RESIDUAL AND CUMULATIVE EFFECTS OF NITROGEN APPLIED TO A SANDY LOAM SOIL

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ABSTRACT

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By

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Residual and cumulative effects of three nitrogen carriers, at three rates of application were studied on a sandy loam soil while growing corn (*Zea mays*). The nitrogen carriers urea, NH_4NO_3, and NH_3 were applied at zero, 84, 168, and 252 kg/ha with one to four annual applications.

Yield benefits from one annual application were observed for three years. These residual benefits were increasingly significant with the two higher rates of application.

Upon repeated annual applications of nitrogen fertilizers, a distinct portion of the total response could be identified with each year of application. Cumulative residual benefits increased with rate of application and with carriers in the order urea $< NH_4NO_3 < NH_3$. As much as 78 percent of the current year's nitrogen response could be ascribed to the

previous two or three years of repeated nitrogen treatments with NH_3 and 50 percent with the other two carriers. The greater response to NH_3 was attributed primarily to decreased nitrogen loss with injection vs. surface application of the other two carriers. The residual effects of the highest application rate of NH_4NO_3 was to decrease corn yields. This result was apparently due to increased inhibitory factors associated with decreasing soil pH.

Cumulative residual soil acidification increased with the rate of nitrogen application and with the carriers in the order $NH_4NO_3 >$ urea $> NH_3$. Repeated annual additions of nitrogen at the higher rates of all three carriers resulted in soil pH values below 5.5 for portions of the growing season.

Maximum retention of nitrogen in the soil after three annual nitrogen applications occurred at the 84 kg/ha rate. Maximum retention of carbon occurred at the 168 kg/ha rate. The net effect of increasing carbon retention was a widening of soil CPN ratio from 12.5:1 in control plots to 15:1 for the 168 kg/ha rate.

After three annual applications of 252 kg/ha, both soil carbon and soil nitrogen were reduced below the level in the controls. The C:N ratio declined abruptly to 13.5:1. These results were taken as evidence that fertilizer nitrogen inputs in excess of crop removal were promoting net mineralization and depletion of soil organic nitrogen.

A highly significant quadratic relationship between soil carbon and nitrogen was obtained over the 160 plots in the experiment. This relationship was taken as evidence for effects of treatment on the active organic fraction, i.e. on organic materials most recently added to the soil. The first derivative of this function indicated that carbon and nitrogen were being immobilized in a ratio of 30:1 in control plots and 15:1 in plots receiving the highest nitrogen rates.

At the highest NH_4NO_3 rate, nitrogen applied in excess of calculated crop removal could not be accounted for to a depth of five feet and was assumed lost by leaching or denitrification. Volatilization losses from surface applied urea were probably responsible for smaller yield responses to residual and current applications of this carrier as compared with NH_3.

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
LITERATURE REVIEW	3
The Effect of Inorganic Nitrogen Application on the Uptake of Soil Nitrogen	7
The Effect of Inorganic Nitrogen Application on Soil Humus	8
Greenhouse Studies	11
Nitrogen Losses From the Soil	13
Soil Nitrogen and Corn Growth	21
EXPERIMENTAL PROCEDURES AND METHODS OF ANALYSIS . .	22
Field Treatments	22
Soil Sampling	23
Soil Testing	25
Statistical Analysis	26
RESULTS AND DISCUSSION	28
Yield History	28
Sources of Variation in 1967 and 1968	31
Residual Effects of Nitrogen on Corn Yields . .	34
Cumulative Effects on Corn	36
Incrementation of Residual Response	40
Relative Efficiency of Carriers	45
Forms of Residual N in Soil	50
Kjeldahl N in the soil	50
Crop residues	59
Mineral nitrogen	62
Other soil sources of N	70
Effects on Soil pH	71
Effects on Soil Calcium and Magnesium Levels .	77
Effects on Soil Phosphorous and Potassium Levels.	81
SUMMARY AND CONCLUSIONS	85
BIBLIOGRAPHY	92
APPENDIX	98

LIST OF TABLES

Table		Page
1.	Basal fertilizer and management	24
2.	Corn yields over a four-year period in relation to residual and cumulative effects of fertilizer nitrogen	29
3.	Monthly rainfall, average temperatures, and deviations from the norm	30
4.	Approximate significance probabilities of F in 1967 for variance associated with experimental design categories	32
5.	Approximate significance probabilities of F in 1968 for variance associated with experimental design categories	33
6.	Absolute increases in yields of corn over controls which received no nitrogen	35
7.	Relative increases in yields of corn expressed as percent of maximum for carrier or rate of nitrogen	41
8.	Relative yield responses incremented over years of N application	42
9.	Soil nitrogen in November 1967	51
10.	Soil carbon in November 1967	53
11.	Soil C:N ratios in November 1967	55
12.	Soil carbon, nitrogen and C:N ratios in relation to annual rates of N application .	58
13.	Nitrate nitrogen in soil sampled August, 1968 .	63
14.	Distribution of ammonium and nitrate with depth on August 14, 1968	64
15.	Effects of nitrogen carrier and rate of application on soil pH	72

Table		Page
16.	Extractable Ca and Mg in soil sampled November, 1967	78
17.	Effects of nitrogen carrier and rate of application on the November 1967 lime requirement	80
18.	Extractable K in soil sampled November, 1967 and August, 1968	82
19.	Extractable P (Bray P_1) in soil sampled November, 1967 and August, 1968	83

LIST OF FIGURES

Figure		Page
1.	Cumulative effects of annual nitrogen applications on relative yields of corn in 1968	37
2.	Cumulative effects of annual nitrogen applications on corn ear weights in 1968 .	38
3.	Cumulative effects of annual nitrogen applications on numbers of fertile stalks in 1968	39
4.	Residual and cumulative effects of N rates on 1968 yield increases over controls . . .	44
5.	Incremented responses of corn in 1968 to residual and current inputs of nitrogen from three fertilizer sources	47
6.	Immobilization ratios in relation to soil carbon and nitrogen contents	57
7.	Soil carbon, nitrogen and C:N ratios in relation to increasing rates of fertilizer N after three annual applications	57
8.	Corn yields on residual plots in 1968 in relation to soil N in November 1967	60

INTRODUCTION

Nitrogen efficiency and losses as related to plant growth have been of concern in agronomic research since 1877 when lysimeter studies of nitrate began at the Rothamstead Experimental Station (Russell and Richards, 1920). This problem is more than of academic interest. As is pointed out by Boawn, Nelson, and Crawford (1963), the efficiency with which the current crop utilizes nitrogen and the extent of carry-over into subsequent growing seasons is important for making good nitrogen fertilizer recommendations.

Furthermore, as the price per pound of nitrogen goes down and the rate of fertilizer application increases, the potential for pollution of surface and ground waters through leaching of nitrate and for adverse residual effects on soil acidity are also becoming of increasing concern.

There is a long history of attempts to identify forms of nitrogen in soils and in plants which could be used as a basis for controlling this nutrient for efficiency in fertilizer practice. In technologically advanced areas of the world, the objective of efficiency in nitrogen use is now coupled with that of identifying criteria and practices which may be used for controlling hazardous accumulations of nitrate in agricultural lands.

The objective of the research reported here was to evaluate residual and cumulative effects of three nitrogen materials at annual rates up to 252 kg N/ha (225 lb N/Acre). The experimental design permitted an estimate in the fourth year of carryover effects from each of three preceding annual applications. Major residual effects were expressed on the response of corn to the current year's nitrogen input. Significant effects on soil pH and nitrate levels were noted.

LITERATURE REVIEW

The literature here reviewed is related to the residual characteristics of fertilizer nitrogen. A detailed survey of the mechanisms by which nitrogen is lost from the soil is beyond the scope of this review, except as it is brought out in the papers dealing with nitrogen studies.

Residual nitrogen studies have been carried out in a variety of ways, both in the field and in the greenhouse. One of the procedures for estimating residual nitrogen as reported by White (1957), Dumenil and Pesek (1958), and White and Pesek (1959), involved the determination of the rate of increase of nitrogen in oats with various rates of nitrogen applied the previous year. With three medium textured soils, 60, 120, and 180 pounds of nitrogen were applied to corn. The residual response represented a carryover of about seven percent of the nitrogen applied to corn the previous year at the 60 lb. rate and about 49 percent at the 180 lb. rate. In soil which had received the latter treatment, 88 pounds of residual nitrogen was found mainly in the form of nitrate at a depth of six to 21 inches. No appreciable quantities of residual ammonium were found.

A mineralization test showed that the effect of the residual nitrogen on nitrifiable forms of nitrogen in these soils was negligible. There was also a high correlation between effects of residual nitrogen and plant uptake of soil nitrate. The small amounts of nitrate in the surface layer, according to White (1957), improved the root growth and thus facilitated the utilization of residual nitrogen in the subsoil by the plants.

In an earlier study by Pesek and Dumenil (1956), under Iowa conditions, the average residual carry-over from 40 to 60 pounds of nitrogen applied to corn, when measured with oats the following year, was about 25 percent. However, following wet seasons the residual effect was usually equivalent to less than a 20 percent carry-over of nitrogen, while following dry seasons it was in the neighborhood of 30 percent. Pesek and Dumenil conclude that the residual response in areas where the rainfall is 30 to 35 inches per year is likely to be of little importance past the second crop-year after application.

In an experiment by Broadbent and Nakashima (1968), tagged nitrogen fertilizers were applied to pots in which an attempt was made to eliminate leaching and denitrification losses through a controlled watering system. When nitrogen was applied on the soil surface as ammonium nitrate and ammonium sulfate, the volatilization loss of ammonia ranged from 24 to 39 percent. However, when these were banded at a depth of 7.5 centimeters, volatile losses were negligible.

Of the various forms of nitrogen applied, the nitrate sources were decidedly superior to other forms with respect to efficiency of plant uptake by a sequence of sudan grass, tomatoes, and corn over a 314 day period. A comparison of plant uptake of tagged ammonium in ammonium nitrate versus tagged nitrate in ammonium nitrate, showed differences ranging from nine to 20 percent in favor of the nitrate.

Since leaching and denitrification were carefully controlled, the extent of selectivity for nitrate over ammonium by the plants grown was likely greater than it would be under field conditions.

A study with corn in a fine sandy loam soil by Boawn et al. (1963) showed an average residual response equivalent to 44 percent of the original ammonium nitrate applied during the first year of nitrogen removal. This percentage was expressed in terms of the current season's nitrogen application needed to produce the same amount of nitrogen uptake as by the residual crop. Residual nitrogen response during the third year of plant growth was insignificant.

Viets (1960) tells of an experiment in which nitrogen was applied at various rates to grass and to a sequence of crops. All the nitrogen removed in the subsequent crops was measured, without additional fertilization until all residual nitrogen was removed. Erosion and leaching losses were minimized by selection of experimental sites and by careful irrigation. The results were quite variable with seven to 50 percent total recovery on the fine textured soils. One fine sandy loam yielded a total recovery of nearly 80 percent. Viets suggests that denitrification after rain or irrigation may have accounted for some of the loss.

The effect of residual nitrogen is influenced by the kind of crop grown, according to the findings of Widdowson and Penny (1965). Their experiment employed an alternating wheat-potato rotation on a clay loam soil. Zero, 50, and 100 pounds of nitrogen per acre were applied to wheat, and zero, 75, and 150 pounds of nitrogen per acre were applied to potatoes. Nitrogen applied to potatoes always increased wheat yields the next year. The residue from 150 pounds of nitrogen for potatoes had the same effect as applying about 55 pounds of nitrogen to the following wheat crop. There was less carry-over effect in the following wheat crop when the wheat was topdressed with nitrogen.

Potato yields were little affected by the application of nitrogen to the preceding wheat crop. The period of residual benefit from nitrogen fertilizer was just one year, in that there was no gain for either crop from nitrogen applied two years before.

The findings of Clark (1964) agree with the findings of these investigators in that he found very little residual effect upon the yield of cotton from nitrogen two years after application. With zero to 400 pounds of nitrogen applied per acre, nitrogen uptake by the cotton varied considerably over the three-year period.

Nitrogen uptake the first year increased from 80 to 110 pounds as the application of nitrogen was increased from 100 to 300 pounds per acre. When the application was increased to 400 pounds per acre, the current year's nitrogen uptake decreased. Residual nitrogen taken up during the second year increased with each successive increase in the rate of application, until it equaled that taken up the first year at the 300 pound rate. At the 400 pound rate, the second year's residual uptake exceeded the first year's direct uptake. By the third year, uptake of nitrogen dropped to about 45 pounds per acre regardless of the rate of application. Apparently by the third year, the fertilizer nitrogen was lost from the soil through crop removal, leaching, volatilization or denitrification, or it had become a part of the organic fraction of the soil through immobilization.

The Effect of Inorganic Nitrogen Application on Uptake of Soil Nitrogen

The addition of fertilizer nitrogen will usually increase the uptake of soil nitrogen by the crop. This phenomenon has been noted in N^{15} studies by several investigators, with a number of explanations being given.

Broadbent and Norman (1947) suggest that increased uptake of soil nitrogen with increased nitrogen fertilization may be due to a rise in the mineralization rate, resulting from a stimulation of the microflora by added mineral nitrogen. In sharp contrast with this explanation is one given by Stewart, Johnson, and Porter (1963), who say that increased uptake of soil nitrogen could be expected if neither immobilization nor mineralization rates changed, simply by fertilizer nitrogen replacing soil mineral nitrogen in the immobilization pool, thus allowing more soil nitrogen to be available for plant uptake.

According to Allison (1965), if crop growth is increased as applied fertilizer nitrogen is increased, there will be a corresponding increase in the size of the root system. The net result is that more nitrogen will be taken up by the plant. He notes that N^{15} studies are conducted under conditions of maximum exploitation of the available nitrogen supply, so higher recovery rates can be expected than under normal field conditions.

The Effect of Inorganic Nitrogen Application on Soil Humus

The effect of added inorganic and organic nitrogen materials upon soil humus has been the object of much study. Allison (1955) summarizes some of the commonly accepted views by saying that soil humus has a C:N ratio of about 10 or 12 to 1, and that 25 to 35 percent of the initial plant carbon will remain to form humus regardless of whether inorganic nitrogen is applied or not. Thus Allison concludes that added nitrogen will not affect the soil humus very much, but will greatly affect crop growth. High nitrogen applications will often result in higher carbon content, but this is due to the production of more residues, not because inorganic nitrogen has resulted in the retention of more crop residue carbon.

Since the nitrogen content of microbial protoplasm is about 3 to 12 percent, the C:N ratio of the added materials must be below 20 to 25, or about 1.5 percent nitrogen or greater, for any appreciable net mineralization of nitrogen (Harmsen and Kolenbrander, 1965). Jansson (1958) warns against being misled by the "priming effect" of fresh additions of organic materials to the soil. These priming effects according to Jansson, may result when an addition of energy-containing material, whether containing nitrogen or not, to the soil may extend and speed up cyclic transformations. This may result in a net mineralization greater than that of the untreated check and possibly, even in a net depletion of total soil organic nitrogen.

Bingeman, Varner, and Martin (1953) in a study with C^{14} tagged additions of alfalfa insolubles and complete alfalfa, found that there was an initial increase in mineralization of native soil carbon. The greatest increase occured in the first two weeks, then a return to near normal mineralization rate. This in itself says nothing of the mineralization of soil nitrogen.

According to Harmsen and Kolenbrander (1965), when starting with a high C:N ratio, the carbon is rapidly liberated and lost as CO_2 while the nitrogen is mainly retained in organic form until the energy per unit nitrogen ratio has become sufficiently reduced to allow for an accumulation of inorganic nitrogen. Only from that moment onward is there a "net mineralization" of nitrogen. During the foregoing stages, the nitrogen of the original substrate may have been mineralized repeatedly, but there was no accumulation of mineral nitrogen. Such temporary, reversible mineralization can be designated as "primary mineralization", whereas the accumulation of inorganic nitrogen is the "net mineralization".

Thus the C:N ratio of the added materials must be considered as well as the C:N ratio of the soil organic matter in predicting the net mineralization of soil nitrogen. Bartholomew, (1965) expresses both positive and negative ideas concerning the value of the C:N ratio. Positively, the C:N ratios reflect nitrogen immobilization and mineralization. In decomposition of organic residues, carbonaceous materials supply the major energy source for microorganisms. The nitrogen is assimilated as protein in microbial tissue as a function of the growth of the organisms concerned.

Negatively, since the C:N ratio involves the normal errors of determination of both the carbon and nitrogen, it is often less reliable as an index of nitrogen immobilization than is nitrogen percentage. Furthermore, interpretations are frequently made which go beyond the understanding of the actual chemical and biological mechanisms of immobilization in the decay process.

Greenhouse Studies

The efficiency of utilization of fertilizer nitrogen by plants in most greenhouse studies is about 85 to 90 percent in the first crop. The residual effect in terms of percent of the initial application is therefore lower than that usually reported under field conditions.

In a six-year greenhouse study with tagged nitrogen on an infertile acid sandy loam soil, Jansson (1963) found that eight to 14 percent nitrogen losses occurred when part of the tagged inorganic nitrogen was still in the soil. Jansson proposed that this loss occurred through denitrification. He also found that once the nitrogen had been organically immobilized it was liable to a very slow net mineralization process. The plant availability of the organic and clay fixed nitrogen averaged about one percent of the fertilizer addition per year.

When oats were harvested at maturity, nitrogen losses were confined to the year of addition. When the harvesting took place at early stages of growth, then losses also occurred during the second year.

