below.

observed on the two most acid treatments but it did not seem to be a major reason for reduced plant growth.

A strong NxP interaction was apparent. There was no increase in foliar P from the application of P in the basal fertilizer unless supplemental nitrogen was also added.

Based on the yield goal of 95 bushel, and the soil test for potassium, only 1/4 to 1/2 of the recommended K was actually applied. The limed plots were lower in soil K than the unlimed plots. However, the foliar analysis for K indicates that the plants contained adequate amounts of K. They contained 25 to 50 percent more potassium than the critical level needed for good growth.

High levels of K resulted in values of .19 to .55 for the foliar ratio of (Ca+Mg)/K. Potassium deficiencies are usually associated with values greater than 3.5. High levels of soil K can, however, suppress the uptake of calcium.

Secondary Nutrients

Foliar calcium levels indicate that calcium was not limiting for any treatment.

Michigan recommendations (53) call for the use of dolomitic limestone to supply Mg to acid sandy loam soils when the soil test for Mg is below 75 pounds per acre. All unlimed treatments except the checks and sodium nitrate (cf. Table 6) were below this level. All limed plots were well above the critical level. Foliar Mg levels revealed the identical relationship: Unlimed treatments were below, limed treatments were above the critical level for foliar Mg. The only exception to this was the unlimed basal treatment, where soil Mg was just above the critical level while foliar Mg was just below the critical level.

Typical Mg deficiency symptoms were observed on scattered plants. But generally, chlorosis and decline in vigour were more prevalent and served to indicate that the poor state of health, as the result of some treatments, was due to more than just Mg deficiency.

The ratio of K to Mg is much more critical in the soil than is the absolute level of Mg. The ratio K/Mg in soil for unlimed plots of NH_4NO_3, NH_4Cl, and $(NH_4)_2SO_4$ was 6.2, 5.0 and 10.5, respectively. All others were less than 4.0. Soil additions of Mg are recommended in Michigan when this ratio exceeds 4.0.

Reductions in yield where lime was not applied were partilly due to deficiencies of Mg in the plant. But the acidifying nature of the carrier may also have unfavorably altered the ratios of K:Mg:Ca. In specific instances, the level of one or more of these elements in the soil and/or in the plant was altered, not because of the acidifying nature of the carrier, but because of the effect in the soil of the cation or the anion of the carrier. The depressing effect of $NaNO_3$ on the K level of the soil is an example of this.

Micronutrients and Other Elements

The most striking nutritional feature of corn on the unlimed plots receiving acidifying nitrogen carriers was the high leaf content of Mn. All were in excess of 400 ppm which is considered to be toxic for corn.

Mechanisms of Mn toxicity are not understood. There seems to be a critical interaction with Fe. Specific iron deficiency is usually associated with foliar Fe levels below 30 ppm. All treatments showed Fe levels well above this. No toxic concentrations of Fe are recognized.

The observed chlorosis and reduced vigor associated with toxic levels of Mn may actually be due to an induced Fe deficiency. Plants may contain sufficient iron, but it is in a form that is unavailable for the metabolic processes of the plant.

It is significant that there was a general tendency for major and secondary nutrients (P, Ca, Mg) to decline in the plant and for micronutrients and nonessential elements (Si, Mn, Fe, Zn, Al) to increase in the plant as the soil pH declined. Only the high levels of Mn or the low levels of Mg, P and N associated with some treatments can be considered to be specifically toxic or deficient, respectively. However, the declining soil pH imposed by the treatments was associated with changes in the total supply or activity of all elemental constituents. Specific changes with declining pH in the form or activity of a given element are unique to that element. These simultaneous, independent changes are further altered by interactions and equilibria within the changing chemical environment of the soil solution and with the chemically active surfaces of soil colloids.

Soil manganese serves as an indicator of declining soil pH. This is probably due to its dynamic redox character which becomes very important below pH 5.0. Plant content of Mn may be a more sensitive indicator of the changing nutritional status of the soil than is pH. However, by the time the Mn levels of a plant, growing in a natural soil, reaches levels known to be toxic by nutrient solution studies, it is unlikely that excess Mn is solely responsible for the associated poor state of health of the plant. It is simply symptomatic of a generally unfavorable nutritional environment, involving the deficiency, toxicity or imbalance of a whole suite of mineral nutrients.

Thus these data suggest no straightforward explanations for the reduced plant growth observed in association with acidifying nitrogen fertilizers and low soil pH.

RESULTS AND DISCUSSION:

2. SEASONAL FLUCTUATIONS IN SOIL TESTS

Tables 2 and 5 both present values for soil pH for the year 1967. Yet parts of the two tables do not agree. Table 2 contains values for samples taken on September 28 while data in Table 5 are for samples taken on July 31. Similar discrepancies in lime requirement data for these two samplings are apparent in Tables 3 and 5.

These apparent discrepancies were not due primarily to random variation in sampling or analysis. Tables 20 to 25 record analytical data obtained for periodic samplings made throughout the season. These may be compared usefully with rainfall distribution in Figure 3 and with the seasonal distribution of ammonium and nitrate in limed and unlimed plots in Figures 4 to 7.

Soil pH

Soil pH values for the four selected treatments which were sampled periodically are given in Table 20. There was less variation during the season on plots which received only basal fertilizer than on those receiving supplemental N fertilizer.

Table 20. Effect of nitrogen carriers and lime on seasonal variation of soil pH in the plow layer in 1967

Treatment		Date										
		5/10	5/31	6/7	6/14	6/21	7/5	7/19	7/31	8/23	9/28	10/25
Basal fertilizer	No lime	5.8	5.7	5.3	5.6	5.6	5.7	5.5	5.8	5.7	5.4	5.8
	Lime	6.7	6.7	6.6	6.7	6.6	6.8	6.8	6.8	6.7	6.7	7.0
$Ca(NO_3)_2$	No lime	5.8	5.2	5.0	5.2	5.0	5.2	5.3	5.5	5.3	5.4	5.6
	Lime	6.8	6.4	6.3	6.1	6.2	6.3	6.4	6.4	6.3	6.6	7.0
NH_4NO_3	No lime	4.8	4.4	4.4	4.4	4.2	4.3	4.0	4.1	3.9	4.0	4.4
	Lime	6.1	5.9	5.5	5.8	5.6	5.7	5.6	5.7	5.4	5.8	6.3
$(NH_4)_2SO_4$	No lime	4.2	4.1	3.9	4.0	4.0	4.0	3.9	3.8	3.7	3.5	3.7
	Lime	5.6	5.4	5.5	5.4	5.1	5.0	5.0	5.1	4.8	5.4	5.7

Table 21. Effect of nitrogen carriers and lime on seasonal variation of lime requirement in the plow layer in 1967

Treatment		Date										
		5/10	5/31	6/7	6/14	6/21	7/5	7/19	7/31	8/23	9/28	10/25
							ppt[3]					
Basal fertilizer	No lime	1.5	1.5	1.8	1.8	1.8	2.2	1.8	2.0	2.2	1.8	2.2
	Lime	.8	.8	.8	.5	1.5	-[1]	-	-	.8	.8	-
$Ca(NO_3)_2$	No lime	1.5	1.8	1.8	2.5	1.8	2.2	1.5	1.8	1.8	2.2	2.5
	Lime	-	.5	.5	.5	.8	-	-	-	.5	-	-
NH_4NO_3	No lime	4.5	3.8	4.5	4.5	3.5	3.8	3.2	4.2	5.0[2]	4.4	4.2
	Lime	1.2	1.2	1.5	1.5	1.2	1.2	1.2	1.5	1.5	1.5	1.5
$(NH_4)_2SO_4$	No lime	5.0[2]	5.0[2]	5.0[2]	4.0	4.5	3.8	4.2	5.0[2]	5.0[2]	5.0[2]	4.5
	Lime	2.5	1.5	1.8	1.5	2.2	2.2	1.5	2.0	1.5	1.5	1.5

[1] Buffer pH values above 6.9 were ignored

[2] Maximum value reported was 5.0

[3] ppt = parts per thousand (tons per acre for 7 inch plow layer)

Table 22. Effect of nitrogen carriers and lime on seasonal variation of exchangeable potassium in the plow layer in 1967

Treatment		Date										
		5/10	5/31	6/7	6/14	6/21	7/5	7/19	7/31	8/23	9/28	10/25
							pp2m					
Basal fertilizer	No lime	246	235	226	240	224	182	178	174	173	157	190
	Lime	250	282	266	282	252	209	190	197	173	146	182
$Ca(NO_3)_2$	No lime	250	278	238	266	244	182	151	151	145	132	146
	Lime	242	286	247	239	236	186	159	155	149	143	135
NH_4NO_3	No lime	164	196	156	163	171	155	163	174	145	124	129
	Lime	219	239	191	228	217	166	132	128	125	118	135
$(NH_4)_2SO_4$	No lime	148	152	136	140	136	140	151	147	165	146	131
	Lime	171	184	183	173	173	124	109	102	106	93	106

Table 23. Effect of nitrogen carriers and lime on seasonal variation of exchangeable calcium in the plow layer in 1967

Treatment		Date										
		5/10	5/31	6/7	6/14	6/21	7/5	7/19	7/31	8/23	9/28	10/25
							pp2m					
Basal fertilizer	No lime	814	923	898	1303	951	773	597	863	568	486	562
	Lime	1152	1364	1152	1739	1390	1304	1127	1391	882	881	881
$Ca(NO_3)_2$	No lime	983	1275	1237	1444	1652	863	1128	1128	725	723	482
	Lime	1489	2035	1955	2043	2000	1826	1566	1913	1274	1275	1196
NH_4NO_3	No lime	218	409	218	863	508	329	240	329	254	91	170
	Lime	729	981	729	1479	952	952	686	952	646	644	408
$(NH_4)_2SO_4$	No lime	39	39	171	686	508	329	150	240	175	91	91
	Lime	389	930	729	1103	927	686	775	952	646	648	486

Table 24. Effect of nitrogen carriers and lime on seasonal variation of exchangeable magnesium in the plow layer in 1967

Treatment		Date										
		5/10	5/31	6/7	6/14	6/21	7/5	7/19	7/31	8/23	9/28	10/25
							pp2m					
Basal fertilizer	No lime	98	86	108	85	107	99	106	92	105	114	100
	Lime	215	214	215	213	242	235	228	242	213	234	213
$Ca(NO_3)_2$	No lime	87	50	65	58	57	35	57	43	85	58	50
	Lime	151	178	157	157	170	156	149	149	98	150	143
NH_4NO_3	No lime	36	29	36	14	42	43	50	28	59	43	31
	Lime	187	228	243	256	270	242	249	256	241	255	220
$(NH_4)_2SO_4$	No lime	15	22	22	14	28	28	14	14	39	36	36
	Lime	179	257	293	335	350	264	314	328	398	345	220

Table 25. Seasonal variation of sulfate-S in the plow layer on ammonium sulfate treated plots without lime

Date	Sulfur
1967	ppm
5/10	1.8
5/31	15.8
6/7	21.8
6/14	20.0
6/21	21.8
7/5	12.5
7/19	15.0
7/31	16.8
8/23	24.2
9/28	10.3
10/25	7.3

