

## INFORMATION TO USERS

This reproduction was made from a copy of a manuscript sent to us for publication and microfilming. While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. Pages in any manuscript may have indistinct print. In all cases the best available copy has been filmed.

The following explanation of techniques is provided to help clarify notations which may appear on this reproduction.

1. Manuscripts may not always be complete. When it is not possible to obtain missing pages, a note appears to indicate this.
2. When copyrighted materials are removed from the manuscript, a note appears to indicate this.
3. Oversize materials (maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or in black and white paper format.\*
4. Most photographs reproduce acceptably on positive microfilm or microfiche but lack clarity on xerographic copies made from the microfilm. For an additional charge, all photographs are available in black and white standard 35mm slide format.\*

**\*For more information about black and white slides or enlarged paper reproductions, please contact the Dissertations Customer Services Department.**

**UMI** University  
Microfilms  
International



8607054

**Burutolu, Ebinimi F. A.**

INFLUENCE OF CULTIVATION, CROPPING SYSTEMS, AND CROP RESIDUES  
ON THE CONTENT AND DISTRIBUTION OF NITROGEN FORMS IN SOILS

*Michigan State University*

PH.D. 1985

University  
Microfilms  
International 300 N. Zeeb Road, Ann Arbor, MI 48106



**PLEASE NOTE:**

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages \_\_\_\_\_
2. Colored illustrations, paper or print \_\_\_\_\_
3. Photographs with dark background \_\_\_\_\_
4. Illustrations are poor copy \_\_\_\_\_
5. Pages with black marks, not original copy \_\_\_\_\_
6. Print shows through as there is text on both sides of page \_\_\_\_\_
7. Indistinct, broken or small print on several pages ✓ \_\_\_\_\_
8. Print exceeds margin requirements \_\_\_\_\_
9. Tightly bound copy with print lost in spine \_\_\_\_\_
10. Computer printout pages with indistinct print \_\_\_\_\_
11. Page(s) \_\_\_\_\_ lacking when material received, and not available from school or author.
12. Page(s) \_\_\_\_\_ seem to be missing in numbering only as text follows.
13. Two pages numbered \_\_\_\_\_. Text follows.
14. Curling and wrinkled pages \_\_\_\_\_
15. Dissertation contains pages with print at a slant, filmed as received \_\_\_\_\_
16. Other \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

University  
Microfilms  
International



INFLUENCE OF CULTIVATION, CROPPING SYSTEMS, AND  
CROP RESIDUES ON THE CONTENT AND DISTRIBUTION  
OF NITROGEN FORMS IN SOILS

By

Ebinimi F. A. Burutolu

A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences

1985

## ABSTRACT

### INFLUENCE OF CULTIVATION, CROPPING SYSTEMS, AND CROP RESIDUES ON THE CONTENT AND DISTRIBUTION OF NITROGEN FORMS IN SOILS

By

Ebinimi F. A. Burutolu

Changes in organic C and total N, and in the distribution of N in fractions obtained by acid hydrolysis were used to evaluate effects of tillage, cropping systems and types of crop residues on N status in soils.

Under cash crop systems on Charity clay and Hodunk sandy loam, total N in the plow layer was lower by 66% than in surface layers of adjacent virgin soils. The corresponding decreases in organic C were 62% in clay and 80% in the sandy loam.

In a livestock operation on Kalamazoo sandy loam, total N was lower by 23% and organic C by 12% than in the virgin soil.

At another location on Charity clay, seven cash crop systems involving different sequences and proportions of corn, navy beans, sugar beets, oats and alfalfa were compared. After 11 years, total N had declined by 2 to 11% from levels found at the beginning of the experiment. Organic C had declined by 13 to 17%.

At all field locations, decreases in the proportion of nonhydrolyzable N and increases in the proportion of hydrolyzable



unknown forms (HUN fraction) indicated that a long-term effect of tillage was to increase exposure and decrease stability of physically protected humic complexes. This increased the proportion of lower molecular weight fragments and precursors. An increase in exposed surface was indicated also by increases in hydrolyzable ammonium. Variable changes in the proportion of hydrolyzable amino acid and amino sugar fractions appeared related to current crop cover.

A Hodunk sandy loam amended with residues of corn, navy beans, sugar beets or alfalfa was incubated for 63 days. Both chemical and biological transformations may have contributed to observed patterns of mineralization-immobilization. The HUN fraction seemed to be a key intermediate in transfers of N among organic fractions and in exchanges with the mineral N pool. Amino acid and amino sugar fractions peaked after major respiratory losses of C has occurred and appeared related to size or activity of microbial populations. Lesser parallel changes in hydrolyzable ammonium indicated its association with active surface sites.