Broadbent and Nakashima (1965) have also shown that once inorganic fertilizer nitrogen is incorporated into the organic cycle in soil, it is remineralized only very slowly. The presence of growing plants on the soil during the period of nitrogen application resulted in more efficient utilization of the fertilizer than where planting was delayed several weeks, regardless of whether straw was added or not.

In an experiment by van der Paauw (1963), over a seven year period, the residual effect of nitrogen applied in the previous year averaged 5.6 percent of the effect of a corresponding fresh application. The residual effect of nitrogen not taken up in the previous crop averaged 13.5 percent. The results were similar with different crops and soils. The residual effect of nitrogen not removed in the first crop was related to rainfall during the intervening winter. As the November-to-February rainfall decreased from 10 to seven inches, the residual effect from nitrogen not accounted for in the first crop increased from two percent to 17 percent.

Legg and Allison (1967) conducted another greenhouse study in which 50 to 200 ppm of nitrogen was applied for oats. They investigated recovery of the nitrogen by the oats and a following crop of sudan grass. The residual nitrogen taken up by the first cutting of sudan grass, as a percent of the tracer nitrogen which was not removed by the previous crop, ranged from 10 to 41 percent and increased with the rate of application. Availability of residual nitrogen to a second cutting of sudan grass dropped to 4.5 percent of the remaining tracer nitrogen.

Nitrogen Losses From the Soil

Nitrogen losses from the soil occur through erosion, leaching, volatilization of ammonia from plants and soil surfaces, microbial denitrification, and chemical reduction of nitrite.

In a brief review of nitrogen losses from the soil, it soon becomes apparent that the form of nitrogen loss that has been studied the most extensively is leaching. Leaching losses have been studied by use of lysimeters since 1877 (Russell and Richardson, 1920). Allison (1965) states that a general study of the data from lysimeters of the type commonly used, that is, shallow, filled-in lysimeters, seems to justify the conclusion that they do not serve as a satisfactory basis for judging the amount of leaching losses of nitrogen under field conditions. However, he feels that they do bring out the importance of the various factors that affect the magnitude of leaching losses. These factors include the cropping system, soil texture, infiltration rate, and ease of water movement through a soil column.

Benson and Barnette (1939) performed a series of leaching studies on four coarse-textured soils after application of several nitrogen sources. Sufficient quantities of water were applied to the test areas to provide three inches of drainage water at intervals of one, four, 10, and 21 days. They found that all the nitrogen that was applied as nitrate was leached, while only one-third of the ammonium applied as ammonium nitrate was leached. The amount of urea leached as urea was dependent upon the time of leaching, with 35 percent removal one day after application and 16 percent when the leaching occurred four days after application. Ammonium nitrogen was retained efficiently until nitrification began, then both ammonium and nitrate nitrogen leached.

Utilizing isotopic nitrogen, Owens (1960) was unable to account for an average of 33 percent of applied nitrogen two years after 120 pounds per acre had been applied as ammonium sulfate. This loss was assumed to have taken place via denitrification since the soils were maintained at field capacity, thus yielding anaerobic conditions in soil micropores. The leaching losses varied from five percent at 12 inches of rainfall over a five-month period to 20 percent at the 24-inch rainfall level. The amount of fertilizer in the soil at the end of the two-year period was 38 percent and was unaffected by the soil moisture treatment.

Some guidelines as to the amount of leaching loss in relation to rainfall have been given by Gardner (1965). He notes that the distance which nitrate will move downward depends not upon total rainfall but upon the amount of rainfall which actually passes through the soil. For this reason, correlation of nitrate leaching losses with rainfall is not as direct as might be expected. This is especially true under cropping conditions when plants are continually extracting water from the soil. Gardner proposes the use of excess rainfall over evapotranspiration to estimate the probability of leaching losses.

Nelson and Uhland (1955) point out that the amount of rainfall which passes through the soil is not the only factor controlling the amount of leaching loss. Where percolation occurs, the amount of nitrogen leached from the root zone depends upon the amount of nitrate in the soil, the fertilizer applied, and the rate of formation of nitrate from ammonium. Among other things, this rate is dependent upon temperature. According to Nelson and Uhland, considerable nitrification can occur over a period of time, even at temperatures of 45°F.

According to studies by Burns et al. (1965), nitrate formation may take place at considerably lower temperatures than 45°F. Their field data show that nitrification proceeds rapidly in the early fall and that complete thermal inhibition does not occur until the soil temperatures approach freezing. The rate of nitrification however, declined rapidly below 50°F. in the fall. It commenced again rather abruptly when this temperature was reached in the spring.

Another factor controlling the amount and rate of nitrification is the availability of water. Fitts, Bartholomew, and Heidel (1955) found that nitrate production will take place over a fairly wide range of soil moisture conditions. One hundred centimeters of tension, or just less than field capacity, provided the optimum moisture for the production of nitrate. Burns (1969) reports similar findings on a loess-derived silt loam. In the soil moisture tension range of zero to 15 bars, the maximum nitrate accumulation rates occurred at 0.1 bar, which corresponds to slightly more water than that held at field capacity.

The importance of factors which control leaching in modifying the residual character of fertilizer nitrogen is apparent in the work of Pearson et al. (1961) in the Southeastern United States. They report that fall-applied nitrogen was only 49 percent as effective as spring-applied nitrogen when measured by corn yields. In terms of nitrogen recovery, the relative effectiveness of fall vs. spring application was about 62 percent. Under similar conditions where 200 pounds of nitrogen per acre was applied to corn in the spring, there was a large residual benefit to two succeeding crops during the following 16 months. Total recoveries of nitrogen amounted to 70 to 77 percent in three crops. Pearson et al. concluded that recoveries can be good even in humid regions, if the nitrogen is applied at a time when leaching is at a minimum and when a crop is present to assimilate it.

The amount of leaching that occurs in relation to rainfall has been examined by Harmsen and Kolenbrander (1965). They report that the vertical downward displacement of nitrogen in sandy soils at field capacity is about 45 centimeters per 10 centimeters of rainfall entering the soil. This figure drops to about 30 centimeters for soils

in which 20 to 40 percent of the particles are less than 20 microns in diameter. They conclude, that complete loss of nitrogen from permeable sandy soils may occur in humid climates even during normal winters. During the summer growing season, nitrate is seldom carried downward beyond the reach of plant roots except during unusually rainy periods.

It may be assumed that any infiltration of water will result in some downward movement of nitrate and that later capillary movement will result in some upward movement within the soil (Wetselaar, 1961). It becomes important to ask how deep must nitrate move before "leaching" or actual nitrogen loss occurs. Any answer must consider rate and height of capillary rise and, thus, the texture of the soil profile.

Wetselaar (1962) reported that the upward movement of nitrate in a clay loam was restricted to the top 18 inches of soil. This implies that any nitrate leached below this depth, in this soil, cannot be returned to the topsoil by capillary movement. If the root system of a given crop extends below this depth, then nitrate below 18 inches is not necessarily an economic loss. On the other hand, any nitrate leached below this depth and below the root zone of crops grown may be considered lost in terms of management and control. This nitrate will, undoubtedly reach the ground water and move to nearby lakes and streams.

Another important mechanism of nitrogen loss, especially in humid regions, is denitrification. Allison (1965) states that there are many opportunities for denitrification to occur under field conditions if nitrate or nitrite are present. In well-drained sandy soils, opportunities for loss of nitrogen by microbial reduction are negligible. In fine textured soil, such losses may be large since oxygen deficiencies, due to poor drainage and/or rainfall in excess of infiltration, occur frequently for periods of several days.

Allison (1963) discusses several mechanisms of chemical denitrification. One such mechanism is by chemical decomposition of nitrous acid. The nitrite ion (NO_2^-) is stable. The undissociated acid (HNO_2) is formed below pH 7.0 and is increasingly unstable with decreasing pH below 6.0. The dismutation in dilute solution may be written:

$$3\ HNO_2 \longrightarrow 2\ NO + HNO_3 + H_2O$$

At higher concentrations the following reaction may be observed (Black, 1968):

$$2\ HNO_2 \longrightarrow NO + NO_2 + H_2O$$

Black cites data from a Ph.D. thesis by D. W. Nelson in which nitric oxide according to the above reactions, appeared only when the atmosphere contained no oxygen. When small amounts of oxygen were present, nitric oxide was oxidized rapidly to nitrogen dioxide. Lack of oxygen would normally occur in saturated conditions. However, water would be available to form nitric acid:

$$2\ NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

Thus no loss of nitrogen dioxide was observed, except at extremely acid pH.

Another chemical reaction that may be more important in terms of denitrification losses is the chemical reduction of nitrous acid by organic matter. The reaction seems to be related to the amount of lignin or of lignin-derived structures in the soil organic fraction. Bremner (1957) found that nitrous oxide was liberated upon treatment of humic acid or lignin with nitrous acid in the Van Slyke reaction. Black (1968) again reporting from Nelson's thesis, says that extracted soil organic matter, prepared lignins, and soils high in content of organic matter all promoted decomposition of nitrite.

Clark and Beard (1960) in earlier experiments obtained similar findings and concluded that since nitrite is an intermediate in the microbial oxidation of ammonium to nitrate and since denitrification of nitrite by soil organic matter is a chemical reaction, then much of the naturally occurring volatile loss of nitrogen from aerobic soils occurs during the nitrification process.

These losses may be large, according to Allison (1965), under conditions where considerable nitrogen as ammonia, urea, or green manure is added to acid sandy soils and ammonia oxidation is delayed at the nitrous acid stage.

The extent of nitrogen loss as a result of volatilization of ammonia is commonly negligible from soils having pH values less than neutral unless there is enough free ammonia to raise the pH locally. These losses increase with increasing pH and temperature and are greatest in soils of low cation exchange capacity (Pesek and Dumenil, 1956).

The greatest loss through volatilization of ammonia occurs in most soils as anhydrous ammonia is being injected in soil. According to Pesek (1964) these losses occur when the soil is too wet or too dry, when the application is too shallow, or when the rate of application per volume of soil is too great. The latter may occur through the use of application furrows which are too far apart.

High potential losses of nitrogen from urea fertilizers may occur if the urea is not mixed well with the soil, or if the surface becomes dry. Urea hydrolyzes rapidly in soil and forms high local concentrations of ammonium carbonate and high pH. The major inefficiencies of urea nitrogen occur through losses of ammonia as a result of surface soils drying out after hydrolysis has taken place on moist soils. These potential losses are magnified, according to Pesek (1964), by high pH, low base exchange capacity, and by high temperatures.

Soil Nitrogen and Corn Growth

Predicting the soil's ability to supply nitrogen for the growth of crops has been the concern of researchers for a long time. A meaningful prediction cannot be made without considering the needs of the plant concerned in relation to its pattern of growth. Romaine (1965) cites data from Ohio showing quite clearly that the time of greatest nitrogen demand by the growing corn plant is during the time that the ear is being formed. These data show that 48 percent of the nitrogen uptake by corn occurs during the third month, and nearly 60 percent during the third and fourth months together.

On the basis of field experience in Michigan, Lucas (1969) has proposed that 40 pp2m of nitrate-nitrogen in the plow soil represents a critical level for estimating the adequacy of nitrogen available to corn during the tasseling, silking and pollination period when its need for nitrogen is greatest.

EXPERIMENTAL PROCEDURES AND METHODS OF ANALYSIS

Field Treatments

In 1965 an experiment was initiated on the Soil Science Experimental Farm at Michigan State University to evaluate residual effects of three different nitrogen carriers at three rates of application. The experiment was designed to follow residual and cumulative effects over a four-year period on continuous corn (*Zea mays*). Ten treatments, including the control, were replicated four times in a randomized complete block design yielding a total of 40 plots. Each plot was 14 by 100 feet (4.26 by 30.4 meters).

To introduce variation in residual and cumulative effects of fertilizer nitrogen, these main plots were subdivided as follows: The entire plot received the nitrogen treatment the first year. Each succeeding year, 25 feet less of each plot received nitrogen until the fourth year, when each 100 foot plot was subdivided into four 25-foot sub-plots. These sub-unit treatments were randomized within blocks, but not within nitrogen treatments. The resulting systematic grid arrangement was taken into consideration in the analysis of variance.

Four rows of corn were planted on each plot, with the planter set to deliver 17,500 to 19,600 kernels per acre (43,000 to 48,000 kernels per hectare). Michigan 400 hybrid seed was used each year.

Basal fertilizer and management were the same on all plots (Table 1).

The nitrogen carriers were urea, ammonium nitrate, and anhydrous ammonia. Each nitrogen carrier was side-dressed on knee-high corn at the rate of 75, 150, and 225 pounds of nitrogen per acre (84, 168 and 252 kg/ha). The anhydrous ammonia was knifed in between each two rows. The urea and ammonium nitrate was spread byhand between each two rows and then mixed with the soil by shallow cultivation.

The soil has been classified as a Hodunk Sandy Loam which belongs to the subgroup Ochreptic Fragiudalf (Schneider, Johnson, and Whiteside, 1967). See the Appendix for the description.

Soil Sampling

In November of the third year, 1967, and in early August of the fourth year, 1968, soil samples were taken. The soil sample for each plot consisted of 20 cores taken to a depth of 10 inches with a soil probe. The 20 cores were taken randomly between the center two rows and their fertilizer bands. They were passed through a one-fourth inch screen in the field and thoroughly mixed. Subsamples of the screened soil were spread

Table 1. Basal fertilizer and management

Date	Operation	Basal fertilizer*			Seed spacing
		Ratio	Rate	Placement	
		$N-P_2O_5-K_2O$	lb/acre		inches
1965 crop:					
May 11	Plow, plant	0-20-20	300	Banded	8 x 42
June 18	Inject NH_3				
June 24	Sidedress NH_4NO_3 and urea, double cultivate				
1966 crop:					
May 5	Plow, plant	0-20-20	300	Banded	9 x 42
June 20	Inject NH_3				
June 23	Sidedress NH_4NO_3 and urea, double cultivate				
1967 crop:					
Nov.15,1966	Basal fertilizer and fall plowing	0-20-20	350	Broadcast and plowed down	
May 20, 1967	Plant	6-24-24	80	Banded	8 x 42
June 27	Inject NH_3				
June 28	Sidedress NH_4NO_3				
July 3	Sidedress urea, double cultivate				
1968 crop:					
May 1	Plow				
May 2	Plant	0-20-20	300	Banded	8 x 42
July 5	Inject NH_3, sidedress NH_4NO_3 and urea, cultivate				

* Total basal fertilizer for each crop (kg/ha N-P-K): 1965 (0-29-56); 1966 (0-29-56); 1967 (5-43-83); 1968 (0-29-56).

shallowly in five-pound paper bags laid on their sides on the drying racks in the soils barn. After one week the samples were ground to pass a two mm screen.

The 1967 samples were placed in one-pint icecream cartons for storage while the 1968 samples were sealed in plastic bags for storage.

Soil Testing

The Michigan State University soil testing lab received approximately one-half of each sample for routine analysis. Soil pH, lime requirement, P, K, Ca, and Mg were determined on the November 1967 samples. The August 1968 samples were analysed only for pH, P, and K.

The November 1967 samples were ground to pass a 100-mesh screen in preparation for the total nitrogen and total carbon analysis. A modified version of Bremner's micro-Kjeldahl method (Bremner 1965) for total nitrogen analysis was used to determine total nitrogen. A complete description of the modified semi-micro-Kjeldahl method may be found in the appendix.

A high induction furnace, model 750-100 Leco, was employed for making the total carbon determination. A sub-sample of soil ranging from 0.1 to 0.2 grams was combusted with about 1.0 gram of tin and 1.5 grams of iron catalyst. In this instrument, the carbon is converted into carbon dioxide which is then quantified by the change in thermal conductivity which results when the carbon dioxide is mixed with oxygen.

The August 1968 soil samples were exposed to ammonia fumes while on the drying racks, thus the ammonium values were all very high and quite meaningless. Nitrate determinations were made on these samples, using the Brucine technique by Greweling and Peech (1965).

Statistical Analysis

In the field, the nitrogen treatments were randomized within each block while the year of nitrogen application was systematically imposed across N treatments. The appropriate analysis of variance is that for a split plot with sub-units in strips (Cochran and Cox, 1957).

An arbitrary decision was made to consider year of application as the unit category and nitrogen treatment as the sub-unit. This choice has no effect on the analysis, since each main effect and treatment interaction is tested by the corresponding interaction with blocks.

Two separate analyses were performed on each observed variable: (1) main effects and interactions with years of ten nitrogen treatments, including the control; and (2) factorial main effects and interactions of carrier and rate (nine treatments), and their first and second order interactions with years.

The factorial interactions with years were also examined by multiple correlation analysis.

Use of facilities in the Michigan State University Computer Center was made possible by support, in part, from the National Science Foundation. Programs developed by Ruble et al. (1969) were used.

RESULTS AND DISCUSSION

Yield History

Corn yields over the four-year period are given in Table 2.

Year-to-year variation in yields was influenced by weather. Non-significant responses to applied N in 1965 were due to critical shortages of moisture from early spring through July (Table 3). There was some evidence that the deeper placement of NH_3, which was injected, may have made more N available from this carrier at the higher rates than from the other two, which were mixed with the surface soil by shallow cultivation.

