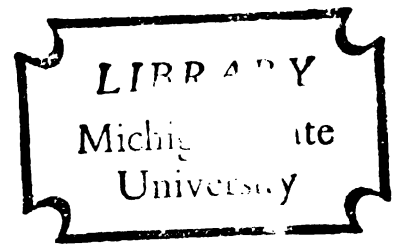


EFFECTS OF LONG-TERM APPLICATION OF HIGH
RATES OF NITROGEN CARRIERS ON SOIL ACIDITY,
EXCHANGEABLE CATIONS AND SOIL ORGANIC MATTER

Thesis for the Degree of M. S.
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ABSTRACT

EFFECTS OF LONG-TERM APPLICATION OF HIGH RATES OF NITROGEN CARRIERS ON SOIL ACIDITY, EXCHANGEABLE CATIONS AND SOIL ORGANIC MATTER

By

Ebinimi F. A. Burutolu

Residual effects of 14 annual applications of eight nitrogen carriers at rates of 300 lb N/A were studied on a Hodunk sandy loam soil. Data collected by others over a period of 16 years from initiation of the experiment are summarized. Data collected by the author in two succeeding years are presented.

The eight nitrogen carriers were applied in a randomized complete block design with four replications. Corn (*Zea mays* L.) was grown each year from 1959 to 1972. A basal fertilizer control and an unfertilized check were included. The ten treatments were discontinued in 1973 when wheat (*Triticum aestivum* L.) was grown with uniform fertilization on all plots, followed by soybeans [*Glycine max* (L.) Merr.] in 1974, 1975 and 1976. Dolomitic lime was applied on two of the four replications in 1965 and again in 1966. The total for the two applications was two times the requirement determined by the SMP buffer test on each plot.

Soil pH in the plow layer was initially about 6.0. With $(\text{NH}_4)_2\text{SO}_4$, soil pH had declined to a limiting low value of about 4.2 in 1962 after four annual applications. A similar limiting value

was reached by other acidifying carriers in the order: NH_4Cl (1965), NH_4NO_3 (1967), urea and ureaform (1970). Occasional values of less than 4.2 were encountered from time to time, indicating the presence of free mineral acid at the time of sampling. With anhydrous NH_3 , a limiting low value of 4.5 was reached in 1971. $\text{Ca}(\text{NO}_3)_2$ had little residual effect on soil acidity, but NaNO_3 maintained a consistently higher pH than in control plots which received only basal fertilizer.

Lime requirement (potential acidity) increased rapidly in the plow layer at about pH 5.0 and then progressed quickly into the sub-soil. By 1971, the increase in potential acidity to a depth of 30 inches was two to three times greater than the expected residual acidity from acidifying N carriers. It appeared that acidity which had accumulated in polymeric Al complexes before the experiment was initiated in 1959 was quickly released as exchangeable Al when the pH dropped below 5.0.

Bray P_1 in the plow layer increased in several treatments in unlimed and limed plots over time. Significant differences were mainly between no fertilizer and plots that received basal fertilizer.

The capacity of the soil to retain exchangeable basic cations was reduced by the high levels of exchangeable Al indicated by the high lime requirement. Exchangeable Ca and Mg were depleted to very low levels throughout the 30" profile by 1975. Similar depletion of exchangeable K did not occur, probably because of rapid release from non-exchangeable forms.

Levels of exchangeable Ca and Mg were restored by addition of dolomite, but a significantly lower level of exchangeable Mg was maintained after liming with NH_4Cl and $\text{Ca}(\text{NO}_3)_2$ than with other carriers. Liming did not completely neutralize accumulated acidity

in $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl plots by 1975. Specific carrier ion effects on persistence of acidity and on retention of cations were observed for Cl^- vs SO_4^{2-} and for Ca^{2+} vs Na^+ .

There was evidence that nitrification of ammonium was retarded in very acid soils. Liming increased nitrification because it provided suitable environmental conditions for the nitrifying bacteria. Detection of substantial quantities of nitrate in acid unlimed plots indicates the presence of acid tolerant strains of bacteria or the spontaneous formation of nitrate from nitrite at very acid pH.

Residual organic matter was higher and had wider C:N ratios in unlimed acid plots than the limed plots, although return of residues as indicated by yields of corn and soybeans had been reduced drastically below pH 5.0 and was restored by liming.

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Ebinimi F. A. Burutolu

A THESIS

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

MASTER OF SCIENCE

Department of Crop and Soil Sciences

TO MY PARENTS

*This thesis is dedicated to my beloved parents
for their prayers and encouragement
all these years.*

ACKNOWLEDGEMENTS

The author would like to express his profound gratitude to Dr. A. R. Wolcott for his wonderful and most rewarding guidance through all phases of the research. The amount of time we spent together in preparing the thesis has been quite invaluable.

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INTRODUCTION

In both the tropics and temperate regions, sustained high production of non-leguminous crops can be accomplished by the application of nitrogen. Admittedly, certain amounts of inorganic nitrogen can be provided from natural sources: crop residues, animal manures, precipitation, symbiotic and non-symbiotic nitrogen fixation. Whether or not the amounts from these sources are sufficient for maximum crop production depends, among other things, on the crop yield potential and nitrogen requirement, soil moisture content, quantity and quality of organic matter and the rate of mineralization from unavailable forms. In the shifting system of cultivation practiced mainly by subsistence farmers in the tropical world, crop production depends solely on the natural ability of the soil to furnish essential nutrients to the crops. Reasonable production is obtained where there is an equilibrium between uptake of nutrients by the crops and their return as litter during the fallow and cropping periods. Crop production cannot depend solely on these natural regenerating systems in this rapidly expanding world, with the change in emphasis from subsistence farming to intensive production-oriented systems.

Thus, natural and biological sources of nitrogen must be supplemented and in some cases entirely substituted with fertilizers.

Soil reactions and crop responses have been investigated extensively since the introduction of fertilizers into farming

systems. Effects of fertilizers on the environment have caused great concern.

The objectives of this research are to investigate the following aspects of applying nitrogen fertilizers:

1. Evaluate the trend of residual effects of several nitrogen carriers applied at high rates (300 lb N/a) on corn and soybean yields over time.
2. Evaluate long-term effects over the same period of time on soil pH, buffer pH, available P and exchangeable K, Ca, Mg.
3. Evaluate long-term effects of these carriers on the organic matter of surface and subsoils.

LITERATURE REVIEW

Soil Acidity and Nitrogen Carriers

Numerous studies have shown that soil acidity tends to increase with the continuous application of heavy rates of some nitrogen fertilizers (Pierre, 1928). The increase in acidity may be due to differential adsorption of cations or anions by plants (Kappen, 1927), microbiological activity (Volk, 1955), or differential retention of anions by complex formation. The rate of acidification depends on the source and rate of nitrogen fertilizer, amount of exchangeable bases removed, soil type, length of time the fertilizer and soil are in contact, and climatic factors.

Wolcott (1964) reported that nitrogen carriers may have direct and/or residual effects which may be basic or acidic depending on the carrier. Any salt may have a direct acidic effect initially. This is due to the salt effect which involves the displacement of H^+ ions by cations as shown below:



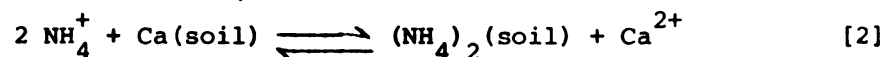
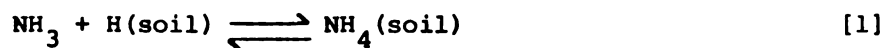
Residual effects may be acidic or basic, depending upon the salt and the extent to which anions or cations are removed differentially by crops or by leaching.

In the case of ammoniacal nitrogen carriers (those which contain or release NH_3 or NH_4^+), residual acidity will arise due to the

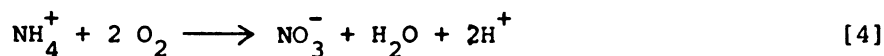
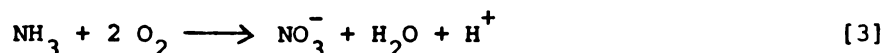
formation of H^+ ions during nitrification (Alexander, 1965). This is the major source of residual acidity, and is the reason why ammoniacal N fertilizers have a much greater acidifying effect on soils than most other fertilizer materials.

Pierre (1928) noted that differential removal of nutrients by crops or by leaching may be an important mechanism for development of residual acidity over a period of years. However, he used the term physiological acidity to describe the substantial acidity formed at the time when fertilizer ammonium is being oxidized to nitrate. Wolcott et al. (1965) pointed out that physiological acidity produced from NH_4^+ is twice that formed from NH_3 . The sequence of reactions involved in development of residual acidity and increasing lime requirement may be summarized by the following:

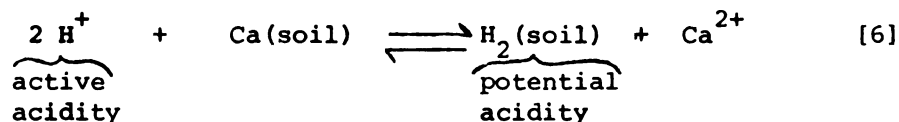
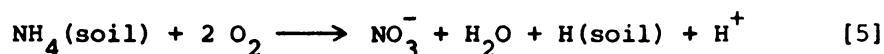
a) Adsorption of ammonia or ammonium by soil colloids:



b) Oxidation of ammonia or ammonium to nitrate:



c) Increase in potential acidity (lime requirement):



Reactions [1] and [2] show that either NH_3 or NH_4^+ , when added to soil that is not highly alkaline, will be adsorbed immediately on the exchange complex as NH_4^+ . Reactions [3] and [4] show that the

expected production of acidity (H^+ ions) will be twice as great from nitrification of NH_4^+ as from NH_3 .

The nitrifying bacteria in soil probably have access only to the adsorbed NH_4^+ formed by reactions [1] or [2]. Nevertheless, the essential reactions of nitrification involve NH_3 , as shown in reaction [3]. As a result, when adsorbed NH_4^+ is nitrified, as in equation [5], part of the acidity produced appears initially as exchangeable H^+ and part of it as H^+ ions in solution.

The equilibrium in equation [6] is very much in favor of adsorption of H^+ from solution onto the soil exchange complex. Thus, much of the acidity produced by nitrification appears initially as exchangeable H^+ on soil mineral and organic colloids. Further reactions are slower, but they lead to incorporations of H^+ ions into complexes with hydrated Al oxides and hydroxides already present in the soil or released by continuing decomposition of aluminosilicate minerals.

In equations [5] and [6], the H^+ ions in solution represent "active" acidity which can be measured with a glass electrode as pH. The H^+ adsorbed on soil represents "potential" acidity or "buffer" acidity. Potential acidity may be defined as the soil's capacity to feed H^+ ions back into solution, by reversal of equation [6], when lime is applied to produce a desired change in pH. Potential acidity, or "lime requirement", can be estimated from the pH change in a standard buffer when soil is added to it.

According to Jackson (1963), the principal form of potential acidity in soils from pH 4.2 to 5.0 or 5.2 involves complexes of exchangeable Al with H^+ . From pH 5.2 to 7.0, the principal forms of potential acidity include organic matter and $Al-H^+$ complexes which

are not exchangeable but which carry positive charge and serve to counter the negative charge at exchange sites.

Both exchangeable and non-exchangeable Al-H^+ complexes serve to reduce the soil's capacity to retain other cations on the exchange complex. For this reason, accumulating potential acidity is usually accompanied by depletion of exchangeable nutrient cations such as Ca^{2+} and Mg^{2+} .

The roles of different forms of aluminum in soil acidity, as well as the roles of other mineral colloids and organic matter, have been treated extensively in the literature (Mirasol, 1920; Paver and Marshall, 1934; Howard and Coleman, 1954; Jenny, 1961; Jackson, 1964; McLean et al., 1964).

The increase in soil acidity with application of ammonium sulphate has long been recognized (Wheeler, 1893; Allison and Cook, 1917; Ruprecht and Morse, 1915; Morgan and Anderson, 1928; White, 1931; Leo et al., 1959). Pierre (1928) compared the relative effects on acidity of sources of nitrogen fertilizers and found it to be of this order: ammonium sulphate > ammonium phosphate > leunasalpeter > urea > ammonium nitrate. A similar result was reported by Kolbe and Scharf (1967).

Brown (1934) reported that application of sodium nitrate increased pH while ammonium sulphate caused a decrease in soil acidity when materials were applied in amounts equivalent to 21 and 63 pounds of nitrogen per acre, respectively, in a greenhouse study. In the dry-land regions of the Northern Great Plains, Power et al. (1972) reported the greatest reduction in pH with $(\text{NH}_4)_2\text{SO}_4$ in an experiment where corn (*Zea mays*) and bromegrass (*Bromus inermis*) were grown on a sandy loam soil of pH 6.5. Soil pH values for $\text{Ca}(\text{NO}_3)_2$ treated

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plots were higher than $(\text{NH}_4)_2\text{SO}_4$ treated plots but similar to those for the check.

On red sandy loam soils of Bangalore, India, Rao et al. (1971) found that at high rates of $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl application, pH decreased in both leached and submerged soils. In the submerged soils, the decrease in pH was directly related to the depletion of exchangeable Ca^{2+} and Mg^{2+} and inversely to the increase in exchangeable H^+ in the soil.

At high rates of application of urea and ammonium nitrate, Volk (1955) found low pH with ammonium nitrate. He attributed this to differential adsorption by plants of bases such as calcium, or to movement of bases along with the nitrate ion into the subsoil.

Nitrogen carriers have been shown to have immediate, but temporary, effects on soil acidity. Residual effects may be counteracted by release of bases through weathering of soil minerals or through additions of liming materials.

The CaCO_3 equivalent of residual acidity or basicity is an important property of fertilizer materials. Thus, anhydrous NH_3 is strongly basic initially but, when it nitrifies, residual acidity equivalent to about 1.8 lb CaCO_3 is produced for each pound of N. The equivalent residual acidity from NH_3NO_3 , urea and ureaform is similar. Residual acidity from $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl is considerably greater because much of the SO_4^{2-} and Cl^- is not removed by plants and these surplus anions promote leaching of bases. Commonly accepted residual acidities are 5.5 lb CaCO_3 per lb N for $(\text{NH}_4)_2\text{SO}_4$ and 5.3 for NH_4Cl (Wolcott, 1964). Residual acidity from the sulphate salt is greater than for the chloride because H_2SO_4 tends to form complexes

with aluminum compounds in soils and is retained as an acidic residue to a greater extent than HCl.

In the case of $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 , nitrate is absorbed more extensively by plants than Ca^{2+} or Na^+ . The surplus cations tend to be retained on the exchange complex and leave a basic residue with a neutralizing value of about 1.8 lb CaCO_3 per lb N.

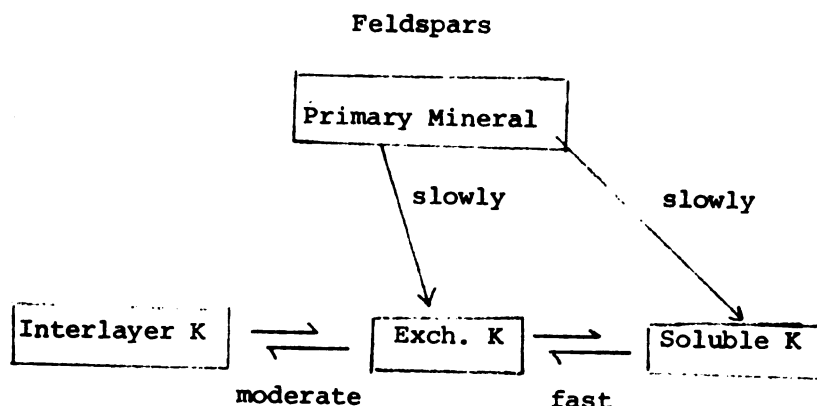
Relationship Between pH and Nutrient Availability

Phosphorus and Potassium

Brown (1934) found that application of $(\text{NH}_4)_2\text{SO}_4$ as nitrogen source reduced pH but had no effect on phosphate availability. Fudge (1928) reported that $(\text{NH}_4)_2\text{SO}_4$ did not only cause an increase in acidity but also caused a marked decrease in phosphate availability, along with some negative effects on calcium. Trogdan and Volk (1949) reported that availability of phosphate depended upon whether the nitrogen fertilizer was banded or broadcast. Banding of N decreased while broadcasting had little effect on availability of applied phosphate. Davis (1938), using Truog's method for determining available P, reported the availability of P decreased with an increase in soil acidity associated with the application of nitrogen fertilizers. Schafer et al. (1968b) reported that all nitrogen carriers, especially anhydrous NH_3 and $(\text{NH}_4)_2\text{SO}_4$, promoted the release of soil phosphorus. The effect of NH_3 was ascribed to the fact that the hydroxyl ion formed from hydrolysis of NH_3 is effective in displacing absorbed phosphorus.

Potassium is an important macronutrient in the soil. It is much greater in content than nitrogen and phosphorus in mineral soils. It exists in exchangeable, soluble, interlayer and primary mineral forms.

The latter two forms may be classified as non-exchangeable. These forms are in equilibrium as shown below:



Removal of K in one form shifts the various equilibria in accordance with mass action. Among other factors, the type of colloid, soil pH, wetting and drying, and temperature affect the K equilibria in soils (Tisdale and Nelson, 1975).