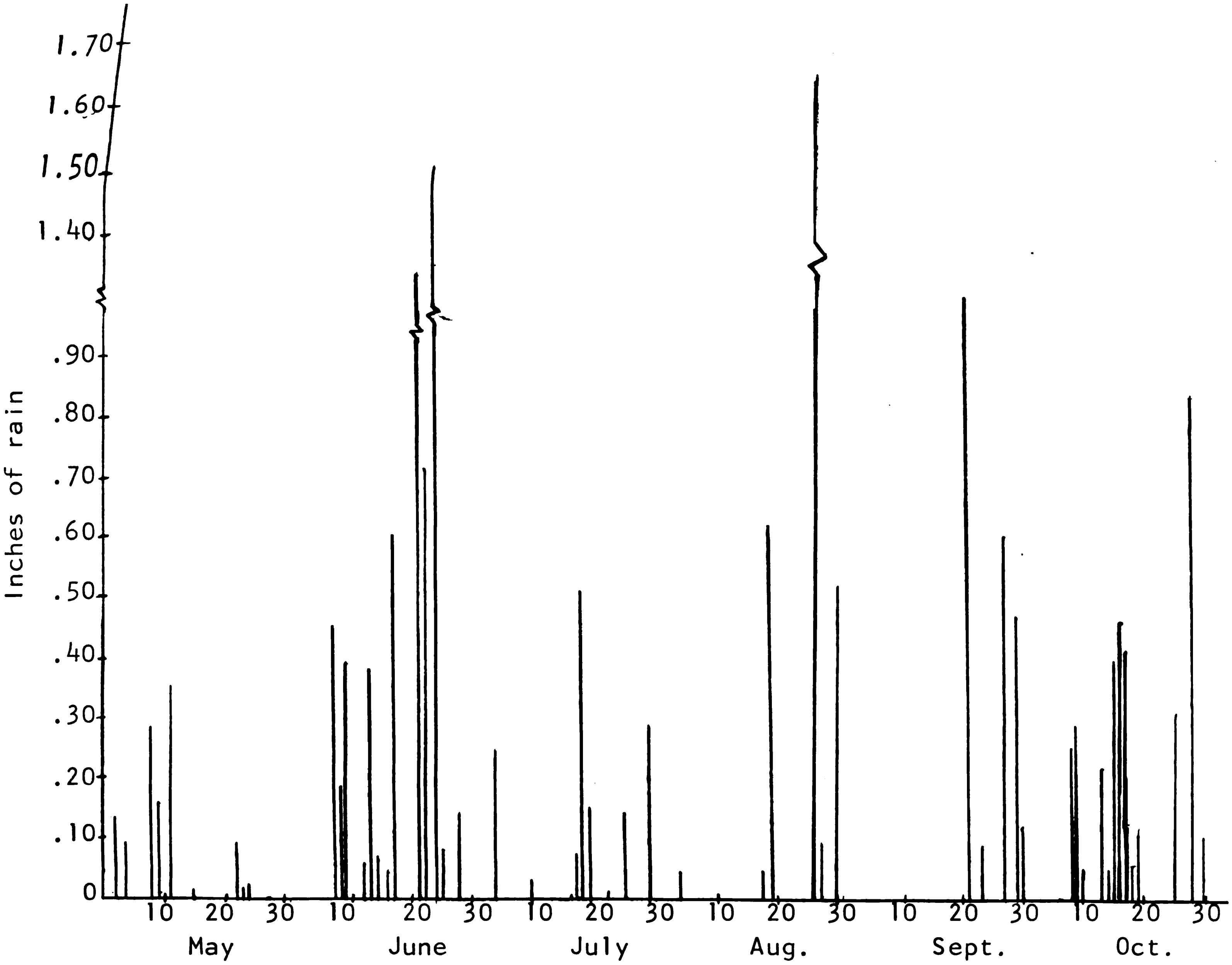


Figure 3. Rainfall distribution for summer 1967, East Lansing, Michigan

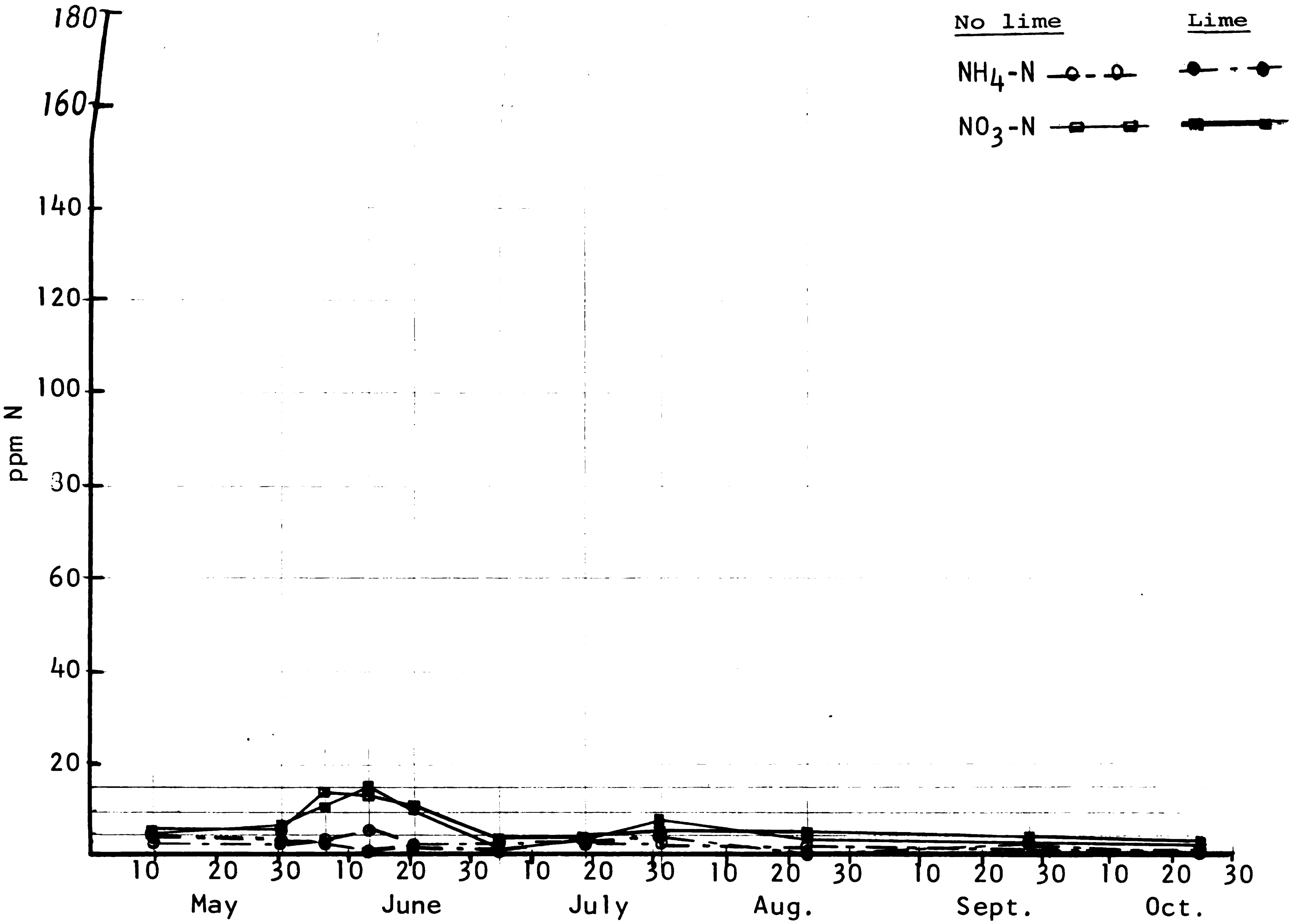


Figure 4. Seasonal fluctuation of ammonium and nitrate nitrogen on soil receiving only basal fertilizer

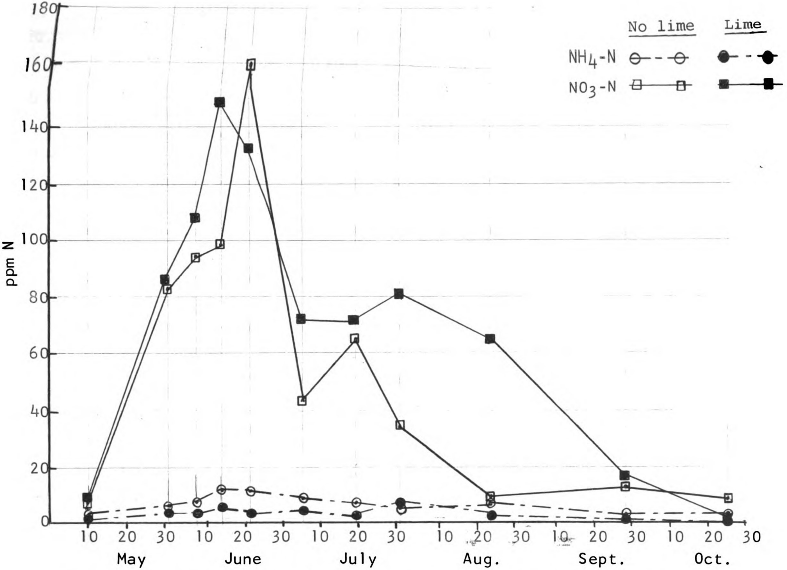


Figure 5. Seasonal fluctuation of ammonium and nitrate nitrogen on calcium nitrate treated soil

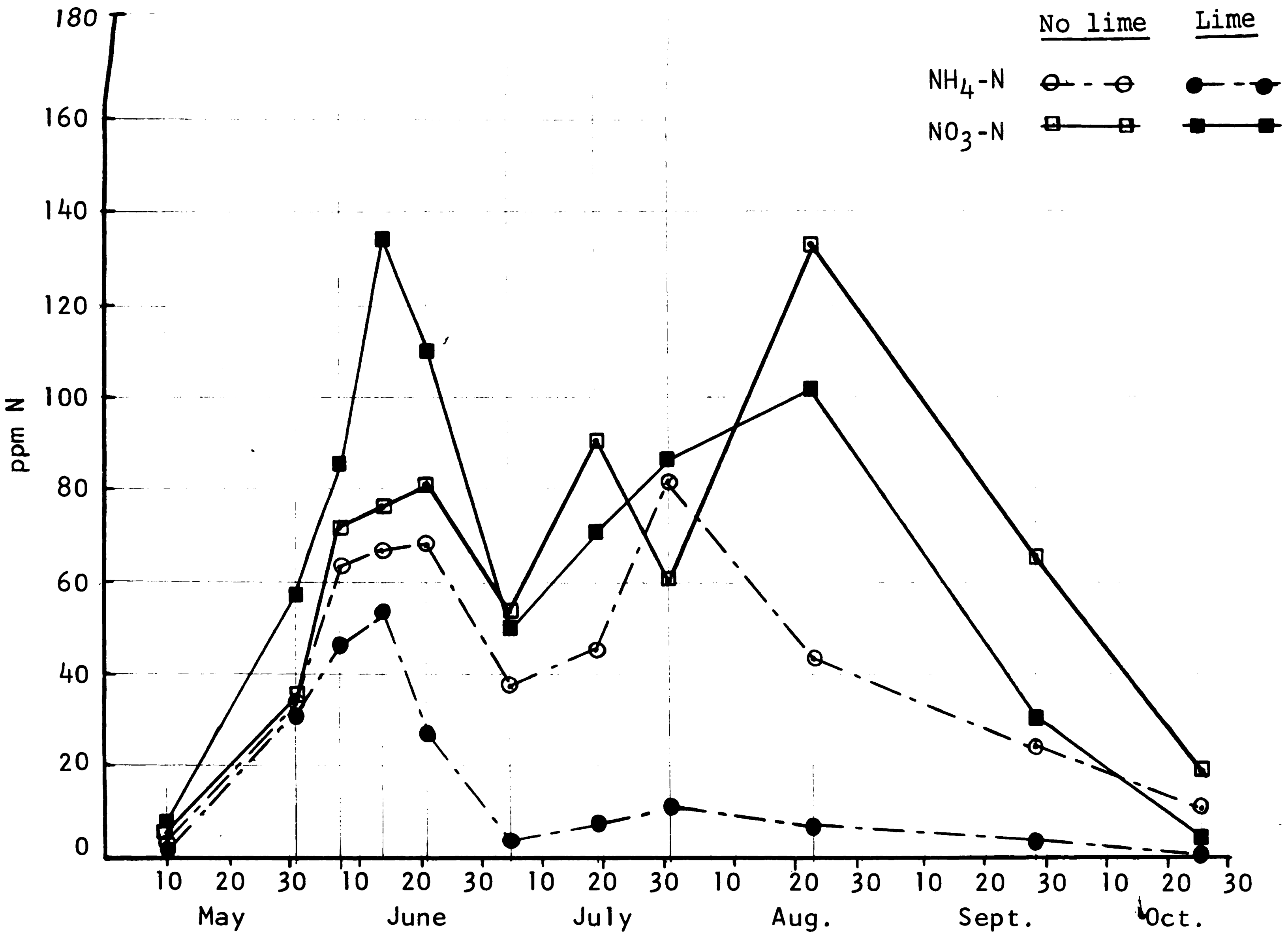


Figure 6. Seasonal fluctuation of ammonium and nitrate nitrogen on ammonium nitrate treated soil

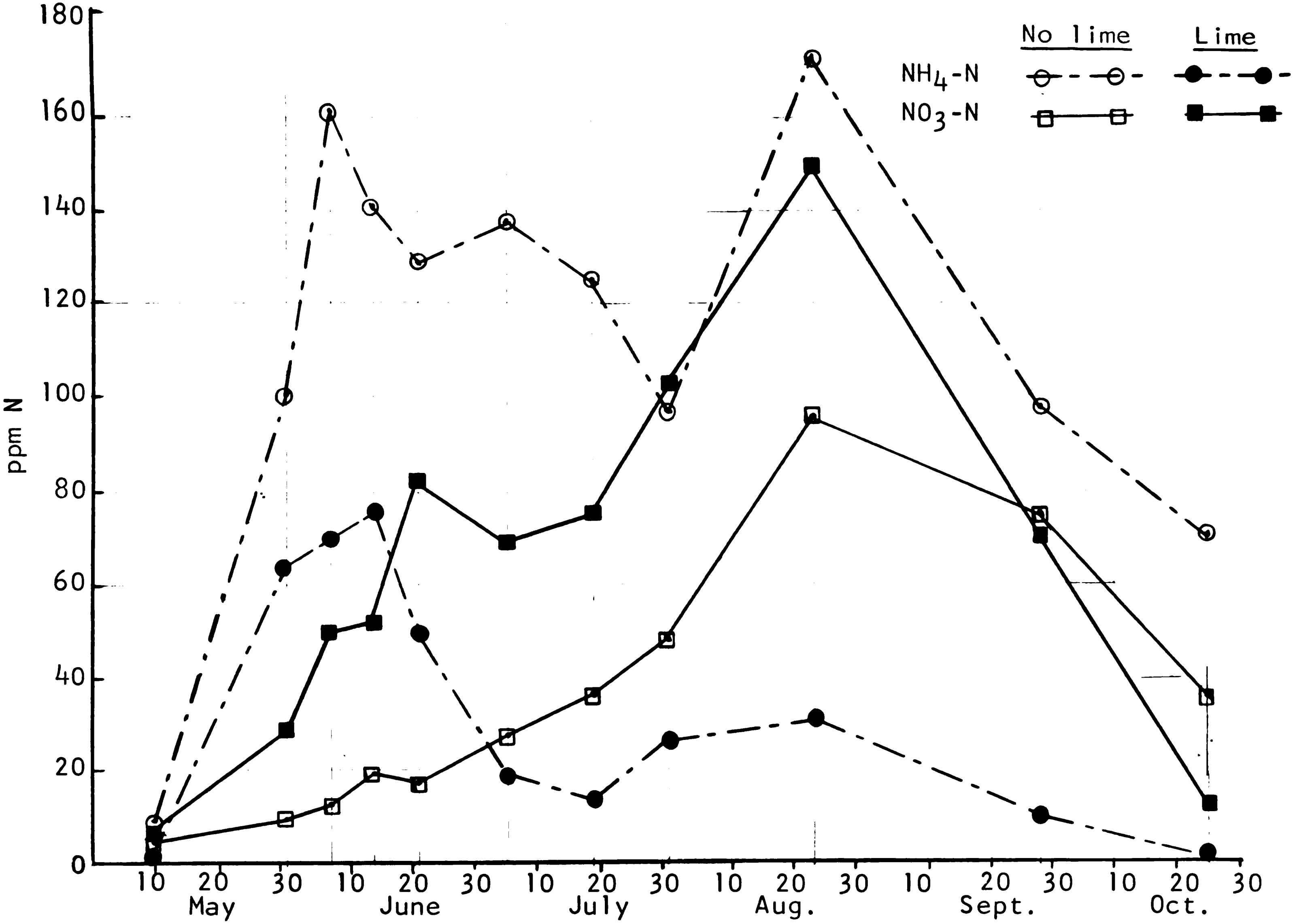


Figure 7. Seasonal fluctuations of ammonium and nitrate nitrogen on ammonium sulfate treated soil

The first samples were taken on May 10, just before the supplemental nitrogen materials were applied on the surface and disced in prior to planting corn. With all treatments, except the limed basal fertilizer, there was a sharp drop in pH over the next two samplings. This is the usual "salt effect" due to displacement of exchange acidity by fertilizer cations. The numerical decrease in pH was greater for calcium nitrate and unlimed basal fertilizer than for either ammonium nitrate or ammonium sulfate. However, actual displacement of exchangeable H^+ into solution was much greater for the ammonium carriers because the pH range was an order of magnitude lower.

It took four to five weeks for this salt effect to express itself fully. This is the time required for the surface applied fertilizers to approach an equilibrium with the bulk of the soil. This is apparent from the increasing recoveries of sulfate in Table 25 and of nitrate and/or ammonium in Figures 5, 6, and 7 over this same period.

Later pH fluctuations followed rather closely the seasonal fluctuations in nitrate and sulfate.

Soil Nitrate

With the basal fertilizer treatment (Figure 4) negligible quantities of nitrate accumulated and only minor variations in soil pH were encountered.

With supplemental nitrogen treatments, large fluctuations in nitrate after the initial peak in June were clearly related to two main factors: (1) crop removal, and (2) the distribution of rainfall.

With $Ca(NO_3)_2$ and NH_4NO_3 in Figures 5 and 6, there was a rapid disappearance of nitrate from the plow layer after the initial peak in June. This coincides with the period of rapid vegetative growth and rapidly increasing demand for nutrients by corn. It also occurred during a period of frequent and moderately heavy rains in 1967 (Figure 3).

In the case of $(NH_4)_2SO_4$, the June peak in nitrate and the succeeding draw-down period was clearly expressed only in limed plots because nitrification and plant removal was very greatly retarded at the low pH of the unlimed plots (Fig. 7).