Nitrogen not used in 1965 was used effectively in 1966. Residual N carried over from 1965 was adequate for maximum yields and there were no significant differences for residual vs. current applications of N in 1966. Yields in 1966 were the highest for the four years of the experiment. This reflects a combination of favorable soil moisture, at planting time, more timely rains in June, July and August and generally higher temperatures in July and August in 1966 than in the other growing seasons.

Table 2. Corn yields over a four-year period in relation to residual and cumulative effects of fertilizer nitrogen

Carrier	N applied	Harvest year: 1965	1966		1967			1968			
		Years of N application									
	kg/ha	1965	1965	1965 1966	1965	1965 1966	1965 1966 1967	1965	1965 1966	1965 1966 1967	1965 1966 1967 1968
		hl/ha*									
Control	0	57.4	83.6	71.3	55.4	49.2	39.1	42.7	38.4	45.1	38.9
Urea	84	68.2	93.2	99.7	62.6	64.3	85.0	44.5	45.5	47.7	50.9
	168	64.7	102.7	103.2	55.0	65.4	87.0	49.8	48.5	60.4	74.4
	252	62.7	103.0	103.0	61.2	81.3	91.9	49.3	51.1	76.1	77.6
NH_4NO_3	84	60.0	96.0	102.5	58.7	68.5	82.2	48.4	50.1	65.2	67.9
	168	65.7	97.6	101.8	65.1	84.3	91.9	50.9	53.5	67.7	69.2
	252	62.7	95.1	105.3	62.8	71.1	89.1	41.6	45.8	64.7	69.9
NH_3	84	65.3	102.0	107.5	60.0	80.3	88.4	46.2	50.4	61.6	84.0
	168	77.3	105.3	100.4	67.0	87.2	87.6	48.3	52.9	66.9	88.2
	252	71.4	105.0	100.9	72.8	95.0	88.7	57.8	68.2	80.8	85.1
LSD(.05)		ns	10.0	10.0	12.1	12.1	12.1	10.6	10.6	10.6	10.6

*hl/ha = 1.15(bu/acre)

Table 3. Monthly rainfall, average temperatures, and deviations from the norm*#

Year		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
1965	Temp.	23.5	24.6	27.7	43.9	63.6	66.4	69.4	68.0	63.4	50.9	40.9	34.2
	Dev.	-0.8	-0.4	-4.7	-1.8	6.5	-1.0	-2.3	-2.2	1.4	0.4	3.0	6.7
	Rain	2.86	1.70	2.13	2.05	1.57	2.84	0.79	3.73	4.78	1.50	2.97	3.40
	Dev.	0.90	-0.25	-0.27	-0.82	-2.16	-0.50	-1.79	0.68	2.18	-1.00	0.76	1.41
1966	Temp.	19.9	26.0	38.6	44.3	53.0	68.0	72.5	68.5	60.3	50.0	40.1	26.4
	Dev.	-4.4	1.8	6.2	-1.4	-4.1	0.6	0.8	-1.7	-1.7	1.3	2.2	-1.1
	Rain	0.43	0.81	2.95	3.26	2.00	4.32	2.33	3.28	1.03	0.82	3.02	1.96
	Dev.	-1.53	-1.14	0.55	0.39	-1.73	0.98	-0.25	0.23	-1.57	-1.70	0.81	-0.03
1967	Temp.	26.6	19.8	33.6	47.9	52.3	69.6	68.7	66.1	60.1	50.7	34.7	30.3
	Dev.	2.3	-4.4	1.2	2.2	-4.8	2.2	-3.0	-4.1	-1.9	-0.6	-3.2	2.8
	Rain	1.81	0.31	0.71	3.71	1.16	5.96	1.46	2.98	2.29	3.59	2.93	3.58
	Dev.	-0.15	-1.64	-1.69	0.84	-2.57	2.62	-1.12	-0.07	-0.31	1.09	0.72	1.59
1968	Temp.	21.8	22.7	38.2	49.5	54.1	66.6	69.7	70.2	64.1	52.3	38.8	26.2
	Dev.	-2.5	-1.5	5.8	3.8	-3.0	-0.8	-2.0	0.0	2.1	1.0	0.9	-1.3
	Rain	0.66	1.79	0.65	1.75	4.39	7.16	2.34	2.23	3.49	1.34	3.38	2.71
	Dev.	-1.30	-1.60	-1.75	-1.12	0.66	3.82	-0.24	-0.82	0.39	1.16	1.17	0.72

May to August, 1968, Rainfall Concentrations

	May 26-28	June 21-29	July 23-27	Aug. 5-8	Aug. 16-17
Rainfall	3.04	6.25	1.90	1.34	0.57

* Rainfall and temperature data from the East Lansing 3SE Weather Bureau Station

\# Deviations from the norm are based upon the norm at the Lansing Weather Bureau

Yields in 1967 and 1968 were limited by deficiencies of moisture and by abnormally low temperatures during critical growth periods. Nevertheless, significant yield responses were associated with both residual and current year's inputs of fertilizer nitrogen.

Sources of Variation in 1967 and 1968

Probabilities in the first column of Tables 4 and 5 show that highly significant components of yield variation were associated with soil variation (replication), years of N application, nitrogen treatment and year x treatment interaction.

Subdivision of treatment variance in the factorial analysis indicates that treatment effects on yield in both seasons were associated with both carrier and rate. In 1968, a significant carrier x rate interaction also appeared.

The number of fertile stalks (harvested ears) per hectare and the weight per ear were strongly influenced by replication, year of N application and treatment. Treatment effects on ear weight included significant effects of both carrier and rate and a significant carrier x rate interaction.

Variance in total soil N in 1967 was not significantly associated with any design category (Table 4). In the case of soil C, variance approaching significance at five percent was associated with replications and years of N application in the plots which received the factorial N treatments. The ratio of carbon to nitrogen varied significantly in association

Table 4. Approximate significance probabilities of F in 1967 for variance associated with experimental design categories

Category	Dependent variables									
	Corn yield	Soil parameters								
		Total N	Total C	C/N	pH	Lime rqmt.	Avail. P	Exchangeable K	Exchangeable Ca	Exchangeable Mg
Split plot analysis:										
Replications	.063	.099	.141	.018	.007	.041	.005	.001	<.0005	.001
Years	.011	.325	.115	.056	.094	.315	.900	.113	.365	.189
Treatments	<.0005	.434	.150	.666	.060	.307	.364	.844	.219	.194
Y x T	<.0005	.286	.218	.251	.006	.037	.555	.180	.809	.572
Factorial split plot analysis:										
Replications	.081	.098	.067	.014	.013	.032	.006	<.0005	<.0005	.001
Years	.009	.228	.068	.035	.081	.287	.887	.079	.382	.176
Carriers	.063	.367	.458	.264	.456	.576	.180	.784	.581	.570
Rates	.040	.360	.182	.618	.057	.803	.974	.403	.413	.549
C x R	.256	.543	.363	.578	.374	.076	.271	.760	.188	.087
Y x C	.020	.559	.221	.884	.024	.058	.633	.342	.990	.659
Y x R	.281	.296	.234	.751	.128	.457	.344	.350	.127	.484
Y x C x R	.539	.689	.552	.038	.150	.187	.459	.611	.823	.455

Table 5. Approximate significance probabilities of F in 1968 for variance associated with experimental design categories

Category	Dependent variables						
	Crop parameters			Soil parameters			
	Yield	Ears per ha	Ear wt.	NO_3-N	pH	Avail P	Exchangeable K
Split plot analysis:							
Replications	.002	.001	.001	.075	.001	.023	.005
Years	<.0005	.002	.005	<.0005	.029	.809	.101
Treatments	<.0005	.007	<.0005	.164	.314	.161	.891
Y x T	<.0005	.560	.010	.185	.216	.135	.715
Factorial split plot analysis:							
Replications	.002	.002	.001	.052	.001	.022	.004
Years	<.0005	.003	.002	<.0005	.030	.779	.108
Carriers	.016	.256	.041	.913	.968	.101	.713
Rates	.040	.241	.016	.051	.113	.734	.631
C x R	.026	.216	.031	.886	.454	.259	.689
Y x C	.006	.524	.410	.988	.979	.691	.128
Y x R	.149	.443	.571	.070	.278	.004	.736
Y x C x R	.153	.664	.086	.813	.088	.665	.815

with the replications, years and the second order interaction: years x carriers x rates.

Other soil tests in Tables 4 and 5 reflected principally soil variation among replications. Residual effects on soil pH tended to be additive as N applications were repeated year after year, but a significant interaction between year of application and carrier was expressed in the November 1967 samples. A year x carrier interaction approaching significance was indicated for lime requirement, also.

The level of available P in soils sampled during the growing season in 1968 reflected a highly significant year x rate interaction.

Residual Effects of Nitrogen on Corn Yields

Both in 1967 and in 1968, corn yields were increased significantly by residual effects of nitrogen applied in previous years (Table 6).

Residual benefit from the 1965 applications was still apparent two years later in 1967 and three years later in 1968. Significant increases over the controls were associated with the higher rates of anhydrous NH_3.

Where a second annual application of nitrogen was made in 1966, the level of residual response in the 1967 and 1968 harvest years was increased substantially. A third annual application in 1967 resulted in additionally increased yields on residual plots in 1968.

Table 6. **Absolute increases in yields of corn over controls which received no nitrogen**

Carrier	N applied	Harvest year 1967			Harvest year 1968			
		Years of N application						
	kg/ha	1965	1965 1966	1965 1966 1967	1965	1965 1966	1965 1966 1967	1965 1966 1967 1968
		hl/ha						
Urea	84	7.1 ab[1]	15.1 e	45.9 a	1.8 ab[1]	7.1 b[1]	2.6 d[1]	12.1 d
	168	-0.5 b[1]	16.2 de	48.2 a	7.1 ab[1]	10.1 b	15.3 c	35.5 abc
	252	5.8 ab[1]	32.1 abcd	52.8 a	6.7 ab[1]	12.7 b	31.1 ab	38.8 abc
NH_4NO_3	84	3.2 ab[1]	19.3 cde	43.1 a	5.8 ab[1]	11.7 b	20.1 bc	30.1 c
	168	9.7 ab[1]	35.1 abc	52.9 a	8.3 ab[1]	15.1 b	22.7 abc	30.4 c
	252	7.4 ab[1]	21.9 bcde	50.0 a	-1.0 b[1]	7.4 b[1]	19.7 bc	31.1 bc
NH_3	84	4.6 ab[1]	31.1 abcd	49.3 a	3.6 ab[1]	12.0 b	16.6 c	45.1 ab
	168	11.6 ab	38.0 ab	48.5 a	5.6 ab[1]	14.5 b	21.9 abc	49.3 a
	252	17.4 a	45.8 a	49.6 a	19.0 a	25.5 a	35.8 a	46.2 a
S_m		4.28	4.28	4.28	3.74	3.74	3.74	3.74

a...e Ranges of equivalence (Duncan, 1955). Means accompanied by the same letter are not different at 5 percent.

1 Not a significant increase over control.

Cumulative Effects on Corn

The cumulative responses of corn in 1968 to residual and current inputs of nitrogen are depicted graphically in Figures 1, 2 and 3.

Actual control values, corresponding to 100 percent on each graph, were 41.2 hl/ha (Fig. 1), 128 g/ear (Fig. 2) and 22,000 ears/ha (Fig. 3).

The last value indicates that only one-half of the planted population survived or obtained sufficient nutriment to produce an ear of corn on the control plots. The number of fertile stalks increased with annual increments of residual nitrogen and with nitrogen applied in 1968 (Fig. 3).

Something less than half of the increased yield in Fig. 1 was due to the increase in number of ears harvested (Fig. 3). The balance was due to a somewhat parallel increase in weight per ear (Fig. 2). Partial correlation coefficients significant at $P < .0005$ were obtained for ear numbers ($r_{yn \cdot w} = .979$) and for ear weight ($r_{yw \cdot n} = .984$) in the following regression:

$$EY = -55.5 + .0022\,N + .3629\,W \qquad (R^2 = .986)$$

where: EY = estimated yield, hl/ha

N = number of ears/ha

W = ear weight, g/ear

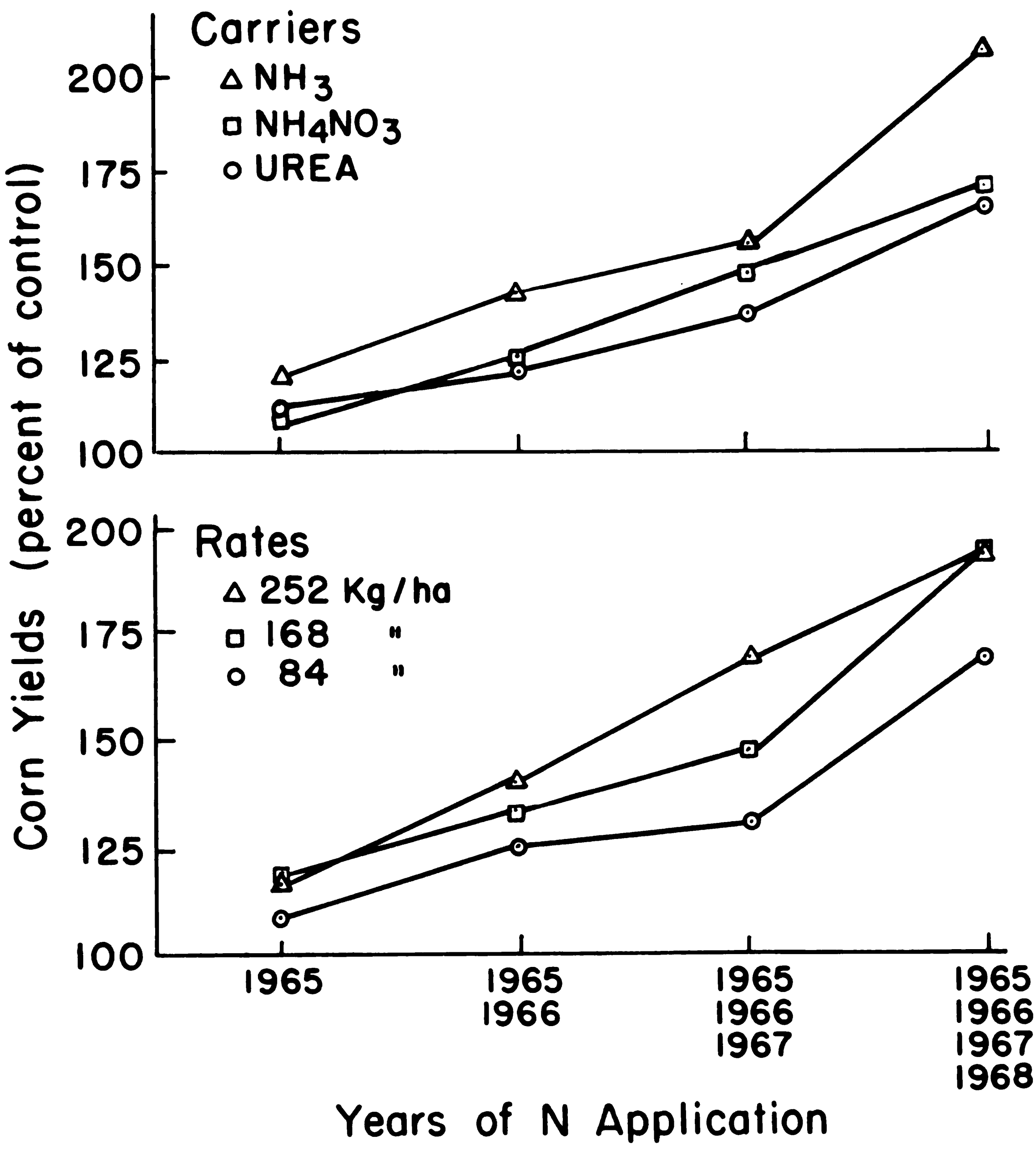

Figure 1. Relative increases in yields of corn in 1968 in relation to residual and cumulative effects of fertilizer nitrogen