Potassium availability is low at low pH. It is likely that K^+ and other cations move down the profile in company with surplus anions. However, Crowther and Basu (1931) reported no evidence that intense acidity caused by nitrogen fertilizers decreased the level of exchangeable K. Prince et al. (1941) reported no apparent nitrogen fertilizer effect on the amount of exchangeable K in a 40-year study of nitrogen fertilizers. The availability of P and K were studied by determining their solubility as indicated by their concentration in displaced solutions and in 1:5 extract using 0.04 N H_2CO_3 or 0.2 N H_2NO_3 . Fudge (1928) concluded that basic fertilizers decrease the amount of water soluble K while acid forming fertilizers caused an increase.

Wolcott et al. (1965) studied the patterns of acidification associated with eight sources of nitrogen applied at annual rates of 40 to 300 lb N per acre in long-term experiments, including the one

used in the present study. They reported that all acidifying carriers maintained exchangeable K at levels higher than basal fertilizer, but that exchangeable K continued to decline over the three-year period beginning the third year after annual applications of N carriers were initiated.

Calcium and Magnesium

In acid, humid region soils, Ca, Al and H^+ ions occur in the greatest quantity on the exchange complex (Tisdale and Nelson, 1975). Plants absorb Ca largely from the soil solution as the ion Ca^{2+} . In soil systems the exchangeable and solution forms are in dynamic equilibrium. There is a definite correlation between pH and the amounts of exchangeable Ca and Mg in humid region soils. A decrease in soil pH is marked by a decrease in the amount of Ca and Mg in the soil solution. It is then to be expected that nitrogen carriers which have significant effect on soil pH will encourage the loss of Ca and Mg if applied in heavy amounts over periods of time.

Crowther and Basu (1931) reported significant reduction of replaceable calcium by $(NH_4)_2SO_4$ compared to $NaNO_3$. The differential effect on replaceable magnesium was so small as to be within experimental error. Davis (1938) also reported a decrease in soil bases with an increase in soil acidity in Olivier silt loam in Louisiana. Prince et al. (1941) summarized results of a 40-year study of the comparative effect of various carriers of nitrogen on nitrogen recovery and on the status of the exchange complex in Penn loam soil in Alabama. They reported that the use of $(NH_4)_2SO_4$ caused a reduction of exchangeable Ca. There were similar effects on exchangeable Mg.

Results of long-term treatments with $(\text{NH}_4)_2\text{SO}_4$ on the soil-calcium status under field conditions in the Northeastern tea growing region of India showed that there was a significant reduction in the calcium content of the soil (Gokhale and Bhattacharyya, 1958). In the tropics, where high rates of nitrogen fertilizers are applied in order to get maximum yields, the residual acidity from $(\text{NH}_4)_2\text{SO}_4$ can cause rapid changes in soil nutrient status. Pearson et al. (1962) reported the use of high rates of acidifying N fertilizers caused a significant downward movement of Ca and Mg in the profiles of typical latosolic and red-yellow podzolic soils used for the production of forage grasses in Puerto Rico.

On the other hand, Chaudhry and Vachhani (1965) reported no effect of long-term applications of $(\text{NH}_4)_2\text{SO}_4$ on exchangeable Ca in rice soils when moderate rates were applied. Yield response of rice increased with increasing rates up to 40 lbs N/a, and continued applications did not affect soil pH.

In the third, fourth, and fifth years of the long-term experiment used in the present study, Wolcott et al. (1965) reported significant losses of exchangeable Ca and Mg where acidifying carriers had been applied annually at 300 lbs N/a. In the eighth year of the same study (1967), Schafer et al. (1968b) observed extreme depletion of exchangeable Ca and Mg as soil pH dropped below 5.0. It was noted that levels of Ca and Mg were influenced by the anion or cation associated with N in the different carriers. For example, the calcium in $\text{Ca}(\text{NO}_3)_2$ maintained soil calcium but accelerated depletion of soil magnesium.

Liming and Nutrient Availability

Liming is an important management practice that has long been recognized. The methods of liming are as varied as the liming materials. The ability of crops to make effective use of applied fertilizers through the influence of liming on plant growth is due to one or more of the following: "supplying Ca and Mg as nutrients; maintaining availability of applied nutrients; improving availability of native soil nutrients; enhancing desired types of microbiological activity; improving root development; and reducing toxic effects of Mn or Al" (Pearson, 1958). These effects may be direct or indirect. The effects of liming have been extensively studied.

Phosphorus and Potassium

One of the anticipated benefits of liming is to increase the availability of phosphorus. Salter and Barnes (1935) reported that liming increased the availability of phosphorus in soil. Over a two-year period on La Terraza and La Vega clay loam soils at Zamorano in Honduras, Awan (1964) observed a significant increase in soil P liberated from the organic fraction with liming. Similar results were reported by Stewart and Pearson (1952) and Davis (1938). Liming increased the availability of phosphate and corrected the detrimental effects of acid-forming nitrogenous fertilizers (Fudge, 1928). Schafer (1968) reported no significant increase in available P where lime had been applied the year before in amounts equal to two times the lime requirement by buffer test. In fact, he found more extractable P in unlimed than in limed plots. This may have been due to interaction effects of anion exchange.

It may also be pointed out that the availability of P with liming depends on what governs the solubility of phosphate in a given soil, the method of extraction and the type of phosphate ion in solution. Phosphate solubility diagrams predict the changes that may be expected with the application of lime where phosphate equilibria are dominated by Fe or Al in the presence of different phosphate minerals (Lindsay and Moreno, 1960).

The availability of K as influenced by liming has been a subject of much confusion. Bradley (1910) found that liming gave increases in soluble K. Gaither (1910) reported that liming did not have any liberating effect on K.

Bradfield (1924) noted that the above disputes were caused by the failure of investigators to consider soil acidity. He said that, unlike CaSO_4 , the Ca in CaCO_3 cannot appreciably liberate other soil bases until the acidity of the soil is neutralized.

MacIntyre et al. (1930) showed a repressive effect of lime on the solubility of K. Jenny and Shade (1934) reported that addition of CaCO_3 liberated K.

After extensive further studies, Peech and Bradfield (1943) concluded that the addition of lime to soils containing neutral salts may have no effect, may decrease, or may increase the concentration of K in soil solution, depending on the initial degree of base saturation of the soil. York and Rogers (1947) studied six soils in Alabama with wide ranges of exchange capacity, total K content and exchangeable bases. They concluded that the addition of lime could result in an increase or decrease in available K depending on the ability of the soil to fix K and, also, on the amount, kind and solubility of K-bearing minerals in the soil. Bonnet (1946), working with lateritic

soils from Puerto Rico, showed a significant increase in available phosphorus and calcium and a decrease in available iron 15 and 23 months after the application of lime.

Calcium and Magnesium

Duley (1924) reported an increase in the concentration of Ca, with liming, in displaced solutions. Rost and Zetterberg (1932) conducted a study on the effect of liming on the exchangeable Ca and Mg content in Southeastern Minnesota. They found that Ca and Mg content increased with liming and that replaceable bases decreased from the surface with depth.

Schafer (1968) assessed the nutrient status of soils in the long term N carrier experiment used in the present study. Samples were taken in the eighth year of the experiment, one year after half of the plots were limed. He found that the limed plots contained more exchangeable Ca and Mg than unlimed plots. In plots treated with $\text{Ca}(\text{NO}_3)_2$, Ca suppressed exchangeable Mg in limed and unlimed plots.

Effect of Anions of Nitrogen Carriers on Ion Retention and/or Losses

The nature and concentration of anions in percolating soil solution influence the vertical movement of exchangeable bases in the soil (Pearson et al., 1962). Gillingham and Page (1965) reported that the enhancing effects of anions on vertical movement of Ca and Mg through the profile and into the leachate were in the order of solubility of their respective salts: $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{=2-} > \text{PO}_4^{=3-}$.

Anions may also affect the adsorption of cations by the soil exchange complex. It appears that the surface charge density of soil materials does not remain constant, but varies with the surface

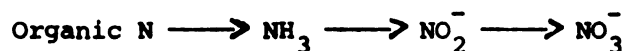
environment. Anions are not considered by some authors to significantly affect adsorption characteristics of soil materials (Eaton, 1950; Marshal, 1949). However, it has been indicated by others (Kelly, 1957; Bower and Truog, 1941; Sommerfeldt, 1962) that such effects may be significant.

Mineral Nitrogen

Wolcott et al. (1965) reported the effect of various nitrogen carriers on the nitrate levels in the long-term experiment used in the present study. They found no evidence of interference of nitrification at low pH in soils. Weber and Gainey (1962) found that nitrate may be produced in soils with pH as low as 4.0. They suggested the presence of acid tolerant strains or that the nitrifying organisms may be protected from acid effects by other mechanisms.

Alexander et al. (1960) defined nitrification as the "biological conversion of nitrogen in organic or inorganic compounds from a reduced to a more oxidized state." This definition includes the possibility of nitrate formation from other compounds such as amides, amines, hydroxylamine, and oximes (Tisdale and Nelson, 1975).

It is not known how important the direct production of NO_3^- from organic N substrates may be in nature. The generally accepted sequence of events, according to Alexander (1961) and Campbell and Lees (1967), is the following:



According to this sequence, organic N is released by decay organisms as NH_3 . The NH_3 is oxidized to NO_2^- by a specific group of bacteria (*Nitrosomonas* spp.). The NO_2^- is oxidized to NO_3^- by another

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specific group (*Nitrobacter* spp.). The two oxidation steps together are referred to as nitrification.

Under normal conditions, nitrification is rapid. Neither NH_4^+ nor NO_2^- accumulates in appreciable concentrations unless environmental conditions are unfavorable for one or both groups of nitrifying bacteria. Whether NH_4^+ or NO_2^- accumulates will be determined by which group is more severely restricted in its activity.

Any of the mineral forms of N (NH_3 , NH_4^+ , NO_2^- , NO_3^-) can be taken up by crops (Allison, 1973). Excessive concentrations of the incompletely oxidized forms can have unfavorable effects on some plants. Under normal conditions, NO_3^- is the principal form available through much of the growing season because nitrification is so rapid in warm, moist, well-aerated soils.

In addition to removal by crops, mineral N forms can be lost from soils in various ways (Allison, 1973). NH_3 can be lost by volatilization if anhydrous NH_3 is improperly injected or if ammoniacal fertilizers or livestock manures are topdressed, particularly on alkaline soils. Nitrite and nitrate can be lost by leaching or by biological denitrification (reduction to N_2O or N_2) under excessively wet conditions. Under acid conditions, NO_2^- can be lost also by chemical denitrification due to chemical reactions of undissociated nitrous acid (HNO_2). Erosion by wind or water can, of course, lead to losses of both organic and mineral forms of N.

Organic Matter as Affected by Nitrogen Carriers

In absence of fertilizers, soil organic matter is important primarily as a source of nitrogen. Except in newly tilled virgin soils, the rate of release of N is too low to support a high level of

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production of cultivated crops. Numerous technologies have evolved to augment or replenish soil organic matter as a source of N: use of livestock manures, legumes, shifting agriculture and, within the last 50 years, the large scale use of nitrogen fertilizers produced industrially.

The use of industrially fixed nitrogen for fertilizer has increased many-fold since World War II, with the result that intensive management systems have developed which make little or no provision for practices that will maintain soil organic matter or retain unused fertilizer N in the soil. However, at the present time, energy shortages and concern for environmental pollution are arousing new interest in the role of soil organic matter in recycling of N and other nutrients. Declining organic matter is suspected to be one of the causes for problems of reduced infiltration, impeded aeration and restricted root development in many intensively cropped soils.

Soil organic matter content of any horizon depends partly on how much organic matter from crops or other vegetation is turned over to the soil every year and partly on what percentage of the organic matter decomposes during the year. The organic matter content is stable when the two processes are balanced, plus or minus allowances for eluviation of humus (Rich and Obenshain, 1943). They reported that fertilizer and cropping practices which tended to increase crop yields tended to increase soil organic matter and cation exchange capacity. On the other hand, Salomon and Smith (1947) found that, despite higher yields in limed plots, more organic matter accumulated in the more acid soils of unlimed soils which received N from the same sources. Apparently the effect of lime was to increase annual

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decomposition rates to an even greater extent than the annual return of crop residues.

Because soil pH can influence both the production of residues and their rate of decomposition, reported effects of liming on soil organic matter are varied and often conflicting. White and Holden (1924) found that soils which received lime treatments showed a significant increase in N above that found in untreated soils. Greater loss of nitrogen was reported on limed plots than unlimed plots (Mooers et al., 1912). Potter and Snyder (1916) reported basically similar findings.

It may be noted that there is a general lack of treatment in the literature of effects of specific nitrogen fertilizers on organic matter. It is generally assumed that any carrier that increases plant growth will increase the organic matter by way of increased crop residues. This may not always be the case.

Dodge and Jones (1948) concluded that there had been a continual loss of soil nitrogen and carbon over the period 1915-1945 in a long-term management experiment, regardless of cropping system or fertilizer treatment. It was found that fertilizer treatment had no influence on the nitrogen trends in the soil or C:N ratios. It may be noted that only NaNO_3 was used as the source of nitrogen. In a 7-year cropping study, Mazurak and Conrad (1966) found that nitrogen fertilizers either minimized the losses or increased the total-N content of the plow layer (0-6"). Scharf (1967) reported a decrease in soil nitrogen which was greatest in plots that received NaNO_3 or $\text{Ca}(\text{NO}_3)_2$ and least in plots that received calcium-ammonium nitrate and ammonium sulphate.

There is not much literature on changes in the C:N ratio with the application of nitrogen carriers. Waksman (1942) considered C:N ratio as the factor that controls most of the liberation of nitrogen in available forms during the decomposition of plant residues. Leo et al. (1959) reported that $(\text{NH}_4)_2\text{SO}_4$ caused a downward movement of organic matter and there was a wider C:N ratio in the subsoil.

Crop Yields as Affected by Nitrogen Carriers

Nitrogen is regarded as one of the primary elements in plant growth. Investigations have been carried out not only to test the effects of rate but also the effects of sources of nitrogen. These research objectives arise from the fact that different types of nitrogen carriers undergo remarkable soil reaction which should cause concern to those who "dump" heavy amounts of fertilizers to get maximum yield.

Tidmore and Williamson (1932) conducted 222 tests, during a 5-year period, with $(\text{NH}_4)_2\text{SO}_4$ and NaNO_3 . They reported that $(\text{NH}_4)_2\text{SO}_4$ produced lower yields than NaNO_3 . They attributed it to low pH caused by the continued use of acid forming fertilizers, and to depletion of soil bases.

Prince et al. (1941) reported that nitrate of soda was the most effective carrier of nitrogen. The average crop yields were greater from the use of this material per unit of nitrogen applied than any other source of nitrogen.

Scarbrook and Cope (1957) summarized the results, from 1925 through 1955, of field experiments on sources of nitrogen for cotton and corn. They reported that a primary cause of reduced yields was the low pH produced by the acid-forming sources of nitrogen, without

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the addition of lime, would eventually cause reduced yields on nearly all soils in Alabama. Sodium nitrate, at rates applied, maintained the soil pH at approximately constant level without the addition of lime. Chaudhry and Vachhani (1965) reported that $(\text{NH}_4)_2\text{SO}_4$ may not be deleterious on a long-term basis, if applied at moderate rates. They found that yield response of rice increased with increasing rates of $(\text{NH}_4)_2\text{SO}_4$ up to 40 lbs N/a, on a silt loam soil, but did not affect soil pH, total-N or C.

Power et al. (1972) found greater corn (*Zea mays*) response to $(\text{NH}_4)_2\text{SO}_4$ than $\text{Ca}(\text{NO}_3)_2$ at 110 Kg/ha than at 55 Kg N/ha. This was due mainly to leaching of the nitrate fertilizer.

Data reported by Schafer (1968) for the eighth season in the long-term N carriers experiment used in the present study show drastic reductions in corn yields where cumulative acidity from N fertilizers at 300 lbs N/a/yr had reduced soil pH to about 5.0 and virtually barren plots at a pH of about 4.0. Corn with the same carriers responded dramatically to lime applied one year earlier.

In an adjacent experiment on similar soils, Starr (1970) observed only moderate reductions in soil pH after three annual applications of NH_3 , NH_3NO_3 and urea at 255 lbs N/a/yr but not at lower rates which did not exceed the maximum yield response range of the corn.

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MATERIALS AND METHODS

Field Treatments

An experiment was initiated in 1959 on the Soil Science Experimental Farm at Michigan State University to study the residual effects of nitrogen carriers on soil and on crop yields. The cropping and basal fertilization history for these plots is given in Table 1-a. Basal fertilizer was broadcast and plowed down before planting.

The nitrogen carriers in Table 1-b were applied annually on corn (*Zea mays* L.) from 1959 to 1972 at 300 lbs N/a/yr (336 Kg/ha/yr). Solid carriers were broadcast after plowing and disced in before planting. Anhydrous NH_3 was injected in row middles when corn was knee-high. These eight treatments, plus an unfertilized check and a control treatment which received only basal fertilizer, comprise the ten treatments for which residual effects are reported in this thesis.