Later seasonal peaks of nitrate accumulation occurred during July or August. This was a long, droughty period when scattered light rains served to maintain capillary contact with the surface and promote mass flow of water and solutes from the subsoil into the plow layer.

These later peak accumulations of nitrate were much reduced by crop removal in $Ca(NO_3)_2$ plots (Figure 5). They were greatly exaggerated in NH_4NO_3 and $(NH_4)_2SO_4$ plots.

Crop removal was less with these two carriers, particularly on unlimed plots where stands and vigor of corn were severely reduced.

However, reduced crop removal cannot account for totals of NH_4^+ and NO_3^- encountered in these plots in August. In the unlimed $(NH_4)_2SO_4$ plots, the total NH_4^+ plus NO_3^- in the surface 10 inches on August 23 was equivalent to 760 pounds of N per acre (2 x (173 + 95) x 10/7). In NH_4NO_3 plots without lime, the total was 510. Only 300 pounds was applied in 1967. It must be assumed that large quantities of nitrate and ammonium had been retained in the subsoil from previous years and had moved with capillary water into the plow layer.

After the August 23rd sampling, nitrate declined with all carriers to the end of the season. Here disappearance must be ascribed principally to leaching by heavy rains on August 27 and September 21 and by the frequent rains which followed through the cold month of October. As will be shown in a later section (p. 156), large accumulations of nitrate were encountered in the subsoil to a depth of 20 inches on October 25, with evidence that additional quantities had leached to greater depths.

Soil Sulfate

The seasonal distribution of sulfate in unlimed ammonium sulfate plots (Table 25) showed the same relationship to rainfall pattern as did nitrate on other plots. Its fluctuations followed very closely those of ammonium in the same plots (cf. Figure 7). As in the case of nitrate, on October 25 there was evidence of downward displacement of sulfate into the subsoil (p. 156).

Extractable Ammonium

As noted in the previous paragraph, ammonium fluctuations in unlimed $(NH_4)_2SO_4$ plots followed very closely the seasonal fluctuations in sulfate. In unlimed NH_4NO_3 plots (Figure 6), fluctuations in ammonium tended to follow fluctuations in nitrate.

In the section on soil nitrate (p. 114) it was observed that total mineral N in the plow layer (0-10 inches) in August exceeded by a factor of approximately 2 the actual 1967 application of N in these two carriers. Is the assumption that this apparent excess must have moved upward from the subsoil by capillarity unfounded? These apparent recoveries may have been analytical artifacts.

Several independent observations argue against such gross analytical errors.

In plots receiving only basal fertilizer (Figure 4), ammonium levels rarely exceeded 2 or 3 ppm, a characteristic level for cultivated soils (13).

In $Ca(NO_3)_2$ plots (Figure 5), ammonium levels during the June flush of microbial activity were somewhat higher, notably in unlimed soil. This is consistent with the much higher yield history and higher N content of corn residues (cf. Table 10) associated with this treatment as compared with the basal fertilizer control. Organic sources of N in the soil would be quantitatively greater and ammonification rates higher when soil temperatures become favorable for microbial activity in the early part of the summer.

There is no evidence of extremely erratic fluctuation during the initial equilibration period when NH_4^+ and NO_3^- were increasing precipitously to the first season peak in June. Nevertheless, totals for NH_4^+ -N plus NO_3^--N in the 10-inch plow layer of unlimed plots at the time of the June peak in Figures 5, 6, and 7 were 496, 420 and 496 for $Ca(NO_3)_2$, NH_4NO_3 and $(NH_4)_2SO_4$, respectively. In limed plots these totals were 453, 537, and 368 pounds N per acre.

In the case of the $Ca(NO_3)_2$ plots, up to 40 pounds of N might have been contributed to this total by mineralization of organic matter (2% organic matter containing 5% N ammonified at the rate of 2% per year). The contribution from organic sources would have been less in NH_4NO_3 and $(NH_4)_2SO_4$ plots because of much lower corn yields and rate of residue return in previous years and the unfavorably low pH for rapid decomposition.

This leaves unaccounted for in these June peaks up to 200 pounds of N per acre for the limed NH_4NO_3 plot (537 lbs. total less 40 lbs. mineralized less 300 lbs. applied).

Errors of this magnitude are not inherent in the distillation procedure used for NH_4^+ and NO_3^-.

It must be assumed that substantial quantities of ammonium and/or nitrate moved into the plow layer from subsoil horizons. The long dry period between May 11 and June 7 would have promoted extensive upward movement of water and solutes by capillarity (Figure 3).

Ammonium could have moved upward in company with chloride, nitrate or sulfate (cf. Table 25). Nitrate could have moved up in association with ammonium or any number of soil cations including K, Ca, Mg, and hydronium complexed with Al or Fe.

In the sections which follow it will appear that mobility of Ca was closely associated with mobility of nitrate and sulfate in both limed and unlimed soils. Magnesium may have contributed to anion mobility in limed soils. Downward movement of K may have been associated with downward movement of nitrate or sulfate, but there was little evidence of upward movement back into the plow layer. In very acid soils there was evidence that components of buffer acidity (lime requirement) moved extensively in both directions in association with nitrate and sulfate.

Exchangeable Calcium

Data for exchangeable Ca in Table 23 show an early season increase to seasonal maxima in the period from June 7 to June 21. This increase is less marked for limed plots of $Ca(NO_3)_2$ amd the basal fertilizer than for other treatment combinations. The increase on unlimed $(NH_4)_2SO_4$ plots is dramatic and parallels the increase in sulfate over the same period (Table 25). In the case of unlimed $(NH_4)_2SO_4$ and both limed and unlimed plots of $Ca(NO_3)_2$ and NH_4NO_3, the seasonal peak in exchangeable Ca coincided with the June peak in soil nitrate (cf. Figures 5, 6 and 7).

Immediately after the June 21 sampling, a total of 3.56 inches of rain fell over a period of four days, and this was followed by humid weather and light rains totaling 0.5 inches just prior to the July 5 sampling (Figure 3). Nitrate and sulfate moved extensively out of the plow layer (cf. Table 25 and Figures 5, 6 and 7). Disappearance of these anions was accompanied by sharp decreases in exchangeable Ca, notably in unlimed soils (Table 23).

Further declines in exchangeable Ca were associated with the massive disappearance of nitrate from all supplemental nitrogen plots after August 23.

Exchangeable Magnesium

Seasonal fluctuations in exchangeable Mg (Table 24) in plots which received basal fertilizer only, or $Ca(NO_3)_2$, were not great and appeared to be random. The same was true for the much lower levels found in unlimed plots of NH_4NO_3 and $(NH_4)_2SO_4$.

In limed plots of these two strongly acid carriers, however, there was a distinct early season rise to a maximum on June 21, similar to that observed for exchangeable Ca. Whether this increase was due to movement from the subsoil or to dissolution of dolomite cannot be said with any certainty. However, levels found on July 5 were distinctly lower, which suggests that some magnesium may have accompanied nitrate or sulfate into the subsoil. A sharp decrease in exchangeable Mg in the last sampling (October 25) also suggests downward movement out of the plow layer and is consistent with the subsoil enrichment actually observed on this date (p. 163).

Exchangeable Potassium

There was not evidence of movement of exchangeable K (Table 22) from the subsoil into the plow layer during the May-June period of nitrate and sulfate accumulation. A sharp drop in level of K in the July 5 sampling for most treatments, and again at the end of the season for the unlimed NH_4NO_3 and $(NH_4)_2SO_4$, suggests that downward movement may have occurred in these very acid soils. (Subsoil enrichment was not as clearly expressed on October 25, however, as was true for magnesium (p. 163)).

The decrease in soil K between June 21 and July 5 was only of the order of 40 to 60 pounds. This would represent a reasonable level of uptake by corn during this period of growth. There was essentially no change in unlimed $(NH_4)_2SO_4$ plots where there were only a very few stunted plants and a change of only 16 pounds in unlimed

NH_4NO_3 plots where stands and growth were also restricted, though not as severely.

Thus the decrease in exchangeable K at this time was more likely due to uptake rather than leaching. This would not have been true for decreases observed at end of the season.

Plant uptake certainly contributed also to in-season disappearance of nitrate and exchangeable Ca and Mg. However, the quantities of nitrate and calcium which disappeared greatly exceeded any reasonable level of uptake.

Lime Requirement

In general, seasonal variations in lime requirement (Table 21) appeared to be random. However, the values for the unlimed plots of NH_4NO_3 and $(NH_4)_2SO_4$ show a mid-season drop followed by an increase to maxima in August which tend again to drop off in the last sampling. This pattern follows those for nitrate (Figures 6 and 7) and sulfate (Table 25).

These data lend support to the view that components of buffer acidity at low pH are highly mobile if suitable anions are present to accompany them in the soil solution.

The dominant cationic components of buffer acidity are generally considered to be hydrated Al-hydronium complexes. However, soil tests in this study showed Fe to be much more readily extracted than Al. During dry weather, iron was deposited in striking, dark brown, cemented crusts on the surface of plots where soil pH was below 5.0.

Cationic species of iron were certainly associated to a significant extent with the observed mobility of nitrate and sulfate. It appears likely that hydronium complexes with Fe rather than Al may have dominated the mobile components of buffer acidity (lime requirement) in the soil of this experiment.

Soil Phosphorus

Soil phosphorus data for this seasonal study are not given. Variation over the season was less than 20 pounds from the respective mean values for the basal fertilizer, NH_4NO_3 and $(NH_4)_2SO_4$ plots. Where $Ca(NO_3)_2$ was applied, the variation was greater but still appeared to be at random. It appeared that the calcium added with the carrier altered phosphate equilibria and the larger fluctuations reflected adjustments to this addition.

Implications of Seasonal Study

The observed mobility of calcium was greater than for magnesium or potassium. This may have been only a superficial observation. Continuing release from decomposing primary and secondary minerals may have served to mask movement of K and Mg.

The great mobility of calcium associated with nitrate and sulfate would lead one to expect that large losses of calcium could have occurred from the lime applied two years earlier. However, by no stretch of the imagination could it be supposed that the 12 tons per acre applied on the $(NH_4)_2SO_4$ plots had been depleted to the same level as in the unlimed basal fertilizer plots. Yet the levels of exchangeable Ca were essentially the same (Table 23). By contrast, levels of exchangeable Mg were 2 to 3 times higher (Table 24). Similar relationships hold for the limed NH_4NO_3 plots.

It may be suggested that this low recovery of exchangeable Ca from very acid soils after liming was a laboratory artifact. However, the fact that soil pH and nutritional restrictions on corn yields had not been corrected argues against this.

It is possible that some complexing mechanism, rather specific for Ca, was operating to block its release from dolomite or to inactivate it after release. On the other hand, the lime inactivating mechanism may have been merely the precipation of soluble iron compounds in the alkaline vicinity of lime particles, with the result that the lime has become embedded in iron concretions. Investigations regarding the latter proposal were not carried out.

RESULTS AND DISCUSSION

3. Incubation Studies

Two incubation experiments were conducted to observe nitrification rates in soils taken from the field experiment. In the first experiment, soils from every plot were used. In the second experiment, samples from the two replicate plots of six selected treatments were used.

Samples for the first incubation were taken July 31; those for the second incubation were taken September 28, 1967. Ammonium and nitrate in the soils at sampling time are shown in Tables 26 and 27.

In the July sampling (Table 26), very high levels of ammonium and total mineral nitrogen were present in unlimed soils from plots receiving NH_3 and the three ammonium salts. The levels were still high for NH_3 and $(NH_4)_2SO_4$ in September (Table 27). The unusually high values for unlimed NH_3 were due to the fact that one of the plots received 300 pounds per acre of N, as urea, by mistake in May, in addition to the same amount of N, as NH_3, in June.

Total mineral nitrogen for several treatments exceeded the 10.5 mg N per 100 g soil which would be equivalent to 300 pounds N per acre distributed through the 10 inch plow layer. Probable reasons for this have been discussed in a previous section (p. 116).

Table 26. Ammonium and nitrate in the plow layer (0-10") on July 31, 1967

Carrier #	Ammonium		Nitrate		NH_4^+ plus NO_3^-	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	mg N/100 g		mg N/100 g		mg N/100 g	
No fertilizer	.3	.4	.3	1.0	.6	1.4
Basal fertilizer	.3	.5	.5	.9	.8	1.4
$NaNO_3$	.8	.4	7.8	6.4	8.6	6.8
$Ca(NO_3)_2$	.5	.5	3.5	8.1	4.0	8.6
NH_3	29.8	5.8	7.3	5.1	37.1	10.9
Urea	2.0	.7	4.6	7.5	6.6	8.2
Ureaform	.9	.5	3.1	2.6	4.0	3.1
NH_4NO_3	8.1	1.2	6.0	8.6	14.1	9.8
NH_4Cl	9.4	3.7	3.6	9.3	13.0	13.0
$(NH_4)_2SO_4$	9.7	2.6	4.8	10.6	14.5	13.2
Lime means	6.2	1.6##	4.2	6.0*	10.4	7.6

*Lime effect significant at 5 percent
##No significant effect of lime
#No significant effect of carriers

Table 27. Ammonium and nitrate in the plow layer (0-10") on September 28, 1967

Carrier	Ammonium		Nitrate		NH_4^+ plus NO_3^-	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	mg N/100 g		mg N/100 g		mg N/100 g	
Basal fertilizer	.1	.2	.4	.5	.5	.7
$Ca(NO_3)_2$	.3	.2	1.3	1.8	1.6	2.0
NH_3	10.3	1.6	7.0	7.2	17.3	8.8
Urea	2.5	.4	5.0	7.4	7.5	7.8
NH_4NO_3	2.4	.4	6.6	3.3	9.0	3.7
$(NH_4)_2SO_4$	9.7	1.1	7.6	7.1	17.3	8.2
Lime means#	4.2	.6	4.7	4.5	8.9	5.1
$LSD_{.05}$ for carriers	NS	NS	6.1	6.1	-	-

#Effects of lime not significant

Incubation Experiment I

It had been the intent to bring all samples to a common ammonium level before incubation. Errors in calculation resulted in the initial ammonium concentrations shown in Table 28.

For comparing treatment effects, ammonium and nitrate recovered after a two week incubation were converted to percentages of initial mineral N. The data confirm the field observation that nitrification was greatly retarded in unlimed acid soils. In soils which had been limed, there were no effects of carriers on the net disappearance of ammonium.

The retardation of nitrification in unlimed soil with ureaform was much less than would have been expected. The pH of this soil was as low as for the urea or NH_4NO_3 plots. This retardation may be attributed to the continuing release of NH_3 which serves to maintain a pH more favorable to the nitrifiers in the immediate microenvironment of the slowly hydrolyzing ureaform particles. The hydrolysis of ureaform during the incubation resulted in a 40 percent increase in total mineral nitrogen. This was equivalent to about 60 pounds per acre, or 1/5 of the annual application of ureaform nitrogen in this experiment.