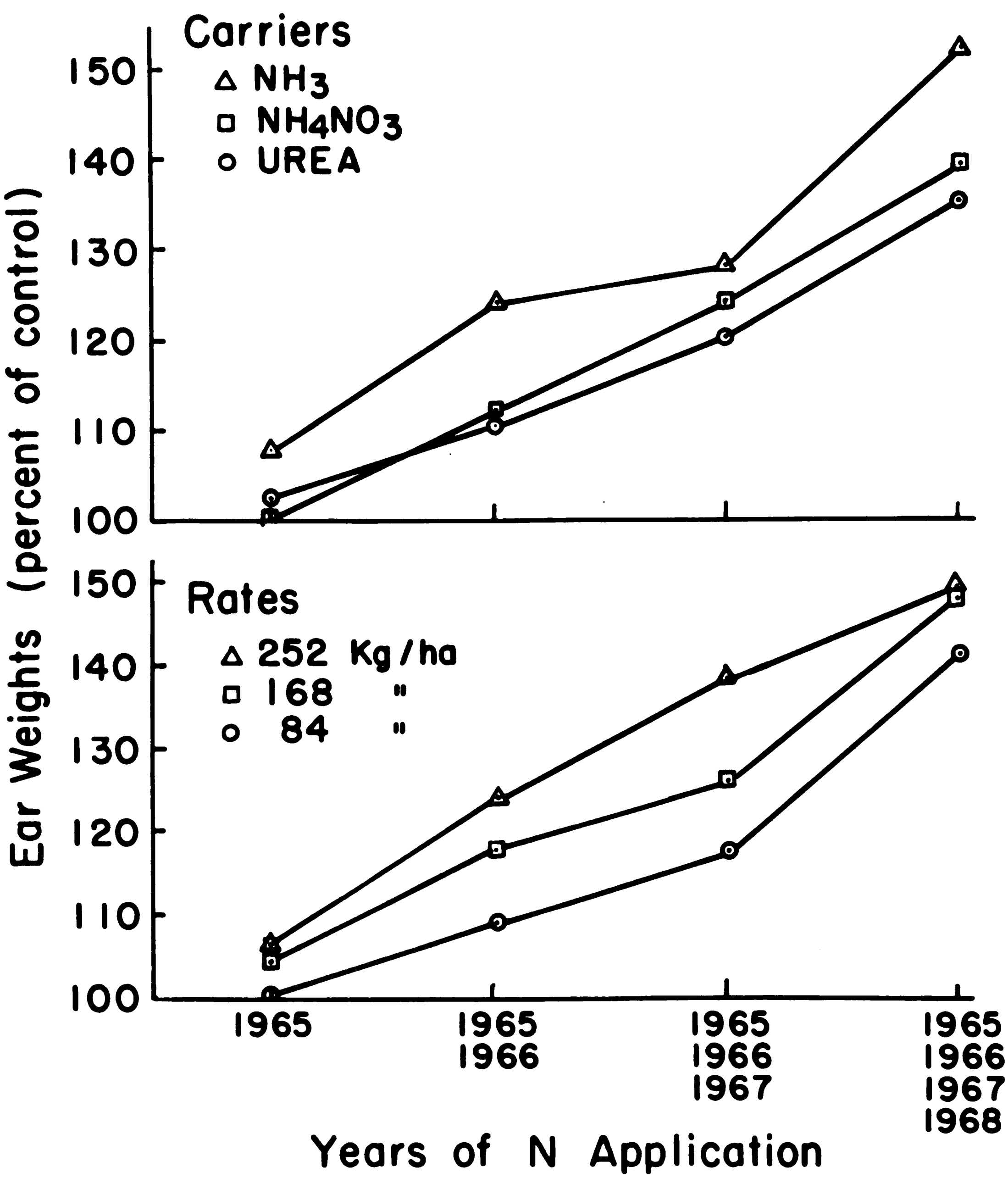

Figure 2. Cumulative effects of annual nitrogen applications on corn ear weights in 1968

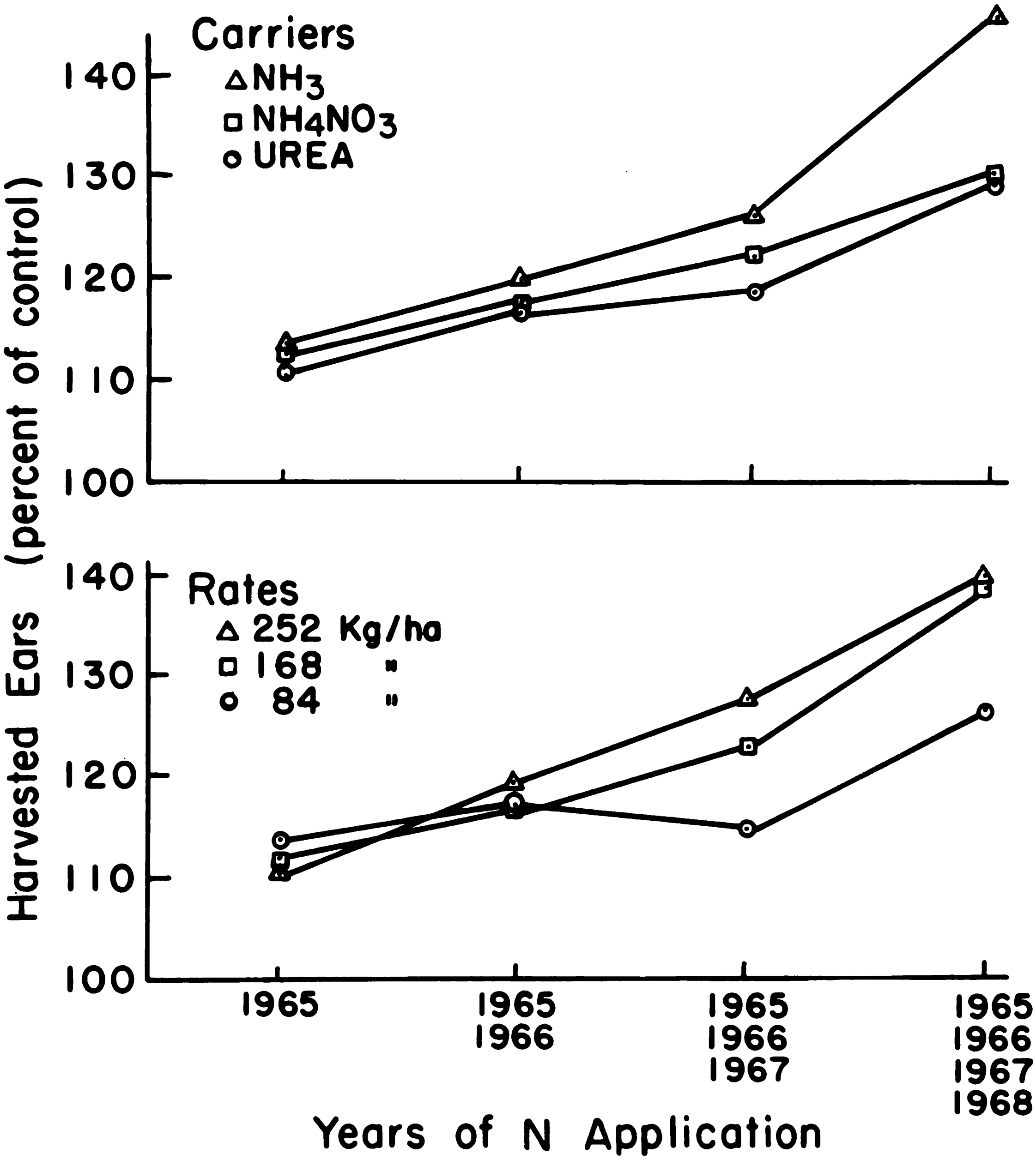

Figure 3. Cumulative effects of annual nitrogen applications on numbers of fertile stalks in 1968

Although weight per ear was calculated from yields and ear numbers, the two independent variables were not highly intercorrelated ($r_{nw} = .227$). The probabilities in Table 5 indicate that variation in ear numbers was associated mainly with soil variation (replication) and with the increasing differential in soil productivity associated with successive annual applications of N. Ear weights and yields, on the other hand, were influenced strongly also by differences in carrier and rate of N application.

Incrementation of Residual Response

In Table 7, main effects of carriers and of rates are considered in terms of relative yield responses in 1967 and 1968. Yields increased with each successive annual application. The rate at which these year-to-year increases occurred also increased with the amount of N applied and with carriers in the order urea $< NH_4NO_3 < NH_3$.

It may be assumed that benefits from nitrogen applied in previous years would have contributed similarly to the yields on plots which received additional nitrogen in the harvest year. On this assumption, the relative increases in Table 7 have been incremented by year of N application in Table 8.

In 1967, there was little difference in total relative response to the three carriers. However, the extent to which residual and current inputs of nitrogen contributed

Table 7. Relative increases in yields of corn expressed as percent of maximum for carrier or rate of nitrogen

Carrier or rate of N	Years of N application: 1965	1965 1966	1965 1966 1967	1965 1966 1967 1968	LSD(.05) for years within N treatments
	-------	-------	percent	-------	-------
1967 harvest year:					
Urea	8.3	43.1	97.7		26.1
NH_4NO_3	13.6	51.6	98.7		26.1
NH_3	22.7	77.8	100.0		26.1
LSD(.05)	ns	16.7	ns		
84(kg/ha)	9.7	43.8	92.4		24.3
168	13.6	59.7	99.8		24.3
252	20.3	66.6	100.0		24.3
LSD(.05)	ns	13.0	ns		
1968 harvest year:					
Urea	11.0	21.3	34.8	61.3	18.4
NH_4NO_3	9.3	24.2	44.4	64.2	18.4
NH_3	17.4	39.9	52.6	100.0	18.4
LSD(.05)	ns	14.0	14.0	14.0	
84(kg/ha)	9.5	26.5	33.9	74.5	24.2
168	18.2	34.2	51.5	99.5	24.2
252	17.9	42.8	74.7	100.0	24.2
LSD(.05)	ns	ns	21.0	21.0	

Table 8. Relative yield responses incremented over years of N application

Carrier or rate of N	Relative yield increases associated with year of N application				Total relative increase
	1965	1966	1967	1968	
	percent				
1967 harvest year:					
Urea	8.3	34.8	54.6		97.7
NH_4NO_3	13.6	38.0	47.1		98.7
NH_3	22.7	55.1	22.2		100.0
84 (kg/ha)	9.7	34.1	48.6		92.4
168	13.6	46.1	40.1		99.8
252	20.3	46.3	33.4		100.0
1968 harvest year:					
Urea	11.0	10.3	13.5	26.5	61.3
NH_4NO_3	9.3	14.9	20.2	19.8	64.2
NH_3	17.4	22.5	12.7	47.4	100.0
84 (kg/ha)	9.5	17.0	7.4	40.6	74.5
168	18.2	16.0	17.3	48.0	99.5
252	17.9	24.9	31.9	25.3	100.0

to the total response varied greatly. In the case of NH_3, about 78 percent of the yield increase could be ascribed to residual N from 1965 and 1966 and only 22 percent to the N applied in 1967. With the other two carriers, approximately half of the response could be assigned to residual sources and half to the current year's application.

In 1968, the response to NH_3 was much greater than to urea or NH_4NO_3. The difference was due principally to more effective use of the current year's application of NH_3. Circumstances of weather in 1968 were responsible for this difference and will be described in the next section.

Increments of residual response in Table 8 increased with rate of N addition. At the 252 kg rate, residual accumulations accounted for about 67 percent of the total yield response in 1967 and about 75 percent in 1968. The 25 percent relative increase which could be ascribed to the 1968 application at this rate was equivalent to an actual increase of about 10 hl/ha (Fig. 4). The resulting ratio of 25 kg N per hl (19 lb N/bu) can hardly be considered economic.

In previously reported studies of residual nitrogen availability, no consideration has been given to the effect of repeated annual applications. Residual incrementation, as illustrated in Table 8 and Fig. 4, must be given increasing attention as more growers use more N year after year on the same acres.

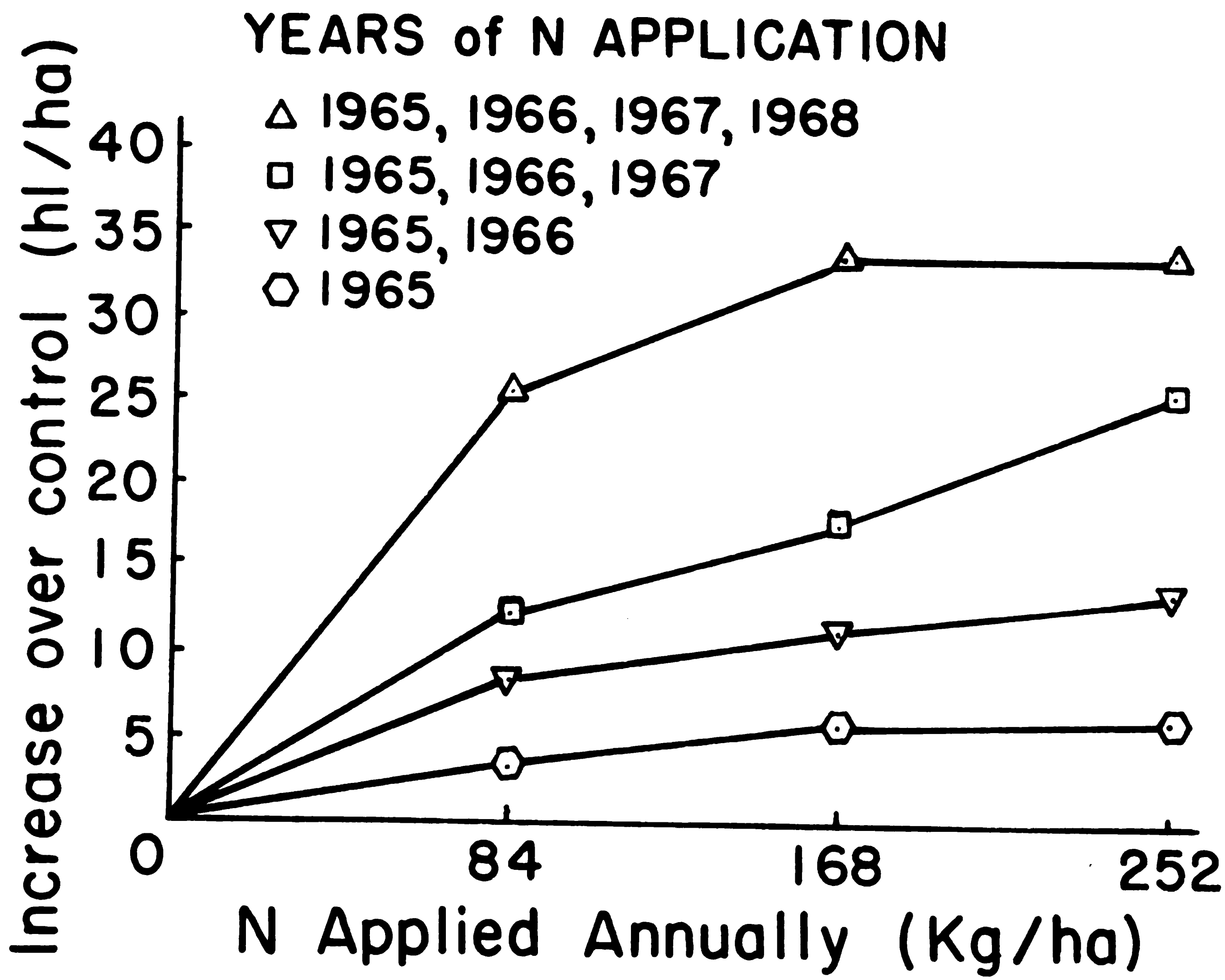

Figure 4. Residual and cumulative effects of nitrogen rates on 1968 yield increases over controls

Relative Efficiency of Carriers

Evidence has been presented in Tables 2, 6, 7, and 8 that residual benefits accumulated more rapidly with NH_3 than with the other two carriers. Also, the total response in 1968 to residual and current year's applications of NH_4NO_3 and urea was only about 60 percent of that for NH_3.

These differences, however, were expressed as main effects. They lead to erroneous generalizations unless circumstances of application and significant interactions between the carriers and rates and years of application are taken into account. These interactions are not readily apparent in tabular data.

A number of mathematical models were examined for their usefulness in describing these interactions in the 1968 yield response data. The function finally chosen made use of a quadratic on number of annual applications to supply a unique constant term for the quadratic on rate of N for each carrier within each application year. The model chosen for the response to N within carrier within year of application had the following form:

$$EY_i = a + bA_i + cA_i^2 + \sum_{j=1}^{A_i} (d_{ij}N_i + e_{ij}N_i^2)$$

where: EY_i = estimated yield increase for an individual carrier

A_i = number of repeated annual applications of the ith carrier

N_i = rate of application of the ith carrier

j = rate of application, coded as 1,2 and 3

The coefficient of multiple determination (R^2 = .658) indicates that only 66 percent of the total variation in yield response was accounted for. Nevertheless, the plotted function in Fig. 5 provides a realistic picture of significant interactions between carriers and rate on yield response to successive annual applications of fertilizer nitrogen.

The curves in Fig. 5 represent the response observed on separate series of plots which received 1, 2, 3 and 4 annual applications of N. The area between the curves is shaded to represent the incremental contribution from each successive annual application. The assumption is made that similar increments of available nitrogen would have contributed to the total response on plots which received all four annual applications.

The percentage points on the vertical axis are relative to the maximum yield increase with NH_3 taken as 100.

Three practically important differences among the three carriers are reflected in Fig. 5.