The application of different carriers on different plots was discontinued after 1972. Only the basal fertilizers in Table 1-a were applied on wheat (*Triticum aestivum* L.) in 1973 or on soybeans (*Glycine max* [L.] Merrill) in 1974, 1975, and 1976.

The ten treatments on corn from 1959 to 1972 were replicated four times in a randomized complete block design. Each plot was 14 x 25 ft (4.3 x 7.6 m). In the spring of 1965 and again in 1966 applications of dolomitic agricultural limestone were made on all

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Table 1-a. Crops and amounts of nutrients used in nitrogen carrier study from 1959 to 1976

Year	Crop	Basal fertilizer		Annual nutrients		
		Annually	Ratio N-P ₂ O ₅ -K ₂ O	N	P	K
		lb/a ^α		lb/a		
1959-72	Corn	200	5-20-20	10	17	33
1973	Wheat	150	6-24-24	9	16	30
1974	Soybeans	350	12-12-12	42	18	35
1975	Soybeans	350	12-12-12	42	18	35
1976	Soybeans	100	0-26-26	0	11	22

^αlb/a x 1.12 = kg/ha.

Table 1-b. Percent N and relative residual acidity of the nitrogen carriers in the field experiment

Carrier used on corn ^α	% N	Relative residual acidity ^β
(NH ₄) ₂ SO ₄	20.5	5.5
NH ₄ Cl	28.0	5.3
NH ₄ NO ₃	32.5	1.8
NH ₃	82.2	1.8
Urea	46.0	1.9
Ureaform	48.0	1.9
Ca(NO ₃) ₂	15.5	-1.3
NaNO ₃	16.0	-1.8

^αSupplemental N carrier applied at 300 lb N/a/yr (336 kg/ha) on continuous corn 1959 to 1971.

^βLbs of CaCO₃ to neutralize a weight of carrier containing one pound of nitrogen (Wolcott, 1964).

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plots in two of the four blocks. The two applications on each plot totalled 2 times the lime requirement by the SMP buffer test on that plot.

Michigan 480 Hybrid corn was used in the early years, but in later years Michigan 300 was grown. The row spacing in early years was 42 inches, but 28-inch rows were adopted in 1967. In 1970, the row spacing changed again to 42 inches when Pioneer 3773 corn hybrid was grown.

In early years, an initial plant population of 25,000 plants per acre was thinned to 16,000 plants per acre. In 1970, plant population was thinned from 21,000 to 18,000 plants per acre. Due to dry weather at planting time in 1971, emergence on most plots was less than 16,000 plants per acre. No observations were made in 1972.

Sources of Data

A number of people have been involved in this study over the years. The field experiment was established by J. F. Davis and H. D. Foth in 1959. Representative soil test data for 1961, 1962 and 1963 were reported by Wolcott et al. (1965). Corn yields, foliar analyses and soil tests in 1967 were reported by J. W. Schafer in a PhD thesis (1968). The 1967 results were summarized at national meetings by Schafer et al. (1968a,b), but never were published. Corn yields and extensive data on foliar analyses and soil tests in 1970 and 1971 were collected by A. R. Wolcott and B. D. Knezek, and recorded in the 1971 Research Report of the MSU Soil Science Farm. Additional data have been collected at various times by students of E. C. Doll, H. D. Foth, J. C. Shickluna and A. R. Wolcott. Many of

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these data were found in files of A. R. Wolcott and have been drawn on for historical background prior to 1975.

Soybean yields in 1975 and 1976 were taken by the author. Soil samples in 1975 were taken and analyzed by the author. Raw data for September 1966 and July 1971 were also reduced and subjected to analysis of variance by the author.

Soil Sampling

On September 25, 1975, soil samples were taken. Twenty cores were taken randomly from the plow layer (0-10") between the center rows of the plot. For the 10-20" and 20-30" depth, 5 core samples were taken from plots treated with basal fertilizer, $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 . A composite sample for each plot was obtained after passing the core samples through a 4-mesh (5 mm) screen. The moist samples were stored at 5°C until analyses for NH_4^+ , NO_2^- and NO_3^- were completed. They were then air dried for 8 days. For total C, $\text{CO}_3\text{-C}$ and Kjeldahl N analyses, an aliquot of the air-dry sample was ground to pass through an 80-mesh screen (0.18 mm). For other analyses, air-dry soil which had passed through a 2 mm screen was used.

Laboratory Procedures

Soil pH was measured with a glass electrode pH meter, using a 1:1 soil-to-water suspension. Available P was extracted with the Bray P_1 extractant using a 5-minute extraction. Exchangeable K, Ca and Mg were extracted with neutral 1 N NH_4OAc (5 minutes, 1:4 soil-to-extractant ratio). The extracted nutrients were determined after filtering through Whatman No. 1 filter paper, by procedures used

routinely in the Soil Testing Laboratory, Michigan State University, East Lansing.

Available P was determined from the color developed, accomplished by utilizing Ammonium Molybdate - Ascorbic Acid Method (Watanabe and Olsen, 1965). The Technicon Auto-Analyzer was used. Exchangeable Ca and Mg were determined after addition of La_2O_3 to an aliquot of the NH_4OAc extract, using the Perkin-Elmer 303 Atomic Absorption Spectrophotometer. Lanthanum was added to prevent ion interference associated with the ground state and excitement of electrons. Exchangeable K was determined in a separate aliquot of the same extract, using a Coleman Model 21/22 Flame Photometer (no lanthanum was added as was done for Ca and Mg determinations).

Lime requirement was estimated, using the p-nitrophenol, triethanol-amine buffer (pH 7.5) of Shoemaker et al. (1961). Lime requirement, as CaCO_3 , was calculated from the decrease in pH of the buffer from neutrality after equilibrating with soil (1:2 ratio of soil to buffer, 30 minutes). The acid equivalent of the buffer is $14.4 \text{ me H}^+ / 100 \text{ g}$ per unit pH, as given in Ohio Ext. Bul. 472 (1970-71):

$$\text{me H}^+ / 100 \text{ g} = 14.4 (7.0 - \text{buffer pH}).$$

Total N (excluding NO_2^- and NO_3^-) and NH_4^+ -N were determined by semi-micro methods described by Bremner (1960), Bundy and Bremner (1972), and Bremner (1965). Potassium sulphate-selenium mixture was used as catalyst in the Kjeldahl digestion for total N. The clear digestion mixture was made alkaline with NaOH, and NH_3 was distilled over into boric acid. See Appendix B. Exchangeable NH_4^+ was determined by distillation of a 1:1 suspension of soil in 2 N KCl in the presence of NaOH, and NH_3 was collected in boric acid. In both cases, NH_3 collected in

boric acid was titrated against standard acid, using a mixed indicator. Organic N was taken as the difference between Kjeldahl N and NH_4^+ -N.

Organic-C was determined by difference between total-C and carbonate-C. Total-C was determined using a LECO carbon analyzer (Belo, 1970; Appendix C). Carbonate-C was determined by the titrimetric method of Bundy and Bremner (1972), using 2 M HCl at room temperature.

Nitrate-N was determined on moist samples which had been stored at 5°C for two weeks after they were taken from the field. An automated procedure for the Technicon Auto-Analyzer (1972) was used. These soluble ions were extracted into saturated CaSO_4 solution (1:1 soil-to-extract ratio, 30 minutes). Nitrite in the extract is determined directly and nitrate after reduction to nitrite in a copper-cadmium reactor column. Nitrous acid then reacts with sulfanilamide under acidic conditions to form a diazo-compound. The compound then couples with N-1-naphthylethylenediamine dihydrochloride to form a reddish azo dye which is measured photometrically.

Statistical Analysis

Analysis of variance was performed on raw data from 1966, 1971, 1975 and 1976, using facilities of the Michigan State University Computer Center.

Data summarized here for years prior to the applications of lime in 1965 and 1966 had been analyzed in accordance with a randomized complete block design, with four replications. Treatments were randomized within each block. Since the two center replications were first limed in 1965, the data have been treated as for a split

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plot design, with lime or no lime as main plots and N treatments as sub-plots. Replications were, thus, reduced from four to two when lime was applied.

In general, split plot design may be used in experiments where the experimental units are large and/or the experimenter wants to compare subsidiary treatments. Also, it is used where the experimenter wants more precision in the sub-plot effects and interactions than the main plot effects (Cochran and Cox, 1965; Federer, 1955; Snedecor and Cochran, 1974; Steel and Torrie, 1960). Characteristically, the sub-treatments have larger degrees of freedom and generally smaller experimental error.

In the present experiment, the original plots were too small (14 x 25 ft) to split for lime on half of each plot. The loss of useful plot area to border effects would have been excessive. The loss of replication has resulted in LSD values which frequently exclude what must be considered to be a real difference. The basis of statistical inference with only one degree of freedom for lime is very weak.

To help overcome this serious weakness in design of the field experiment, data that have been collected over the course of the experiment are presented, in addition to those collected personally by the author. Changes over time serve to support differences which may not be statistically significant in any given year.

RESULTS AND DISCUSSION

History of Corn and Soybean Yields

Yields of corn in many years of the experiment were not taken or were of doubtful value because of damage from wildlife entering from an adjacent orchard. Representative yields in Table 2 reflect changes which were observed visually in the vegetative development of corn with different carriers, as noted in reports by Schafer (1968) and Schafer et al. (1968b).

Yields without lime with the two non-acidifying carriers, $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 , represent near maximum response of corn to nitrogen on this sandy loam soil without irrigation. By contrast, yields with the three ammonium salts declined sharply. The rate of decline from 1961 to 1971 was in the order: $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{NH}_4\text{NO}_3$.

In the early years of the experiment, maximum yields were obtained with anhydrous NH_3 , urea and ureaform. By 1971, the effectiveness of these carriers had declined to the point where yields were no different than for no fertilizer or for basal fertilizer only.

Addition of lime in 1965-66 did not affect yields on plots which received $\text{Ca}(\text{NO}_3)_2$, NaNO_3 or no supplemental N. Yields were increased dramatically by lime on all plots where acidifying carriers were used.

The long term trends in corn yields and the responses to lime reflect observed changes in germination and in survival and vigor of emerged plants, as is seen in the data for plants per acre in 1971

(Table 2). As will be seen, declining yields in plots which received acidifying carriers without lime were associated with declining soil pH and depletion of Ca and Mg. Analyses of seedlings in 1971 showed deficient levels of Mg and toxic concentrations of Mn for these treatments (Wolcott et al., 1971). Both of these nutritional imbalances were corrected where lime had been applied.

The nitrogen carrier treatments were discontinued after 1972. Nevertheless, residual effects of carriers were still apparent in soybeans in unlimed plots in 1974 and 1975 (Table 3). These residual effects were not apparent in limed plots.

In 1976, soybean yields on all plots were very low. This may have been due, in part, to the fact that no fertilizer nitrogen was applied in 1976 (Table 1-a). Also, the weather was very dry at flowering and during the pod setting period (rainfall in August was 0.56" and 1.85" in September, compared with the 15-year average for these months of 2.95" and 2.64"). Additional factors may have been build-up of disease due to growing soybeans three years in a row and declining fertility due to the low annual return of residues from soybeans.

Soil Test Changes Over Time

Soil pH and Lime Requirement

Some of the variation in pH values given in Tables 4-a,b and c is due to the fact that the determinations were performed by different analysts in different years. The determination is sensitive to variation in manipulation of the sample. The author found variations as great as 0.3 pH units between duplicate soil samples.

Table 2. Representative yields and stands of corn on plots which received 300 lb N/a/yr from various sources, beginning in 1959

Carrier	Bus. corn/acre ^δ			Plants/acre in ^δ			
	No lime		Plus lime ^α	No lime		Plus lime	
	1961	1967	1971	1967	1971	Emerged	Ears at harvest
No fertilizer ^β	56.3	26.0	29.2	38.8	54.2	14261	7390
Basal fertilizer ^β	48.0	53.6	29.9	46.2	44.3	14520	7130
(NH ₄) ₂ SO ₄	52.4	1.0	0	44.0	54.0	6093	0
NH ₄ Cl	64.0	14.3	0	59.4	40.2	6482	0
NH ₄ NO ₃	74.7	26.4	0.5	77.2	73.3	10372	389
NH ₃	93.4	70.4	38.2	94.7	65.0	14261	10242
Urea	89.9	69.0	22.3	50.2	73.1	11927	5575
Ureaform	94.8	72.0	25.6	62.8	62.3	13224	5186
Ca(NO ₃) ₂	86.4	85.3	83.0	83.8	60.7	13483	11668
NaNO ₃	85.6	64.2	81.4	77.6	77.8	13872	11798
LSD(.05) carriers within lime	17.0	25.6	34.5	25.6	34.5	5402	6756
LSD(.05) lime within carriers	-	-	-	22.0	31.2	---	---

^αDolomitic limestone, split into 2 applications (spring 1965, spring 1966) totaling 2 times lime requirement in early spring 1966.

^βBasal fertilizer: 200 lb/acre 5-20-20 (N-P-K=10-18-33).

^γData from 1971 Research Report, M.S.U. Soils Farm, East Lansing, Michigan.

^δMetric conversions:

Bus. corn/acre x .63 = quintals/hectare
Plants/acre x 2.47 = plants/hectare

Table 3. Residual effects on soybean yields of 14 annual applications (1959 to 1972) of nitrogen carriers (300 lb N/a/yr) on continuous corn

Carrier used on corn	Soybean yields			Lime Applied ^α T/a	Soybean yields		
	No lime				Plus lime		
	1974	1975	1976		1974	1975	1976
	—————Bu/a ^γ —————				—————Bu/a—————		
No fertilizer	19.3	15.9	5.9	4	20.4	15.3	9.3
Basal fertilizer ^β	17.6	13.9	5.3	6	18.9	17.3	8.0
(NH ₄) ₂ SO ₄	2.1	6.9	3.8	12	16.6	16.5	8.0
NH ₄ Cl	4.4	4.6	1.9	10	17.5	14.2	5.8
NH ₄ NO ₃	5.4	5.8	2.4	8	17.8	16.9	8.1
NH ₃	8.9	10.9	2.8	6	24.9	17.8	8.0
Urea	8.0	14.1	5.5	8	19.5	17.4	10.0
Ureaform	12.5	14.8	7.0	8	18.7	15.3	7.7
Ca(NO ₃) ₂	20.6	11.9	4.4	4	22.6	15.7	7.6
NaNO ₃	23.7	10.0	4.2	4	16.9	17.4	7.3
LSD (.05) carriers within lime	2.2	4.1	3.1		2.2	4.1	3.1
LSD (.05) lime within carriers					2.4	4.4	ns

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test. (T/a x 2.24 = TM/ha).

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γBu/a x .67 = quintals/ha.

Table 4-a. Changes in soil pH, plow layer, unlimed plots, 1961 to 1975

Carrier used on corn 1959-72	Soil pH in the plow layer ^Y of unlimed plots									
	Jul 61	Aug 62	Jul 63	1965	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Sep 75
No fertilizer	5.9	5.7	5.7	5.2	6.0	5.8	5.8	6.1	5.3	5.3
Basal fertilizer ^β	5.7	5.9	5.9	5.6	5.9	5.8	5.6	5.5	5.1	5.1
(NH ₄) ₂ SO ₄	4.5	4.2	4.0	4.1	3.9	3.8	3.8	4.1	3.8	4.2
NH ₄ Cl	4.9	4.6	4.4	4.3	4.0	4.0	3.8	4.3	3.7	4.4
NH ₄ NO ₃	5.4	4.8	4.8	4.4	4.4	4.1	4.2	4.5	3.8	4.2
NH ₃	5.2	5.4	5.1	5.6	5.1	5.2	4.5	4.7	4.6	4.5
Urea	5.1	4.9	4.9	4.8	4.7	4.3	4.2	4.5	3.9	4.4
Ureaform	5.4	5.3	5.0	5.0	4.8	4.6	4.2	4.5	4.1	4.3
Ca(NO ₃) ₂	5.7	5.8	5.8	5.6	5.7	5.4	5.8	5.8	5.3	5.3
NaNO ₃	5.9	6.0	6.2	6.2	6.4	6.2	6.4	6.5	5.6	5.6
LSD(.05) carriers within lime	0.5	0.4	0.5	No AOV	0.7	0.7	0.7	1.0	0.5	0.8

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^Y Data for depths by years: 1961(0-6"); 1962(0-8"); 1963, 1965, 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

Table 4-b. Changes in soil pH, plow layer, limed plots, 1965 to 1975

Carrier used on corn 1959-72	Lime applied ^α T/a	Soil pH in the plow layer ^γ of plots limed in 1965-1966							
		1965	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Oct 74	Sep 75
No fertilizer	4	5.8	6.5	6.7	7.2	7.0	6.7	6.7	6.7
Basal fertilizer	6	6.3	6.9	6.8	6.9	6.9	6.6	6.5	6.8
(NH ₄) ₂ SO ₄	12	4.2	4.4	5.1	5.4	5.8	5.5	6.0	6.2
NH ₄ Cl	10	4.5	4.6	5.0	5.0	5.6	4.9	5.4	5.3
NH ₄ NO ₃	8	5.0	5.5	5.6	6.0	6.5	5.9	6.4	6.7
NH ₃	6	5.1	5.7	6.1	6.1	6.2	5.8	5.7	6.2
Urea	8	4.6	5.6	5.7	6.2	6.6	5.4	6.7	6.7
Ureaform	8	5.0	5.7	6.2	6.4	6.6	6.3	6.0	5.9
Ca(NO ₃) ₂	4	6.2	6.7	6.4	7.0	7.0	6.5	6.2	6.8
NaNO ₃	4	6.2	7.0	6.9	7.3	7.2	6.5	6.4	7.0
LSD(.05) carriers within lime		No AOV	0.7	0.7	0.7	1.0	0.5	0.8	0.8

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γData for depths by years: 1965, 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

Table 4-c. Changes in soil pH, upper subsoil, unlimed and limed plots, 1961 to 1975

Carrier used on corn 1959-72	Soil pH in the upper subsoil ^γ									
	No lime					Plus lime ^α				
	Jul 61	Aug 62	Jul 63	Sep 66	May 71	Sep 75	Sep 66	May 71	Sep 75	
No fertilizer	6.4	5.5	5.7	6.4	6.3	---	6.2	6.7	---	
Basal fertilizer ^β	6.3	5.8	5.9	6.1	6.0	5.4	6.6	6.7	6.9	
(NH ₄) ₂ SO ₄	5.3	4.5	4.6	4.5	4.0	4.2	4.7	4.8	5.4	
NH ₄ Cl	5.8	5.2	4.9	4.7	4.0	4.5	4.8	4.6	4.9	
NH ₄ NO ₃	6.0	5.1	5.2	5.1	4.5	---	5.5	5.4	---	
NH ₃	5.9	4.5	5.1	5.1	5.0	---	5.1	5.4	---	
Urea	5.8	5.4	4.5	4.5	5.4	---	5.4	5.6	---	
Ureaform	5.8	5.4	5.7	5.7	5.4	---	5.9	5.6	---	
Ca(NO ₃) ₂	6.3	5.6	5.8	5.8	6.0	5.7	6.7	6.8	6.9	
NaNO ₃	6.7	6.0	6.7	6.7	6.8	6.4	6.6	6.4	6.6	
LSD(.05) carriers within lime	ns	0.6	0.5	0.7	1.6	1.9	0.7	1.6	1.9	

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γSampled upper subsoil depth for years: 1961(12-18"); 1962, 1963, 1966(10-15"); 1971, 1975(10-20").