## DEDICATION

This dissertation is dedicated to my wife Comfort and our children, Taripreye, Ebitari and Taritonye for their encouragement, sacrifice, patience and love.

## ACKNOWLEDGMENTS

The author would like to express sincere appreciation to Drs. D. R. Christenson and A. R. Wolcott for their very useful guidance and support in the research and preparation of this dissertation.

I am also grateful to other members of my guidance committee, Drs. B. G. Ellis, S. A. Boyd and O. D. Meaders for their advice and useful suggestions throughout my program.

My thanks are due to Dr. C. Cress for his advice in the statistical analysis. I am also grateful to Mr. Calvin Bricker for his rewarding assistance in the field and laboratory work during my program. Assistance from other faculty, staff and graduate students is gratefully acknowledged.

The author also wishes to thank the Rivers State University of Science and Technology, Port Harcourt, Nigeria, for their financial support.

Special thanks and praises to God the Father, the Son and the Holy Spirit for making me "like a tree planted by the rivers of water, that bringeth forth his fruit in his season; his leaf shall not wither; and whatsoever he doeth shall prosper" (ps. 1:3 KJV).

## TABLE OF CONTENTS

	Page
LIST OF TABLES . . . . .	vi
LIST OF FIGURES . . . . .	x
 Chapter	
I. INTRODUCTION . . . . .	1
LITERATURE CITED . . . . .	3
II. EFFECT OF CULTIVATION ON THE CONTENT AND DISTRIBUTION OF NITROGEN FORMS IN SOME MICHIGAN SOILS . . . . .	5
Effect of Cultivation on Organic Matter and Total N . . . . .	5
Cultivation and Content of Organic-N Forms . . . . .	8
Cultivation and Profile Distribution of Organic N Forms . . . . .	9
Objectives of Present Research . . . . .	11
MATERIALS AND METHODS . . . . .	13
Experimental Sites . . . . .	13
Soil Sampling . . . . .	13
Laboratory Analyses . . . . .	13
RESULTS AND DISCUSSION . . . . .	16
Distributions of N in Virgin and Cultivated Profiles . . . . .	16
Total Kjeldahl N and Organic Carbon . . . . .	16
Fractional Forms of N . . . . .	18
Effects of Cultivation on Distribution of N in Surface Soil Layers . . . . .	27
Changes in Total Kjeldahl N . . . . .	27
Changes in Fractional Forms of N . . . . .	30
Fractional Contributions to Total Kjeldahl N Loss . . . . .	35
SUMMARY AND CONCLUSIONS . . . . .	40
LITERATURE CITED . . . . .	42

Chapter	Page
III. INFLUENCE OF CROPPING SYSTEMS ON FORMS OF NITROGEN IN A CLAY SOIL . . . . .	47
MATERIALS AND METHODS . . . . .	53
Field Experiment . . . . .	53
Soil Type . . . . .	54
Soil Sampling . . . . .	54
Laboratory Analyses . . . . .	56
Statistical Analyses . . . . .	56
RESULTS AND DISCUSSION . . . . .	57
Effect of Cropping System on the Distribution of N Over Time . . . . .	57
Changes in Total Kjeldahl N and Organic Carbon . . . . .	57
Changes in Fractional Forms of N . . . . .	59
SUMMARY AND CONCLUSIONS . . . . .	65
LITERATURE CITED . . . . .	67
IV. EFFECT OF TYPE AND RATE OF CROP RESIDUES ON THE CONCENTRATION AND DISTRIBUTION OF NITROGEN FORMS DURING INCUBATION . . . . .	72
MATERIALS AND METHODS . . . . .	76
Laboratory Analyses . . . . .	77
Statistical Analyses . . . . .	77
RESULTS AND DISCUSSION . . . . .	78
Apparent Gains and Losses of N . . . . .	78
Changes in Exchangeable Ammonium . . . . .	86
Changes in Nitrified N . . . . .	88
Changes in Organic N Fractions . . . . .	90
Total Hydrolyzable N and Nonhydrolyzable N . . . . .	90
Changes Among Hydrolyzable Forms of N . . . . .	95
SUMMARY . . . . .	106
CONCLUSIONS . . . . .	110
LITERATURE CITED . . . . .	112
APPENDICES . . . . .	115