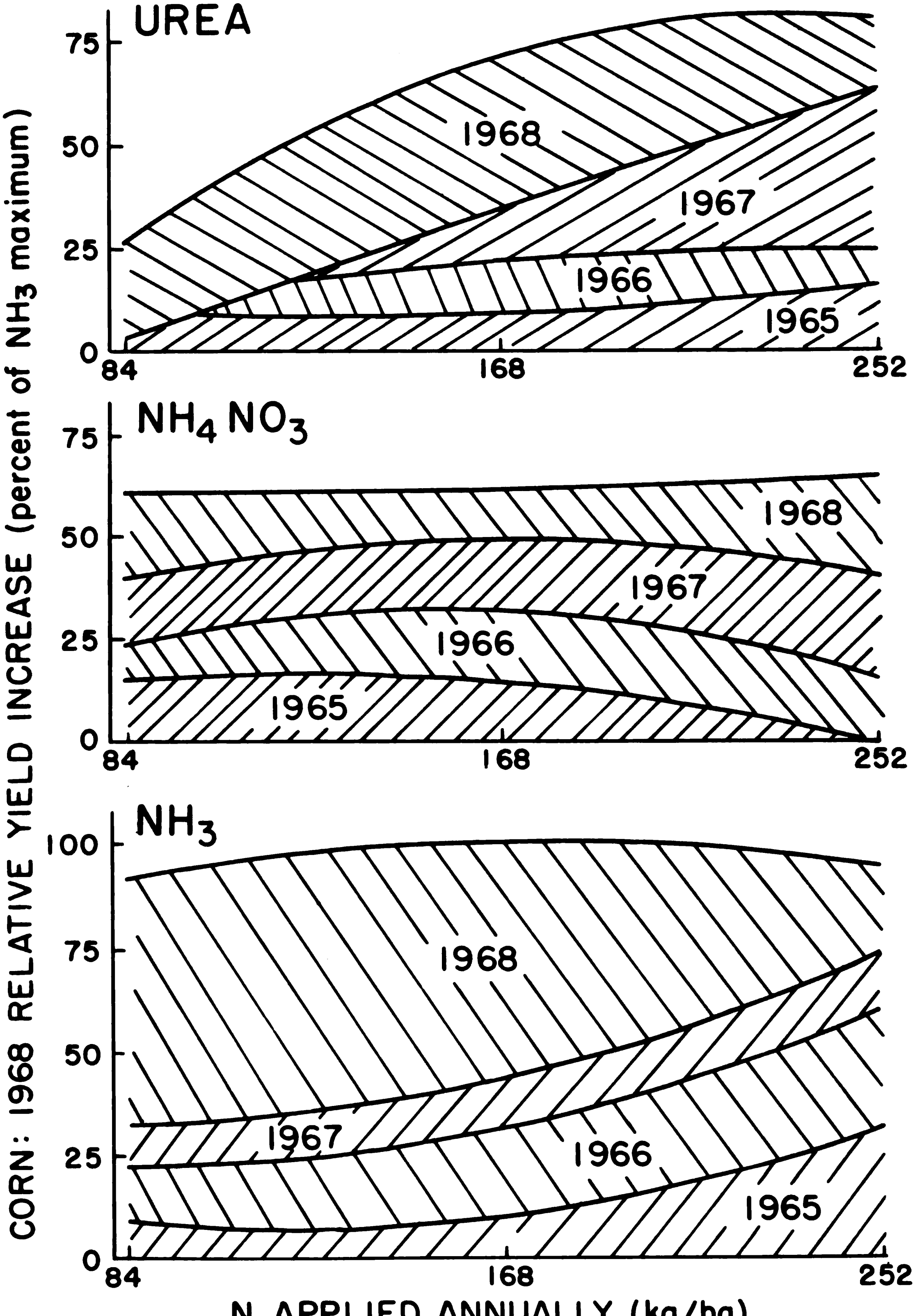

Figure 5. Incremented responses of corn in 1968 to residual and current inputs of nitrogen from three fertilizer sources

The most striking difference is in the response of corn to the 1968 application of the carriers. At the 84 and 168 kg level, NH_3 applied in 1968 was much more effective than urea or NH_4NO_3. Referring to Table 2, a similar differential response in favor of NH_3 had been expressed in 1965, but it did not appear in the case of current year's applications in 1966 or 1967.

The 1965 differences were not statistically significant, but they may have reflected a moisture advantage in a dry year for deep placement (injection) of NH_3 (cf. Table 3).

The uniquely greater effectiveness (observed in Table 8 and Fig. 5) of NH_3 applied in 1968 is readily explained by sequences of rainfall associated with the times of application of the three carriers in 1968 (cf. Table 1). The three carriers were applied between two periods of above average rainfall (Tables 1 and 3). The soil remained near field capacity during this period. It may be assumed that the 1.90 inches of rain from July 23-27 and the 1.34 inches of rain from August 5-8 resulted in considerable percolation.

The relative inefficiency of urea and NH_4NO_3 applied in 1968 can be ascribed to leaching of urea and/or volatilization of NH_3 released by its hydrolysis and to leaching and/or denitrification of the N applied as nitrate in the salt.

A second feature of difference in Fig. 5 is the evidence that, at the 84 kg level of N application, the residual benefit from urea applied in previous years was less than with the other two carriers. As noted in Table 1, both urea and NH_4NO_3 were sidedressed (broadcast by hand) and mixed in by shallow cultivation. This is a very inefficient placement for urea (Benson and Barnette, 1939, Pesek and Dumenil, 1956, Pesek, 1964).

In 1965, 1966, and 1967, sidedressings were followed by periods of 9 to 16 days before precipitation occurred which might have moved urea down to a safer depth or have promoted absorption of NH_3 released by hydrolysis. Single light rains five days after application in 1966 (.21 inches) and the day after application in 1967 (.25 inches) would have promoted hydrolysis but little movement. Hydrolysis of urea and volatilization of NH_3 would have been enhanced also by periods of high temperature after application (5 to 14 consecutive days with maximums of 80 to 95°F).

Volatilization losses due to inappropriate placement of urea were not reflected in yield responses to the current application of N in these earlier years (Table 2). Differences in residual response were, however, significant (Tables 7 and 8).

A third difference among carriers in Fig. 5 relates to residual behavior at the highest rate of N application. In the case of urea and NH_3, the residual contributions to 1968 yields increased with rate of N over the entire range of treatment. With NH_4NO_3, however, residual benefits reached a maximum and then declined at higher rates of application.

The declining residual benefit from NH_4NO_3 can be explained if residual effects on soil acidity are taken into consideration. At the 252 kg level of N addition, soil pH in August 1968 was 5.3, 5.5 and 5.7 for NH_4NO_3, urea and NH_3, respectively. These may be compared with pH 6.0 for control plots.

Effects on soil pH will be discussed in greater detail in connection with Tables 11 and 12. It is apparent, however, that unfavorably acid soil conditions had developed more quickly with NH_4NO_3 and that these would have tended to oppose beneficial residual effects at high rates of this carrier.

Forms of Residual N in Soil

It may be assumed that residual benefits to corn were due, mainly, to carryover of available nitrogen at depths in the soil within reach of the roots of succeeding crops of corn. Forms of nitrogen which might have been carried over include organic N in soil humus or in corn residues, nitrate in the soil solution and ammonium adsorbed on the exchange complex or fixed reversibly by collapsible clay minerals.

Kjeldahl N in the soil

Values for total N in Table 9 would have excluded nitrate but would have included both organic N and ammonium.

Table 9. Soil nitrogen in November 1967

Carrier	Rate of N	Treatment means				Carrier means			
		Years of N application			LSD(.05)	Years of N application			LSD(.05)
	kg/ha	1965	1965 1966	1965 1966 1967	Years within treatments	1965	1965 1966	1965 1966 1967	Years and yrs within carriers
Control	0	.087	.081	.090	ns				
Urea	84	.092	.098	.096	ns	.093	.088	.093	ns
	168	.102	.084	.090	ns				
	252	.086	.082	.082	ns				
NH_4NO_3	84	.094	.092	.085	ns	.094	.091	.085	ns
	168	.093	.090	.082	ns				
	252	.096	.090	.088	ns				
NH_3	84	.090	.102	.092	ns	.095	.095	.089	ns
	168	.100	.095	.090	ns				
	252	.096	.087	.084	ns				
LSD(.05)		ns	ns	ns		ns	ns	ns	
Means(years) for plots receiving N:						.094	.091	.089	ns

Analytical and sampling errors in the determination of total N and total C are high relative to variation which may have practical significance in the field. For example, a difference of .001 percent N in Table 9 is equivalent to 30 lb/acre to the 10-inch depth that was sampled. A difference of .01 percent C in Table 10 is equal to 300 lb/acre.

None of the variation in percent N or C was related to treatment or years of application with statistical significance. However, significant year-to-year variations in C:N ratio (Table 11) did reflect net removals of N and/or net addition of C by the large crops of corn which were harvested in 1966 (cf. Table 2).

A detailed examination of the relationships between C and N in these soils will help to evaluate the extent to which N may have been immobilized and carried over in soil organic matter from one year to the next. The relationships observed also illustrate a number of principles which have been established in the extensive literature on soil nitrogen (Allison, 1955; Bartholomew, 1965; Harmsen and Kolenbrander, 1965; Jansson, 1958).

The quantity of organic matter in the soil is largely determined by the balance between annual inputs of C in plant debris and annual losses of C by respiration. The C:N ratio is an important consideration since it influences the extent to which immobilization of mineral N or mineralization of organic N will occur. A critical

Table 10. Soil carbon in November 1967

Carrier	Rate of N	Treatment means				Carrier means			
		Years of N application			LSD(.05)	Years of N application			LSD(.05)
	kg/ha	1965	1965 1966	1965 1966 1967	Years within treatments	1965	1965 1966	1965 1966 1967	Years and yrs within carriers
Control	0	1.13	1.12	1.12	ns				
Urea	84	1.31	1.34	1.16	ns	1.24	1.23	1.19	ns
	168	1.24	1.26	1.30	ns				
	252	1.16	1.09	1.11	ns				
NH_4NO_3	84	1.19	1.34	1.20	ns	1.28	1.29	1.20	ns
	168	1.35	1.23	1.19	ns				
	252	1.29	1.29	1.21	ns				
NH_3	84	1.20	1.46	1.28	ns	1.25	1.34	1.21	ns
	168	1.31	1.36	1.25	ns				
	252	1.24	1.21	1.11	ns				
LSD(.05)		ns	ns	ns		ns	ns	ns	
Means(years) for plots receiving N:						1.26	1.29	1.20	ns

ratio for normal crop residues is C:N = 30 or 35 to 1, which corresponds to an N content of about 1.5 percent.

The linear regression of C on N for the 120 plots sampled in the fall of 1967 was highly significant ($r = .663$) and indicated that there was, on the average, a 600-lb/acre change in soil C for each 30-lb change in soil N.

The ratio of change was 20:1, which is wider than the C:N ratio of the soils themselves (Table 11). This ratio reflects changes in the more active fractions of soil organic matter —those portions most recently derived from decomposition of corn residues in which the C:N ratio was of the order of 45:1 or higher.

The change in proportion of C to N was not linear. A highly significant ($P = .007$) quadratic term was expressed in the polynomial of Fig. 6. The derivative of this function

$$dN/dC = -.089 + .110\ C$$

was used to calculate the ratios of C to N immobilized in the active soil organic fraction at each level of soil C.

As seen in Fig. 6, this immobilization ratio, at the lowest C and N contents, was about 30:1. This would have been the situation in control plots where no inputs of fertilizer N were made and where inputs of C were limited by reason of low yields and restricted production of corn residues (cf. Table 2).

Table 11. Soil C:N ratios in November 1967

Carrier	Rate of N	Treatment means				Carrier means			
		Years of N application			LSD(.05)	Years of N application			LSD(.05)
	kg/ha	1965	1965 1966	1965 1966 1967	Years within treatments	1965	1965 1966	1965 1966 1967	Years and yrs within carriers
Control	0	13.1	14.0	12.4	1.85				
Urea	84	14.3	13.9	12.0	1.85	13.4	14.2	13.0	1.06
	168	12.4	15.2	14.4	1.85				
	252	13.6	13.4	13.6	ns				
NH_4NO_3	84	12.6	14.6	14.1	1.85	13.6	14.3	14.1	ns
	168	14.6	13.8	14.5	ns				
	252	13.5	14.5	13.8	ns				
NH_3	84	13.4	14.6	13.8	ns	13.1	14.3	13.6	1.06
	168	13.0	14.4	13.9	ns				
	252	13.0	14.0	13.1	ns				
LSD(.05)		ns	ns	ns		ns	ns	ns	
Means(years) for plots receiving N:						13.4	14.3	13.6	0.67

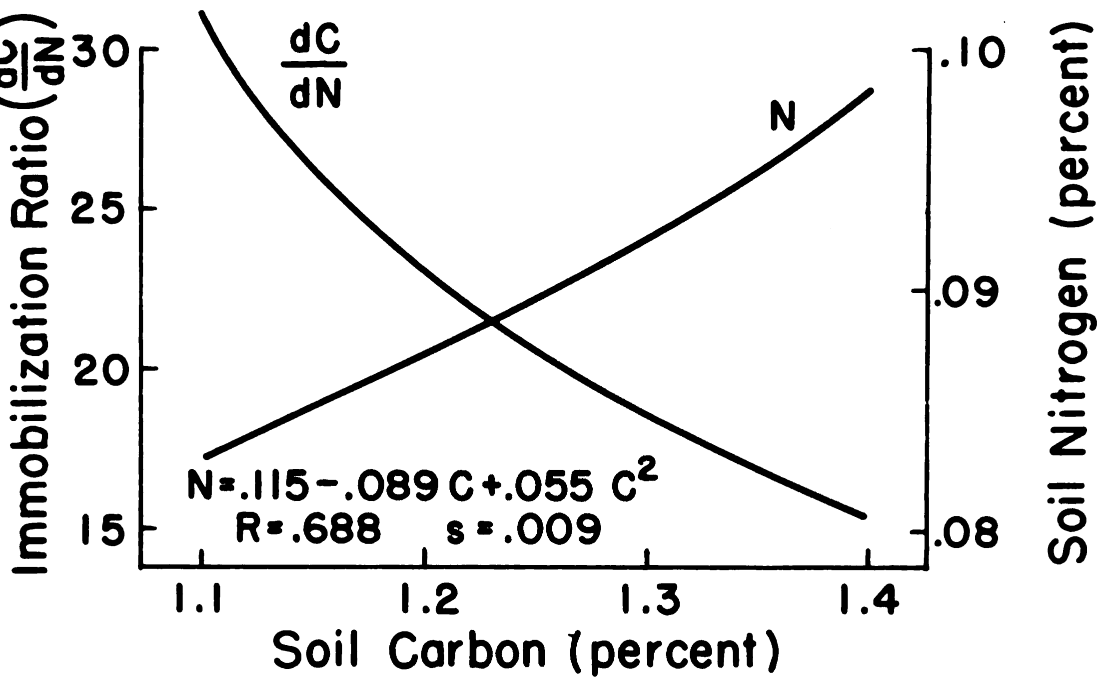

Figure 6. Immobilization ratios in relation to soil carbon and nitrogen contents

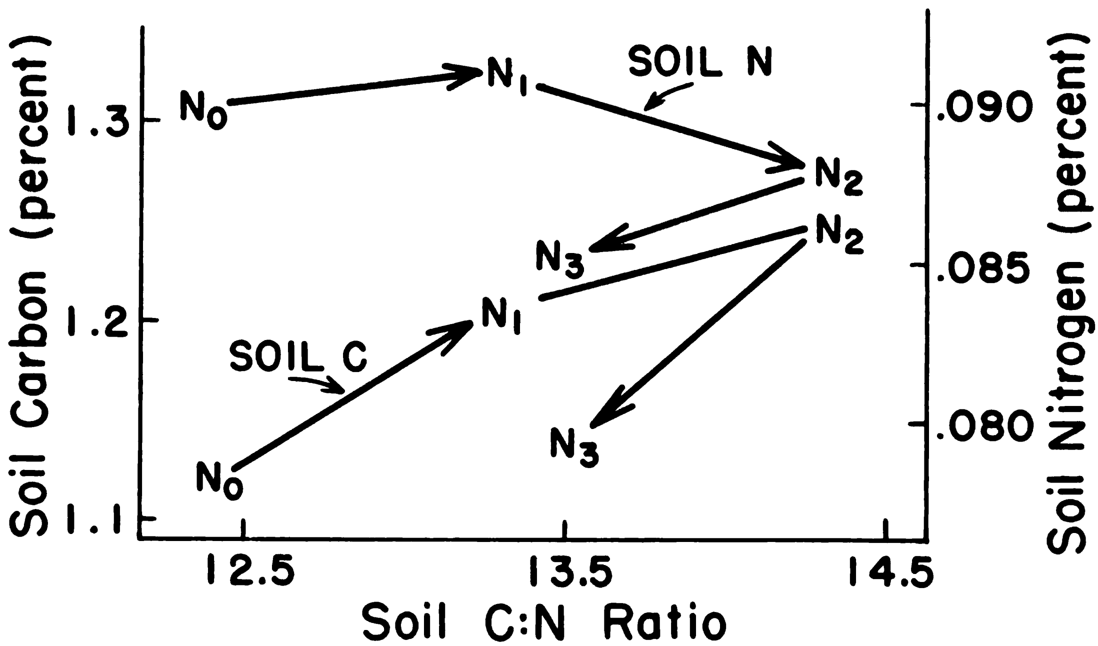

Figure 7. Soil carbon, nitrogen and C:N ratios in relation to increasing rates of fertilizer nitrogen after three annual applications (N_o = control; N_1, N_2, N_3 = 84, 168, 252 kgN/ha)

The immobilization ratio in Fig. 6 decreased with increasing C and N contents, approaching the C:N ratio of the soils themselves as a limit (cf. Table 11).

When inputs of fertilizer N exceeded the capacity of the crop to respond by producing an appropriate excess of residual C, the balance in favor of immobilization and increasing C and N contents was abruptly reversed (Fig. 7).

In relation to theory, the 30:1 ratio at low N and C contents in Fig. 6 is in the critical range where an increase in C would promote net immobilization of N, whereas an increase in N would permit net mineralization.

Over the range of Fig. 6, increasing C was accompanied by increasing retention of N. The increase in C, however, was due to increased growth of corn in response to fertilizer N which also increased the size of the microbial population and the annual rate of decomposition. This increase in respiratory loss of C was responsible for the narrowing immobilization ratio.

Maximum quantities of N were retained in humified soil organic matter when fertilizer N was used at the 84 kg rate (Fig. 7, Tables 9 and 12). Additional increases in C occurred at the 168 kg rate. The increased C produced by corn at this rate, however, was insufficient to maintain a balance in favor of immobilization and retention of N. At the 252 kg rate, residual levels of both N and C declined sharply.