Another source of variation is the season of the year when soil samples were taken. Except in highly buffered soils, pH declines during the forepart of the growing season because of the nitric acid produced by nitrification (Eno and Blue, 1957). As nitrification slows down, accumulated acidity is slowly neutralized by various soil buffer systems so that, by the spring of the following year, soil pH tends to return to the level of the previous spring. This annual fluctuation is apparent in plow layer data for several treatments over the sequence August 1970, May 1971, July 1971 (Table 4-a).

According to Jackson (1963), the ultimate buffer system in soils is the release of bases by decomposing primary and secondary silicate minerals. Because of mineral decomposition, most soils cannot remain long at a pH less than the "ultimate" pH of 4.2 unless free acids, such as sulfuric or nitric, are present.

This ultimate pH had been reached in the plow layer by 1962 after four annual applications of $(\text{NH}_4)_2\text{SO}_4$ at the rate of 300 lbs N/a/yr (Table 4-a). This pH was approached less quickly by other carriers but had been reached by 1970 with all acidifying carriers except NH_3 . The rate of decline in soil pH over this period was approximately in the order: $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{NH}_4\text{NO}_3 > \text{urea} > \text{ureaform} > \text{NH}_3$. The order of declining pH parallels rather well the order of declining corn yields (Table 2).

After the last application of N carriers at high rates in 1972, there was a tendency for the very low pH developed earlier to increase. However, the data for 1975 indicate that soil acidity was still being controlled mainly by decomposition of soil minerals at near the ultimate pH of 4.2.

Residual basicity from NaNO_3 maintained pH in the plow layer at levels distinctly higher than control plots which received only basal fertilizer. $\text{Ca}(\text{NO}_3)_2$ had little residual effect on soil pH at any time.

The lime applied in 1965-66 produced immediate increases in plow layer pH (cf. Tables 4-a and 4-b). However, by September 1966, full correction to the desired pH of 6.5 to 6.8 had been achieved only with the two control treatments and with $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 . The lime reacted very much more slowly with the acidity produced by acidifying carriers. With $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl and NH_3 , full correction was never achieved through 1975.

Soil pH in the plow layer of limed plots (Table 4-b) reached a maximum for several carriers in the May 1971 sampling. This spring sampling represents a seasonal high and should be ignored in assessing long-term trends. If only summer and fall samples are considered, it would appear that lime applied in 1965-66 was still reacting with residual acidity from several carriers through the last sampling in 1975.

Residual acidity from acidifying carriers moved quickly from the plow layer into the upper subsoil (Table 4-c). The rate of downward movement through May 1971 was greater for $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl than for other carriers.

Lime applied in 1965-66 had resulted in substantial correction of subsoil pH by 1971. Additional increases in pH of the upper subsoil had occurred by 1975. These findings are in agreement with reports of Blair (1934), Brown and Munsell (1936) and Brown et al. (1956) that lime applied to the plow layer had marked effect in reducing acidity in the subsoil.

Lime requirements from 1961 to May 1971 in Tables 5-a and 5-b were recalculated to make them directly comparable with those for later samplings. The recalculations included changing the assumed acid equivalence of the buffer from 10.0 to 14.4 me H^+ /100 g, and conversion of T/a for varying sample depths to a common basis (T/a - $6\frac{2}{3}$ ", or ppm $\times 10^3$). Data from 1964, 1965 and 1967 could not be adjusted to a common basis because buffer pH values were not recorded, and lime requirements greater than 5 T/a were recorded at 5 T/a.

Lime requirement in the plow layer increased dramatically when soil pH dropped to 5.0 or less (cf. Tables 4-a and 5-a). The increase occurred earlier with $(NH_4)_2SO_4$ than with other carriers. By August 1970, lime requirement with all six acidifying carriers had reached the range of 9 to 14 $\times 10^3$ ppm at soil pH values of 4.5 or less. In most cases, lime requirement remained in this range as long as high annual applications of N were being made. In the case of NH_3 , the relatively low value of 4.3×10^3 ppm in July 1971 may reflect alkalinity from the injection of NH_3 in late June.

The N treatments were discontinued in 1973, and all plots have been fertilized uniformly at much reduced N rates since then (Table 1-a). Lime requirements in unlimed plots which had received acidifying carriers had fallen sharply by 1974 (Table 5-a). Further decreases occurred in 1975 for several treatments which had been discontinued in 1973.

These decreases in lime requirement may have been due, in part, to leaching of exchangeable Al and other mobile components of potential acidity. The greatest downward development of lime requirement by 1971 had occurred with $(NH_4)_2SO_4$ and NH_4Cl (Table 5-b). The plow layer with these two carriers had been very strongly acid (pH 4.5 or

Table 5-a. Changes in lime requirement, plow layer, unlimed and limed plots, 1961 to 1975

Carrier used on corn 1959-72	Lime requirement in the plow layer ^γ								Lime requirement in the plow layer ^γ Plus lime				
	No lime								Lime applied ^α T/a				
	Jul 61	Aug 62	Jul 63	Aug 70	May 71	Jul 71	Oct 74	Sep 75	Aug 70	May 71	Jul 71	Oct 74	Sep 75
	ppm x 10 ⁻³								ppm x 10 ⁻³				
No fertilizer ^β	2.3	3.0	4.5	6.5	1.0	3.6	4.3	2.6	0.0	0.4	0.0	0.0	0.0
Basal fertilizer ^β	2.6	2.9	3.3	4.3	5.6	4.3	4.3	2.2	0.3	0.4	0.7	0.0	0.0
(NH ₄) ₂ SO ₄	6.6	8.9	10.9	12.2	9.6	11.5	5.8	5.8	5.0	5.8	3.6	2.2	2.2
NH ₄ Cl	4.3	4.3	8.6	13.0	12.0	9.4	6.5	5.0	10.5	6.5	3.6	4.3	1.4
NH ₄ NO ₃	3.3	4.3	7.2	9.4	7.9	9.4	5.0	4.3	1.4	1.0	2.9	0.7	0.0
NH ₃	4.5	4.6	6.9	13.0	12.2	4.3	5.8	5.0	4.3	2.9	2.2	3.6	0.0
Urea	4.0	3.2	7.2	13.0	8.6	8.6	5.0	5.4	1.4	0.7	3.6	0.7	0.0
Ureaform	3.3	3.7	6.2	14.4	10.8	6.5	6.5	5.8	1.2	1.4	0.7	2.2	0.0
Ca(NO ₃) ₂	2.6	2.0	2.6	4.3	4.3	3.6	4.3	2.9	0.0	0.0	0.0	1.4	0.0
NaNO ₃	3.3	2.3	2.2	6.5	6.8	2.9	4.3	2.5	0.0	0.0	0.0	0.7	0.0
LSD(.05)	1.8	2.5	2.4	5.6	7.5	3.2	ns	2.6	5.6	ns	3.2	2.4	ns

^α Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γ Data for depths by years: 1961(0-6"); 1962(0-8"); 1963(0-5"); 1970(0-7"); 1971, 1974, 1975(0-10").

^δ ppm x 10⁻³ = T/a - 6 2/3 = MT/ha - 17 cm.

Table 5-b. Changes in lime requirement, upper subsoil, unlimed and limed plots, 1961 to 1975

Carrier used on corn 1959-72	Lime requirement in the upper subsoil ^γ									
	No lime					Plus lime ^α				
	Jul 61	Aug 62	Jul 63	Sep 66	Sep 75	Jul 61	Aug 62	Jul 63	Sep 66	Sep 75
ppm x 10 ⁻³ δ										
No fertilizer	2.9	2.2	2.2	0.7	---	1.4	0.0	---	---	---
Basal fertilizer β	2.2	1.2	1.9	1.9	0.0	1.2	1.0	0.0	1.4	0.0
(NH ₄) ₂ SO ₄	3.6	3.3	5.6	2.6	5.0	2.6	12.2	4.0	2.6	3.6
NH ₄ Cl	3.3	1.9	3.5	2.6	3.6	2.9	11.5	6.8	2.9	1.4
NH ₄ NO ₃	3.0	1.9	2.9	2.2	---	1.4	3.9	7.2	1.4	---
NH ₃	3.6	3.3	4.5	2.6	---	2.2	4.3	5.8	2.2	---
Urea	2.6	1.6	2.7	1.9	---	2.2	3.3	3.9	2.2	---
Ureaform	2.9	1.6	2.2	1.9	---	1.4	3.3	1.0	1.4	---
Ca(NO ₃) ₂	2.9	1.4	3.3	1.9	0.0	0.0	1.9	0.4	0.0	0.0
NaNO ₃	0.7	1.4	3.3	0.7	0.0	0.0	0.4	1.9	0.0	0.0
LSD(.05)	1.5	1.3	2.4	1.1	0.7	1.1	8.1	ns	1.1	0.7

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γSampled upper subsoil depth for years: 1961(12-18"); 1962, 1963, 1966(10-15"); 1971, 1975(10-20").

^δppm x 10⁻³ = T/a - 6 2/3" = MT/ha - 17 cm.

less) for a longer period than with other carriers (Table 4-a). Very high levels of potential acidity had accumulated earlier also (Table 5-a). It is reasonable to expect that downward movement of potential acidity would have occurred with other carriers but somewhat later in time. The data for 1971 (Table 5-b) are consistent with this expectation. Unfortunately, subsoil samples were not taken for the other acidifying carriers in 1975.

Lime applied in 1965-66 reacted slowly with the potential acidity from $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl (Table 5-a). Data for subsoils in limed plots of NH_4NO_3 , NH_3 and urea in 1971 (Table 5-b) suggested that one effect of liming may have been to displace exchangeable Al and promote its downward movement.

Available P and Exchangeable K

There are significant differences in available P among treatments over the years, except in 1961, 1962 and 1974, both in unlimed and limed plots (Tables 6-a and 6-b). The significant differences were mainly between no fertilizer and all other plots which received basal fertilizer. Bray P_1 levels increased in all treatments in unlimed and limed plots over time.

In unlimed plots, this increase over time paralleled the record of increasing acidity. However, phosphate normally is less available at the very low pH levels which developed with acidifying carriers in this study. Looking at the data for 1967, Schafer et al. (1968b) suggested that nitrogen carriers, especially NH_3 and $(\text{NH}_4)_2\text{SO}_4$, promoted the release of soil phosphate by displacement with anions which were at high concentration because of the annual rates of application of N carriers. They noted that sulphate is particularly

Table 6-a. Available P, plow layer, unlimed plots, 1961 to 1975

Carrier used on corn 1959-72	Available P in the plow layer ^Y									
	No lime									
	Jul	Aug	Jul	Sep	Jul	Aug	May	Jul	Oct	Sep
	61	62	63	66	67	70	71	71	74	75
No fertilizer	34	22	29	43	30	37	45	45	72	52
Basal fertilizer ^β	48	36	52	70	62	102	111	104	90	97
(NH ₄) ₂ SO ₄	47	44	64	98	92	112	115	108	116	102
NH ₄ Cl	43	43	60	98	80	98	111	117	129	110
NH ₄ NO ₃	49	47	59	89	80	120	125	104	99	110
NH ₃	51	41	53	80	82	85	117	103	111	100
Urea	50	38	52	77	77	113	102	122	117	99
Ureaform	45	32	50	72	79	103	107	106	90	101
Ca(NO ₃) ₂	50	33	54	84	76	90	102	110	122	99
NaNO ₃	44	34	49	73	72	69	96	92	108	82
LSD(.05)	ns	ns	12.0	52.8	20.0	29.5	42.7	26.4	ns	27.5

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^Y Data for depths by years: 1961(0-6"); 1962(0-8"); 1963, 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^δ ppm x 2 = lb/a - 6 2/3; ppm x 2.24 = Kg/ha - 17 cm.

Table 6-b. Available P, plow layer, limed plots, 1966 to 1975

Carrier used on corn 1959-72	Available P in the plow layer ^Y Plus lime ^a						
	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Oct 74	Sep 75
	ppm δ						
No fertilizer β	30	21	24	26	31	68	63
Basal fertilizer ^{β}	69	71	86	98	94	111	96
(NH ₄) ₂ SO ₄	77	77	108	107	98	124	111
NH ₄ Cl	84	80	101	99	108	103	96
NH ₄ NO ₃	82	80	101	96	104	113	85
NH ₃	83	65	71	86	100	78	85
Urea	77	73	87	90	110	120	89
Ureaform	59	67	82	105	94	130	86
Ca(NO ₃) ₂	67	63	76	79	88	129	85
NaNO ₃	64	56	56	77	86	109	79
LSD(.05)	52.8	20.0	29.5	42.7	25.9	58.4	27.5

^aLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^{β} Basal fertilizer: 200 lb/a 50-20-20 (N-P-K=10-18-33).

^YData for depths by years: 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^{δ} ppm x 2 = lb/a - 6 2/3; ppm x 2.24 = Kg/ha - 17 cm.

Table 6-c. Available P, upper subsoil, unlimed and limed plots, 1961 to 1975

Carrier used	Available P in the upper subsoil ^γ									
	No lime					Plus lime ^α				
	Jul	Aug	Jul	Sep	May	Sep	Jul	May	Sep	May
on corn	61	62	63	66	71	75	66	71	75	75
1959-72										
ppm ^δ										
No fertilizer	23	21	18	24	19	--	18	13	--	--
Basal fertilizer ^β	34	22	29	34	31	38	35	36	56	56
(NH ₄) ₂ SO ₄	24	23	20	23	35	30	25	33	38	38
NH ₄ Cl	30	23	21	26	35	29	35	27	30	30
NH ₄ NO ₃	39	22	23	30	40	--	27	27	--	--
NH ₃	30	22	17	28	20	--	27	37	--	--
Urea	32	13	12	15	23	--	20	25	--	--
Ureaform	38	21	19	34	39	--	20	22	--	--
Ca(NO ₃) ₂	40	27	28	47	35	40	20	14	23	23
NaNO ₃	26	18	17	23	23	28	20	22	39	39
LSD(.05)	ns	ns	12.0	ns	ns	ns	ns	ns	ns	ns

^α Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γ Sampled upper subsoil depth for years: 1961(12-18"); 1962, 1963, 1966(10-15"); 1971, 1975(10-20").

^δ ppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

effective in displacing adsorbed phosphates as are hydroxyl ions released from the hydrolysis of NH_3 .

Extractable P levels were lowered rather consistently by liming (cf. Tables 6-a and 6-b). However, the reduction was not statistically significant in any year. There were scattered significant differences among nitrogen carriers, but there were no consistent differences relative to the basal fertilizer treatments.

Most of the available P was retained in the plow layer because low levels of phosphorus were found in the subsoil for all treatments over the years (Table 6-c). There is some evidence that more of the subsoil P remained in extractable forms with $\text{Ca}(\text{NO}_3)_2$ than with other carriers.