In contrast with this net mineralization release of N from ureaform, 25 percent of the ammonium which disappeared

Table 28. Changes in mineral N (NH_4^+ and NO_3^-) during two weeks' incubation in Experiment I

Carrier	Initial ammonium[2]		Percent of initial mineral N[1] present after incubation as				Change in mineral N during incubation	
			Ammonium		Nitrate			
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	mg N/100 g		%	%	%	%	%	%
No fertilizer	4.5	4.6	13	8	97	88	+10	-4
Basal fertilizer	4.5	4.7	10	4*	96	100	+6	+5
$NaNO_3$	4.9	4.4	4	4	92	102	-3	+6
$Ca(NO_3)_2$	4.7	4.6	6	3	95	101	+1	+4
NH_3	31.4	8.8	32	3*	75	112*	+7	+15
Urea	5.8	4.8	26	3*	81	99*	+7	+1
Ureaform	5.0	4.6	12	6*	128	139*	+40	+44
NH_4NO_3	10.6	5.2	26	3*	49	104*	-25	+7
NH_4Cl	11.6	7.2	76	3*	26	101*	+1	+5
$(NH_4)_2SO_4$	11.9	6.3	67	2*	29	104*	-3	+5
Lime means#	9.5	5.5	27	4	77	105	+4	+9
$LSD_{.05}$ for carriers	NS	NS	10.1	NS	19.5	19.5	21.2	21.2

[1] Initial mineral N included soil NH_4^+, soil NO_3^-, and NH_4^+ added as $(NH_4)_2CO_3$

[2] Initial ammonium after adding $(NH_4)_2CO_3$. Error in calculated addition was responsible for non-uniform starting levels.

*Lime effect within carrier significant at 5 percent.

#No significant average effect of lime.

Table 29. Changes in mineral nitrogen and evolution of CO_2 during two weeks'

Table 29. Changes in mineral nitrogen and evolution of CO_2 during two weeks' incubation in Experiment II

Carrier	Decrease in ammonium[1]		Increase in nitrate		Change in mineral N during incubation		CO_2 evolution	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	mg N/100 g		mg N/100 g		%	%	mg C/100 g	
Basal fertilizer	6.0	8.3*	5.0	6.8*	-10	-16	18	15
$Ca(NO_3)_2$	5.5	8.2*	4.9	7.6*	-6	-6	21	22
NH_3	3.5	8.1*	2.8	6.8*	-4	-9	22	25
Urea	2.6	8.3*	1.6	6.6*	-7	-10	7	17
NH_4NO_3	0.6	8.4*	0.3	6.7*	-2	-14	14	25
$(NH_4)_2SO_4$	0.0	8.0*	-.9	5.4*	-5	-16	2	21
Lime means	3.0	8.2*	2.3	6.6*	-6	-12	-	-
$LSD_{.05}$ for carriers	1.34	NS	1.37	1.37	NS	NS	-	-

[1] Ammonium N in field samples was augmented with $(NH_4)_2CO_3$ to give 9.0 mg/100 g NH_4^+-N at the beginning of incubation.

*Lime effects significant at 5 percent.

from the unlimed NH_4NO_3 soil failed to appear as nitrate. This cannot be ascribed to microbial immobilization or denitrification because of the low organic matter content of the soil. It could have been due to loss of N_2 or N_2O from reactions of nitrous acid which is an intermediate in nitrification and unstable at low pH. If this were true, there is no apparent reason why it should not have occurred also at the even lower pH of the NH_4Cl and $(NH_4)_2SO_4$ soils.

Incubation Experiment II

In the second incubation experiment, soils were incubated in glass jars so that CO_2 could be collected in alkali as a measure of general microbial activity. The data are presented in Table 29.

All soils were adjusted to a common initial ammonium level, except for soil from the one erratic NH_3 plot which contained 18 mg. N per 100 g.

The essential relationships were the same as in the first incubation. Nitrification was increasingly inhibited as soil pH was lowered by acidifying carriers. Where lime had been applied, there were no differences in the extent to which ammonium disappeared in two weeks.

Notall of the ammonium coverted appeared as nitrate. Unlike the first experiment, there was a net loss of mineral nitrogen with all treatments. This may have been due to the presence of a greater concentration of fine root debris in the September samples. This would have promoted immobilization. However, there is no correspondence between the extent of N disappearance and the level of microbial activity as reflected in CO_2 evolution.

It is of interest to note that the unlimed $(NH_4)_2SO_4$ soil is approaching sterility as indicated by its failure to nitrify and the near absence of respiratory activity. This further reinforces observations made throughout this study that the effect of pH changes in the soil below pH 5.0 are of a much different nature than those changes taking place above pH 5.0.

RESULTS AND DISCUSSION

4. Mineralogical Studies

Cation Exchange Capacity

Cation exchange capacity and its dependency upon pH were estimated conductometrically after potentiometric titration in BaOAc buffer with $Ba(OH)_2$ or HOAc to equilibrium at various reference pH's. In the conductometric procedure described by Mortland and Mellor (56), CEC is estimated graphically from the intersection of the horizontal baseline, which represents displacement of exchangeable Ba by Mg, and the linear increase in conductivity resulting from concentration of the titrant $MgSO_4$ in solution after the exchange complex has been Mg saturated.

Barium chloride was used as a final saturating wash and disappearance of Cl^- in subsequent distilled water washes was used as the criterion for removal of soluble salts. With soils in this study, this criterion was not fully adequate. Insufficient washing and excessive washing with distilled water both resulted in baseline conductivities higher than the desired minimum. However, it was found that neither the slope or the horizontal displacement of the rising leg of the conductance curve varied appreciably with additional washing after chloride could no longer be detected with silver nitrate. To avoid the variability associated with floating baselines, the endpoint was estimated by extrapolating the rising leg of the conductance curve to zero.

Cation exchange values obtained in this way are presented in Table 30 for limed and unlimed soils from four selected field treatments. The range of values is not great, but consistent trends associated with treatment and equilibrium pH can be noted.

The exchange capacity decreased with decreasing equilibrium pH and decreasing pH associated with acidifying carriers. Such pH dependency is characteristic for organic matter and for amphoteric clay minerals such as allophane and to a lesser extent kaolinite.

However, it must be observed that the degree to which this relationship to soil pH was reversed by liming was very different for the different carriers and at different equilibrium pH's.

The largest increases in CEC after liming occurred with $Ca(NO_3)_2$ and basal fertilizer. These increases ranged from 0.4 to 0.9 me at equilibrium pH's of 5 to 8. With the two strongly acidifying carriers which had reduced soil pH in the field to the vacinity of 4.0, liming had had little effect. In fact, with these two carriers, as well as with $Ca(NO_3)$, liming tended to suppress exchange sites active at an equilibrium pH

Table 30. Effect of nitrogen carriers and lime on cation exchange capacity of plow layer and its pH dependence

Carrier	Equilibrium pH												
	8.0		7.0		6.0		5.0		4.0		Average		
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Overall
	CEC - me per 100 g												
Basal fertilizer	5.0	5.4	3.8	4.0	3.1	3.6	2.4	3.0	1.4	1.5	2.9	3.5	3.2
$Ca(NO_3)_2$	5.0	5.4	4.2	4.6	2.9	3.8	2.4	2.8	1.8	1.6	3.2	3.6	3.4
NH_4NO_3	4.8	4.9	4.0	3.6	2.4	2.6	1.4	1.8	1.6	1.4	2.8	2.9	2.8
$(NH_4)_2SO_4$	4.4	4.6	4.2	4.2	2.2	2.4	1.8	2.0	1.8	1.4	2.9	2.9	2.9
Average	4.8	5.1	4.0	4.1	2.6	3.1	2.0	2.4	1.6	1.5	3.0	3.2	3.1

of 4.0. It should be pointed out that the samples used here were taken in the spring of 1966, only one year after lime application. The pH values of the unlimed basal, calcium nitrate, ammonium nitrate and ammonium sulfate and the limed basal, calcium nitrate, ammonium nitrate and ammonium sulfate treated soils were 5.9, 5.8, 4.8, 4.4 and 6.5, 6.6, 5.4 and 4.5, respectively.

It would appear that long exposure to high rates of the two very strongly acidifying carriers has resulted in irreversible loss of pH dependent exchange materials which become active in the pH range of 5 to 6. As a result, one year after liming, the CEC of these soils was 0.8 and 1.2 me lower than in soils which had received basal fertilizer alone or with $Ca(NO_3)_2$. The difference was less at equilibrium pH's of 7 and 8.

(The determination of CEC at pH 7.0 was difficult to duplicate because the titration curve for $Ba(OH)_2$ vs HOAc is very steep in this region. Barium acetate is probably an inappropriate buffer for estimating CEC at pH 7.0 if the potentiometric method for barium saturation is used.)

The observed reduction in CEC with declining pH is a third factor contributing to the great mobility of cations observed in these soils and described in a later section

(p. 155-165). The roles of hydrogen ions formed during nitrification and the associated anions will be discussed at that time.

A question yet to be considered is: what is the nature and fate of exchange materials which appear to have been altered or removed in the process of soil acidification?

The apparent pH dependency suggests that they include organic matter and amphoteric clay minerals. Increases in activity of Al, Fe and Si were indicated by soil tests and foliar analysis and have been offered in evidence that crystalline clay minerals were also breaking down.

Clay Minerals

Figure 8 shows the x-ray diffraction pattern for clays isolated from the unlimed basal treated soil and the unlimed ammonium sulfate treated soil. X-ray patterns were also obtained from clays isolated from the unlimed ammonium nitrate and the limed ammonium sulfate plots but are not shown here. The soil samples were taken in the spring of 1966.

The peaks at 3.3 Å and 4.3 Å indicate the presence of quartz. Part of the quartz is in the sample, and part is contained in the device used to hold the clay during analyses.

The peaks at 3.2 and 3.8 Å are due to feldspars. The former may be due to any feldspar while the latter is usually due only to plagioclase feldspars.

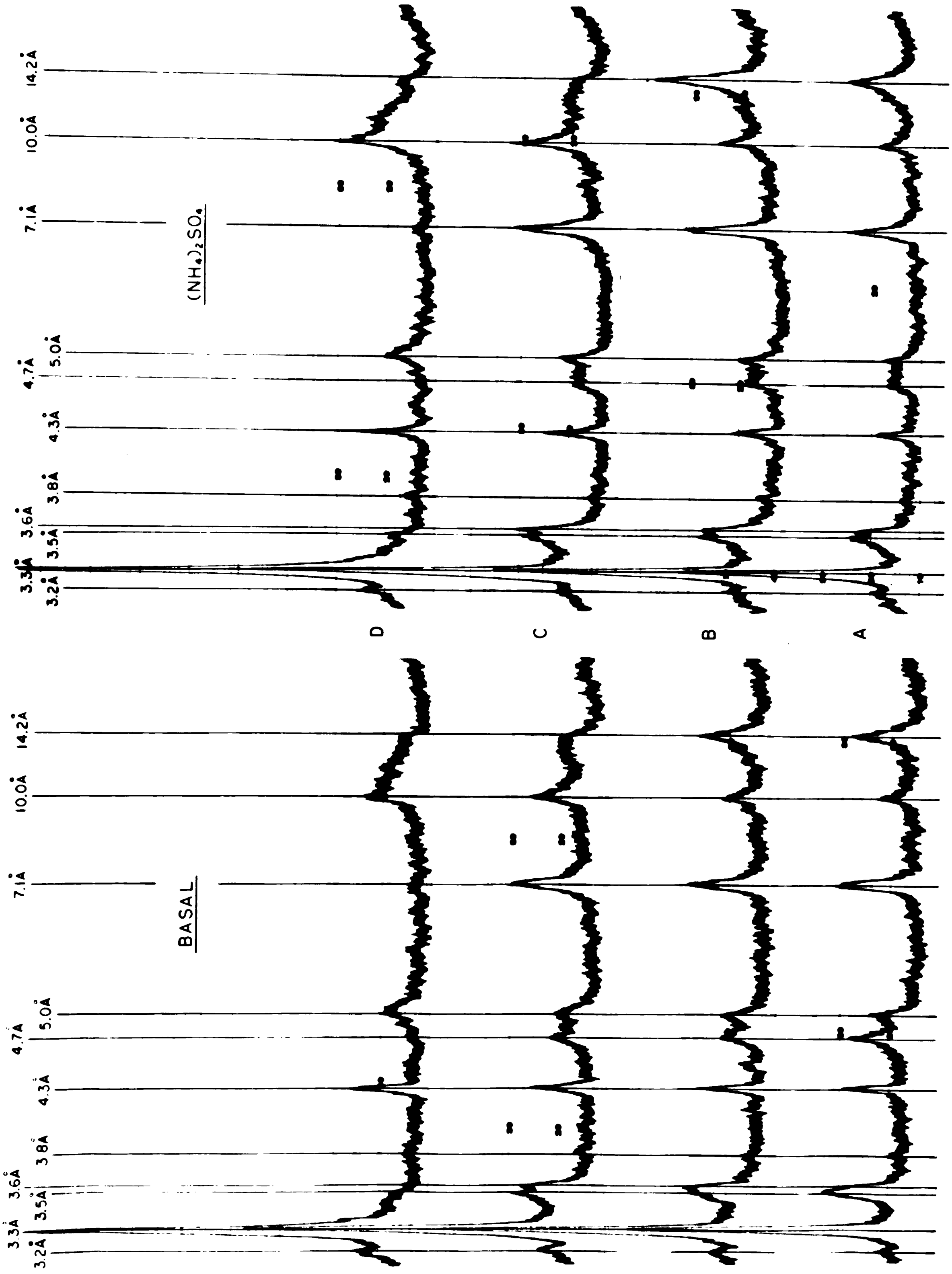
Table 31. Interpretation of x-ray peaks in the clay analyses

Peak at	Due to
14.2	001 chlorite 001 vermiculite (prior to heating to 330)#
10.0	001 illite 001 vermiculite (after heating to 330)
7.0	001 kaolinite (prior to heating to 550) 002 chlorite 002 vermiculite (prior to heating to 330)
5.0	002 illite 002 vermiculite (after heating to 330)
4.7	003 chlorite 003 vermiculite (prior to heating to 330)
4.3	quartz
3.8	plagioclase feldspars
3.5 and 3.6*	002 kaolinite (prior to heating to 550) 004 chlorite 004 vermiculite (prior to heating to 330)
3.3	quartz 003 illite 003 vermiculite (after heating to 330)
3.2	feldspars

*Reason for shadow at 3.6 not known

#Pure vermiculite will collapse without heating. Soil vermiculite usually requires heating.

Figure 8. X-ray diffraction tracings of oriented soil clay films from the unlimed basal and ammonium sulfate treated soils on porous ceramic plates. Treatments: A, Mg-saturated, glycerol-solvated, no heat treatment; B, K-saturated, no heat treatment; C, K-saturated and heated to 330 C; D, K-saturated and heated to 550 C. Scale of horizontal axis is linear for degrees 2θ. Vertical axis is radiation intensity at a scale factor of 8.