Table 12. Soil carbon, nitrogen and C:N ratios in relation to annual rates of N application

Rate of N	Year of N application 1965	1965 1966	1965 1966 1967	Average for rate of N
kg/ha		Percent total N in soil		
0	.087	.081	.090	.086
84	.092	.097	.091	.095
168	.099	.090	.088	.092
252	.093	.087	.085	.088
LSD(.05)	ns	ns	ns	ns
		Percent total C in soil		
0	1.132	1.123	1.121	1.125
84	1.231	1.383	1.214	1.276
168	1.302	1.286	1.246	1.278
252	1.230	1.200	1.142	1.191
LSD(.05)	ns	ns	ns	ns
		Soil C:N ratio		
0	13.1	14.0	12.4	13.2
84	13.4	14.4	13.3	13.7
168	13.3	14.5	14.3	14.0
252	13.4	14.0	13.5	13.6
LSD(.05)	ns	ns	ns	ns

The sharp reversal towards narrowing C:N ratios in Fig. 7 is evidence that the annual balance between inputs of C and N at the 252 kg rate now favors net mineralization and depletion of humified soil organic matter.

This depletive balance of C and N may be inferred also from the relationship in Fig. 8 between kjeldahl N in soil samples taken November 1967 and corn yields in 1968 for the 120 plots which received no N in 1968. Only 14 percent of the total yield variation was accounted for, but the overall relationship was highly significant ($P < .0005$) and the coefficient for the squared term approached significance ($P = .06$). Maximum yields were associated with the lower levels of residual N in the plow soil.

It is clear that the higher rates of N which produced maximum yields of corn did not produce increases in residual organic or ammonium forms of N in the plow soil, as determined by the kjeldahl procedure. Rather, the reverse was true.

The question remains, where did the N come from to produce the residual responses observed at high rates of urea or NH_3 in Fig. 5 ?

Crop residues

The soil samples taken in the fall of 1967 did not include surface residues from the 1967 corn crop. These were avoided in sampling or were removed by screening.

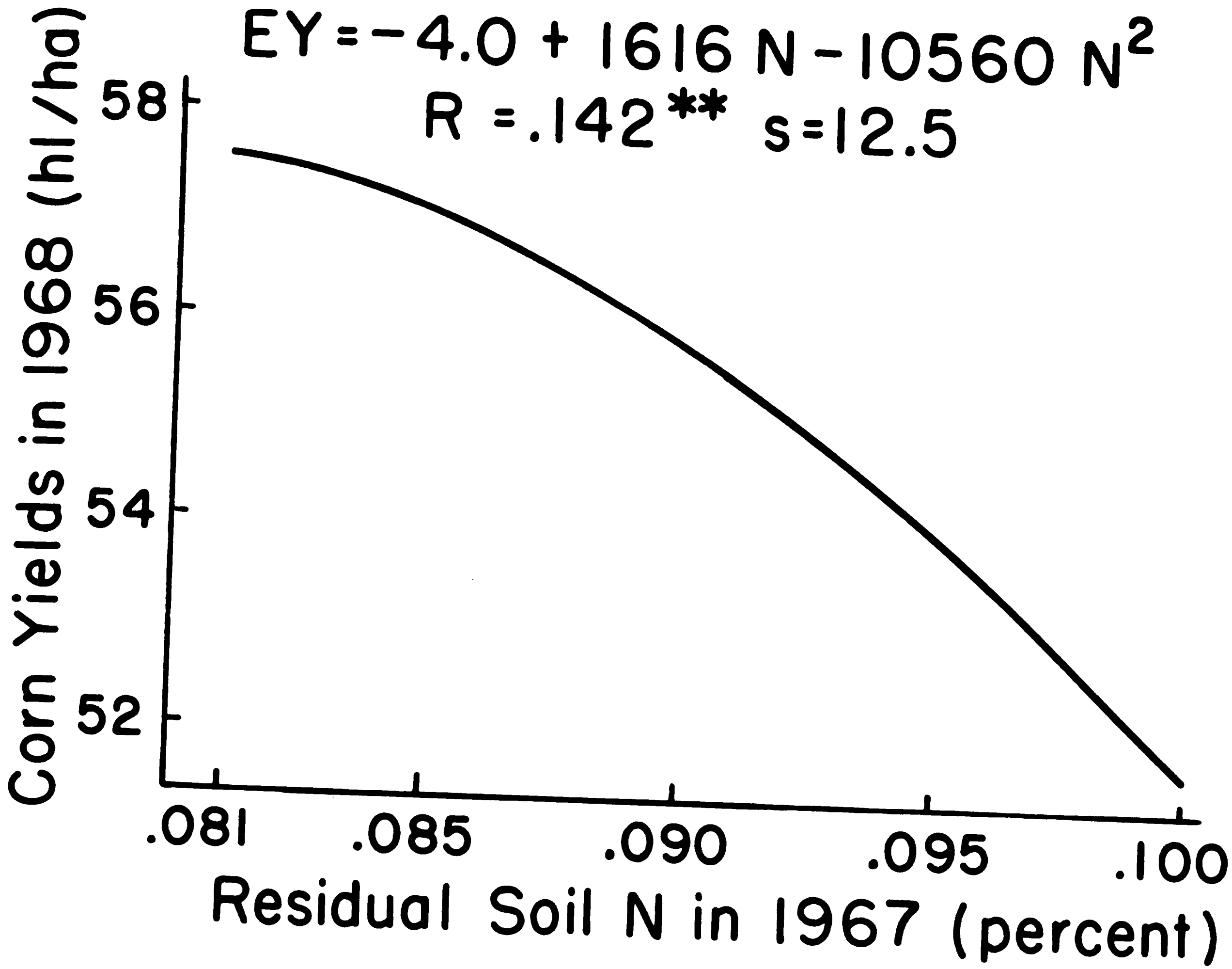

Figure 8. Corn yields on residual plots in 1968 in relation to soil nitrogen in November 1967.

No measurements of stover production or N content were made. A tentative estimate of N that might have been carried over in the stover can be calculated from the yields of grain.

Romaine (1965) notes that a 150-bushel corn crop grown under optimum fertility will contain 135 pounds of N in the grain and cobs and 65 pounds in the stover (about 1 percent N). On this basis, stover left on the control plots in 1967 would have contained about 20 pounds of N per acre (cf. Table 2). The carryover from plots which produced 90 hl/ha or more (80 bu/acre) would have been about double this, if no allowance is made for the fact that the stover on these plots probably would have contained a higher percentage of N. If it is assumed that N content of stover at the higher rates of N application was 1.5 percent (Cook, 1962), the carryover would have been about 60 pounds (67 kg/ha).

With their low N content, the stover from control plots would be expected to immobilize additional N during their decomposition whereas the high N residues would be expected to release some N to the 1968 crop. A release of 25 or 30 percent (15 to 20 pounds of N) would have produced the 12 to 13 bushels of corn which is represented in Table 8 as a 31.9 percent incremental increase attributable to carryover from the 1967 N application at the 252 kg rate.

These calculations are illustrative only. They do indicate that significant residual benefits from fertilizer N may be carried over in the form of increased quantities of stover of increased N content.

Mineral nitrogen

Data in Table 13 show that nitrate in the plow soil (0 to 10 inches) at the time of tassel appearance was uniformly low in all plots except those which received fertilizer N in 1968. Ammonium concentrations in these same samples were unusually high, but there were reasons to suspect that this was due to contamination from atmospheric sources during storage in paper bags.

According to Lucas' (1969) proposed "critical nitrate-nitrogen" level, all of the nitrate values in Table 13 are in the positive response range except that for the highest 1968 application of N. Comparison with Table 7 shows that, in fact, a significant increase in yield of corn was obtained with the 168 kg application in 1968 but no further response was obtained with 252 kg.

The fact that corn yields should be related to the capacity of the soil to maintain a moderately high level of nitrate in the plow soil is surprising in view of the quantities of nitrate and much larger quantities of ammonium which were present in the root zone (surface 24 inches) of these soils (Table 14).

Table 13. Nitrate nitrogen in soil sampled August, 1968

Carrier	Rate of N kg/ha	Years of N application 1965	1965 1966	1965 1966 1967	1965 1966 1967 1968	Averages Treatment	Carrier
		ppm					
Control	0	17.0	17.0	16.0	16.5	16.6	
Urea	84	17.3	15.3	18.8	33.5	21.2	22.9
	168	18.8	18.8	21.3	34.5	23.3	
	252	15.3	17.8	15.8	47.8	24.1	
NH_4NO_3	84	15.8	14.0	18.5	25.5	18.4	22.2
	168	16.3	23.3	15.0	39.3	23.4	
	252	18.8	18.8	19.5	41.8	24.7	
NH_3	84	15.3	20.0	17.3	30.8	20.8	22.1
	168	19.5	15.3	19.3	35.5	22.4	
	252	16.5	17.5	19.3	39.5	23.2	
LSD(.05)		ns	ns	ns	ns	ns	ns

Table 14. Distribution of ammonium and nitrate with depth on August 14, 1968

Soil depth cm (in.)	Ammonium-N		Nitrate-N	
	Control	252 kg/ha N as NH_4NO_3	Control	252 kg/ha N as NH_4NO_3
	---- Lb. N per acre-foot ----			
0 - 30.5 (0-12)	129	292	26	72
30.5 - 61 (12-24)	36	36	41	36
61 - 91.5 (24-36)	36	31	31	41
91.5 - 122 (36-48)	17	115	(*)	46
122 - 152.5 (48-60)	27	17	31	36
Total: 0 to 24 in.	165	328	67	108
Total: 24 to 60 in.	80	163	(62)	123
Total: 0 to 60 in.	245	491	(129)	231

(*) Missing data

Soil samples for Table 14 were stored in sealed glass containers to avoid contamination by atmospheric NH_3. The unusually high ammonium levels in the surface 12 inches must, therefore, be taken seriously. They can be explained in terms of effects of unusually wet soil conditions associated with several periods of rainfall concentration in 1968 (Table 3).

The surface soils of this experiment are underlain by a moderately impermeable sandy clay loam B horizon at about 16 to 25 inches (Appendix A). They were periodically saturated and remained near field capacity for periods up to two weeks after each of the rainfall concentrations in May, June, July and August. Higher than normal temperatures were associated with each of these periods.

Nitrification is retarded by restricted aeration under conditions of high moisture to a much greater extent than are heterotrophic processes of organic matter decomposition. A major effect of restricted aeration on decomposition is to reduce the extent to which N is immobilized in the presence of carbonaceous substrates (Bartholomew, 1965; Harmsen and Kolenbrander, 1965).

The residues from the 1967 corn crop would have decomposed under conditions favoring rapid decomposition with minimal immobilization and restricted nitrification of released ammonium. Conditions favoring denitrification would have occurred also from time to time.

The quantities of ammonium in the surface 12 inches (Table 14) greatly exceeded the amount added as NH_4NO_3 or the quantities that might have been carried over in stover from the 1967 corn crop. This indicates that soil humic N had been extensively ammonified. The normal immobilizing effect of corn residues during early stages of decomposition was not expressed with either treatment. Instead, its rapid decomposition may have supplied energy to support microbial attack on humified organic materials which are not normally utilized because of their low energy content. This is the phenomenon referred to in the literature as the "priming action" of fresh residues on decomposition of soil organic matter (Bingeman, et al., 1953; Winsor, 1958; Jansson, 1958).

Below the 12-inch depth, there was essentially no difference in quantities of either ammonium or nitrate in either profile, except for a marked accumulation of ammonium in the 36 to 48-inch layer under the NH_4NO_3 treatment. This indicates that considerable ammonium had leached to this depth. It was detained by sorption in the clay loam B horizon and protected against nitrification because this horizon remains saturated or near saturation for much longer periods of time than upper horizons after heavy rains or during seasons of low evapotranspiration.

Except for the surface 0-12 inches, the two profiles are analogous to two chromatographic columns with essentially similar capacities for retaining ammonium or nitrate. Since they were not loaded the same, it must be assumed that much more mineral nitrogen had moved to depths greater than five feet under the NH_4NO_3 treatment than in the control plot. Major movement would have been as nitrate, but ammonium has leached also as indicated by the build-up at 36 to 48 inches.

Total mineral N (NH_4^+ plus NO_3^-) in the control profile was 374 pounds per acre to a depth of five feet. The total for the NH_4NO_3 plot was 722 pounds.

A total of 900 pounds of N per acre had been applied as NH_4NO_3 over the 4-year period. A calculated 200 pounds had been removed in the 257 bushels of grain and cobs harvested over the previous three years. This plus the 722 pounds found in the profile would account for all of the fertilizer N that had been applied.

However, it must be assumed that additional mineral N was released from soil sources. This release from soil sources would have been at least as great as in the control plot since the analyses for kjeldahl N, which would have included ammonium, were similar (Table 9).

The estimate of soil release in the control plot must take into account the 130 pounds of N in 168 bushels of corn and cobs harvested over the first three years. This plus 374 pounds found in the control profile gives an estimate of 504 pounds of N which must have been mineralized from soil sources, since no fertilizer N had been applied.

If a similar release from soil sources had occurred in the NH_4NO_3 plot, then an equal quantity must have been lost by denitrification or by leaching to depths greater than five feet.

On first thought, a loss of 500 pounds of N per acre is staggering. On an annual basis, however, it is only 125 pounds per year. This is the difference between the 225 pound annual rate used on this plot and 100 pounds, which is the maximum recommendation to farmers for corn on soils of similar productivity without irrigation in Michigan (CES Bul. E-550, 1966). Thus, 125 pounds more N was applied each year than could be expected reasonably to enter into the crop or into biological systems involved in its decomposition.

The crop and biological systems associated with it in the surface horizons appear to be the only mechanisms for retaining N in the soil for any period of time. Data in Table 13 indicate that these systems are mainly operative in the surface 12 inches. Foth (1962) has shown that this is where 80 to 90 percent of the corn root system is to be found. It includes the plow soil (0 to 10 in.) where decomposition of surface residues takes place after plowing.

It may be concluded that the plow soil dominates the nutritional environment of the corn plant. In turn, the crop and the microflora of the plow soil, which are supported by the crop, dominate the N economy of the total profile. Some recycling of mineral N from the 12 to 24-inch depth can be expected to occur by capillarity and by root uptake, since eight to ten percent of the corn root system is to be found here. Recycling from the 24 to 36-inch layer will be minor since corn roots extend only randomly to this depth and mass capillary movements upward from this depth occur infrequently (Wetselaar, 1962).

Most of the mineral N below 24 inches has, therefore, moved beyond recovery. How much of the N above 24 inches may yet be recovered will depend upon crop and climatic factors affecting its uptake, conversion from one form to another and its vertical movement. If 50 percent of it were to carry over usefully to the 1969 season, as Pesek (1964) suggests, a 60-bushel corn crop could be predicted on the control plot. This is a reasonable expectation (cf. Table 2).

The predicted 1969 yield on the NH_4NO_3 plot would be 135 bu/acre. This exceeds the yield potential for this soil without irrigation. Residual yields of 95 to 105 bu/acre were obtained at this level of N addition in the favorable 1966 season.

Data in Table 14 indicate that mineral N in excess of crop response will be quickly lost beyond recovery. Only N which is retained in the upper 24 inches of the soil by recycling through the crop and its associated microflora can contribute significantly to residual carryover for the benefit of succeeding crops. Under the soil and climatic conditions of this experiment, beneficial effects of fertilizer N were carried over by these systems for three years. It appeared, however, that beneficial residual effects of the 1965 applications would not have been detected in a fourth season.

Other soil sources of N

The data and discussion in the previous section suggest that as much as 500 pounds of mineral N were released from soil sources. If this all came from organic matter in the plow soil, it would represent a decrease in organic N of .017 percent.

Changes this great were observed in plots which received N treatments, if allowance is made for up to .005 percent ammonium which have been included in the kjeldahl N determinations of Table 9.

Since these samples were all taken at the same time, there is no basis for inferring any trend over time in the control plots. The data in Table 14, however, show that extensive release of mineral N has occurred. The release must be at a substantially high rate in order to maintain nitrate concentrations in the soil solution equal to those under NH_4NO_3 through the entire profile below 12 inches.

Mineralization of soil organic matter probably has resulted in declines in soil organic nitrogen. The rate of depletion has been less rapid at lower N rates than the heavier N applications. This reflects more efficient recycling and immobilization due to lower N content of corn residues. The possibility exists, also, that non-symbiotic fixation of atmospheric N may be supported by these low N residues (Jensen, 1965).

Another possible source of N in these soils may have been ammonium previously fixed by clay minerals. Preliminary analysis of surface soil from a control and an NH_4NO_3 plot indicated the presence of vermiculite to the extent of five to 20 percent of the clay fraction. Since the clay fraction represents only 18 percent of the surface soil, fixed ammonium must be dismissed as a significant source of N.

Effects on Soil pH

Probable sources of soil pH variation were noted in connection with tables 4 and 5. Soil pH variation in relation to N treatments for the November 1967 and the August 1968 samplings is shown in table 15.

Increases up to 0.5 pH units occurred on most plots between the November 1967 sampling and the following August sampling. A decrease in soil pH during the summer months has been observed by several investigators (van der Paauw, 1962; Collins, Whiteside, and Cress, 1970). Although reasons for seasonal and year-to-year changes in soil pH are not well understood, there is agreement on some of the fundamental processes involved.