## LIST OF TABLES

Table	Chapter II	Page
1. Location and management of soils, description of profiles, and pH and carbon content of sampled soil depths . . . . .		14
2. Organic carbon and total Kjeldahl nitrogen in cultivated and virgin soil profiles . . . . .		17
3. Content and distribution of total hydrolyzable N in cultivated and virgin soil profiles . . . . .		19
4. Content and distribution of hydrolyzable ammonium N in cultivated and virgin soil profiles . . . . .		20
5. Content and distribution of $\alpha$ -amino acid N in cultivated and virgin soil profiles . . . . .		21
6. Content and distribution of serine plus threonine N in cultivated and virgin soil profiles . . . . .		22
7. Content and distribution of amino sugar N in cultivated and virgin soil profiles . . . . .		23
8. Content and distribution of hydrolyzable unknown N(HUN) in cultivated and virgin soil profiles . . . . .		24
9. Content and distribution of nonhydrolyzable N in cultivated and virgin soil profiles . . . . .		25
10. Distribution of organic N fractions in cultivated and virgin surface soils . . . . .		29
11. Effect of cultivation on $\text{NH}_4$ and unidentified N in acid hydrolysates in relation to nonhydrolyzable N . .		36
Chapter III		
1. Crops grown and supplemental N applied to cropping systems from 1972 to 1983 . . . . .		55
2. Effect of cropping system on total Kjeldahl N and organic carbon levels and carbon-nitrogen ratio in a Charity clay soil . . . . .		58

Table	Page
3. Effect of cropping system on the concentration of nitrogen forms and percentage change . . . . .	60
4. Effect of cropping system on the distribution of total Kjeldahl N among organic N fractions and percent change.	61
5. Effect of cropping system on total hydrolyzable N(THN), hydrolyzable ammonium (AN), and hydrolyzable unknown N(HUN) in relation to nonhydrolyzable N(NHN) . . . . .	62
6. Effect of cropping system on hydrolyzable $\text{NH}_4^+$ (AN), amino acid N (AAN), amino sugar N (ASN) and hydrolyzable unknown N (HUN) in relation to the total hydrolyzable N(THN) . . . . .	64
Chapter IV	
1. Composition of crop residues used in the incubation study . . . . .	78
2. Effect of type and rate of crop residue and time of incubation on organic carbon . . . . .	84
3. Effect of type and rate of residue and time of incubation on exchangeable ammonium N . . . . .	87
4. Effect of type and rate of crop residues and time of incubation on the concentration of nitrate plus nitrate.	89
5. Effect of type and rate of crop residues and time of incubation on the concentration of total N . . . . .	96
6. Effect of type and rate of crop residues and the time of incubation on the concentration of total hydrolyzable nitrogen . . . . .	97
7. Effect of type and rate of crop residues and time of incubation on the concentration of nonhydrolyzable N . . . . .	98
8. Effect of type and rate of crop residues and time of incubation on the concentration of hydrolyzable unknown N . . . . .	99
9. Effect of type and rate of crop residues and time of incubation on the concentration of hydrolyzable ammonium N . . . . .	100
10. Effect of type and rate of crop residues and time of incubation on the concentration of amino acid N . . . . .	101

Table	Page
11. Effect of type and rate of crop residues and time of incubation on the concentration of amino sugar N . .	102
APPENDIX A	
1. Probabilities for significance of main effects and interactions of residues, rates, and time of analyses for carbon and forms of nitrogen . . . . .	117
2. Probabilities for significance of main effects and interactions of residues, rates, and times on the proportion of fractional forms of N . . . . .	118
3. Effect of type and rate of crop residues and time of incubation on the concentration of total organic nitrogen . . . . .	119
4. Effect of crop residue type and time of incubation on the proportion of total N as total hydrolyzable N . .	120
5. Effect of type and rate of crop residues on the proportion of total N as total hydrolyzable N . . . . .	121
6. Effect of crop residue rate and time of incubation on the proportion of total N as total hydrolyzable N . .	122
7. Effect of type and rate of crop residue on the concentration of nonhydrolyzable N . . . . .	123
8. Effect of residue rate and time of incubation on the concentration of nonhydrolyzable N . . . . .	124
9. Effect of type and rate of crop residue on the proportion of total N as nonhydrolyzable N . . . . .	125
10. Effect of residue rate and time of incubation on the proportion of total N as nonhydrolyzable N . . . . .	126
11. Effect of residue type and time of incubation on the concentration of hydrolyzable ammonium N . . . . .	127
12. Effect of type and rate of crop residues on the concentration of hydrolyzable ammonium N . . . . .	128
13. Effect of residue rate and time of incubation on the concentration of hydrolyzable ammonium N . . . . .	129
14. Effect of residue type and time of incubation on the proportion of total N as hydrolyzable ammonium N . .	130