3.2Å
3.3Å
3.5Å
3.6Å
3.8Å
4.3Å
4.7Å
5.0Å
7.1Å
10.0Å
14.2Å
(NH₄)₂SO₄
BASAL
D
C
B
A

The lack of an 18 Å peak with magnesium saturation and glycerol solvation indicates a lack of montmorillonitic type clays.

The small 14.2 Å peak after the vermiculite shift indicates a small amount of discrete chlorite is present. The 10.0 Å peak before this shift shows the presence of illitic clays. The disappearance of the 7.1 Å peak after heating to 550 C indicates the presence of kaolinite.

The two peaks at 3.5 and 3.6 Å are not fully understood. A peak in this region is expected for the 1/2 cell unit height of kaolinite and should disappear after heating to 550 C. The 1/4 unit cell height of chlorite should remain or shifts slightly upon heating due to dehydration of the mineral. The reason for the double peak in some of the tracings is not understood.

The real significant difference between these two tracings is the vermiculite peak. The peak height for vermiculite both before and after the shift at 330 C, relative to the kaolinite peak, is greater where ammonium sulfate was applied than when only the basal fertilizer was applied. (This shift is due to the collapse of the plate from 14 Å to 10 Å. In pure vermiculite, K-saturation in water is sufficient to accomplish this, but in soil, hydrated Al and other cations between the plates require additional energy to remove the water before they collapse).

It was postulated from potassium levels in the soil (Table 7) that under acidic conditions illite was being converted to vermiculite (p. 57). The gain in vermiculite noted in Figure 8 provides some evidence for this. Whether this is a random occurrence or a treatment effect is difficult to decide since there is evidence supporting both alternatives.

Evidence that this is a treatment effect includes the following.

(1) The samples X-rayed are a composite from plots in the first and second block which would tend to reduce the influence of random field variation.

(2) The tracings for the unlimed ammonium nitrate and the limed ammonium sulfate plot showed vermiculite peak heights similar to the ammonium sulfate tracing shown in Figure 8. This would tend to support a real effect of acidic fertilizers.

(3) The failure of the tracing pattern to return to the base level between the 14.2 and 10.0 peaks indicates the presence of some random interstratified crystalline material. Some of these minerals may contain interlayer K and this may be the source of the vermiculite rather than discrete illite.

On the other hand, there is evidence that the conversion of illite to vermiculite is not occuring.

(1) The peak height for illite is not different between treatments.

(2) The illite content of these clays (based on a total K_2O analysis) was 31.8, 30.8, 32.3, and 30.3 percent for the unlimed basal, ammonium nitrate and ammonium sulfate and the limed ammonium sulfate treatments, respectively. A loss of illitic clays is not indicated by these data.

(3) A conversion of illite to vermiculite is accompanied by an increase in soil cation exchange capacity. Acidifying treatments decreased exchange capacity.

There is a difference in the vermiculite level of these soils. Differences of less than 5 percent are usually not detected by X-ray analysis. There is no evidence of changes in illite in either the illite peaks or in the K_2O analysis. But it is postulated here that the source of this vermiculite is the micas in the silt fraction of the soil. Under the acid soil conditions of this experiment, silt sized micas, if present, are being weathered. This would result in a release of potassium into the soil solution and the appearance of vermiculite. Not all of the silt sized mica would be weathered to vermiculite. Some would appear in the clay fraction of the soil as illite. It might be possible then that the illite level of the soil would be maintained and even increased slightly.

This should be accompanied by an increase in soil cation exchange capacity. However, this increase may be overshadowed by the changes in pH dependent buffering systems at these low pH values, resulting in a net loss in exchange sites.

Amorphous Material

Alumnium and silicon that becomes soluble when the clay fraction of the soil is boiled in sodium hydroxide, was determined on clays isolated from each of the eight treatments used in the cation exchange study. From these data the amount of allophane in the soil was estimated. The allophane content of these treatments varied from 11.5 to 13.7 percent, as indicated in the following table.

Table 32. Effect of nitrogen carriers and lime on sodium hydroxide soluble SiO_2 and Al_2O_3 and an estimation of allophane in the clay fraction of the soil

Carrier	SiO_2		Al_2O_3		Allophane	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	%	%	%	%	%	%
Basal	7.5	6.8	3.7	3.2	13.6	12.2
$Ca(NO_3)_2$	7.8	6.8	3.5	3.5	13.7	12.6
NH_4NO_3	7.4	6.4	3.2	3.2	12.8	11.5
$(NH_4)_2SO_4$	6.8	7.0	3.2	3.6	12.1	12.6

These data represent small and statistically nonsignificant changes. There validity in interpretation of what changes are occuring in the soil is supportive rather than conclusive. The fact that amorphous material classed as allophane was less in the more acid soils before liming is consistent with the observation that cation exchange materials which disappeared were pH dependent.

The implications of the altered distribution of amorphous Al and Si compounds after liming are not obvious. In all soils, the addition of lime would have promoted polymerization of any charged species of Al and Si that may have been present. The solubility in alkali of these polymerization products would reflect both the pH and the specific anion and cation populations of the environment in which the polymerization occurred.

Data in previous sections show that these genetic parameters were drastically different in soils subjected to these four fertilizer treatments, even after liming.

The differences in alkali extractable Al and Si in Table 32 for limed soils reflect these differences, although they give no clue to the specific nature of the chemical structures from which they came. Certainly, the Al and Si extracted from colloidal fractions of the limed NH_4NO_3 and $(NH_4)_2SO_4$ soils did not represent strongly allophanic structures because their cation exchange behavior showed but little dependency on pH in the range from 5.0 to 6.0 (Table 30).

Organic Matter

No attempt was made in this study to evaluate the role of organic fractions in cation exchange or any other phenomenon observed. No analyses for organic carbon or organic matter were made.

The organic matter content of this sandy loam soil is low, however, probably of the order of 2 percent in the surface layer. Nevertheless, organic colloids probably contributed at least as much to CEC as the clay fractions.

It must be assumed that significant differences in organic matter content between treatments would have been found because of the very great differences in yield history and level of annual return of corn residues. Ammonium sulfate and ammonium nitrate plots in particular would likely be much lower in humus content because they have had no significant return of organic residues for several years.

It appears likely that some of the decrease in pH dependent CEC observed for these two treatments was due to depletion of soil organic matter.

Summation

The observed variations in CEC associated with fertilizer and lime treatments strongly support earlier inferences from soil tests and plant analyses that soil buffering systems are qualitatively and quantitatively altered during acidification.

These changes are tremendously accelerated below pH 5.0. This in itself is evidence that the activity of aluminum compounds is uniquely involved.

The evidence from CEC behavior and from alkali-extractable Al and Si in isolated colloidal fractions suggests that dissolution of allophane-like minerals in this soil may have been a major source of Al and Si found in corn leaves (Tables 14 and 15), as well as of mobile buffering systems which probably contributed to the observed mobility of anions (Figures 5, 6, and 7) and seasonal variations in lime requirement (Table 21).

The suggestion from X-ray patterns that vermiculite may have increased in acid soils by migration of K out of illite supports the earlier inference that mobility of K (p. 55) may have been masked by continuing release from decomposing minerals.

Although the formation of vermiculite is inconsistent with decreasing CEC, it must be conceded that observed changes in CEC could well have been dominated by changes in amorphous minerals and in organic fractions.

RESULTS AND DISCUSSION

5. Subsoil Studies

Texture of the Subsoil

Several attempts to take subsoil samples during the summer of 1967 were unsuccessful. The soil was impossible to penetrate with sampling tools beyond the plow sole. Only in the spring or fall was the subsoil soft enough to allow sampling.

During heavy rains, surface water would collect for several hours at the north end of the experimental area, covering a large part of the unlimed half of replication 2. Infiltration was slow. For several days after such a rain, surface soil here was visibly more moist than the southern half of the plot area (replication 1).

Changes in friability with depth, observed in the spring, indicated the presence of a dense, impermeable layer at 10 or more inches from the surface. This is a little shallow for the typical Hodunk soil series, in which a massive horizon or fragipan is expected at 16 to 25 inches.

Mechanical analyses of the 10 - 15 inch layer from all plots showed a range in clay content from 12 to 24 percent (average of 15 percent). Clay plus silt ranged from 28 to

41 percent, with an average of 36 percent. Thus, the soil at this depth fell in the same sandy loam textural class as the plow layer.

These data would suggest that observed differences in friability and permeability were due to structural rather than textural changes below the plow layer.

Soil Test Variation With Depth

In the summer of 1966, soil samples were taken from the unlimed plots receiving either ammonium nitrate plus starter or no fertilizer. These were taken to a depth of 66 inches. It was intended to investigate ammonium and nitrate nitrogen found at these depths. But the samples were stored moist for a period of time, and thus, they no longer reflected soil nitrogen conditions in the field. They were, however, sent to the soil testing laboratory for routine analysis. These results are reported in Tables 33-38.

Differences in the nutritional status of the 0 to 12 inch layer can be explained largely on the basis of soil treatment. The low values for soil pH, Ca and Mg on the ammonium nitrate plots at the 12-24 inch depth and for pH at the 24-36 inch depth, indicates that the acidifying and base depleting effect of this fertilizer treatment was not limited to the plow layer.

Table 33. Variation of soil pH with depth in the profile[1]

Depth	No-fertilizer		Ammonium nitrate	
	Rep 1	Rep 2	Rep 1	Rep 2
0-12	5.9	6.0	4.5	4.5
12-24	6.4	6.2	5.0	5.2
24-36	6.5	5.7	4.9	6.1
36-48	6.7	6.4	7.3	7.6
48-60	6.7	7.0	7.7	8.3
60-66	8.0	6.8	7.3	8.2

[1] Soil samples taken summer 1966

Table 34. Variation of lime requirement with depth in the profile[1]

Depth	No-fertilizer		Ammonium nitrate	
	Rep 1	Rep 2	Rep 1	Rep 2
		ppt		
0-12	1.5	1.5	5.0[2]	5.0
12-24	1.0	1.0	1.5	1.0
24-36	0	1.5	1.5	1.0
36-48	0	.4	0	0
48-60	0	0	0	0
60-66	0	0	0	0

[1] Soil sample taken summer 1966

[2] Buffer pH values above 7.0 were ignored

Table 35. Variation in soil phosphorus with depth in the profile[1]

Depth	No fertilizer		Ammonium nitrate	
	Rep 1	Rep 2	Rep 1	Rep 2
	pp2m			
0-12	59	93	126	162
12-24	20	10	20	51
24-36	25	10	12	16
36-48	25	18	12	17
48-60	8	14	4	3
60-66	4	14	10	3

[1] Soil samples taken summer 1966

Table 36. Variation in soil potassium with depth in the profile[1]

Depth	No fertilizer		Ammonium nitrate	
	Rep 1	Rep 2	Rep 1	Rep 2
	pp2m			
0-12	97	97	167	120
12-24	89	89	128	82
24-36	60	181	167	120
36-48	60	136	120	89
48-60	120	97	105	105
60-66	97	60	39	112

[1] Soil samples taken summer 1966

Table 37. Variation in soil calcium with depth in the profile[1]

Depth	No fertilizer		Ammonium nitrate	
	Rep 1	Rep 2	Rep 1	Rep 2
	pp2m			
0-12	1160	960	560	560
12-24	800	1012	560	400
24-36	659	1752	1604	1308
36-48	800	1456	3346	4057
48-60	1900	1012	6480	6621
60-66	3212	800	800	6903

[1] Soil samples taken summer 1966

Table 38. Variation in soil magnesium with depth in the profile[1]

Depth	No fertilizer		Ammonium nitrate	
	Rep 1	Rep 2	Rep 1	Rep 2
	pp2m			
0-12	176	122	56	56
12-24	112	136	56	32
24-36	68	344	404	220
36-48	68	506	568	220
48-60	416	288	404	232
60-66	372	164	122	244

[1] Soil samples taken summer 1966

The high levels of calcium in the lower part of both profiles receiving ammonium nitrate; the high level of potassium in the profile from the second replication of the unfertilized treatment and in the profile from the first replication of the ammonium nitrate treated plot in the 24-36 inch layer; and the high magnesium level in the same two profiles at the 36-48 inch depth, would appear not to be due to fertilizer treatment. It is suggested that these results are due to natural variation in the subsoil due to the heterogenous nature of the till of the Lansing moraine where this soil is found. Corn roots penetrating to these depths will absorb nutrients, and yields will not entirely reflect fertilizer treatment of the surface soil.

The Influence of Treatment on the Subsoil

On October 25, 1967, soil samples were taken at 0-10, 10-15, and 15-20 inch depth in the soil. Soil test data for this sampling were not subjected to analysis of variance. Like the data in Tables 33 to 38, there was considerable variation between replications at depths below 10 inches. Means are presented in Tables 39 to 46. Detailed graphical and mathematical treatment of the original data is beyond the scope of this report.

Table 39 shows the ammonium level in these samples. As noted earlier, this late in the season the ammonium level of the soil was generally low. The unlimed ammonium nitrate and sulfate plots showed accumulations of ammonium in the plow layer due to retarded nitrification at low pH (Table 41). These surface accumulations were reflected also in the 10-15 inch layer with both materials and at 15 to 20 inches with ammonium sulfate.

The retarded oxidation of ammonium in soils below pH 4.5 was expected in view of the known sensitivity of nitrifiers to low pH. In this connection, three features of the nitrate data in Table 40 are of great fundamental interest:

(1) Extensive nitrification had occured at soil pH well below 4.0 in unlimed ammonium sulfate plots.

(2) Nitrate had accumulated extensively in the subsoil. From the observed distribution, it must be inferred that large quantities of nitrate would have been found at depths greater than 20 inches.

(3) Retention of nitrate in unlimed soil was greater at all depths with acidifying carriers than with calcium nitrate.