Statistically significant differences in exchangeable K were found in both unlimed and limed plow layer soils (Tables 7-a and 7-b). All treatments that received basal fertilizer maintained exchangeable K at higher levels than the no fertilizer treatment. There is some evidence that the retentive capacity for K in the plow layer was maintained at a higher level with the NaNO_3 treatment than with other carriers. Liming appears to have increased the retention of exchangeable K, especially after the large annual applications of acidifying carriers were discontinued in 1973.

Exchangeable K levels in the upper subsoil were much lower than in the plow layer but do reflect the annual additions of basal fertilizer (Table 7-c).

Exchangeable Ca and Mg

Exchangeable Ca (Tables 8-a, b and c) and Mg (Tables 9-a, b and c) were affected much more dramatically by residual acidity from

Table 7-a. Exchangeable K, plow layer, unlimed plots, 1961 to 1975

Carrier used	Exchangeable K in the plow layer ^γ									
	No lime									
	Jul	Aug	Jul	Sep	Jul	Aug	May	Jul	Oct	Sep
on corn										
1959-72	61	62	63	66	67	70	71	71	74	75
	ppm									
No fertilizer	67	47	48	57	43	54	66	50	83	46
Basal fertilizer ^β	118	92	86	100	87	88	120	94	115	64
(NH ₄) ₂ SO ₄	125	118	91	93	74	75	71	92	115	48
NH ₄ Cl	120	113	105	106	87	73	86	86	122	56
NH ₄ NO ₃	116	133	102	83	78	71	102	55	86	51
NH ₃	114	103	102	104	110	86	85	103	120	58
Urea	103	88	101	106	78	86	120	127	136	57
Ureaform	95	80	104	98	78	92	87	103	125	50
Ca(NO ₃) ₂	117	81	87	109	76	87	124	103	117	59
NaNO ₃	128	109	144	125	126	122	143	140	151	73
LSD(.05) carriers	21.0	25.2	15.6	49.7	26.0	31.0	54.7	26.2	45.4	16.0
within lime										

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γ Data for depths by years: 1961(0-6"); 1962(0-8"); 1963, 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^δ ppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = kg/ha - 17 cm.

Table 7-b. Exchangeable K, plow layer, limed plots, 1966 to 1975

Carrier used on corn 1959-72	Exchangeable K in the plow layer ^γ Plus lime ^α						
	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Oct 74	Sep 75
	ppm						
No fertilizer	57	49	54	62	57	98	43
Basal fertilizer ^β	106	99	112	118	114	107	73
(NH ₄) ₂ SO ₄	82	51	77	96	107	102	59
NH ₄ Cl	94	64	59	96	94	138	63
NH ₄ NO ₃	97	64	77	120	125	122	64
NH ₃	130	91	88	107	116	128	71
Urea	102	64	94	141	126	120	66
Ureaform	86	64	94	120	98	120	61
Ca(NO ₃) ₂	102	78	98	118	128	115	66
NaNO ₃	121	124	126	143	152	133	77
LSD(.05) carriers within lime	49.7	26.0	31.0	54.7	26.2	ns	16.0

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γData for depths by years: 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^δppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 7-c. Exchangeable K, upper subsoil, unlimed and limed plots, 1961 to 1975

Carrier used on corn 1959-72	Exchangeable K in the upper subsoil ^γ									
	No lime					Plus lime ^α				
	Jul 61	Aug 62	Jul 63	Sep 66	May 71	Sep 75	Sep 66	May 71	Sep 75	
No fertilizer	51	35	31	41	57	--	43	43	--	
Basal fertilizer ^β	63	44	45	66	89	51	66	75	61	
(NH ₄) ₂ SO ₄	65	62	62	72	54	38	66	49	42	
NH ₄ Cl	66	53	63	74	113	34	78	78	40	
NH ₄ NO ₃	65	44	48	66	73	--	72	74	--	
NH ₃	72	39	47	60	64	--	58	74	--	
Urea	83	42	46	82	103	--	66	83	--	
Ureaform	75	42	42	64	54	--	61	92	--	
Ca(NO ₃) ₂	79	44	42	70	64	57	68	80	57	
NaNO ₃	77	42	43	61	76	53	66	78	53	
LSD(.05)	ns	12.6	15.6	ns	56.0	ns	ns	ns	ns	

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γSampled upper subsoil depth for years: 1961(12-18"); 1962, 1963, 1966(10-15"); 1971, 1975(10-20").

^δppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 8-a. Exchangeable Ca, plow layer, unplowed plots, 1961 to 1975

Carrier used on corn 1959-72	Exchangeable Ca in the plow layer ^Y									
	No lime									
	Jul 61	Aug 62	Jul 63	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Oct 74	Sep 75
	ppm ^δ									
No fertilizer	492	450	336	530	520	378	560	398	273	388
Basal fertilizer ^β	624	498	418	490	432	304	367	167	306	338
(NH ₄) ₂ SO ₄	396	231	158	240	120	95	126	75	102	45
NH ₄ Cl	618	339	238	340	165	137	126	121	69	50
NH ₄ NO ₃	528	360	231	280	165	95	174	121	102	75
NH ₃	510	384	270	405	299	178	222	167	102	88
Urea	588	366	341	365	254	137	222	121	140	75
Ureaform	498	396	264	365	254	137	126	75	104	88
Ca(NO ₃) ₂	720	648	539	530	564	430	463	441	306	405
NaNO ₃	636	504	425	580	520	430	560	398	271	413
LSD(.05)	ns	166.7	71.2	ns	196.0	164.5	311.3	137.9	179.5	201.3

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^Y Data for depths by years: 1961(0-6"); 1962(0-8"); 1963, 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^δ ppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 8-b. Exchangeable Ca, plow layer, limed plots, 1966 to 1975

Carrier used	Exchangeable Ca in the plow layer ^Y Plus lime ^a						
	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Oct 74	Sep 75
ppm δ							
No fertilizer	493	564	430	511	490	481	528
Basal fertilizer ^{β}	604	696	514	607	536	447	825
(NH ₄) ₂ SO ₄	280	476	304	463	398	342	258
NH ₄ Cl	330	476	262	367	352	306	300
NH ₄ NO ₃	380	476	378	463	490	445	480
NH ₃	506	564	378	511	490	340	513
Urea	340	608	378	463	398	444	463
Ureaform	365	476	378	511	441	342	515
Ca(NO ₃) ₂	802	957	683	801	767	549	615
NaNO ₃	580	564	472	560	490	481	538
LSD(.05) carriers within lime	357.7	196.0	164.5	311.3	137.9	179.6	201.3

^aLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^{β} Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^YData for depths by years: 1966(0-15"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^{δ} ppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 8-c. Exchangeable Ca, upper subsoil, unlimed and limed plots, 1961 to 1975

Carrier used on corn 1959-72	Exchangeable Ca in the upper subsoil ^γ									
	No lime					Plus lime ^α				
	Jul 61	Aug 62	Jul 63	Sep 66	May 71	Sep 75	Sep 66	May 71	Sep 75	
	ppm ^δ									
No fertilizer	42	396	320	453	511	---	527	367	---	
Basal fertilizer ^β	492	414	368	405	767	325	601	479	490	
(NH ₄) ₂ SO ₄	360	299	277	265	189	35	340	222	138	
NH ₄ Cl	480	420	314	340	334	43	365	271	113	
NH ₄ NO ₃	516	371	349	340	126	---	453	367	---	
NH ₃	384	234	255	340	415	---	330	222	---	
Urea	534	486	374	453	560	---	490	367	---	
Ureaform	408	381	329	340	463	---	490	511	---	
Ca(NO ₃) ₂	575	552	417	440	463	338	879	753	500	
NaNO ₃	492	390	372	393	367	84	567	469	84	
LSD(.05)	ns	ns	71.2	ns	ns	260.3	ns	ns	260.3	

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γSampled upper subsoil depth for years: 1961(12-18"); 1962, 1963, 1966(10-15"); 1971, 1975(10-20").

^δppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 9-a. Exchangeable Mg, plow layer, unlimited plots, 1961 to 1975

Carrier used	Exchangeable Mg in the plow layer ^Y									
	No lime									
	Jul	Aug	Jul	Sep	Jul	Aug	May	Jul	Oct	Sep
1959-72	61	62	63	66	67	70	71	71	74	75
	ppm									
No fertilizer	35	69	48	65	67	56	78	58	40	48
Basal fertilizer ^β	55	79	49	48	46	36	46	19	38	40
(NH ₄) ₂ SO ₄	25	38	10	4	7	10	7	12	8	9
NH ₄ Cl	50	38	19	19	18	16	14	16	5	13
NH ₄ NO ₃	83	50	23	12	14	10	17	12	2	13
NH ₃	25	49	23	28	32	16	17	12	10	13
Urea	48	42	30	21	28	13	21	16	20	10
Ureaform	36	50	31	21	21	13	14	12	15	15
Ca(NO ₃) ₂	52	57	33	25	21	29	25	20	28	28
NaNO ₃	56	70	42	72	64	59	71	54	44	63
LSD(.05)	ns	24.9	12.7	59.6	32.0	28.0	45.3	27.8	ns	27.3

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^Y Data for depths by years: 1961(0-6"); 1962(0-8"); 1963, 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^δ ppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 9-b. Exchangeable mg, plow layer, limed plots, 1966 to 1975

Carrier used on corn 1959-72	Exchangeable Mg in the plow layer ^γ Plus lime ^α						
	Sep 66	Jul 67	Aug 70	May 71	Jul 71	Oct 74	Sep 75
	ppm ^δ						
No fertilizer	92	117	132	146	143	135	158
Basal fertilizer ^β	95	121	110	121	123	113	163
(NH ₄) ₂ SO ₄	75	164	117	129	147	106	148
NH ₄ Cl	72	142	86	89	108	86	103
NH ₄ NO ₃	62	128	117	128	139	139	148
NH ₃	99	128	111	117	135	97	145
Urea	66	146	117	135	135	126	138
Ureaform	59	121	117	153	135	111	158
Ca(NO ₃) ₂	65	74	73	71	73	103	118
NaNO ₃	92	103	114	121	116	139	148
LSD(.05) carriers within lime	ns	32.0	28.0	45.3	27.8	ns	27.3

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γData for depths by years: 1966(0-5"); 1967, 1970(0-7"); 1971, 1974, 1975(0-10").

^δppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

Table 9-c. Exchangeable Mg, upper subsoil, unlimed and limed plots, 1961 to 1975

Carrier used on corn 1959-72	Exchangeable Mg in the upper subsoil ^γ									
	No lime					Plus lime ^α				
	Jul 61	Aug 62	Jul 63	Sep 66	May 71	Sep 75	Sep 66	May 71	Sep 75	
	ppm ^δ									
No fertilizer	51	39	37	59	67	--	86	103	--	
Basal fertilizer ^β	54	51	49	37	49	40	96	71	90	
(NH ₄) ₂ SO ₄	38	42	39	25	7	6	52	53	78	
NH ₄ Cl	46	47	31	45	25	2	52	74	43	
NH ₄ NO ₃	71	45	43	38	14	--	79	96	--	
NH ₃	54	37	31	21	119	--	44	63	--	
Urea	43	52	41	49	71	--	72	117	--	
Ureaform	49	45	40	25	46	--	78	150	--	
Ca(NO ₃) ₂	50	58	37	11	35	13	79	67	80	
NaNO ₃	53	48	40	48	53	58	82	103	85	
LSD(.05)	ns	ns	12.7	ns	ns	34.5	ns	ns	34.5	

^α Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γ Sampled upper subsoil depth for years: 1961(12-18"); 1962, 1963, 1966(10-15"); 1971, 1975(10-20").

^δ ppm x 2 = lb/a - 6 2/3"; ppm x 2.24 = Kg/ha - 17 cm.

N carriers than was exchangeable K. The capacity of soils to retain these cations in the plow layer decreased as potential acidity increased. A comparison of Tables 4-a, 5-a and 8-a indicates that large increases in lime requirement did not occur until exchangeable Ca had decreased to less than 400 ppm at a pH of about 5.0. Below that pH rapid adsorption of protons by exchangeable Al would have reduced the capacity of the soil to retain basic cations, but accelerating decomposition of soil minerals would have served to maintain K levels at the expense of Ca and Mg (Wolcott et al., 1965; Schafer, 1968).

Marked depletion of exchangeable Ca was first observed with $(\text{NH}_4)_2\text{SO}_4$ (Table 8-a). Depletion progressed more rapidly with the three ammonium carriers as a group than with NH_3 , urea or ureaform, but all were at the same low level by 1971. Additional decreases have occurred in the plow layer since annual application of these acidifying carriers was discontinued in 1973.

Ca added in $\text{Ca}(\text{NO}_3)_2$ tended to maintain exchangeable Ca at higher levels during the early years of the study. However, since 1966, values for both $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 in unlimed soil have been similar and somewhat higher than for no fertilizer or for basal fertilizer only.

The additions of lime in 1965-66 had restored exchangeable Ca in the plow layer by 1967 to levels comparable to those found in 1961 (cf. Tables 8-a and 8-b). In the case of $\text{Ca}(\text{NO}_3)_2$, exchangeable Ca after liming was higher than for any other treatment and remained higher through the last sampling in 1975. In the case of $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl , maximum values were obtained in 1971 and have shown a marked tendency to decline since then.

Marked evidence for depletion of Ca from upper subsoils (Table 8-c) was obtained only for the three ammonium salts and NH_3 . Reductions for $(\text{NH}_4)_2\text{SO}_4$ and NH_3 were significant in 1963 and for $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl in 1975. It must be recognized that levels found in the subsoil represent a balance between illuviation and eluviation. There were variations from year to year, but no evidence that Ca lost from the plow layer had accumulated in the upper subsoil.

There have been both increases and decreases in subsoil Ca since lime was applied. The largest increases were in $\text{Ca}(\text{NO}_3)_2$ plots. Smaller increases in $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl plots may reflect reduced capacity to retain basic cations due to exchangeable Al retained in the subsoil as potential acidity (Table 5-b).

Exchangeable Mg in the plow layer (Table 9-a) was depleted in much the same pattern as Ca. The levels at the beginning of the experiment were already rather low in all plots. Mg deficiency symptoms were observed in corn on $(\text{NH}_4)_2\text{SO}_4$ plots as early as 1961. In 1967, foliar analyses for Mg were at deficient levels for corn in unlimed plots of all carriers except NaNO_3 (Schafer, 1968). Exchangeable Mg for the same treatments (Table 9-a) remained at the 1967 levels, or dropped still further, during the remaining years of the study. The Na in NaNO_3 appears to have had a sparing action on displacement of Mg, similar to that noted earlier for exchangeable K.

Mg released from dolomitic lime applied in 1965-66 increased exchangeable Mg to levels 3-fold or more greater than 1961 (cf. Tables 9-a and 9-b). The increases by July 1967 were related in a general way to the quantities of lime applied (Table 5-a). However, levels in $\text{Ca}(\text{NO}_3)_2$ plots were less than in NaNO_3 plots and have remained so, even though both treatments received 4 T/a of lime. Mg is adsorbed

less strongly than Ca in cation exchange reactions and would not have displaced Ca previously adsorbed from $\text{Ca}(\text{NO}_3)_2$. The greater retention of Mg in NaNO_3 plots again reflects the sparing action of Na which is adsorbed less strongly and remains in solution as the dominant complementary cation accompanying nitrate as it leaches through the profile.

With acidifying carriers, Mg in limed plots fluctuated considerably from year to year, with no consistent tendency to increase or decrease. Levels were frequently significantly lower in NH_4Cl plots than with other carriers. This may reflect differences in the exchange reactions of Al complexes with Cl^- as compared with Al complexes with polyvalent anions such as sulphate or phosphate (Jackson, 1963).

Evidence for progressive depletion of Mg in the upper subsoil of unlimed plots was obtained only for the three ammonium carriers (Table 9-c). Year to year fluctuations with NH_3 , urea and ureaform suggest that there were periods of net eluviation and net illuviation. The sparing action of Na relative to Ca is again expressed in the data for the two nitrate salts.

There is evidence that Mg from the dolomitic limestone had moved quickly into the upper subsoil, but that less was retained in the very acid plots. These differences are undoubtedly real even though statistical significance was achieved only in 1975 because of inadequate replication of the lime treatment.

Profile Changes After Treatments Were Discontinued

In May 1971, all plots were sampled in 10" increments to 30". In September 1975, the same depth increments were sampled for the

basal fertilizer control and for the two most acidifying carriers, $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl , and the two non-acidifying carriers, $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 . Soil tests for these two samplings (Tables 10 to 15) provide a picture of changes that have taken place in the profile since annual applications of the different carriers at high rates were discontinued in 1973.

In Tables 5 to 9, lime requirements and nutrients in the 0-10" and 10-20" increments were given in units of concentration. These have been converted in Tables 11 to 15 to T/a or lb/a in each 10" increment so that totals to 30" can be compared. The English units were used because they are still the basis for lime and fertilizer recommendations in Mich. Ext. Bul. E-550 (1976).

Soil pH and Lime Requirement

The striking change in Table 10 from 1971 to 1975 is the sharp decrease in pH at 20-30" for $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl . These decreases occurred in both limed and unlimed plots.