Table 15. Effects of nitrogen carrier and rate of application on soil pH

Carrier	Rate of N kg/ha	Years of N application: 1965	1965 1966	1965 1966 1967	1965 1966 1967 1968	Averages: Treatment	Carrier	Rate of N
November 1967								
Control	0	5.75	5.75	5.83		5.78		
Urea	84	5.75	5.68	5.73		5.79	5.62	5.68
	168	5.58	5.83	5.48		5.63		5.49
	252	5.45	5.53	5.33		5.44		5.46
NH_4NO_3	84	5.73	5.63	5.60		5.65	5.58	
	168	5.63	5.78	5.72		5.71		
	252	5.58	5.38	5.18		5.38		
NH_3	84	5.75	5.50	5.55		5.60	5.53	
	168	5.65	5.45	5.20		5.43		
	252	5.68	5.70	5.30		5.56		
LSD(.05)		ns	0.33	0.33		ns	ns	ns
August 1968								
Control	0	6.18	6.17	5.93	5.98	6.06		
Urea	84	5.90	5.88	5.98	5.78	5.88	5.78	5.88
	168	5.83	5.85	5.83	5.63	5.78		5.78
	252	5.73	5.75	5.75	5.48	5.68		5.73
NH_4NO_3	84	5.93	6.05	6.00	5.73	5.93	5.81	
	168	5.78	5.95	6.03	5.83	5.89		
	252	5.93	5.60	5.63	5.32	5.62		
NH_3	84	5.85	5.85	5.95	5.70	5.84	5.80	
	168	5.73	5.68	5.68	5.53	5.65		
	252	5.93	6.05	5.85	5.75	5.90		
LSD(.05)		ns	ns	ns	ns	ns	ns	ns

Initiating processes of soil acidification involve differential accumulation of anions in excess of basic cations in the soil. Plants tend to take up cations and anions in approximately equivalent quantities. However, nitrate and sulfate are reduced to amino and sulfhydryl forms when they are assimilated by the plant. Protons and anions are produced when they are released by decomposition and are oxidized again to nitrate and sulfate.

Because of the great reactivity of the H ion, the protons which appear initially with surplus anions in solution quickly react with the exchange complex or with soil minerals to release bases. A cation-anion balance in the soil solution, and a buffered pH, are achieved through this release of soil bases which accumulate as residual free salts in the absence of leaching.

The decrease in soil pH with time during the growing season is usually attributed, in part, to the effect of these free salts. Thus in the absence of leaching, soluble salts tend to accumulate through the growing season. This increasing salt concentration shifts cation exchange equilibria in the direction of increasing H ion activity (the "salt effect"). For this reason, soil pH determined in water tends to reach a minimum in temperate climatic zones in the fall of the year. It tends to return to a higher level, characteristic for the soil, in the spring or early summer as surplus salts are removed by leaching.

The leaching of residual free salts is the essential process whereby soils are depleted of bases and made residually more acid. The development of residual acidity is expressed by an increase in buffer acidity (lime requirement) and/or by the failure of soil pH each year to return to the previous year's pH.

That seasonal soil pH variation is controlled by mechanisms other than the "salt effect" has been shown by Collins et al. (1970). Just what these other mechanisms are is not clearly understood.

The normal acidification process is greatly affected by nitrogen fertilization. The three N carriers used in this experiment are considered to have essentially similar residual acidifying effects, on soil pH (Wolcott, 1964). However, the initial reactions of these carriers are not the same. Urea and NH_3 have an initial basic effect whereas the NH_4NO_3 has an initial acidic effect. The reactions by which these initial effects take place may be written as equations (1) to (3). The initial increase in soil pH with urea and NH_3 is due to the formation of the ammonium ion upon hydrolysis:

$$NH_3 \overset{HOH}{\rightleftharpoons} NH_4NO_3 \rightleftharpoons NH_4^+ + OH^- \quad (1)$$

$$(NH_2)_2CO \longrightarrow (NH_4)_2CO_3 \overset{HOH}{\rightleftharpoons} NH_4HCO_3 + NH_4^+ + OH^- \quad (2)$$

NH_4NO_3, the salt of a weak base and a strong acid upon hydrolysis results in an immediate decrease in pH:

$$NH_4NO_3 \overset{HOH}{\rightleftharpoons} NH_4OH + H^+ + NO_3^- \quad (3)$$

The initial akalizing effect of urea and NH_3 is reversed as the basic cation, NH_4^+, is oxidized by nitrifying bacteria to nitrate, disengaging two protons in the process. Under most humid soil conditions, nitrite is oxidized to nitrate by Nitrobacter faster than ammonium is converted to nitrite by Nitrosomonas, thus the complete reaction may be written as:

$$NH_4^+ \xrightarrow{2O_2} 2H^+ + NO_3^- + HOH \qquad (4)$$

Adams and Pearson (1967) point out that the ultimate acidity that develops from fertilizer in a particular horizon is realized only after the residual salts are removed from that horizon by leaching. The comparison of the August 1968 pH values in the current year's N addition plots (Table 15) with the residual N treatment plots supports this statement.

The most pronounced effect in terms of soil pH variation occurred in the current year's N addition for both the 1967 and 1968 samplings. The residual acidifying effects of the N carriers may be seen in the plots receiving N treatments in other than the year of sampling.

In addition to the N carrier, the rate of N application is also an important factor in the potential acidification of the soil. Increasing acidification with rate of application is expected within each carrier as the rate of application exceeds the ability of the crop to respond in additional growth, and with the increasing production of H ions from reactions (3) and (4).

Within the current year's N addition in 1967 and 1968, pH was sharply depressed by high rates of urea and NH_4NO_3. This was true for NH_3 in 1967, but not in 1968. Due to the weakly to moderately developed fragipan in the B-horizon of this soil, water movement through the profile is restricted. The upper profile was saturated during abnormal rainfall concentrations in May and June of 1968 (Table 3). The soil remained unseasonably wet and was periodically saturated above the B-horizon during the more normal rainfall concentrations in July and August. Thus, for two-thirds of the growing season the soil was much wetter than normal, hence less well aerated. As a result, the higher pH values for NH_3 in August 1968 are likely due to the inhibition of nitrification of injected NH_3 to a greater extent than in the case of surface applied urea or ammonium in NH_4NO_3. It should be noted from equation (4) that N from urea or NH_3 must be 50 percent nitrified to neutralize alkalinity released when they are hydrolyzed, equations (1) and (2).

In the non-current year's N addition plots, the greatest acidifying effects were associated with the highest rates of application. This buildup in residual acidity was highest with NH_4NO_3 and the lowest with NH_3. Annual increments of acidity which exceed the capacity of more readily decomposed soil minerals to release bases will accumulate in the soil in the form of aluminohexahydronium and protonated hydroxy aluminum and iron (Coleman and

Thomas, 1967). This in effect increases the potential acidity (lime requirement) of the soil. The rate of annual accumulation of potential acidity is greatly accelerated at pH levels below 5.5 and becomes a principle buffering mechanism below pH 5.0 (Wolcott, et al., 1965).

It is apparent in Table 15, that plots receiving the higher rates of N in the form of any of these carriers are experiencing pH's of 5.5 or less for at least portions of the year. Accelerated increases in lime requirement can be expected, even if pH is seasonally restored to higher levels by leaching of surplus salts arising from nitrification and mobilization of soil bases (Wolcott, et al., 1965; Coleman and Thomas, 1967; Schafer, 1968).

Soil pH's associated with current year's treatments in Table 15 are in a range where toxicities of Mn or other nutritional derangements can be expected to begin showing up. Such effects on corn nutrition may have contributed to the lower yield responses to NH_4NO_3 than to the other two carriers.

Effects on Soil Calcium and Magnesium Levels

According to the F statistics in Table 4, the only factor associated significantly with Ca and Mg levels was soil variation (replications). A carrier x rate interaction approaching significance (P = .087) was expressed for Mg. Some of the variations associated with treatments in Table 16 are of interest.

Table 16. Extractable Ca and Mg in soil sampled November, 1967

Carrier	Rate of N kg/ha	Years of N application 1965	1965 1966	1965 1966 1967	Treatment means
		------------	------------ pp2m	------------	------------
Calcium					
Control	0	920	1240	800	980
Urea	84	1120	1040	1120	1090
	168	1280	1320	1280	1290
	252	1000	1000	1000	1000
NH_4NO_3	84	1360	1240	1200	1270
	168	1360	1280	1240	1290
	252	800	800	760	790
NH_3	84	1120	920	1160	1070
	168	1080	1000	960	1010
	252	1200	1240	1040	1160
LSD(.05)		ns	ns	ns	ns
Magnesium					
Control	0	89	106	83	93
Urea	84	105	96	106	102
	168	96	116	89	100
	252	73	83	71	75
NH_4NO_3	84	115	99	93	102
	168	121	141	109	124
	252	86	74	64	72
NH_3	84	102	86	86	91
	168	86	74	74	78
	252	121	119	80	107
LSD(.05)		ns	ns	ns	ns

Irreversible declines in soil pH are due to base depletion. Acidity produced by a process such as nitrification results, not only in displacement of exchangeable bases, but in release of bases by mineral decomposition. In the absence of leaching, displaced and released bases accumulate in the soil solution as free salts of surplus anions. Ammonium acetate extraction as used in this study makes no distinction between exchangeable bases and their free salts.

It is not surprising, therefore, that extractable Ca and Mg as determined here were frequently higher in soils receiving N fertilizers than in the controls. This increased level of extractable Ca and Mg also affected the lime requirement (Table 17), resulting in a less pronounced increase in potential acidity for many of the treatments than might have been expected.

The accumulation of surplus free salts and their subsequent removal by leaching is closely related to the production of surplus nitrate and its removal from the soil profile by leaching. It was estimated earlier (p. 68) for the 252 kg/ha rate of NH_4NO_3 addition that as much as 125 pounds of N per acre could not be accounted for. If it is assumed that this was entirely lost by leaching of nitrate, the equivalent associated annual leaching loss of Ca would have been 180 pounds, or 98 pounds of Mg.

The low values for Ca and Mg in Table 16 at the 252 kg/ha rate of NH_4NO_3 suggest that their annual rate

Table 17. Effects of nitrogen carrier and rate of application on the November 1967 lime requirement

Carrier	Rate of N kg/ha	Years of N application 1965	1965 1966	1965 1966 1967	Averages Treatment	Carrier	Rate of N
Control	0	2.50	2.00	2.00	2.16		
Urea	84	2.75	2.38	2.50	2.54	2.45	2.36
	168	2.13	2.38	2.00	2.16		2.46
	252	2.25	2.38	3.13	2.59		2.50
NH_4NO_3	84	2.00	2.25	1.63	1.96	2.30	
	168	3.00	2.63	2.00	2.54		
	252	2.63	3.88	2.63	3.04		
NH_3	84	2.13	2.75	2.88	2.58		
	168	2.50	3.50	3.50	3.17		
	252	2.50	2.38	1.75	2.21		
LSD(.05)		0.37	0.37	0.37	0.19	ns	ns

of loss with this treatment exceeded the rate at which these bases are released by mineral decomposition.

The sum of exchangeable plus soluble bases extracted with ammonium acetate represents a balance between removal by crops or leaching and release by mineral decomposition. The data in Table 16, therefore, do not reflect base depletion as reliably as the evidence for irreversible pH changes in residual plots discussed in connection with Table 15, or the evidence for displacement of bases by exchangeable Al in Table 17.

Effects on Soil Phosphorous and Potassium Levels

The effects of N treatment on extractable K and P are shown in Tables 18 and 19. The primary factor related to changes in soil K and P was soil variation (replication) according to the probabilities shown in Tables 4 and 5. However, there was a high probability for a significant year by rate interaction for P in 1968 (Table 5).

Due to the close relationship between soil pH and the solubility of various Al, Fe, and Ca phosphate compounds it would be expected that extractable P would be directly related to soil pH. A comparison of Tables 15 and 19 shows this not to be the case. This lack of correlation is likely due to the complications introduced by soil variation and to the time lag for phosphate solubilities to come to equilibrium with changing soil pH.

Table 18. Extractable K in soil sampled November, 1967 and August, 1968

Carrier	Rate of N (kg/ha)	Years of N application: 1965	1965 1966	1965 1966 1967	1965 1966 1967 1968	Averages: Treatment	Averages: Carrier
November 1967		ppm					
Control	0	126	102	119		117	
Urea	84	127	130	106		117	112
	168	124	104	97		106	
	252	118	122	109		115	
NH_4NO_3	84	126	114	113		117	117
	168	129	108	103		111	
	252	134	124	118		123	
NH_3	84	122	136	115		123	114
	168	118	114	105		111	
	252	126	104	103		109	
LSD(.05)		ns	ns	ns		ns	ns
August 1968							
Control	0	136	119	109	113	119	
Urea	84	127	130	121	126	126	119
	168	127	111	113	121	118	
	252	128	102	113	111	114	
NH_4NO_3	84	132	111	108	113	116	115
	168	134	109	104	102	112	
	252	132	128	104	106	117	
NH_3	84	117	123	115	121	119	115
	168	123	113	96	100	108	
	252	126	148	95	106	118	
LSD(.05)		ns	ns	ns	ns	ns	ns

Table 19. Extractable P (Bray P_1) in soil sampled November, 1967 and August, 1968

Carrier	Rate of N kg/ha	Years of N application 1965	1965 1966	1965 1966 1967	1965 1966 1967 1968	Averages Treatment	Carrier
November 1967		------	------	------	pp2m	------	------
Control	0	93	86	95		92	
Urea	84	92	90	92		91	89
	168	90	78	85		84	
	252	97	94	90		90	
NH_4NO_3	84	71	78	79		77	79
	168	82	72	70		74	
	252	91	95	81		87	
NH_3	84	94	90	85		88	89
	168	93	96	101		98	
	252	83	81	79		80	
LSD(.05)		ns	ns	ns		ns	ns
August 1968							
Control	0	67	74	67	78	71	
Urea	84	81	86	83	89	85	85
	168	90	84	83	103	90	
	252	91	75	83	70	80	
NH_4NO_3	84	70	66	66	76	69	72
	168	75	61	60	63	65	
	252	91	88	79	72	82	
NH_3	84	83	91	76	84	83	81
	168	87	90	95	89	90	
	252	79	73	70	56	69	
LSD(.05)		ns	ns	ns	ns	ns	ns

There is no evidence for depletion of K in Table 18. The leaching equivalent of 125 pounds N per year would be 350 pounds K per acre. It must be assumed that K as well as Mg and Ca accompanied nitrate into drainage. Fertilizer inputs of 60 pounds per year plus release of K by decomposition of soil minerals apparently offset leaching and crop removal of exchangeable plus soluble K.

SUMMARY AND CONCLUSIONS

Information from earlier experimenters indicate that in most years one can expect approximately 50 percent residual benefit in the crop year following N additions and no significant residual benefit thereafter. These reported experiments have had one serious limitation, though, in view of the common practice of monoculture. That limitation is the lack of more than one year of N application.

The field experiment used here was designed to determine the effects of three N carriers at three rates of application, with systematically incremented and systematically deleted annual N additions over a four-year period. Variation in yields of corn and soil tests were noted in response to these treatments.

Residual benefits to corn were observed in these experiments in each of the three years following just one annual application of N. These benefits were highly significant with the two higher rates of application of NH_3. With repeated annual N additions, residual yield benefits were cumulative. A portion of total residual response could be identified with each year of application up to the fourth year.

Cumulative carryover benefits increased with the carriers in the order urea $< NH_4NO_3 < NH_3$. In the 1967 harvest year about 78 percent of the yield could be ascribed to residual benefits from NH_3 and about 50 percent from the other two carriers.

In 1968, with four annual N applications, the response to NH_3 was nearly 40 percent greater than for the other two carriers. This advantage for NH_3 was ascribed to deeper N placement and to less loss due to volatilization, denitrification and/or leaching. It would be inappropriate to conclude from this experiment alone that NH_3 will give the greatest efficiency in N uptake and the least N loss. Rather, when evaluating N carriers, the circumstances of weather and application methods must be given consideration.

Increments of residual response increased with the rate of N addition. In the year of the fourth successive N application, about 50 percent of the yield response to N at 84 kg/ha could be ascribed to carryover from the three previous annual applications. About 75 percent of the yield response in the fourth successive year of N application could be ascribed to carryover from the three previous annual applications at the 252 kg/ha rate.

Cumulative residual effects on corn yields were due to incremented increases in ear number (fertile stalks) and ear weight. However, as the productivety capacity of the soil was approached, or as limitation of crop yields was effected by declining soil pH, then the yields leveled off or declined.

Incrementation of residual response to N is an important consideration for N fertilization and management whenever N is applied two or more years in succession.

Although variation in total N and C in the soil could not be correlated significantly with treatment, the interrelationships between soil N and C were highly significant.

The C:N ratios of the soils ranged from 12.0 to 14.6. The relationship between treatment and C:N ratios was not readily apparent. However, a linear regression of C on N indicated that C varied with N in a ratio of about 20:1. This ratio of change represents effects of treatment upon the active fraction of soil organic matter. A highly significant quadratic term showed that the change in soil N with change in soil C was not linear.

The derivative of this quadratic function was used to calculate the ratios of C to N immobilized in the active soil organic fraction at each level of soil C content.

The highest immobilization ratio of about 30:1 occurred when no N was applied during the four years of the experiment, resulting in limited production of corn residues. Thus with low N fertilizer application and low C fixation by corn, the C:N ratio of the active organic fraction was at its highest. As the rate of applied N increased, the total C and N increased and their ratio increased until the limit of the soil's productive capacity was approached.