A number of factors may have been contributed to this last observation. Crop yields and crop removal have been greater over a period of years with calcium nitrate than

Table 39. Effect of nitrogen carriers on soil ammonium at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				ppm NH_4-N				
0-10	2.0	.2	3.1	1.7	13.8	1.6	71.8	2.1
10-15	1.6	1.0	3.4	2.6	5.0	1.8	9.6	2.9
15-20	2.8	0	.9	2.4	.9	1.1	6.0	1.3

[1] Soil samples taken October 25, 1967

Table 40. Effect of nitrogen carriers on soil nitrate at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				ppm NO_3-N				
0-10	2.6	.4	8.6	3.0	19.0	3.5	35.1	11.8
10-15	2.8	2.0	25.0	17.2	34.6	26.8	48.1	36.7
15-20	2.2	1.8	14.0	33.4	23.6	34.2	39.6	39.3

[1] Soil samples taken October 25, 1967

Table 41. Effect of nitrogen carriers on soil pH at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
0-10	5.8	7.0	5.6	7.0	4.4	6.3	3.7	5.7
10-15	5.8	6.8	5.8	6.8	4.6	5.8	3.8	4.6
15-20	6.0	6.8	5.8	6.5	4.8	5.8	4.2	4.4

[1] Soil samples taken October 25, 1967

Table 42. Effect of nitrogen carriers on lime requirement at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				ppt[3]				
0-10	2.2	--[2]	2.5	--	4.2	1.5	4.5	1.5
10-15	1.5	0.5	1.5	--	2.8	.8	4.5	3.0
15-20	0	--	1.0	--	1.5	.8	5.0	1.8

[1] Soil samples taken October 25, 1967

[2] Buffer pH above 7.0 ignored

[3] ppt = parts per thousand

Table 43. Effect of nitrogen carrier on soil phosphorus at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				pp2m				
0-10	133	113	128	103	146	140	157	150
10-15	48	60	72	44	64	47	46	70
15-20	26	32	45	20	32	25	82	30

[1] Soil samples taken October 25, 1967

Table 44. Effect of nitrogen carriers on soil potassium at three depths[1]

Depth	Basal fertlizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				pp2m				
0-10	190	182	146	135	125	135	132	106
10-15	135	132	156	96	176	128	150	114
15-20	96	118	120	100	121	124	178	135

[1] Soil samples taken October 25, 1967

Table 45. Effect of nitrogen carriers on soil calcium at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				pp2m				
0-10	565	881	486	1196	175	407	91	486
10-15	486	723	565	1118	249	407	91	249
15-20	486	880	407	1354	328	565	249	249

[1] Soil samples taken October 25, 1967

Table 46. Effect of nitrogen carriers on soil magnesium at three depths[1]

Depth	Basal fertilizer		Calcium nitrate		Ammonium nitrate		Ammonium sulfate	
	No lime	Lime	No lime	Lime	No lime	Lime	No lime	Lime
				pp2m				
0-10	100	213	50	143	36	220	36	220
10-15	94	171	50	129	121	171	36	192
15-20	115	213	50	192	100	199	58	192

[1] Soil samples taken October 25, 1967

with ammonium nitrate and over the entire 9 years of the experiment than with ammonium sulfate. Nitrate applied directly as calcium nitrate in the spring is subject to leaching and denitrification losses through the entire season. Some in-season losses are greatly reduced when nitrification of spring applied ammonium is retarded in very acid soils.

Theoretically, a third factor may have influenced greater retention of nitrate in acid soils. This would have involved anion exchange or complex formation with compounds of Fe and Al. Soil tests and tissue analyses both indicate that the activity of sesquioxides was greatly enhanced by acidifying carriers (cf. Tables 9 and 14).

Lime requirements in Table 42 indicate that the acidity of sesquioxide buffering systems in very acid soils was not completely neutralized two years after application of twice the theoretical lime requirement. However, reductions in buffer acidity were apparent to a depth of 20 inches. The formation of stable anion-sesquioxide complexes would permit retention of nitrate from year to year in the face of intensive fall, winter and spring leaching which normally reduces nitrate to very low levels by planting time. Consistent with this view is the fact that mineral nitrogen (NH_4^+ plus NO_3^-) recovered in the top 20 inches of the ammonium sulfate plots totaled

445 pounds per acre (71.8 (2) + 9.6 + 6.0 + 35.1 (2) + 48.1 + 39.6 = 317.1; x 2 x (5/7) = 445). This is nearly 50 percent greater than the amount actually applied in the spring of 1967. Since 65 pounds were found in the 15 to 20 inch layer, it must be assumed that substantial additional quantities would have been found at greater depths. Quantities of nitrogen in the total profile in excess of 300 pounds per acre would necessarily have come from previous years' accumulations from fertilizer or biological sources. Since these plots have been continuously in a non-leguminous crop, it is unlikely that biological fixation could have contributed to mineral nitrogen levels in these soils.

Although nitrification was drastically retarded in ammonium sulfate plots, nitrification still did occur at pH's as low as 3.7. This raises the question as to what mechanisms of nitrification are active in extremely acid soils. This represents an intriguing area for further fundmental research.

The data for soil pH and lime requirement in Tables 41 and 42 and for exchangeable Ca and Mg in Tables 45 and 46 show that the acidifying and base depleting effects of ammonium nitrate and ammonium sulfate had been expressed through the entire 20-inch sampling depth. Displacement of Mg by Ca, applied as calcium nitrate, was also apparent to 20 inches.

Surprisingly, the effects of liming on pH, Ca and Mg were apparent throughout the sampled profile. This unexpected mobility of Ca and Mg applied two years previously as dolomite is perhaps less surprising when it is considered in relation to the very great mobility of nitrate (cf. Table 40). For cations to move in the soil solution, they must be accompanied by anions.

In ammonium sulfate treated plots, the sulfate would have provided a second accompanying anion for downward moving bases. Lime promoted downward movement of sulfate. This is indicated by the following data for sulfate-S in soils from the ammonium sulfate plots:

Depth	Sulfate-S (ppm)	
	No lime	Lime
0-10 inch	8.7	5.9
10-15 inch	7.8	9.5
15-20 inch	7.5	10.0

Less than 2 ppm of SO_4-S were found in plots other than those which received ammonium sulfate.

Data for nitrate in Table 40 shows a similar tendency for lime to promote movement of the anion to greater depths in the soil. Less Ca was found in subsoils of limed ammonium sulfate plots than where lime was applied with other carriers (Table 45). The presence of both nitrate and sulfate anions may have enhanced mobility of calcium and resulted in its movement to greater depths than those samples or, Ca may have been immobilized by sesquioxide complexes.

Equally effective in promoting mobility of calcium in ammonium sulfate plots would have been its mass action displacement by complexed hydronium-sesquioxide cations which would have retained a high degree of mobility at pH's of 4.6 and 4.4 observed in the subsoil layers (Table 41).

The observed mobility of Ca and Mg is of great practical significance. It implies that surface applications of lime can effectively neturalize subsoil acidity, although it may take considerably longer than if the lime were incorporated directly into the subsoil by expensive deep tillage methods.

On the other hand, the data clearly demonstrates the hazards of allowing soils to become too acid. Nutritional imbalances, in a crop such as corn, may not become apparent until soil pH is reduced to 5.0 or less. However, the nature of soil buffering systems which come into play below this pH are such that lime requirements quickly become excessively high. Furthermore, the actual lime requirement of such acid soils cannot be assessed by currently available soil tests.

Extractable P in the 0-10 inch layer (Table 43) increased with increasing acidity of the carrier. This can only be understood in terms of displacement of phosphate by high concentrations of nitrate and/or sulfate. Phosphorus availability normally decreases below pH 5.5 because of the formation of insoluble compounds with iron and aluminum.

Exchangeable K in the 0-10 inch layer decreased with increasing acidity of the carrier, whereas in the 15-20 inch layer it increased (Table 44). This suggests that increasing surface acidity promoted displacement of K to lower depths in the soil.

Effects of lime on soil P and K were not consistent from treatment to treatment or from one depth to another.

Subsoil Influence on Crop Response

The data obtained from analyses of the subsoil has pointed out the importance of considering the properties of the subsoil in interpreting crop response in field experiments.

The variability of the deep subsoil was noted in Tables 33-38. As plants send roots into the lower parts of the soil profile, they will go beyond the region where the treatments were applied. Nutrients or toxic elements not observed in the analyses of the surface soil may have considerable influence on crop response. In this experiment the presence of free lime and accumulations of exchangeable Ca and Mg were noted in the upper six feet of the soil profile. The presence of Mg is of particular interest because the Mg level of the plow sole may have been limiting to plant growth in some cases.

Accessibility of the subsoil nutrients in this experiment may have been restricted in a variable manner by the variation in the development of the fragipan and its impedence to root growth. Subsoil nutrients and moisture are completely unavailable to plants if the surface soil is so acid that normal root growth is prevented.

Fertilizer treatments did influence soil conditions well below the plow layer. Lime applied to the most acid soils had not corrected the infertility of the subsoil to the extent it had in the plow layer.

There is strong evidence that the seasonal moisture variation does result in vertical movement of mobile nutrients in the profile. This can be of considerable importance when upward movement during dry periods concentrates toxic materials from the subsoil in the plow layer.

SUMMARY AND CONCLUSIONS

Effect of Nitrogen Carriers on Soil Acidity

Acidifying carriers rapidly decreased the pH of the soil. The extent of the reduction for the carriers was, in general, related to the residual acidity of the carrier. Ammonium nitrate, however, resulted in a pH more comparable to ammonium chloride or sulfate treated soils than to the other moderately acid carriers (urea, ureaform, and anhydrous ammonia). This is likely due to the excessive rates used in this study. High concentrations of nitrate, in excess of crop demand, added as NH_4NO_3 would contribute to mobility of cations displaced by protons released during nitrification in the same way as the sulfate or chloride in the other two ammonium carriers. The mobilized cations would be subject to leaching by spring and early summer rains. During this period, mobility of cations would be suppressed by the direct alkalinity associated with NH_3, urea and ureaform prior to nitrification.

Two years after liming at twice the recommended rates (based on the buffer pH tests for each plot), the soil pH was still well below the desired value of 6.5 to 6.8. Values for the two most acidic carriers had barely risen to pH 5.0.

In this study the pH of the soil for NH_4Cl and $(NH_4)_2SO_4$ dropped to about 4.5 in the first two or three years and remained at this very low level for the remaining six or seven years of the experiment, except for the two replications which were limed in the seventh and eighth years. This long exposure to low pH produced drastic changes in chemical properties and fertility status of the soil.

A major chemical change was the accumulation of potential acidity measured by buffer test and reported as lime requirement. In soils below pH 5.0, a major component of potential acidity appeared to be highly mobile, giving rise to seasonal fluctuations in lime requirement. These fluctuations coincided with major fluctuations in nitrate and sulfate which, in turn, coincided with weather patterns conducive to mass movement of water and solutes vertically between the plow layer and the subsoil.

Marked differences in extractability of iron and aluminum in these extremely acid soils indicated that mobile components of potential acidity may have been dominated by cationic hydronium complexes with iron. This interpretation was supported by the formation of brown iron oxide crusts on the surface of these soils during periods of dry weather. Also by greatly increased Fe concentrations in the leaves of corn.

Detectable levels of aluminum were found in potassium chloride extracts of soils from the three most acid treatments. Increased amounts of aluminum were also found in plant tissue from most of the treatments involving acidifying carriers. These results are consistent with the expectation of exchangeable aluminum contributing significantly to total potential acidity. It was also likely present among the mobile components.

Addition of twice the lime requirement (indicated by buffer test) failed to neutralize the buffer acidity or raise the pH of soils below pH 5.0 to the desired range of 6.5 to 6.7. It is suggested that lime particles may have been coated by precipitated mobile components of buffer acidity, most probably by iron oxides formed in the alkaline environment in the vicinity of particles of lime. The reactivity of the lime was thereby greatly reduced. It appeared, however, that release of calcium from the dolomite was retarded to a greater extent than magnesium.

Effects On Elements of Soil Fertility

From the standpoint of fertility, nitrogen was supplied with all supplemental carriers in amounts greatly in excess of crop requirements. The proportion of NH_4^+ to NO_3^-, however, varied greatly.

Over the entire season, much higher proportions of the available nitrogen was present as NH_4^+ with anhydrous NH_3 and the three ammonium salts than with other carriers. This was due to the greatly retarded nitrification in the most strongly acid soils and to delayed time of application in the case of anhydrous ammonia.

Corn is considered to use nitrate more effectively than ammonium. Even with treatments where NH_4^+/NO_3^- ratios were high, nitrate was present in amounts more than adequate for corn. Much of this was nitrate which had accumulated in the subsoil from previous years and moved up quickly into the plow layer during dry periods in May and June and again in July and August.

Acidifying carriers resulted in rapid and progressive depletion of exchangeable Ca and Mg over the years of the experiment. Exchangeable K also decreased progressively over the years, but residual levels remained higher in the more acid soils, which indicated that K was being released by mineral decomposition more rapidly in acid environments. This release of exchangeable K from soil minerals appeared to be enchanced by NH_3 and the sodium in $NaNO_3$. They may have been due to displacement of interlayer K, promoted in the case of anhydrous ammonia by the greater ease of penetration of uncharged NH_3 at high pH as compared with NH_4^+ at lower pH. The calcium in $Ca(NO_3)_2$, on the other hand, promoted depletion of exchangeable Mg by displacement from the exchange complex.

Addition of lime tended to suppress exchangeable K. It did result in increased levels of exchangeable Ca and Mg. The resulting levels of exchangeable Mg reflected the increasing rates of application of dolomite with increasing acidity of nitrogen carriers. This was not true for exchangeable Ca. The levels of Ca were not significantly different among acidifying carriers in limed soil and the Ca levels with these carriers after liming was no different.than the unlimed controls. The common factor controlling release of calcium from dolomite in these acid soils may have been the deposition of sesquioxides around lime particles.

Extractable phosphorus was increased by soil acidification and reduced by liming. Phosphorus is normally fixed by the formation of insoluble aluminum and iron phosphates at low pH. It must be inferred that the solution chemistry of these very acid soils was drastically altered by the ionic activities of sulfate, chloride, nitrate, hydroxyl and bicarbonate associated with acidifying nitrogen carriers or their transformations in soil. Abnormally high concentrations of these anions were attained in this experiment because nitrogen was supplied at rates greatly in excess of crop requirements.

The extractability of soil zinc and iron increased as soil pH decreased. Extractable Mn was also higher with moderately acidifying carriers but decreased sharply in soil which had receive NH_4Cl and $(NH_4)_2SO_4$. Whether this decrease in the most acid soils represented depletion or complexation in nonextractable forms was not ascertained.

Extractable aluminum appeared in detectable quantities only in soils of pH 4.6 or less. It is known that charged species of aluminum become increasingly exchangeable below pH 5.0 and dominate acid buffering systems in the range from pH 4.0 to 5.0 or 5.5. Normal potassium chloride appears to have been an in appropriate buffer for displacing exchangeable aluminum over this range. It is likely, too, that exchangeability of aluminum species in the very acid soils of this experiment may have been reduced by complexing with anions such as sulfate and nitrate, the concentrations of which were very high.

Nevertheless, the very great difference in extractability of Fe and Al supports the view that mobile buffering systems in these acid soils were dominated by hydronium complexes with iron.

Sulfate sulfur and exchangeable sodium accumulated in soils where they were applied as the nitrogen carrier. Extractable copper was not detected in any of the soils.

Effects on Crop Nutrition

Foliar nitrogen, deficient in unfertilized and basal fertilizer controls, increased to fully sufficient levels with all supplemental nitrogen treatments. In spite of the extremely high concentrations of mineral nitrogen in the soil, there was no evidence of abnormal uptake in the leaf tissues.

Phosphorus was at near deficient levels in corn on the unfertilized check and responded to fertilizer phosphorus supplied in the basal fertilizer only when supplemental nitrogen was also applied. Increases in plant phosphorus were essentially similar for all supplemental nitrogen carriers. This again supports the inference that phosphate activity in acid soils is influenced strongly by mass action relationships in anion displacement or exchange reactions.

Foliar K, Ca and Mg reflected the variations associated with carrier and lime that were observed in soil tests for these nutrients. As with soil tests for exchangeable Mg, foliar Mg increased after liming to a greater extent than did foliar Ca. The calcium in $Ca(NO_3)_2$ tended to depress foliar Mg both before and after liming.