In unlimed plots, decreases in pH at 20-30" for both acidifying carriers were accompanied by decreases in lime requirement at each depth and in the total to 30" (Table 11). In limed plots, much of the accumulated potential acidity from NH_4Cl had disappeared by 1975, even though pH at all depths remained low. By contrast, in limed $(\text{NH}_4)_2\text{SO}_4$ plots it seems that potential acidity displaced from upper soil layers had accumulated at the 20-30" depth. The greater retention of potential acidity from $(\text{NH}_4)_2\text{SO}_4$ than from NH_4Cl , in both limed and unlimed plots, is consistent with the greater stability of exchangeable Al complexes with sulphate than with monovalent anions (Jackson, 1963). The sulphate complexes also have a greater tendency

Table 10. Soil pH, profile changes, 1971 to 1975

Carrier used on corn 1959-72	Soil pH No lime			Lime ^α T/a	Soil pH Plus lime ^α		
	0-10"	10-20"	20-30"		0-10"	10-20"	20-30"
A. <u>May 1, 1971</u> ^γ							
No fertilizer	6.1	6.3	6.2	4	7.0	6.7	5.8
Basal fertilizer ^β	5.5	6.0	5.8	6	6.9	6.7	6.6
(NH ₄) ₂ SO ₄	4.1	4.0	5.0	12	5.8	4.8	5.6
NH ₄ Cl	4.3	4.0	5.7	10	5.6	4.6	6.2
NH ₄ NO ₃	4.5	4.5	4.8	8	6.5	5.4	5.9
NH ₃	4.7	5.0	4.6	6	6.2	5.4	5.0
Urea	4.5	5.4	6.2	8	6.6	5.6	6.2
Ureaform	4.5	5.4	5.2	8	6.6	5.6	6.0
Ca(NO ₃) ₂	5.8	6.0	6.0	4	7.0	6.8	6.0
NaNO ₃	6.5	6.8	6.4	4	7.2	6.4	6.8
LSD(05) Carriers within lime	1.0	1.6	NS		1.0	1.6	NS
LSD (05) Lime within carriers	-	-	-		1.8	ns	ns
B. <u>September 25, 1975</u>							
No fertilizer	5.3	-	-	4	6.7	-	-
Basal fertilizer ^β	5.1	5.4	6.6	6	6.8	6.9	6.6
(NH ₄) ₂ SO ₄	4.2	4.2	4.4	12	6.2	5.4	4.8
NH ₄ Cl	4.4	4.5	4.8	10	5.3	4.9	4.9
NH ₄ NO ₃	4.2	-	-	8	6.7	-	-
NH ₃	4.5	-	-	6	6.2	-	-
Urea	4.4	-	-	8	6.7	-	-
Ureaform	4.3	-	-	8	5.9	-	-
Ca(NO ₃) ₂	5.3	5.7	5.7	4	6.8	6.9	7.2
NaNO ₃	5.6	6.4	6.8	4	7.0	6.6	6.3
LSD(.05) Carriers within lime	0.83	0.83	1.90		0.83	0.83	1.90
LSD(.05) Lime within carriers					0.79	ns	ns

^α

Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test. (T/a x 2.24 = TM/ha).

^β

Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γ

Data for 1971 from 1971 Research Report, M.S.U. Soils Farm, East Lansing, Michigan.

Table 11. Lime requirements, profile changes, 1971 to 1975

Carrier used on corn 1959-72	Lime requirement				Lime ^a T/a	Lime requirement			
	No lime					Plus lime ^a			
	0-10"	10-20"	20-30"	0-30"		0-10"	10-20"	20-30"	0-30"
	----- T/a ^δ -----					----- T/a -----			
A. <u>May 1, 1971</u> ^Y									
No fertilizer	1.5	0.0	0.6	2.1	4	0.6	0.0	0.6	1.2
Basal fertilizer ^β	8.4	1.5	1.6	11.5	6	0.6	2.1	0.0	2.7
(NH ₄) ₂ SO ₄	14.4	18.3	10.2	42.9	12	8.7	6.0	2.7	17.4
NH ₄ Cl	18.0	17.2	2.7	37.9	10	9.8	10.2	3.7	23.7
NH ₄ NO ₃	4.8	5.8	5.5	23.1	8	1.5	10.8	3.7	16.0
NH ₃	18.3	6.4	14.5	39.2	6	4.4	8.7	7.6	20.7
Urea	12.9	5.0	2.7	20.6	8	1.0	5.8	1.2	8.0
Ureaform	16.2	5.0	5.5	26.7	8	2.1	1.5	0.6	2.9
Ca(NO ₃) ₂	6.4	2.8	2.7	4.9	4	0.0	0.6	0.0	0.6
NaNO ₃	11.2	0.6	1.6	12.4	4	0.0	2.8	1.2	4.0
LSD(05) Carriers within lime	11.2	12.1	9.4	22.3		NS	NS	NS	22.3
LSD(05) lime within carriers	-	-	-	-		NS	NS	NS	21.3
B. <u>September 25, 1975</u>									
No fertilizer	3.9	-	-	-	4	0	-	-	-
Basal fertilizer ^β	3.2	0	0	3.2	6	0	0	0	0
(NH ₄) ₂ SO ₄	8.6	7.6	4.3	20.5	12	3.2	5.4	10.8	19.4
NH ₄ Cl	7.6	5.4	2.2	15.2	10	2.2	2.2	0	4.4
NH ₄ NO ₃	6.5	-	-	-	8	0	-	-	-
NH ₃	7.6	-	-	-	6	0	-	-	-
Urea	7.6	-	-	-	8	0	-	-	-
Ureaform	8.6	-	-	-	8	0	-	-	-
Ca(NO ₃) ₂	4.3	0	0	4.3	4	0	0	0	0
NaNO ₃	3.2	0	0	3.2	4	0	0	0	0
LSD(.05) Carriers within lime	2.6	5.4	NS	13.0		NS	5.4	6.0	13.0
LSD(.05) Lime within carriers						NS	NS	NS	NS

^a Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirements by buffer test. (T/a x 2.24 = MT/ha).

^β Basal fertilizer: 200 lbs/a 5-20-20 (N-P-K = 10-18-33).

^Y Data for 1971 from 1971 Research Report, M.S.U. Soils Farm, East Lansing, Michigan.

^δ T/a x 2.24 = MT/ha

to form immobile polymers with increasing pH than does exchangeable Al itself.

As will be seen, decreases in pH from 1971 to 1975 in Table 10 were accompanied by extensive depletion of exchangeable cations, notably Ca and Mg. It is likely that these basic cations were displaced by exchangeable Al and its complexes as they moved downward through the profile.

Available P and Exchangeable K

Profile totals and profile distributions for available P in 1975 were remarkably similar to those found in 1971 (Table 12). Uniform fertilization on all plots in 1973, 1974 and 1975 had not eliminated the significant differences in the plow layer between plots which had previously received no fertilizer and all other treatments which had received basal fertilizer.

There is no theoretical explanation for the uniquely high level of P at 20-30" with ureaform in 1971. It is probably not practically significant and cannot be taken seriously since no subsoil samples were taken in 1975 to verify it.

Exchangeable K was much lower in September 1975 than in May 1971 for most treatments at all depths. This difference probably reflects both seasonal variation and differences in laboratory techniques of different analysts. Significant differences in the plow layer in 1975 still reflected the differences observed over the years of the experiment between no fertilizer and other treatments and the greater retention of exchangeable K with NaNO_3 and with lime applied to very acid soils.

Table 12. Available P, profile changes, 1971 to 1975

Carrier used on corn 1959-72	Bray P ₁							
	No lime				Plus lime ^a			
	0-10"	10-20"	20-30"	0-30"	0-10"	10-20"	20-30"	0-30"
----- lb/a ^δ -----								
A. May 1, 1971^γ								
No fertilizer	136	56	36	227	78	40	36	154
Basal fertilizer ^β	334	93	33	459	294	108	45	448
(NH ₄) ₂ SO ₄	345	105	36	484	321	98	39	458
NH ₄ Cl	333	105	39	477	297	82	28	407
NH ₄ NO ₃	376	120	39	535	288	82	30	401
NH ₃	351	60	66	478	258	110	42	410
Urea	306	68	30	404	270	74	39	382
Ureaform	321	117	108	546	316	66	36	418
Ca(NO ₃) ₂	306	104	32	441	237	42	44	322
NaNO ₃	288	72	36	396	231	66	51	349
LSD(05) carriers within lime	128	NS	56	212	128	NS	NS	212
LSD(05) lime within carriers	-	-	-	-	NS	NS	56	NS
B. September 25, 1975								
No fertilizer	155	-	-	-	188	-	-	-
Basal fertilizer ^β	290	113	53	455	287	167	108	561
(NH ₄) ₂ SO ₄	305	90	62	456	296	114	54	464
NH ₄ Cl	329	86	60	474	333	89	56	477
NH ₄ NO ₃	329	-	-	-	288	-	-	-
NH ₃	299	-	-	-	255	-	-	-
Urea	296	-	-	-	267	-	-	-
Ureaform	303	-	-	-	258	-	-	-
Ca(NO ₃) ₂	296	119	53	467	254	69	54	377
NaNO ₃	246	84	59	389	236	116	59	410
LSD(.05) carriers within lime	82.4	NS	NS	NS	82.4	NS	NS	NS
LSD(.05) lime within carriers					NS	NS	NS	NS

^a Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^β Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γ Data for 1971 from 1971 Research Report, M.S.U. Soils Farm, East Lansing, Michigan.

^δ lb/a x 1.12 = kg/ha.

Table 13. Exchangeable K, profile changes, 1971 to 1975

Carrier used on corn 1959-72	Exchangeable K							
	No lime				Plus lime ^a			
	0-10"	10-20"	20-30"	0-30"	0-10"	10-20"	20-30"	0-30"
----- lb/a ^δ -----								
A. May 1, 1971^Y								
No fertilizer	198	171	178	548	186	130	130	448
Basal fertilizer ^β	360	267	177	803	354	224	192	770
(NH ₄) ₂ SO ₄	213	162	268	643	288	147	204	638
NH ₄ Cl	255	338	321	915	288	234	244	767
NH ₄ NO ₃	306	220	272	798	360	222	177	760
NH ₃	255	192	303	752	321	222	225	768
Urea	360	309	234	903	423	250	162	834
Ureaform	261	162	202	625	360	276	177	813
Ca(NO ₃) ₂	372	192	182	745	354	240	166	760
NaNO ₃	428	228	182	838	429	234	222	886
LSD(05) Carriers within lime	164	168	NS	NS	164	NS	NS	NS
LSD(05) Lime within carrier	-	-	-	-	NS	NS	NS	NS
B. September 25, 1975								
No fertilizer	139	-	-	-	130	-	-	-
Basal fertilizer ^β	193	152	135	480	222	182	109	512
(NH ₂) ₄ SO ₂	143	113	116	372	177	125	138	440
NH ₄ Cl	168	102	146	415	188	120	160	469
NH ₄ NO ₃	152	-	-	-	192	-	-	-
NH ₃	173	-	-	-	213	-	-	-
Urea	171	-	-	-	199	-	-	-
Ureaform	149	-	-	-	182	-	-	-
Ca(NO ₃) ₂	178	160	133	471	197	171	125	550
NaNO ₃	220	140	182	484	231	159	90	481
LSD (.05) Carriers within Lime	48.0	NS	NS	NS	48.0	NS	NS	NS
LSD (.05) Lime within carriers					21.8	NS	NS	NS

^a Lime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^β Basal fertilizer: 200 lb/acre 5-20-20 (N-P-K=10-18-33).

^Y Data for 1971 from 1971 Research Report, M.S.U. Soil Science Farm, East Lansing Michigan.

^δ lb/a x 1.12 = kg/ha.

The effect of NaNO_3 is apparent in both limed and unlimed plots. Sodium is adsorbed less strongly than K by cation exchange and is more likely to move with anions in percolating soil solution. Thus, Na would have a sparing action on displacement of K and other cations. Also, at the higher pH in NaNO_3 plots and in all plots after liming the concentration of charged Al compounds would have been less and these are mainly responsible for displacing basic cations in very acid soils (Jackson, 1963).

Exchangeable Ca and Mg

Residual effects of N carriers had extended through the soil profile between 1971 and 1975, as shown by data for exchangeable Ca and Mg in Tables 14 and 15. These changes were related to changes in pH (Table 10) and lime requirement (Table 11).

In the unlimed plots, levels of exchangeable Ca in the plow layer were substantially higher for the two controls and for $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 than all the six acidifying carriers (Table 14). These differences, which were obvious in 1971 (the last application of N carriers was made in 1972), had increased by 1975. There were substantial reductions (or losses) of exchangeable Ca in the plow layer and subsoils in all treatments except in plots that received basal fertilizer. The greatest reductions were associated with the acidifying carriers. The profile totals indicate reductions from 1971 to 1975 in all three layers, especially in the 20-30" layer of $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl plots. Losses from plots that received $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 were mainly from the 20-30" layer and were greater for $\text{Ca}(\text{NO}_3)_2$ than for NaNO_3 .

Table 14. Exchangeable Ca, profile changes, 1971 to 1975

Carrier used on corn 1959-72	Exchangeable Ca							
	No lime				Plus lime ^α			
	0-10"	10-20"	20-30"	0-30"	0-10"	10-20"	20-30"	0-30"
	----- lb/a ^δ -----							
A. <u>May 1, 1971</u> ^γ								
No fertilizer ^β	1680	1534	2402	5615	1534	1101	1245	3881
Basal fertilizer ^β	1101	1534	1389	4025	1822	957	1968	4748
(NH ₄) ₂ SO ₄	378	378	1389	2146	1390	666	2691	4748
NH ₄ Cl	378	668	2979	4025	1101	812	2980	4893
NH ₄ NO ₃	622	378	1534	2435	1390	1101	2256	4748
NH ₃	666	1245	957	2869	1534	666	957	3158
Urea	666	1680	522	8506	1390	1101	2402	4893
Ureaform	378	1390	1245	2291	1534	1534	2256	5326
Ca(NO ₃) ₂	1390	1389	2258	5038	2402	2258	2256	6916
NaNO ₃	1680	1101	1101	3881	1680	1389	1534	4603
LSD (05) Carrier within lime	934	NS	NS	NS	934	NS	NS	NS
LSD (05) Lime within carrier	-	-	-	-	909	NS	NS	NS
B. <u>September 25, 1975</u>								
No fertilizer ^β	1163	-	-	-	1583	-	-	-
Basal fertilizer ^β	1013	975	4508	6495	2475	1470	1328	5272
(NH ₄) ₂ SO ₄	135	105	210	450	773	413	795	1980
NH ₄ Cl	150	128	525	803	900	338	923	2160
NH ₄ NO ₃	225	-	-	-	1440	-	-	-
NH ₃	263	-	-	-	1538	-	-	-
Urea	225	-	-	-	1388	-	-	-
Ureaform	263	-	-	-	1545	-	-	-
Ca(NO ₃) ₂	1215	1013	675	2903	1845	1500	3863	7208
NaNO ₃	1238	1013	555	2805	1613	1013	1238	3863
LSD (.05) Carriers within lime	604	781	NS	3942	604	781	NS	3942
LSD (.05) Lime within carriers					1178	NS	NS	NS

^a Lime applied in two applications (1965 to 1966) to supply 2 times the lime requirement by buffer test.

^β Basal fertilizer: 200 lb/acre 5-20-20 (N-P-K=10-18-33)

^γ Data for 1971 from 1971 Research Report, M.S.U. Soils Farm, East Lansing.

^δ lb/a x 1.12 = kg/ha.

Table 15. Exchangeable Mg, profile changes, 1971 to 1975

Carrier used on corn 1959-72	Exchangeable Mg ^α							
	No lime				Plus lime			
	0-10"	10-20"	20-30"	0-30"	0-10"	10-20"	20-30"	0-30"
----- 1b/a ^δ -----								
A. May 1, 1971^γ								
No fertilizer	234	201	376	808	438	309	286	1033
Basal fertilizer ^β	138	147	244	530	363	212	354	937
(NH ₄) ₂ SO ₄	21	21	147	190	286	159	513	958
NH ₄ Cl	42	74	288	403	266	222	549	1037
NH ₄ NO ₃	52	42	255	350	384	288	450	1121
NH ₃	52	357	159	567	351	190	213	754
Urea	63	213	406	682	405	351	405	1162
Ureaform	42	138	74	254	460	450	428	1337
Ca(NO ₃) ₂	74	105	266	445	212	201	276	688
NaNO ₃	213	159	234	604	362	309	330	1000
LSD (05) Carrier within lime	136	NS	NS	NS	136	NS	NS	NS
LSD (05) Lime within carrier					204	NS	NS	NS
B. September 25, 1975								
No fertilizer	143	-	-	-	473	-	-	-
Basal fertilizer ^β	120	120	383	623	489	270	263	1022
(NH ₄) ₂ SO ₄	26	18	49	93	443	233	323	998
NH ₄ Cl	38	5	90	133	308	128	323	758
NH ₄ NO ₃	38	-	-	-	443	-	-	-
NH ₃	38	-	-	-	435	-	-	-
Urea	30	-	-	-	413	-	-	-
Ureaform	45	-	-	-	473	-	-	-
Ca(NO ₃) ₂	83	38	90	210	353	240	413	1005
NaNO ₃	188	173	210	451	443	255	218	916
LSD (.05) Carriers within lime	82	103.4	NS	NS	82	103.4	NS	NS
LSD (.05) Lime within carriers					182	204	NS	NS

^α Lime applied in two applications (1965 and 1966) to supply 2 times the Lime requirement by buffer test.