Maximum N was retained in the soil at the 84 kg/ha rate of application. Total N decreased at higher rates of application. Maximum C was retained at the 168 kg/ha rate.

At the 252 kg/ha rate, total C decreased abruptly and was accompanied by an abrupt change from widening to narrowing C:N ratio. Clearly, and in accordance with theory, net retention of N was associated with widening C:N ratio, and net mineralization of soil N was associated with narrowing C:N ratio.

Calculations were made which illustrate that significant residual benefits from fertilizer N would be carried over in the form of increased amounts of plant residues of increased N content. This could have amounted to an additional 40 pounds of residual N for the 252 kg/ha rate over the control.

Nitrate-N in the plow soil at the time of tasseling in 1968 was uniformly low in all plots except those which received fertilizer N in 1968. Corn yields were related to these nitrate-N levels.

Ammonium N in the plow soil at this time was high, reflecting the abnormally wet season and retarded nitrification of ammonium N applied in fertilizer or released by mineralization from organic sources.

Relatively large quantities of mineral N were observed from 12 to 60 inches in two profiles: a control and a plot which received 1008 kg/ha N as NH_4NO_3 over the four-year period. Sufficient leaching had taken place so that there was a marked buildup of nitrate and ammonium at the three to four foot depth.

It was estimated that 125 pounds per acre per year were lost by denitrification and/or leaching to depths

greater than five feet on the 252 kg/ha NH_4NO_3 plots. This is equal to the amount of N applied in excess of that currently being recommended on this soil by the Crop and Soil Sciences Department at Michigan State University.

Mineral N in excess of crop response will thus be quickly lost beyond recovery. The economic loss of surplus fertilizer N is of negligible concern relative to the depletion of soil bases and the eutrophication of surface waters which accompanies nitrate movement.

Soil N retained in the upper 24 inches of the soil by recycling through crop residues and associated microflora can contribute significantly to residual carryover for the benefit of succeeding crops. Under the soil and climatic conditions of this experiment, beneficial effects of fertilizer N were carried over by these systems for three years. Carryover of beneficial effects into the fourth year appeared unlikely.

Soil pH was determined in November and August of the third and fourth treatment years respectively. An increase in soil pH, up to 0.5 pH units, was observed from November to the following August in plots receiving N during the sampling year. This "seasonal" pH variation was attributed in part to the leaching of salts through the fall, winter, spring and early summer, thereby reducing the "salt effect" on the pH determination itself. The August determination, therefore, reflected more realistically the characteristic growing season acidity ascribable to N carriers when they are applied annually on this soil.

Inhibited nitrification in the fourth year was, apparently, the cause of a significantly higher pH for the current year's injection of anhydrous NH_3 as compared with surface applied urea and NH_4NO_3. In November of the previous year, acidity and free salts from nitrification produced comparably low soil pH values with all three carriers.

Net residual acidity from N carriers was best estimated in residual plots which did not recieve N in the current year. Residual acidifying effects for the three carriers were in the order $NH_3 <$ urea $< NH_4NO_3$.

The greatest acidifying effects were associated with the highest rates of N application. This buildup in residual acidity resulted in soil pH values of 5.5 or less for all three N carriers for at least portions of the year. The net effect of these low pH's is to accelerate depletion of bases and increases in lime requirement and to greatly increase the probabilities of toxicities of Mn and Al.

The change in the base status was not readily apparent from the tests for Ca, Mg and K extractable with $\underline{N}$ NH_4OAc. Ca and Mg levels remained at or above the controls for all treatments excepting for the plots with the lowest pH (the NH_4NO_3 plots receiving 252 kg/ha). Potassium levels did not vary significantly from those for the controls. These results were likely due to a continued release of bases from primary and secondary minerals through action of hydrogen ions released by nitrification. Released bases would have accumulated partly on the exchange complex and partly as free salts, mainly nitrates. Ammonium acetate extraction as used here did not distinguish between exchangeable bases and bases present as free salts. Thus the soil tests for Ca, Mg and K did not give an indication of the extent to which bases were removed from the soil. Irreversible declines in soil pH and increases in lime requirement do reflect the fact that basic cations are being replaced by acidic Al on the exchange complex and that base supplying minerals are being depleted.

There were no discernible effects of N treatment on extractable P. There was a high probability for a significant year by rate interaction for P in 1968. However, interpretable relationships were not apparent in the data. This may have been due to the complications introduced by soil variation and to the time lag for phosphate solubilities to come to equilibrium with the decreasing soil pH.

BIBLIOGRAPHY

Adams, F., and Pearson, R. W. 1967. Crop response to lime in the southern United States and Puerto Rico. In R. W. Pearson and F. Adams, (ed.) Soil Acidity and liming. Agronomy 12:161-206.

Allison, F. E. 1955. Does nitrogen applied to crop residues produce more humus? Soil Sci. Soc. Amer. Proc. 19:210-211.

Allison, F. E. 1963. Losses of gaseous nitrogen from soils by chemical mechanisms involving nitrous acid and nitrites. Soil Sci. 96:404-409.

Allison, F. E. 1965. Evaluation of incoming and outgoing processes that affect soil nitrogen. In W. Bartholomew and F. Clark, (ed.)Soil Nitrogen. Agronomy 10:573-606.

Alexander, M. 1965. Nitrification. In W. Bartholomew and F. Clark (ed.) Soil Nitrogen. Agronomy 10:309-346.

Benson, N., and Barnette, R. M. 1939. Leaching studies with various sources of nitrogen. Agron. J. 31:44-54.

Bingeman, C. W., Varner, J. E., and Martin, W. P. 1953. The effect of the addition of organic materials on the decomposition of an organic soil. Soil Sci. Soc. Amer. Proc. 17:34-48.

Black, C. A. 1968. Soil-Plant Relationships. 2nd. Ed., John Wiley & Sons, Inc. New York.

Boawn, L. C., Nelson, J. L., and Crawford, C. L. 1963. Residual nitrogen from ammonium sulfate fertilizer and from alfalfa plowed under. Agron. J. 55:231-235.

Bremner, J. M. 1965. Total nitrogen. In C. A. Black (ed.) Methods of soil Analysis. II. Chemical and Microbiological Properties. Agronomy 9:1149-1178.

Bremner, J. M. 1957. Studies on soil humic acids; observations on the estimation of free amino groups; reactions of humic acid and lignin preparations with nitrous acid. J. Agr. Sci. 48:352-360.

Broadbent, F. E. 1965. Effect of fertilizer nitrogen on the release of soil nitrogen. Soil Sci. Soc. Amer. Proc. 29:692-696.

Broadbent, F. E., and Norman, A. G. 1947. Some factors affecting the availability of the organic nitrogen in soil - a preliminary report. Soil Sci. Soc. Amer. Proc. 11:264-267.

Broadbent, F. E., and Nakashima, T. 1965. Plant recovery of immobilized nitrogen in greenhouse experiments. Soil Sci. Soc. Amer. Proc. 29:55-60.

Broadbent, F. E., and Nakashima, T. 1968. Plant uptake and residual value of six tagged nitrogen fertilizers. Soil Sci. Soc. Amer. Proc. 32:388-392.

Burns, R. S. 1969. Influence of soil moisture tension on nitrate accumulation in soils. Soil Sci. Soc. Amer. Proc. 33:263-266.

Burns, R. S., Bartholomew, W. V., Shaw, R., and Pesek, J. 1956. Influence of temperature on nitrification in soils. Soil Sci. Soc. Amer. Proc. 20:357-360.

Clark, R. E. 1964. Direct and residual effects of two mixtures of nitrogen and phosphorous upon the growth of acala cotton in the Pecos Valley. Agron. J. 56:18-20.

Clark, F. E., and Beard, W. E. 1960. Influence of organic matter on volatile loss of nitrogen from soil. Trans. Intern. Congr., Soil Sci. 7th Congr., Madison II:501-508.

Cochran, W. G. and Cox, G. M. 1957. Experimental Designs, 2nd ed., John Wiley & Sons, Inc., New York.

Coleman, N. T., and Thomas, G. W. 1967. The basic chemistry of soil acidity. In R. W. Pearson and F. Adams, (ed.) Soil Acidity and Liming. Agronomy 12:1-34.

Collins, J. B., Whiteside, E. P., and Cress, C. E. 1970. Seasonal variability of pH and lime requirement in several southern Michigan soils when measured in different ways. Soil Sci. Soc. Amer. Proc. 34:56-61.

Cook, R. L. 1962. Soil Management for Conservation and Production. John Wiley & Sons, Inc., New York.

Duncan, D. B. 1955. Multiple range and multiple F tests. Biometrics 11:1-42.

Fitts, J. W., Bartholomew, W. V., and Heidel, H. 1955. Predicting nitrogen fertilizer needs of Iowa soils: I. Evaluation and control factors in nitrate production and analysis. Soil Sci. Soc. Amer. Proc. 19:69-73.

Foth, H. D. 1962. Root and top growth of corn Agron J. 54:49-52.

Gardner, W. R. 1965. Movement of nitrogen in soil. In W. Bartholomew and F. Clark (ed.) Soil Nitrogen. Agronomy 10:550-572.

Gerretsen, F. C., and DeHoop, H. 1957. Nitrogen losses during nitrification in solutions and in acid sandy soils. Can. J. Microbiol. 3:359-380.

Grewling, T., and Peech, M. 1965. Chemical soil tests. Cornell Univ. Agric. Exp. Sta. Bul. 960.

Harmsen, G. W., and Kolenbrander, G. J. 1965. Soil inorganic nitrogen. In W. Bartholomew and F. Clark, (ed.) Soil Nitrogen. Agronomy 10:43-92.

Jansson, S. L. 1958. Tracer studies on nitrogen transformations in soil with special attention to mineralization-immobilization relationships. Kungl. Lantbrukshögskolans Ann. 24:101-361.

Jansson, S. L. 1963. Balance sheet and residual effects of fertilizer nitrogen in a six-year study with N-15. Soil Sci. 95:31-37.

Legg, J. O., and Allison, F. E. 1967. A tracer study of nitrogen balance and residual nitrogen availability with twelve soils. Soil Sci. Soc. Amer. Proc. 31:403-406.

Legg, J. O., and Stanford, G. 1967. Utilization of soil and fertilizer nitrogen by plants in relation to the available nitrogen status of soils. Soil Sci. Soc. Amer. Proc. 31:215-219.

Lucas, R. E. 1969. Cultural trials on irrigated corn. Mich. Agr. Exp. Sta. Rep. 84.

Nelson, L. B., and Uhland, R. E. 1955. Factors that influence loss of fall-applied fertilizers and their probable importance in different sections of the United States. Soil Sci. Soc. Amer. Proc. 19:492-496.

Owens, L. D. 1960. Nitrogen movement and transformations in soils as evaluated by a lysimeter study utilizing isotopic nitrogen. Soil Sci. Soc. Amer. Proc. 24:372-376.

Pearson, R. W., Jordan, H. V., Bennett, O. L., Scarsbrook, C. E., Adams, W. E., and White, A. W. 1961. Residual effects of fall and spring-applied nitrogen fertilizers on crop yields in the southeastern United States. U.S.D.A. Tech. Bul. 1254.

Pesek, J. T., and Dumenil, L. 1956. An extra dividend from fertilizer use. Plant Food Rev. 2(3):4-6;31-32.

Pesek, J. T. 1964. Comparing efficiency of nitrogen fertilizers. In V. Sauchelli, (ed.) Fertilizer Nitrogen. A.C.S. Monograph 161:365-391.

Romaine, J. D. 1965. When fertilizing consider plant food content of your crops. Better Crops with Plant Food May-June:1-8.

Ruble, W. L., Kiel, D. F., and Rafter, M. E. 1968. Mich. Agr. Exp. Sta. Stat. Series Descriptions 5,14,16.

Russell, E. J., and Richards, E. H. 1920. The washing out of nitrates by drainage water from uncropped and unmanured land. J. Agr. Sci., Part I, 10:22-43.

Scarsbroad, D. E. 1965. Nitrogen availability. In W. Bartholomew and F. Clark, (ed.) Soil Nitrogen. Agronomy 10:486-507.

Schafer, J. W. 1968. Nitrogen carrier induced changes in chemical, mineralogical and microbial properties of a sandy loam soil. Ph.D. Thesis, Mich. State Univ., E. Lansing, Mich.

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

Steward, F. A., Johnson, D. D., and Porter, L. K. 1963. The availability of fertilizer nitrogen immobilized during decomposition of straw. Soil Sci. Soc. Amer. Proc. 27:656-659.

United States Dept. Commerce. Climatological Data. Mich. Section. 1965-1968.

van der Paauw, F. 1963. Residual effect of nitrogen fertilizer on succeeding crops in a moderate marine climate. Plant and Soil. 19:324-331.

van der Paauw, E. 1962. Periodic fluctuations of soil fertility. Plant and Soil 17:155-182.

Viets, F. G. 1960. Recovery of fertilizer nitrogen on irrigated and dryland soils of the western United States. Trans. Intern. Congr., Soil Sci. 7th Congr., Madison II:486-493.

Wetselaar, R. 1961. Nitrate distribution in tropical soils. II. Extent of capillary accumulation of nitrate during a long dry period. Plant and Soil. 15:121-133.

Wetselaar, R. 1962. Nitrate distribution in tropical soils. III. Downward movement and accumulation of nitrate in the subsoil. Plant and Soil 16:19-31.

White, W. C. 1957. Nature and effects of residual soil nitrogen. Iowa State Col. J. Sci. 32:286-288.

White, W. C., Dumenil, L., and Pesek, J. 1958. Evaluation of residual nitrogen in soils. Agron. J. 50:255-259.

White, W. C., and Pesek, J. 1959. Nature of residual nitrogen in Iowa soils. Soil Sci. Soc. Amer. Proc. 23:39-42.

Widdowson, F. V., and Penny, A. 1965. Experiments measuring the residual effects of nitrogen fertilizers. In Soils and Fertilizers 29:198.

Winsor, G. W., and Pollard, A. G. 1956. Carbon-nitrogen relationships in soil. I. The immobilization of nitrogen in the presence of carbon compounds. J. Sci. Food Agric., 7:134-141.

Wolcott, A. R. 1964. The acidifying effects of nitrogen carriers. Agr. Ammonia News July-Aug.:1-4.

Wolcott, A. R., Foth, H. D., Davis, J. F., and Shickluna, J. 1965. Nitrogen Carriers: I. Soil effects. Soil Sci. Soc. Amer. Proc. 29:405-410.

APPENDICES

APPENDIX A

HODUNK SERIES

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

Soil Profile:		Hodunk sandy loam
A_p	0-7"	Dark grayish brown (10YR 4/2) to very dark grayish brown (10YR 3/2); sandy loam; moderate fine, granular structure; friable when moist and soft when dry; medium content of organic matter; medium to slightly acid; abrupt smooth boundary. 6 to 11 inches thick.
A_2	7-16"	Yellowish brown (10YR 5/4); pale brown (10YR 6/3) or light yellowish brown (10YR 6/4); sandy loam; weak, fine, granular to 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 (10YR 5/3) to pale brown (10YR 6/3); sandy loam to light sandy clay loam; massive to weak, thick, platy structure; firm when moist and brittle when dry; weak to moderately developed fragipan; few thin clay flows; medium to strongly acid; clear wavy boundary. 4 to 12 inches thick.

B_{2g}	25-46"	Brown (10YR 5/3) to yellowish brown (10YR 5/4) mottled with yellowish brown (10YR 5/8) and dark brown (7.5YR 4/4), mottles are common, medium, distinct; sandy clay loam; few thin clay flows; weak, medium, subangular block 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.
C_g	46+"	Light yellowish brown (10YR 6/4) to brown (10YR 5/3) mottled with yellowish brown (10YR 5/6 - 5/8), mottles are common, medium, distinct; sandy loam; massive to very weak coarse, subangular block structure; friable when moist and hard when dry; calcareous.

Topography: Gently to moderately sloping till plains and moraines.

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

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

APPENDIX B

MODIFIED SEMI-MICRO KJELDAHL METHOD FOR SOILS

A. Reagents:
   1. Concentrated H_2SO_4.
   2. 10 Normal NaOH solution.
      a. Prepare from 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 solution.
      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.
   4. Potassium sulfate-catalyst mixture: mix by grinding 15 g. K_2SO_4; 1 g. $CuSO_4 \cdot 5H_2O$; and .7 g. Se.
   5. 0.01 N H_2SO_4.
   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: .1 g methyl red + .1 g brom-cresol green in 250 ml methanol.

B. Procedure (excluding nitrate):
   1. Grind soil sample to pass 32-40 mesh screen.
   2. Weigh duplicate samples containing 0.5000 g. on weighted 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.
   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.
   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 to temperature.
   10. Add 3 ml of H_3BO_3 solution to a 25 ml erlenmeyer flask which is marked at a volume of 15 ml.
   11. Add one 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 one ml of 10 N NaOH to funnel at start, note height in funnel, then add 10 ml more NaOH.
14. Insert Kjeldahl flask into distillation apparatus.
15. Drop 10 ml of the 10 N NaOH into the flask, close stop cock, 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 .01 N H_2SO_4.
20. Calculate percent nitrogen.

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

T = ml sample nitrated
B = ml blank titrated
N = normality of H_2SO_4 used in titration
S = sample weight in mg