The most striking evidence of nutritional imbalance was the high concentration (400 to 700 ppm) of manganese in leaves of corn on all plots which had received acidifying carriers (NH_3, urea, ureaform, NH_4NO_3, NH_4Cl, $(NH_4)_2SO_4$. The soil pH in these plots was 4.6 or less. In previous years, sharply increased levels of tissue Mn were the first plant abnormality to appear in corn as soil pH declined below 5.0. This appeared before any detectable visual symptoms or depressions in yield.

Liming depressed these high leaf Mn concentrations, but in corn on limed ammonium chloride and sulfate plots they remained near 400 ppm which is usually associated with toxicity. The high availability to plants of Mn in these two extremely acid soils when unlimed (both below pH 4.0) is in contrast to the sharply reduced extractability of soil Mn using phosphoric acid as the extractant. It is not clear whether reduced extractability reflected depletion of soil Mn or if manganese compounds or complexes are being formed which are available to the plant but not H_3PO_4 extractable.

Iron, aluminum, zinc and silicon in corn leaves also increased with the use of acidifying nitrogen carriers. All declined when limed was applied.

Crop Response

Corn yields were drastically reduced by all acidifying nitrogen sources. In general, the lower the soil pH the greater the reduction. Very few plants survived beyond germination where ammonium sulfate was used and soil pH was 3.8.

The application of lime greatly improved yields with most treatments. However, residual effects injurious to corn were still apparent after liming in ammonium sulfate and chloride plots. These injurious effects appeared in the field in the forms of a general chlorosis and reduced vigour, as well as in restricted yields.

High Mn contents were the most conspicuous nutritional feature associated with responses of corn to long continued use of acidifying nitrogen fertilizers. Nevertheless, it is unlikely that injurious effects can be interpreted in terms of a specific manganese toxicity. Rather, high Mn contents are the most obvious symptom of the qualitatively different nutritional environment which plant roots find in soils below pH 5.0 as compared with higher pH.

qu
su
ir

t'
e
d
v
m

H
c
s

Chemical tests in the subsoil indicate that these qualitative changes in the soil environment under acidifying surface treatments had penetrated to depths of 24 to 36 inches.

In practical soil management, the fertility status of the subsoil must also be considered. The soil volume actually explored by plant roots is important. The present study demonstrates that it is also important to consider the volume of soil which comes under the influence of seasonal mass movements of water and solutes.

Greatly increased use of commercial fertilizers at higher rates of application have increased the concentration of solutes in the water which percolates downward through soils or moves upward by capillarity in response to evapotranspiration. The mobilizing effect on soil constituents of fertilizer ions was strickingly illustrated in this study.

The implications for continued high soil productivity when accelerated weathering accompanies increased fertilization rates has been ignored by soil scientists and agronomists alike.

Effects on Microbial Activities

Microbial activity was reduced in acid soils. Nitrification was materially reduced in all soils below pH 5.0 and became negligible during a two weeks' incubation in soils below pH 4.5. In the field, continuing slow nitrification resulted in progressive disappearance of NH_4^+ in soils as low as pH 4.0. In $(NH_4)_2SO_4$ treated soils where pH's were 4.0 or below, fluctuations in nitrate and ammonium may have been due principally to mass vertical movements in solution in response to rainfall and periods of drought.

Evolution of CO_2 during incubation of unlimed $(NH_4)_2SO_4$ soils was extremely low, indicating that these soils were approaching a condition of almost complete sterility.

Ionic Effects of Carriers

There is ample evidence in this study that residual effects of fertilizers on soils cannot be understood simply in terms of their recognized residual acidity. Specific effects of anions and cations must also be considered.

Calcium added as $Ca(NO_3)_2$ accelerated the disappearance of exchangeable Mg. Sodium from $NaNO_3$ promoted increases in exchangeable Ca and Mg and increased the level of both exchangeable Na and K relative to the acidifying carriers.

Anhydrous NH_3 also promoted increases in exchangeable K. This unique difference between NH_3 and other acidifying carriers reflects differences in the reactions which can be entered into by uncharged NH_3 and charged NH_4^+ as well as differences in effects of OH^- released by hydrolysis with NH_3 and of HCO_3^-, NO_3^-, Cl^- or SO_4^{--} released initially by solution or hydrolysis of the other carriers.

Unique differences in effects of urea and ureaform likely reflect mass action effects associated with their very difference rates of hydrolysis to release HCO_3^- and NH_4^+. One of the effects of rapid hydrolysis of urea to ammonium carbonate is a temporary large increase in pH and a shift in the equilibrium between NH_3 and NH_4^+:

$$(NH_4)_2CO_3 + HOH \rightleftarrows 2NH_4^+ + HCO_3^- + OH^-$$

$$NH_4^+ + OH^- \rightleftarrows NH_3 + HOH$$

Temporary high concentrations of NH_3 during hydrolysis of urea would have provided conditions similar to those associated with injections of anhydrous ammonia, except for the difference in proportions of OH^- and HCO_3^-.

This difference in anion population may well have influenced the nature of initial equilibration reactions between these two carriers and soil constituents. A second factor contributing to observed differences in residual effect would have been the fact that urea was always surface applied at planting time, whereas anhydrous NH_3 was injected when corn was about knee high. A third factor which materially influenced 1967 results was the erroneous application of both carriers on one of the NH_3 plots in the unlimed series.

In contrast with the initially alkaline environment associated with NH_3, urea and ureaform, is the direct acidic "salt effect" associated with all fertilizer salts, but notably with ammonium salts since these involve a weak base and strong acids. This direct acidifying effect reinforced the residual acidity which arose during nitrification. As a result, acidifying effects of NH_4NO_3 after nine years were often more comparable to the chloride and sulfate salts than to the moderately acidifying carriers with which it is usually classed.

Even these two very acidifying ammonium salts showed very marked differences in rate of soil acidification in this experiment. Sulfate was more effective than chloride in reducing soil pH, but sulfate treated soils showed a greater degree of response to liming. This can be understood in terms of the more basic nature of sesquioxide complexes with divalent anions than those with monovalent anions. Cationic species of sesquioxide -SO_4 would have been more effective in displacing basic cations from the exchange complex as soil pH decreased. These sulfate complexes would also have been more susceptible to inactivation by polymerization when lime was applied than the complexes associated with chloride.

Ionic Mobility

Both downward and upward movement of ions was observed in all soils receiving supplemental nitrogen. Seasonal movements of sulfate and nitrate into and out of the plow layer were accompanied by parallel movements of NH_4^+, Ca^{++} and Mg^{++}. Evidence for seasonal fluctuations in exchangeable K^+ was less clear and may have been masked by continuing release of K^+ from soil minerals.

In addition to these cations, mobile components of buffer acidity contributed to the very great mobility of sulfate and nitrate observed in the more acid soils.

Cations and anions play a reciprocal role in promoting mobility of solutes in mass seasonal movements of water in soils. Neither negatively nor positively charged species can move with the soil solution unless there is electrical balance in the solution. High rates of fertilizer associated with modern soil management practices have greatly accelereated the dynamics of chemical equilibria in soils. The extent to which this undoubtedly contributes to accelerated weathering of soil minerals has not begun to be appreciated.

Effects on Soil Colloids

Both direct and indirect evidence was obtained that soil colloids were extensively altered by acidifying carriers.

Direct evidence includes the observed reduction in pH dependent cation exchange. Although the reduction was only of the order of 1 me/100 g, this represented 25 to 30 percent of the CEC active in the range from pH 5.0 to 6.0 in control soils.

A portion of this decrease in pH dependent CEC may have been due to declining organic matter content in very acid soils. No organic matter determinations were made to evaluate this relationship. However, declines in allophane-like constituents of the isolated colloidal fractions suggest that decomposition of amphoteric clay minerals may have contributed extensively to the increased activity of Al and Si which was reflected in both soil tests and tissue analyses.

X-ray tracings gave evidence that vermiculite may have increased through release of K from mica in acid soils. This would be consistent with the fact that tissue tests and yields reflected a higher availability of soil K than soil tests and applied rates of fertilizer K would have indicated for this soil. Also, the lower apparent mobility of K relative to Ca or Mg led to the inference that K fluctuations were masked by continuing release from decomposing soil minerals.

The major indirect evidence of alteration in soil colloids was the very large increase in lime requirements in soils below pH 5.0. Quantitatively, this increase greatly exceeded the cation exchange capacity of these soils. It cannot, therefore, be ascribed to exchangeable aluminum on the exchange complex. The bulk of these buffering materials must have accumulated outside the exchange complex. Significant proportions of these were mobile, as indicated by seasonal fluctuations in lime requirement in very acid soil. However, their mobility was dependent upon the presence of high concentrations of anions as shown by data for treatments in which associated fluctuations in SO_4^{-2} and NO_3^- were observed. Their essentially colloidal character must be inferred from the extensive literature which implicates hydronium complexes of Al and Fe with soil buffering systems below the range of pH

5.0 to 5.5. Polymerization and depolymerization of these complexes is known to be extremely dynamic in very acid soils.

Other indirect evidence of accelerated decomposition of soil minerals and accelerated alteration of soil colloidal fractions associated with soil acidification in this experiment are the increased activities, reflected in soil tests and plant analyses, of Fe, Mn, Al, Zn, and Si.

Colloidal forms of Fe may have dominated over Al in components of buffer acidity (lime requirement) which were apparently mobilized in the presence of high concentrations of anions contributed by acidifying nitrogen carriers.

Implications

In the future, economics of production and handling will dictate more extensive use of highly acidic fertilizers. New varieties and higher yield goals will dictate more intensive use of fertilizers.

Three important implications can be drawn from this study. First, Agronomists have very little understanding of the chemistry of very acid soils. Specific changes with declining pH in pure systems have been rather intensively studied, particularly with respect to aluminum. But the soil system is made up of a great many chemical systems that are individually affected by pH in specific ways. Simultaneous independent changes in these systems are further modified by interactions and equilibria in the complex and continuously changing chemical environment of the soil.

Studies in less acid soil systems have been concerned mainly with the cationic species. The anionic species must be given equal importance in the study of acidic soil chemistry.

Secondly, it is apparent from data presented that specific ion effects are also important in altering the residual fertility status of soils. The chemical equilibria in soils respond to mass action effects of each chemical species introduced into soils in the form of a fertilizer amendment. The dynamic nature of these equilibria is greatly enhanced as the concentration of individual chemical species is increased by the high rates of fertilizer application employed in modern soil management. In order to control these equilibria in ways that will contribute to continued or increasing high productivity of soils, it will be necessary to consider specifically the effects of each chemical species added in fertilizer. Research in soil chemistry and soil fertility in the past has ignored effects of carrier species. This is particularly true of carrier anions such as chloride and sulfate which have no nutritional significance or are only of secondary nutritional importance.

Finally, from a practical soil management point of view, without careful monitoring of changes in soil pH and buffer acidity, continued use of residually acidifying fertilizers will, sooner or later, depending upon soil type, result in excessive soil acidity. There is no evidence yet from this experiment that there may not be residual effects of extreme acidity which lime alone cannot correct. Even if it develops that lime applied in this experiment results in complete restoration of soil productivity, it will have been a slow and expensive process.

LITERATURE CITED

1. Abruna, F., R. W. Pearson, and C. B. Elkins. 1958. Quantitative evaluation of soil reaction and base status changes resulting from field application of residually acid-forming nitrogen fertilizers. Soil Sci. Soc. Amer. Proc. 22:539-542.
2. ___________, and J. Vicente-Chandler. 1960. The effect of ammonium sulfate and lime rates on profile acidity of a red-yellow podsol and a latosol under field conditions. Proc. Assoc. Southern Agr. Workers. 57:74-75.
3. Adams, F. and R. Pearson. 1967. Crop response to lime in the Southern United States and Puerto Rico. In R. Pearson and A. Adams (ed.) Soil acidity and liming. Agronomy 12:161-206.
4. Alexander, M. 1965. Nitrification, In W. Bartholomew and F. Clark (ed.) Soil nitrogen. Agronomy 10:309-346.
5. Allison, F. E. 1963. Losses of gaseous nitrogen from soils by chemical mechanisms involving nitrous acids and nitrites. Soil Sci. 96:404-409.
6. Andrews, W. B. 1954. The response of crops and soils to fertilizers and manure. W. B. Andrews, State College, Miss.

7. ______________ and R. Cowart. 1939. The use of the harvested part of the crop in estimating the effect of cotton fertilizers on the base supply of the soil. Soil Sci. Soc. Amer. Proc. 4:275-280.

8. Anomine, S. and M. L. Jackson. 1959. Allophane determination in ando soils by cation-exchange capacity delta value. Soil Sci. Soc. Amer. Proc. 23:210-214.

9. Bardsley, C. E. and J. D. Lancaster. 1965. Sulfur. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:1102-1116.

10. Barshad, I. 1960. The effect of the total chemical composition and crystal structure of soil minerals on the nature of the exchangeable cations in acidified clays in naturally occuring soils. Trans. 7th Intern. Congr. Soil Sci. 2:435-444.

11. Bergin, P. 1959. Observations for eleven years of liming trial. Econ. Proc. Roy. Dublin Soc. 4:119-136. Biol. Abst. 36:15173. (1961).

12. Bouyoucous, G. 1936. Directions for making mechanical analysis of soils by the hydrometer method. Soil Sci. 42:225-230.

13. Bremner, J. M. 1965. Inorganic forms of nitrogen. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:1179-1237.

14. ______________ 1965. Nitrogen availability indexes. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:1324-1345.

15. Brydon, J. E. and F. J. Sowden. 1959. A study of the clay-humus complexes of a chernozemic and a podzal soil. Can. J. Soil Sci. 39:136-143.

16. Chodan, G. Personal communication.

17. Clark, J. S. 1964. Aluminum and iron fixation in relation to exchangeable hydrogen in soils. Soil Sci. 98:302-306.

18. ___________ 1966. The pH value of soils suspended in dilute salt solutions. Soil Sci. Soc. Amer. Proc. 30:11-14.

19. Cochran, W. G. and G. M. Cox. 1950. Experimental design. Wiley, Inc., New York.

20. Coleman, N. L. and D. Craig. 1961. The spontaneous alteration of hydrogen clay. Soil Sci. 91:14-18.

21. ______________ and G. W. Thomas. 1967. The basic chemistry of soil acidity. In R. Pearson and F. Adams, (ed.) Soil acidity and liming. Agronomy 12:1-42.

22. ______________,S. B. Weed, and R. J. McCracken. 1959. Cation-exchange capacity and exchangeable cations in piedmont soils of North Carolina. Soil Sci. Soc. Amer. Proc. 23:146-149.

23. Cornfield, A. H. 1952. The mineralization of the nitrogen of soils during incubation: Influence of pH, total nitrogen, and organic carbon contents. J. Sci. Food Agr. 3:343-349.

24. Eno, C. F., and W. G. Blue. 1957. The comparative rate of nitrification of anhydrous ammonia, urea, and ammonium sulfate in sandy soils. Soil Sci. Soc. Amer. Proc. 21:392-396.