^β Basal fertilizer: 200 lb/acre 5-20-20(N-P-K=10-18-33)

^γ Data for 1971 from 1971 Research Report, M.S.U. Soils Farm, East Lansing, Michigan.

^δ 1b/a x 1.12 = kg/ha.

There were less dramatic losses in exchangeable Mg from 1971 to 1975 in the plow layer of unlimed plots, though differences for treatments were statistically significant in both years (Table 15). In the subsoils, recoveries of exchangeable Mg were substantially lower in $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl and $\text{Ca}(\text{NO}_3)_2$ plots in 1975 than in 1971. Quantitative changes in the subsoil and in the profile totals were less for Mg than Ca, but the relation to carriers was essentially the same as described for Ca.

Losses of bases from the different soil layers are most likely due to displacement by exchangeable Al which moved down the profile along with the bases. This is reflected in the decrease of lime requirement from 1971 to 1975 in the plow layer and upper subsoil of $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl plots (Table 11). This trend would have been expected for other acidifying carriers because of the large quantities of accumulated acidity in the plow layer and subsoil in 1971. However, the expected trend for these other carriers was not determined because subsoil samples were not taken for them in 1975. The very low levels of exchangeable Ca and Mg (Tables 14 and 15) which remained in 1975 may be mainly due to continuing release from decomposition of soil minerals.

The effects of liming in the plow layer were significant in 1971 and 1975 for exchangeable Ca (Table 14). The greatest increases of exchangeable Ca in 1971 with liming were associated with the acidifying carriers in all layers. However, large losses had occurred from the total profile since 1971 for $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl treated plots. There is evidence that Ca in $\text{Ca}(\text{NO}_3)_2$ plots had been displaced downward into the 20-30" layer, also.

In the limed plots, levels of exchangeable Mg were higher in 1975 than in 1971 in the plow layer in all treatments (Table 15). This indicates continued release from dolomitic lime applied in 1965-66. Profile totals show an increase for $\text{Ca}(\text{NO}_3)_2$ due to increases at all depths. In NH_4Cl plots, the profile total shows a decrease due to decreases in both subsoil layers. The subsoils of other treatments showed either a decrease or an increase in exchangeable Mg.

Exchangeable Mg in the plow layer of plots that received $\text{Ca}(\text{NO}_3)_2$ was uniquely lower over the years of the experiment than those that received NaNO_3 . This difference had progressed in unlimed plots, to both subsoil layers in 1975 (Table 15). This indicates interaction between Ca^{2+} and Mg^{2+} ions. Calcium has greater exchange potential compared to Mg and therefore tends to displace Mg from the exchange complex and promote its downward movement in the soil solution.

Exchangeable Mg was displaced from both subsoil layers in plots that received NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ in unlimed plots (1971 to 1975). In limed plots, in 1975, exchangeable Mg in the plow layer and upper subsoil was lower in NH_4Cl plots than $(\text{NH}_4)_2\text{SO}_4$ (Table 15). This was shown in earlier years (Table 9-b). The differential effect of the Cl^- and $\text{SO}_4^{=}$ ions in moving the bases below the root zone appears to be related to differences of Al complexes formed in the presence of Cl^- as against $\text{SO}_4^{=}$ (Table 11). Complexes of Al with $\text{SO}_4^{=}$ are very stable, and the complexed $\text{SO}_4^{=}$ contributes to potential acidity (Jackson, 1963).

Relationship Between Lime Requirement
and Exchangeable Cations

The relationship between lime requirement and the CaCO_3 equivalent sum of exchangeable K + Ca + Mg is shown in Figure 1. The numbers used to identify treatments are the same as were used by Wolcott et al. (1965) in similar graphs for data obtained in 1961, 1962, and 1963.

In those early years of the experiment, lime requirement increased rapidly when soils reached a pH of about 5.0 and then more slowly at lower pH. The authors of the 1965 report noted that exchangeable Al buffers strongly at about pH 5.0 or 5.2.

By 1975, the ten treatments without lime had separated into two groups: (1) the six acidifying carriers with high lime requirements at about pH 4.0 to 4.5 and (2) the two nitrate salts and the two control treatments with moderate lime requirement at pH 5.1 to 5.6.

Exchangeable Al has higher replacing power in exchange reactions than K, Ca or Mg. As seen in Figure 1, the high levels of potential acidity at pH 4.0 to 4.5 had reduced the capacity of soils to retain cations drastically. It is likely that the very low levels of cations in this very low pH range were maintained mainly by decomposition of soil minerals. As had been seen in previous sections in this thesis, exchangeable K levels were maintained more effectively than Ca or Mg.

Additions of lime in 1965-66 had fully neutralized or displaced potential acidity from the plow layer by 1975, except in $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl plots. These two treatments had received the heaviest applications of lime (12 and 10 T/a, respectively). However, extreme acidity had developed earlier than with other acidifying carriers. From this and other data, it seems that the longer soils are allowed

Figure 1. Lime requirement and exchangeable bases in relation to soil pH in 1975.

KEY TO TREATMENTS

1 - $(\text{NH}_4)_2\text{SO}_4$

2 - NH_4Cl

3 - NH_4NO_3

4 - NH_3

5 - Urea

6 - Ureaform

7 - $\text{Ca}(\text{NO}_3)_2$

8 - NaNO_3

9 - Basal fertilizer

10 - No fertilizer

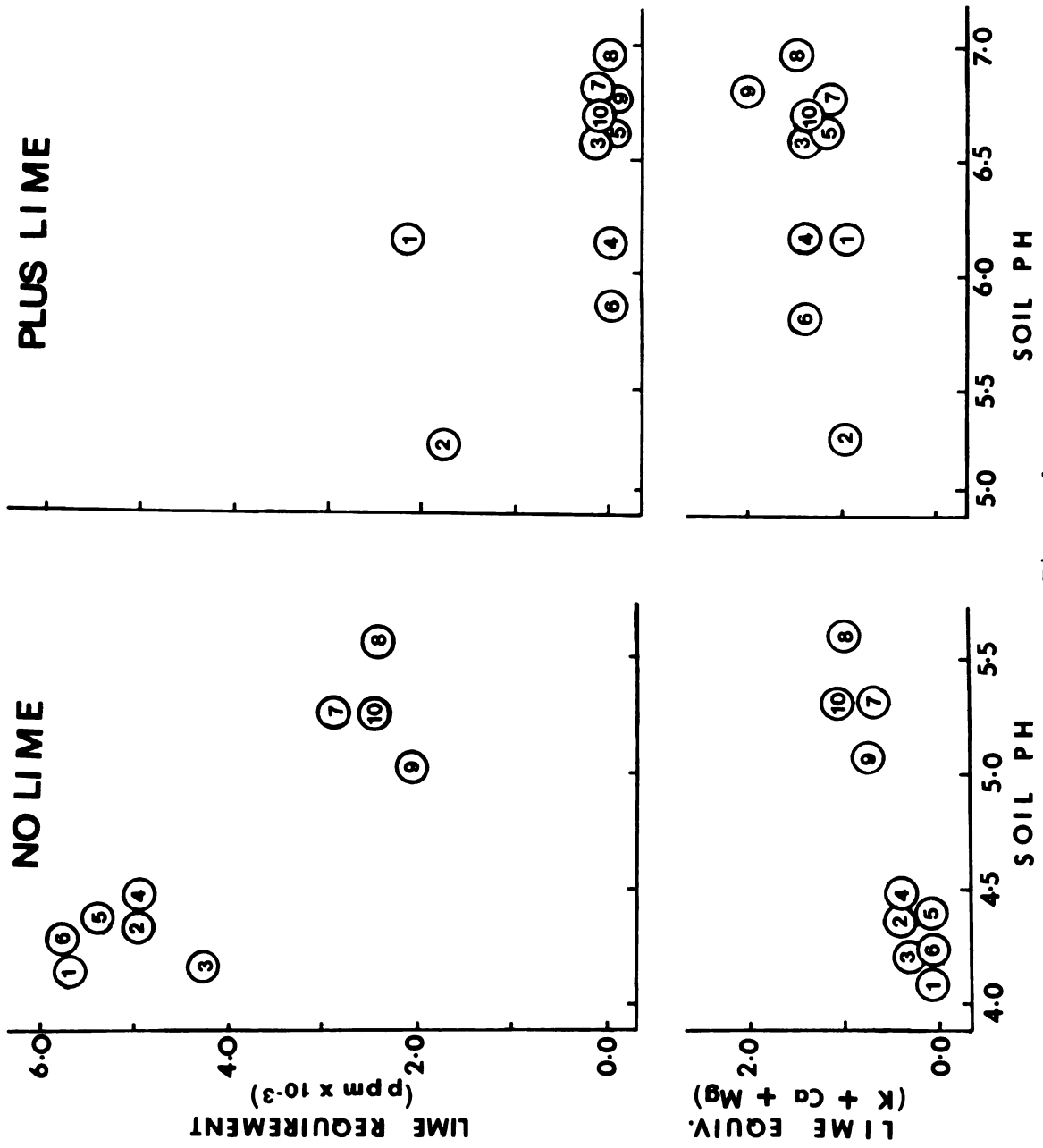


Figure 1

to remain very acid, potential acidity becomes more difficult to correct.

As pointed out in earlier sections, the $\text{SO}_4^{=}$ and Cl^- ions of the nitrogen carriers behave fairly differently. It seems that potential acidity due to complexed $\text{SO}_4^{=}$ may be more stable at higher pH than is the potential acidity which develops in the presence of Cl^- , as shown in the figure with lime. Potential acidity which remained after treatment with lime was still effective in occupying the exchange sites, reducing the capacity of the soil to retain exchangeable ions. The cations replaced in this manner may be taken up by plants or lost to the subsoils as indicated in earlier sections (Tables 13, 14 and 15).

Mineral Nitrogen in 1975

Ammonium N

Accumulation of NH_4^+ or of NO_2^- (the intermediate mineral form in nitrification) is due to unfavorable conditions for one or both groups of nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*.

In the unlimed plots, there were small accumulations of NH_4^+ -N in September 1975 in the plow layer in all treatments, especially in plots that had received acidifying carriers (Table 16). The 42 pounds of N applied on all plots for soybeans in 1975 (Table 1-a) was probably mainly ammoniated phosphate or urea, although there are no records to verify this. Differences in NH_4^+ -N in the total profile were statistically significant, and there is evidence that *Nitrosomonas* may have been inhibited during the growing season in the very acid soils (pH 4.2 to 4.4) of plots which had received $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl in earlier years. The first step of nitrification, itself, is

Table 16. Profile distribution of NH_4^+ , September 25, 1975

Carrier used on corn 1959-72	Ammonium-N					
	No lime			Plus lime ^a		
	0-10"	10-20"	20-30"	0-10"	10-20"	20-30"
	—lb/a ^d					
No fertilizer	0.6			0.2		
Basal fertilizer ^b	1.7	0.0	0.3	0.3	0.5	0.5
$(\text{NH}_4)_2\text{SO}_4$	3.3	0.0	0.0	0.3	0.3	0.2
NH_4Cl	5.9	0.0	0.0	0.9	0.0	0.8
NH_4NO_3	4.5			0.8		
NH_3	3.3			0.5		
Urea	3.9			0.2		
Ureaform	4.4			0.2		
$\text{Ca}(\text{NO}_3)_2$	1.1	0.0	0.0	0.2	0.2	0.3
NaNO_3	0.6	0.0	0.0	0.0	0.3	0.0
LSD(.05) carriers within lime	ns	ns	ns	ns	ns	ns
LSD(.05) lime within carriers				ns	ns	ns

^aLime applied in two applications (1965 and 1966) to supply 2 times the time requirement by buffer test.

^bBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^dlb/a x 1.12 = Kg/ha.

an acidification process that tends to limit the effectiveness of the organisms that carry it out.

Lime applied in 1965-66 continued to be released to effect favorable conditions for nitrification in 1975, as indicated by the very low levels of NH_4^+ -N in the limed plots in all treatments.

Nitrate-N

Nitrification leads to the production of nitrite which is oxidized to nitrate. Soil samples taken and analyzed for NO_2^- in 1975 did not show detectable nitrite. This may be due to delay between the time samples were collected from the field in 1975 and when actual analysis was performed on them.

Soil samples collected in 1976 (about the same time as in 1975) and run immediately showed traces of NO_2^- , up to 1 ppm, in the limed plots, but no trace was found in the unlimed plots. Nitrous acid is unstable at acid pH (Allison, 1973). Mineral N can be lost by chemical denitrification in reactions of nitrous acid with organic and inorganic constituents of acid soils. These reactions lead to the release of oxides of nitrogen and/or elemental nitrogen as gases. Because of the production of nitrous acid as an intermediate in nitrification, these losses can be significant in acid soils and may have contributed to somewhat lower recoveries of nitrate in the most acid unlimed plots (Table 17). Greater leaching may have occurred in these plots also, as is indicated by significantly higher NO_3^- in the 20-30" layer.

Accumulation of nitrate in limed plots (Table 17) is evidence that nitrification of nitrite was not inhibited in the pH range of 5.3 to 7.0, which is favorable for most nitrifiers. Detection of

Table 17. Profile distribution of NO_3^- , September 25, 1975

Carrier used on corn 1959-72	Nitrate-N						
	No lime			Plus lime ^a			
	0-10"	10-20"	20-30"	0-30"	0-10"	10-20"	20-30" 0-30"
	lb/a ^d						
No fertilizer	58				26		
Basal fertilizer ^b	28	9	2	39	29	8	3 40
(NH_4) ₂ SO ₄	17	9	8	34	23	2	1 26
NH_4Cl	11	8	5	24	36	4	2 42
NH_4NO_3	17	--	--	--	30	--	-- --
NH_3	23	--	--	--	32		
Urea	18	--	--	--	26		
Ureaform	35	--	--	--	35		
$\text{Ca}(\text{NO}_3)_2$	35	9	2	46	29	3	1 33
NaNO_3	33	6	1	40	28	6	3 37
LSD(.05) carriers within lime	ns	ns	2.7		ns	ns	ns
LSD(.05) lime within carriers					ns	ns	ns

^a Lime applied in two applications (1965 and 1966) to supply 2 times the time requirement by buffer test.

^b Basal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^d lb/a x 1.12 = Kg/ha.

substantial quantities of nitrate in the unlimed acid soils in the pH range of 4.2 to 4.5 may be due to the presence of acid tolerant strains of *Nitrobacter*, as reported by Weber and Gainey (1962). However, chemical reactions of nitrous acid in acid soils can produce nitrate spontaneously in the absence of *Nitrobacter*, as shown in sterile soils by workers cited by Broadbent and Stevenson (1966).

Soil Organic Matter in 1975

The content of soil organic matter in any horizon depends partly on what percentage of organic matter decomposes during the year and partly on the annual turnover of crop residues or other vegetation.

Organic Matter Levels

Organic matter levels in unlimed plots in the plow layer were substantially higher than limed plots by a factor of 2 in several treatments (Table 18). This is unexpected since higher yields of corn and soybeans had been maintained over a period of years in limed plots than in unlimed plots of acidifying treatments (Tables 3 and 4). However, Leo et al. (1959) also reported greater accumulations of organic matter in the acid topsoil than where pH had been raised by lime. This is an indication that the extent of decomposition of vegetative materials had been reduced by unfavorable pH in unlimed plots compared to limed plots.

Organic matter declined with depth, as expected, since most of the organic residues in both cultivated and virgin soils are deposited on or incorporated in the surface layer.

Table 18. Residual effects of nitrogen carriers on percent soil organic matter (September 25, 1975)

Carrier used on corn 1959-72	Organic Matter ^δ				
	No lime		Plus lime ^α		
	0-10"	10-20"	20-30"	0-10"	10-20" 20-30"
No fertilizer	1.6	---	---	---	---
Basal fertilizer ^β	0.7	0.4	0.7	0.9	0.5
(NH ₄) ₂ SO ₄	1.5	0.6	0.2	0.9	0.2
NH ₄ Cl	1.5	0.5	0.5	1.0	0.3
NH ₄ NO ₃	0.9	---	---	0.9	---
NH ₃	1.3	---	---	1.1	---
Urea	1.5	---	---	0.9	---
Ureaform	1.9	---	---	0.8	---
Ca(NO ₃) ₂	1.7	0.9	0.7	0.9	0.5
NaNO ₃	1.6	0.5	0.2	0.9	0.5
LSD(.05) carriers within lime	0.9	ns	ns	ns	ns
LSD(.05) lime within carriers				ns	ns

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K-10-18-33).

^δOrganic matter = organic-C x 1.724.

C:N Ratios and Organic Nitrogen

Organic-N levels were not affected by treatments at any depth (Table 19). They did decline with depth as expected.

Carbon:nitrogen ratios in Table 20 were consistently wider in the plow layer of unlimed than in limed plots for all carriers except NaNO_3 , and this difference extended into the upper subsoil. The effect of lime was not significant statistically, but the difference in C:N ratio is consistent with the probability that residual organic matter was quantitatively different in limed plots than in those where acidity from N carriers had been allowed to accumulate.

Carbon:nitrogen ratios tend to become narrower as decomposition proceeds. Thus, the wide C:N ratios in unlimed plots support the earlier inference that decomposition was less complete than at more favorable pH in limed soil.

The higher C content of most unlimed, very acid soils suggests that the residual organic matter may have had a higher content of organic acids. The fulvic acid fraction of humus includes compounds which form soluble chelates with polyvalent cations (Allison, 1973). These may have promoted depletion of Ca and Mg in acid soils, as well as downward movement of both basic cations and exchangeable Al.

During the formation of soils under natural conditions, fulvic acid complexes with polyvalent cations, such as Ca, Al and Fe, tend to be precipitated in the B horizon. This would account for the wide C:N ratios at 20-30" in unlimed plots of several treatments in Table 19 and of all treatments in limed plots.

Table 19. Residual effects of nitrogen carriers on organic nitrogen (September 25, 1975)

Carrier used on corn 1959-72	Organic nitrogen ^γ					
	No lime			Plus lime ^α		
	0-10"	10-20"	20-30"	0-10"	10-20"	20-30"
No fertilizer	0.09	---	---	0.08	---	---
Basal fertilizer ^β	0.09	0.04	0.02	0.08	0.04	0.02
(NH ₄) ₂ SO ₄	0.08	0.02	0.01	0.08	0.03	0.02
NH ₄ Cl	0.07	0.03	0.02	0.10	0.04	0.02
NH ₄ NO ₃	0.09	---	---	0.08	---	---
NH ₃	0.07	---	---	0.09	---	---
Urea	0.09	---	---	0.07	---	---
Ureaform	0.10	---	---	0.09	---	---
Ca(NO ₃) ₂	0.09	0.03	0.02	0.09	0.03	0.02
NaNO ₃	0.11	0.03	0.02	0.07	0.03	0.02
LSD(.05) carriers within lime	ns	ns	ns	ns	ns	ns
LSD(.05) lime within carriers				ns	ns	ns

^αLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

^γOrganic nitrogen = Kjeldahl-N - NH₄⁺-N.

Table 20. Residual effects of nitrogen carriers on carbon:nitrogen ratio (September 25, 1975)

Carrier used on corn 1959-72	Carbon:Nitrogen Ratio					
	No lime			Plus lime ^a		
	0-10"	10-20"	20-30"	0-10"	10-20"	20-30"
No fertilizer ^β	9.6	---	---	7.0	---	---
Basal fertilizer ^β	5.2	7.7	13.5	6.9	7.5	11.2
(NH ₄) ₂ SO ₄	11.9	18.7	8.8	6.5	8.9	10.0
NH ₄ Cl	12.4	13.1	13.5	6.0	6.5	16.7
NH ₄ NO ₃	8.0	---	---	6.7	---	---
NH ₃	11.4	---	---	7.7	---	---
Urea	10.3	---	---	7.3	---	---
Ureaform	10.4	---	---	6.1	---	---
Ca(NO ₃) ₂	10.4	19.2	16.8	6.2	5.8	13.2
NaNO ₃	8.1	11.9	6.0	9.0	14.1	14.3
LSD(.05) carriers within lime	6.1	ns	ns	ns	ns	ns
LSD(.05) lime within carriers				ns	ns	ns

^aLime applied in two applications (1965 and 1966) to supply 2 times the lime requirement by buffer test.

^βBasal fertilizer: 200 lb/a 5-20-20 (N-P-K=10-18-33).

One further inference may be made regarding treatments and horizons with wide C:N ratios in Table 19. Jackson (1963) pointed out that humus carboxyl groups are an important buffer system over the pH range of 5.2 to 6.5 or 7.0. Carboxyl groups would have contributed to increases in potential acidity as soils which received acidifying carriers declined over this pH range during the earlier years of the experiment. When pH increased again into this range after lime was applied, humic and fulvic acids may have contributed to the persistence of potential acidity, as was observed for $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl .

SUMMARY AND CONCLUSIONS

Residual effects of 14 annual applications of nitrogen carriers at rates in excess of crop needs (300 lb N/a/yr) have produced a wide range of effects on crop yields, pH, nutrients, inorganic and organic components in the soil. The nitrogen treatments produced effects in 1975 which had continued to develop after the N treatments were discontinued in 1973.

Residual acidity of nitrogen carriers, especially ammonium salts, drastically reduced corn and soybean yields over the entire period. Non-acidifying carriers maintained fairly constant stable yields of corn better than the check plots. The devastating effects of acidifying carriers on yields of both corn and soybean were corrected by dolomitic lime applied in the seventh and eighth years of the study. It is apparent from the data that the lime should have been applied much earlier, as soon as buffer tests indicated the need.

Environmental factors, such as drought, insect and disease build-up, undoubtedly influenced crop yields, especially of soybeans. Other factors, such as Mn and Al toxicity and Mg deficiency associated with low pH, were probably directly responsible for reducing yields.

Soil pH continued to decline with repeated application of acidifying carriers without lime over the years. The rate of acidification was related to their relative residual acidities (Table 1-b). The general rate of decline of pH over time was in the order: $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{NH}_4\text{NO}_3 > \text{urea} > \text{ureaform} > \text{NH}_3$. This order is based on changes

observed from year to year and is reflected, also, in the sequence of years when the "ultimate" pH of 4.2 was first observed for acidifying carriers: $(\text{NH}_4)_2\text{SO}_4$ /1962, NH_4Cl /1965, NH_4NO_3 /1967, urea and ureaform/1970. Soil pH fluctuated near this limiting level through 1971 and showed only slight tendency to increase by 1975 after annual applications were discontinued in 1973. With NH_3 , soil pH reached 4.5 in 1970 and this was the limiting value through 1975.

Calcium nitrate had little effect on soil pH, but residual basicity from sodium nitrate tended to maintain a pH in the plow layer somewhat higher than in plots which received only basal fertilizer.

Soil pH in the subsoil decreased rapidly when the pH of the plow layer was reduced below 5.0.

Lime requirements in the plow layer increased rapidly at about pH 5.0 and then increased quickly in subsoil layers. Increase in profile lime requirements greatly exceeded the acidity which could have been produced as residual acidity from N fertilizers. For example, lime requirements to 30" in 1971 (Table 11) were 42.9 T/a for $(\text{NH}_4)_2\text{SO}_4$ and 11.5 T/a for basal fertilizer. The difference between these two treatments is 31.4 T/a, or 62,800 lb. If this is divided by 3900 lb N applied in 13 annual applications (1959 to 1971) the indicated increase in potential acidity is 16 lb. CaCO_3 per pound of N applied. This is about 3-fold greater than the accepted equivalent acidity, 5.5 lb. CaCO_3 /lb. N, for $(\text{NH}_4)_2\text{SO}_4$ (Table 1-b).

This greatly accelerated increase in potential acidity below pH 5.0 has been referred to as "runaway" acidity (Wolcott, 1964). It is likely that the greater than expected increase in potential acidity at low pH is due to release of hydrogen ions which had

accumulated in non-exchangeable polymeric complexes with Al at pH's above 6.0 before the experiment started. Release of acidic species of Fe may have been involved also, as evidenced by reddish crusts which formed during dry weather (Wolcott et al., 1965) and greatly increased extractability of Fe in soils below pH 5.0 (Schafer, 1968).

Potential acidity which had accumulated before liming in plots which remained extremely acid for the longest periods of time in $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl treatments had not been completely neutralized or displaced from the plow layer into the subsoil by 1975. Residual potential acidity was retained, after liming, at a higher pH in $(\text{NH}_4)_2\text{SO}_4$ plots than where NH_4Cl had been used (pH 6.2 vs 5.3). This is consistent with retention of sulphuric acid in complexes with exchangeable Al that are more stable than the complexes formed in the presence of Cl^- (Jackson, 1963).

Effects of nitrogen carriers or lime on the extractability of exchangeable potassium (K), calcium (Ca), and magnesium (Mg) were dramatic and often statistically significant throughout the 10-year period, despite greatly reduced degrees of freedom for testing significance after lime was applied on two of the four replications in 1965-66. These effects often progressed rapidly into the subsoil.

Effects on available P were less marked than for cations. However, the data indicated that the release of available P was promoted by acidifying carriers. Major increases were for basal fertilizer over no fertilizer. Most of the Bray P_1 phosphorus was retained in the surface soil, which confirms the low mobility of P. However, some increased quantities from basal fertilizer were detected in the subsoil over time.

Exchangeable K was higher in all treatments, including N carriers, that received basal fertilizer than in the no-fertilizer treatment. Higher levels were maintained with NaNO_3 than with other carriers. Liming increased retention of exchangeable K. Exchangeable K moved into the subsoil although, in most treatments, greater levels of K were held in the plow layer.

Acidifying carriers accelerated the disappearance of exchangeable Ca and Mg from the plow layer in both unlimed and limed plots. In unlimed plots, displacement of these two cations from the profile continued after applications were discontinued so that extreme depletion was apparent in the 20 to 30" layer in 1975. Dolomitic lime applied in 1965 and 1966 restored exchangeable Ca to levels observed near the beginning of the experiment and exchangeable Mg to levels 3-fold greater for most treatments. The recovery in exchangeable Mg was significantly less in NH_4Cl and $\text{Ca}(\text{NO}_3)_2$ plots. This result for $\text{Ca}(\text{NO}_3)_2$ reflects the greater exchange potential of Ca^{2+} compared with Mg^{2+} . In the case of NH_4Cl , it appeared that Cl^- had accelerated downward movement of Mg. It did appear that unspent dolomite was continuing to release Ca and Mg and maintain or increase levels in the plow layer for all treatments through 1975.

Ca applied as $\text{Ca}(\text{NO}_3)_2$ accelerated the loss of exchangeable Mg in the profile of both unlimed and limed plots. On the other hand, Na applied as NaNO_3 increased the levels of exchangeable K, Ca and Mg, especially in the plow layer. The differences reflect known differences in replacing power among the four cations in exchange reactions: $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$ (Foth and Turk, 1972).

Significant differences among carrier anions, such as sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-), were observed. Effects of

carbonate ($\text{CO}_3^{\text{--}}$) produced by hydrolysis of urea and ureaform, and effects of hydroxyl from hydrolysis of NH_3 may have influenced patterns of acidification also.

Sulphate was more effective in reducing pH initially than the chloride. However, soil pH in chloride plots was less responsive to liming. Disappearance of exchangeable bases (Ca and Mg) was more rapid initially with $(\text{NH}_4)_2\text{SO}_4$ than with NH_4Cl . Both left more persistent forms of potential acidity than any of the other acidifying carriers. The data support the idea that the sulphate ion forms more stable complexes with Al at higher pH than those formed in the presence of the chloride ion. Liming did not completely neutralize the potential acidity and that which remained reduced the soil's capacity to retain exchangeable K, Ca and Mg.

Levels of mineral nitrogen in the soil in September 1975 indicated that nitrification may have been inhibited earlier in the season in unlimed acid soils. Lime applied in 1965 and 1966 continued to release basic components that reduced soil acidity to a favorable level for nitrification to proceed. This was confirmed by the uniformly high levels of nitrate nitrogen in the limed plots. However, presence of substantial quantities of nitrate nitrogen in very acid unlimed soils indicates the existence of acid tolerant species of *Nitrosomonas* and *Nitrobacter* or the production of nitrate from nitrite by other processes occurring spontaneously at acid pH.

Organic matter was greater in unlimed acid soils than in limed soils. This was due to higher carbon content, since the organic nitrogen level was fairly uniform for all treatments, unlimed and limed. The resulting wide C:N ratios are indicative of reduced microbial activities that cause decay and important differences in

quality of residual humus in acid versus limed soils. Liming promoted decay giving lower carbon content with consequent narrow C:N ratios. As expected, organic matter declined with depth in limed and unlimed plots.

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APPENDICES

APPENDIX A

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 also developed on calcareous sandy loam till.

Soil Profile: Hodunk sandy loam

Ap	0-7"	Dark grayish brown (10 YR 4/2) to very dark grayish brown (10 YR 3/2); sandy loam; moderately 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.
A ₂	7-16"	Yellowish brown (10 YR 5/4); pale brown (10 YR 6/3) or light yellowish brown (10 YR 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.
B _{1m}	16-25"	Brown (10 YR 5/3) to pale brown (10 YR 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.
B _{2g}	25-46"	Brown (10 YR 5/3) to yellowish brown (10 YR 5/4) mottled with yellowish brown (10 YR 5/8) and dark brown (7.5 YR 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 (10 YR 6/4) to brown (10 YR 5/3) mottled with yellowish brown (10 YR 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, oak, and hickories.

Source: Schneider et al., 1967.

APPENDIX B

TOTAL N PROCEDURE

A. Reagents:

1. Concentrated H_2SO_4 .
2. 10 Normal NaOH solution:
 - a. Prepare N-free flakes in deionized water and allow to stand several days.
 - b. Equip with aspirator bulb and ascarite tube to prevent absorption of CO_2 .
3. Boric acid indicator:
 - a. Heat 1800 ml of deionized water to boiling to remove CO_2 .
 - b. Add 40 g boric acid, stopper, swirl to dissolve and cool in cold water bath. Add 30 ml of Fisher's methyl purple indicator.
4. Potassium sulfate-catalyst mixture:
 - a. Mix by grinding 100 g K_2SO_4 , 10 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 1 g Se.
5. 0.01 N H_2SO_4 :
 - a. Make up N/10 H_2SO_4 : 3 ml conc. H_2SO_4 made up to 1:1 with deionized water.
 - b. Make up N/100 H_2SO_4 : 200 ml N/10 H_2SO_4 made up to 2:1 with deionized water.
 - c. Titrate N/100 H_2SO_4 against primary Standard base (0.05 N THAM; equivalent wt. = 121.136).
6. 30% H_2O_2 in brown bottle with glass stopper may be needed to rinse soil particles down flask during digestion.
7. Cigarette paper.
8. Indicator.

B. Procedure (excluding nitrate):

1. Grind soil sample to pass 32-40 mesh screen.
2. Weigh duplicate samples containing 0.5000 grams on weighed cigarette paper, roll and drop into Kjeldahl flask.
3. Add 2 ml H_2O , swirl, allow to stand for 30 minutes.
4. Add 0.8 g K_2SO_4 catalyst mixture.
5. Add 2 ml concentrated H_2SO_4 , heat cautiously on digestion stand until water is removed and frothing stops.
6. Heat until digest clears (a light green color develops).
7. Continue to boil gently for at least one hour, regulating heat so that the H_2SO_4 condenses about 1/3 way up the neck of the flask. Allow to cool to touch.
8. Slowly, and with swirling, add 10 ml deionized water; continue swirling until undissolved materials are in suspension.
9. Flush out distillation apparatus for 5 minutes with steam to clean and bring it up to temperature. (Teflon stop-cocks should be loosened during warmup to avoid freezing and possible splitting to barrels due to expansion of the teflon.)
10. Add 3 ml of H_3PO_3 solution to a 25 Erlenmeyer flask which is marked at a volume of 15 ml.
11. Add 1 drop of indicator.
12. Place Erlenmeyer flask under the condenser of the distillation apparatus so that the tip is about 4 cm above solution.
13. Add 1 ml of 10 N NaOH to funnel at start, note height in funnel, then add 10 ml more NaOH.
14. Insert Kjeldahl flask to distillator.
15. Drop 10 ml of the 10 N NaOH into the flask, close stopcock, open steam system, close steam by-pass.
16. Collect 15 ml of distillate in 3-5 minutes.
17. Remove Erlenmeyer flask.
18. Flush system out.
19. Titrate to first pink color with the 0.01 N H_2SO_4 .
20. Calculate % N.

$$\% N = \frac{(T-B) (N) (1400)}{S}$$

where T = ml of sample titration

B = ml of blank titration

N = normality of H_2SO_4

S = sample wt. in mg.

APPENDIX C

TOTAL C PROCEDURE

Operation:

One hundred milligrams of finely ground soil (80 mesh) is weighed into a special ceramic crucible and one scoop (approx. 1 gram) each of Iron Chip and Tin accelerators are added. The crucible is then placed on the combustion table of the induction furnace through which O_2 is being passed. As the cycle is started, the sample is combusted at a temperature of over $1670^\circ C$, and the Carbon in the sample is oxidized to CO_2 . After leaving the induction furnace, the gas mixture is passed through (1) a dust trap to filter out the solid Tin and Iron oxides, (2) a Sulfur trap containing MnO_2 to absorb Sulfur gases which may have been oxidized during the combustion of the sample, and (3) a heated catalyst to convert any CO formed to CO_2 . Moisture is removed from the gas mixture before it enters the analyzer by an anhydrous trap.

After combustion and passing through the Purification Train, the gas mixture (O_2 and CO_2) is passed into a thermal conducting cell housed in a temperature-controlled oven ($45^\circ C$) in the analyzer. The output of the Thermal Conductivity Cell is read on a special DC digital Voltmeter as percent carbon (% C). The instrument is calibrated to read a one gram sample. So all readings of 100 mg sample size must be multiplied by 10 to get % C in the soil (Belo, 1970).

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