25. __________, and J. M. Good, Jr. 1955. The effect of anhydrous ammonia on nematodes, fungii, bacteria and nitrification in some Florida soils. Soil Sci. Soc. Amer. Proc. 19:55-58.

26. Federer, W. T. 1955. Experimental designs. Macmillan Co., New York.

27. Fiskell, J. G. 1965. Copper. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:1078-1089.

28. Godoy, P. H. 1963. Effect of prolonged use of some nitrogen fertilizers on soil pH. São Paulo Agric. 5:17-19. Abst. in Soils and Fertilizers 27:2972 (1964).

29. Gorbunov, N. I., G. S. Dzyadevich, and B. M. Tunik. 1961. Methods of determining non-silicate amorphous and crystalline sesquioxides in soils and clays. Soviet Soil Sci. 1252-2159.

30. Greenland, D. J. 1965. Interaction between clays and organic compounds in soils: Part I. Mechanisms of interaction between clays and defined organic compounds. Soils and Fertilizers 28:415-425.

31. Grim, R. E. 1953. Clay mineralogy. McGraw Hill Co., New York.

32. Hallsworth, E. G., and G. K. Wilkinson. 1958. The contributions of clay and organic matter to the cation-exchange capacity of the soil. J. Agr. Sci. 51:1-3.

33. Harris, S. A. 1961. Soluble aluminum in plants and soils. Nature 189:513-514. Abst. in Soils and Fertilizers 24:1197 (1961).

34. Helling, C. S., G. Chesters, and R. B. Corey. 1964. Contributions of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solution. Soil Sci. Soc. Amer. Proc. 28:517-520.

35. Hiltbold, A. E., and F. Adams. 1960. Effect of nitrogen volatilization on soil acidity changes due to applied nitrogen. Soil Sci. Soc. Amer. Proc. 24:45-47.

36. Hoff, D. J. and H. S. Medereski. 1958. The chemical estimation of plant available soil manganese. Soil Sci. Soc. Amer. Proc. 22:129-132.

37. Hsu, P. H. and C. I. Rich. 1960. Aluminum fixation in a synthetic cation-exchanger. Soil Sci. Soc. Amer. Proc. 24:21-25.

38. Jackson, M. L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J.

39. ______________ 1963. Aluminum bonding in soils: A unifying principle in soil science. Soil Sci. Soc. Amer. Proc. 27:1-10.

40. ______________ 1964. Chemical composition of soils. In F. E. Bear (ed.) Chemistry of the soil. p. 7-141. Reinhold Pub., New York.

41. ______________ 1965. Free oxides, hydroxides, and amorphous aluminosilicates. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:578-603.

42. ______________ 1967. Physiological effects of soil acidity. In R. Pearson and F. Adams, (ed.) Soil acidity and liming. Agronomy 12:43-124.

43. Jenny, H. 1961. Reflections of the soil acidity merry-go-round. Soil Sci. Soc. Amer. Proc. 25:428-432.

44. Kunze, G. W. 1965. Pretreatment for mineralogical analysis. In C. A. Black, et al. (ed.). Methods of soil analysis. Agronomy 9:568-577.

45. Laflamme, Y. 1967. Determination of aluminum in soils by atomic absorption spectroscopy. Atomic Absorption Newsletter 6:70-71.

46. Lindsay, W. L., M. Peach, and J. S. Clark. 1959. Determination of aluminum ion activity in soil extracts. Soil Sci. Soc. Amer. Proc. 23:266-269.

47. MacLeod, L. M. and L. P. Jackson. 1967. Water soluble and exchangeable aluminum in acid soils as affected by liming and fertilization. Can. J. of Soil Sci. 47:203-210.

48. McIntosh, T. H. and L. R. Frederick. 1958. Distribution and nitrification of anhydrous ammonia in a Nicollet sandy clay loam. Soil Sci. Soc. Amer. Proc. 22:402-405.

49. McKeague, J. A. and M. G. Cline. 1963. Silica in soils. Advance Agron. 15:339-396.

50. McLean, E. O., W. R. Hourigan, H. E. Shoemaker, and D. V. Bhumbla. 1964. Aluminum in soils: V. Form of aluminum as a cause of soil acidity and a complication in its measurement. Soil Sci. 97:119-126.

51. _______________, M. R. Heddleson, R. J. Bartlett, and N. Halowaychuk. 1958. Aluminum in soils: I. Extraction methods and magnitudes in clays and Ohio soils. Soil Sci. Soc. Amer. Proc. 22:382-387.

52. Melton, J. R. Personal communication.

53. Michigan Agricultural Extension Service. 1966. Fertilizer recommendations for Michigan vegetables and field crops. Ext. Bul. E-550. 24 p.

54. Mitchell, B. D., V. C. Farmer, and W. J. McHardy. 1964. Amorphous inorganic materials in soils. Advance Agron. 16:327-384.

55. Mitra, R. P., and K. S. Rajagapalan. 1952. Origin of the base exchange capacity of clays and the significance of its upper limiting value. Soil Sci. 73:349-360.

56. Mortland, M. M. and J. L. Mellor. 1954. Conductometric titration of soils for cation-exchange capacity. Soil Sci. Soc. Amer. Proc. 18:363-364.

57. Mutatkar, V. K. and W. L. Pritchett. 1966. Influence of added aluminum on carbon dioxide production in tropical soils. Soil Sci. Soc. Amer. Proc. 30:343-346.

58. Noll, C. F., F. D. Gardner, and C. J. Irvin. 1931. Fiftieth anniversary of the general fertilizer tests. Penn. Agr. Exp. Sta. Bul. 264. 24 p.

59. R. V. Olson. 1966. Iron. <u>In</u> C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:963-973.

60. Pailoor, G. 1966. A study of manganese availability in several Michigan soils. M.S. Thesis, Michigan State University.

61. Peech, M. 1965. Hydrogen-ion activity. <u>In</u> C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:914-926.

62. Pierre, W. H. 1934. The equivalent acidity and basicity of fertilizers as determined by a newly proposed method. J. of Assoc. Off. Agr. Chem. 17:101-107.

63. ____________, S. A. Aldrich and W. P. Martin. 1966. Advances in corn production. Iowa State U. Press, Ames, Iowa.

64. Pratt, P. F. 1961. Effect of pH on the cation-exchange capacity of surface soils. Soil Sci. Soc. Amer. Proc. 25:96-98.

65. ____________ 1965. Digestion with hydrofluoric and perchloric acids for total potassium and sodium. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:1019-1021.

66. ____________ 1965. Sodium. In C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:1031-1034.

67. Ragland, J. L. and N. T. Coleman. 1960. The hydolysis of aluminum salts in clay and soil systems. Soil Sci. Soc. Amer. Proc. 24:457-460.

68. Rich, C. I. and G. W. Thomas. 1960. The clay fraction of soils. Advance Agron. 12:1-41.

69. Ross, C. J., K. Lawton, and B. G. Ellis. 1964. Lime requirement related to physical and chemical properties of nine Michigan soils. Soil Sci. Soc. Amer. Proc. 28:209-212.

70. Russell, E. J. 1931. Artificial fertilizers. Brit. Min. Agr. Fish. Bul. 28. Cited in Andrews, W. B. 1954. The response of crops and soils to fertilizers and manure. W. B. Andrews, State College, Miss.

71. Sauchelli, V. 1960. Chemistry and technology of fertilizers. Reinhold Pub., New York.

72. Samuels, G. and F. Gonzalez-Vélez. 1962. The influence of ammonium sulfate fertilization on the pH of sugarcane soils. J. Agric. Univ. Puerto Rico. 46:297-306. Abst. in Soils and Fertilizers 26:3193 (1963).

73. Scarsbroad, C. E. 1965. Nitrogen availability. In W. Bartholemew and F. Clark, (ed.) Soil nitrogen. Agronomy 10:486-507.

74. Schneider, I. F., R. W. Johnson, and E. P. Whiteside. 1967. Tentative placements of Michigan soil series in the new soil classification system. Soil Science Dept., Michigan State University.

75. Schofield, R. K. 1950. Effects of pH on electrical charges carried by clay particles. J. Soil Sci. 1:1-8.

76. ________________ and A. W. Taylor. 1955. The measurement of soil pH. Soil Sci. Soc. Amer. Proc. 19:164-167.

77. Schwertmann, V. and M. L. Jackson. 1964. Influence of hydroxy aluminum ions on pH titration curves of hydronium-aluminum clays. Soil Sci. Soc. Amer. Proc. 28:179-183.

78. Shoemaker, H. E., E. D. McLean, and P. F. Pratt. 1961. Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminum. Soil Sci. Soc. Amer. Proc. 25:274-277.

79. Snedecor, G. 1956. Statistical methods. Iowa State Coll. Press, Ames, Iowa.

80. Thomas, G. W. and N. T. Coleman. 1964. The fate of exchangeable iron in acid clay systems. Soil Sci. 97:229-232.

81. Tidmore, J. W. and J. T. Williamson. 1932. Experiments with commercial nitrogenous fertilizers. Ala. Agr. Exp. Sta. Bul. 238.

82. Tisdale, S. and W. L. Nelson. 1966. Soil fertility and fertilizers. Macmillan Co., New York.

83. Turner, R. C. 1965. A study of lime potential: 4. The lime potential during titration of Wyoming bentonite originally saturated with ferric ions. Soil Sci. 99:88-92.

84. ____________ 1965. A study of lime potential: 5. Significance of the lime potential in aqueous acid clay systems. Soil Sci. 100:14-19.

85. ____________ and J. E. Brydon. 1965. Factors affecting the solubility of $Al(OH)_3$ precipitated in the presence of montmorillonite. Soil Sci. 100:176-181.

86. ____________ and J. S. Clark. 1965. Lime potential and degree of base saturation of soils. Soil Sci. 99:194-199.

87. ____________ and W. E. Nichol. 1958. The pH of strongly acid soils. Can. J. of Soil Sci. 38:63-68.

88. ____________. 1962. A study of lime potential: I. Conditions for the lime potential to be independent of salt concentration in aqueous suspensions of negatively charged clays. Soil Sci. 93:374-382.

89. ____________. 1962. A study of lime potential: 2. Relation between lime potential and percent base saturation of negatively charged clays in aqueous salt suspensions. Soil Sci. 94:58-63.

90. ____________ and J. E. Brydon. 1963. A study of lime potential: 3. Concerning reactions responsible for the magnitude of the lime potential. Soil Sci. 95:186-191.

91. Tyler, K. B. and F. E. Broadbent. 1960. Nitrate transformation in California soils. Soil Sci. Soc. Amer. Proc. 24:279-282.

92. United States Dept. Commerce. Climatological Data. Michigan Section. 1967.

93. Van Olphen, H. 1965. An introduction to clay colloidal chemistry. Wiley, Inc., New York.

94. Volk, B. J. 1955. Factors determining the effect of various fertilizer materials on acidity in the soil profile. Florida State Hort. Soc. Proc. 68:220-226.

95. Weber, D. F. and P. L. Gainey. 1962. Relative sensitivity of nitrifying organisms to hydrogen ions in soils and in solution. Soil Sci. 94:138-145.

96. Whiteside, E. P. Personal communication.

97. Whittig, L. D. 1965. X-ray diffraction techniques for mineral identification and mineralogical composition. _In_ C. A. Black, et al. (ed.) Methods of soil analysis. Agronomy 9:671-698.

98. Wiklander, L. 1964. Cation and anion exchange phenomenon. _In_ F. E. Bear (ed.) Chemistry of the soil. Reinhold Pub., New York, p. 1963-203.

99. Williams, R. 1932. The contribution of clay and organic matter to the base exchange capacity of soils. J. Agr. Sci. 22:845-851.

100. Wolcott, A. R. and H. D. Foth. 1964. Lime takes the "sting" out of acid forming N fertilizers. Crops and Soils. 17:8-10.

101. ______________________________, J. F. Davis, and J. C. Shickluna. 1965. Nitrogen Carriers: I. Soil effects. Soil Sci. Soc. Amer. Proc. 29:405-410.

102. ______________________________, J. C. Shickluna and J. F. Davis. 1964. Soil reaction key helps select best N fertilizers. Crops and Soils. 16:21.

103. Wright, K. E. and B. A. Donahue. 1953. Aluminum toxicity studies with radioactive phosphorus. Plant Physiol. 28:674-680.

104. Yuan, T. L. 1963. Some relationships among hydrogen, aluminum and pH in solution and soil systems. Soil Sci. 95:155-163.

105. Zhukov, M. S. 1958. Acidity changes in sandy soils as affected by the hill method of applying fertilizers (in Russian) Prochvovedenie 10:1135-1141. Biol. Abst. 36:5733, (1961).

APPENDIX

HODUNK SERIES

The Hodunk series consists of moderately well drained Gray-Brown Podzolic (Ochreptic fragudalf) soils with fragipans which developed on calcareous sandy loam glacial till. Hodunk soils are found in association with the well drained Hillsdale and moderately well drained Elmdale series which are also developed on calcareous sandy loam till.

Soil Profile:		Hodunk sandy loam
Ap	0-7"	Dark grayish brown (10YR 4/2) to very dark grayish brown (10YR 3/2); sandy loam; moderate fine, granular structure; friable when moist and soft when dry; medium content of organic matter; medium to slightly acid; abrupt smooth boundary. 6 to 11 inches thick.
A2	7-16"	Yellowish brown (10YR 5/4); pale brown (10YR 6/3) or light yellowish brown (10YR 6/4); sandy loam; weak, fine, granular to weak, fine, subangular blocky structure; very friable when moist and soft when dry; medium acid; abrupt wavy boundary. 6 to 20 inches thick.
B1m	16-25"	Brown (10YR 5/3) to pale brown (10YR 6/3); sandy loam to light sandy clay loam; massive to weak, thick, platy structure; firm when moist and brittle when dry; weak to moderately developed fragipan; few thin clay flows; medium to strongly acid; clear wavy boundary. 4 to 12 inches thick.

B2g	25-46"	Brown (10YR 5/3) to yellowish brown (10YR 5/4) mottled with yellowish brown (10YR 5/8) and dark brown (7.5YR 4.4), mottles are common, medium, distinct; sandy clay loam, heavy sandy loam, or light clay loam; few thin clay flows; weak, medium, subangular blocky structure; firm when moist, strongly to medium acid in the upper part and slightly acid in the lower part; abrupt irregular boundary. 15 to 30 inches thick.
Cg	46"+	Light yellowish brown (10YR 6/4) to brown (10YR 5/3) mottled with yellowish brown (10YR 5/6 - 5/8), mottles are common, medium, distinct; sandy loam; massive to very weak, coarse, subangular blocky structure; friable when moist and hard when dry; calcareous.

Topography: Gently to moderately sloping till plains and moraines.

Drainage and Permeability: Moderately well drained. Surface runoff is slow to moderate. Permeability is moderate to slow depending upon the degree of development of the fragipan.

Natural Vegetation: Deciduous forest consisting of sugar maple, beech, oaks, and hickories.