Table		Page
15.	Effect of type and rate of crop residues on the proportion of total N as hydrolyzable ammonium N . . . .	131
16.	Effect of residue rate and time of incubation on the proportion of total N as hydrolyzable ammonium N . .	132
17.	Effect of type and rate of crop residues and time of incubation on the proportion of total N as amino acid N . . . . .	133
18.	Simple effect of type of crop residues and time of incubation on the concentration and proportion of total N as amino sugar N . . . . .	134
19.	Effect of type and rate of residue on the proportion of total N as amino sugar N . . . . .	135
20.	Simple effect of time of incubation on the proportion of total N as hydrolyzable unknown N . . . . .	136

## LIST OF FIGURES

Figure	Chapter II	Page
1.	Content of organic N fractions in cultivated (C) and virgin (V) surface (0-0.15m) in a Charity clay soil . .	31
2.	Content of organic N fractions in cultivated (C) and virgin (V) surface (0-0.15m) in a Kalamazoo sandy loam study . . . . .	32
3.	Content of organic N fractions in cultivated (C) and virgin (V) surface (0-0.15m) in a Hodunk sandy loam soil . . . . .	33
4.	Decrease in content of organic N fractions expressed as percent of total N loss due to cultivation . . . . .	37
	Chapter IV	
1.	Effect of type and rate of alfalfa residues and time of incubation on the concentration of total nitrogen . .	80
2.	Effect of type and rate of sugar beet residues and time of incubation on the concentration of total nitrogen .	81
3.	Effect of type and rate of corn residues and time of incubation on the concentration of total nitrogen . .	82
4.	Effect of type and rate of navy bean residues and time of incubation on the concentration of total nitrogen .	83
5.	Concentration of nitrogen fractions during incubation at 50 g/kg alfalfa residue addition . . . . .	91
6.	Concentration of nitrogen fractions during incubation at 50 g/kg sugar beet residue addition . . . . .	92
7.	Concentration of nitrogen fractions during incubation at 50 g/kg navy bean residue addition . . . . .	93
8.	Concentration of nitrogen fractions during incubation at 50 g/kg corn residue addition . . . . .	94

## CHAPTER I

### INTRODUCTION

The nature and status of soil organic matter and nitrogen are important factors in crop production. Organic matter contributes important physical, chemical, and biological properties to soils. Nitrogen is an essential element in plant nutrition. When soil is cultivated, soil organic matter and total N decline with time. The decline is rapid and appears linear in the earlier years after virgin soils are brought under cultivation, but gradually slows and ultimately reaches a new equilibrium after 50 to 100 years of cultivation.

The rate and magnitude of organic matter and total N loss is influenced by the cropping system and sequence (4, 5, 7, 8, 15, 17, 18), crops grown (7, 20), specific management practices (4, 5, 14, 15, 16, 2), the original soil N content (3, 5, 6, 7, 17, 18), climate (9, 10), soil type (1, 15), and length of cultivation. The rate of establishment of equilibrium is provided by change and the magnitude of the term  $(N_0 - \frac{A}{r}) \exp(-rt)$  in the equation of Bartholomew and Kirkham (2):

$$N = \frac{A}{r} - (N_0 - \frac{A}{r})e^{-rt}$$

where  $N_0$  is the initial N content  
 $r$  is the annual rate of N loss  
 $A$  is the annual rate of addition

More than 90% of the total N in most surface soils is in organic form. About one-half of the organic N has not been adequately characterized. Inorganic N plays a primary and direct role in plant nutrition. The involvement of organic N in plant nutrition is at best regarded as secondary and indirect, that is, through the process of mineralization.

Different kinds of N compounds and complexes differ in their susceptibility to mineralization. It might be expected that their importance as sources of N for plants will vary accordingly.

The content and proportions of various organic N fractions have been influenced by the management system. These organic N fractions shift from one form to another during cultivation and other management practices.

Many researchers have attempted to identify the forms of organic N that might be useful as predictive soil tests (11, 12, 13, 19). The present study was undertaken to determine the nature and magnitude of changes in content and distribution of N forms under the following three systems:

1. Virgin soils and their cultivated analogues under three types of management
2. Rotational cropping for eleven years
3. Incubation systems involving various residue types and rates for a 63-day period.

## LITERATURE CITED

1. Anderson, M. A., and G. M. Browning. 1950. Some physical and chemical properties of six virgin and six cultivated Iowa soils. Soil Sci. Soc. Amer. Proc. 14: 370-364.
2. Bartholomew, W. V., and D. Kirkham. 1960. Mathematical descriptions and interpretations of culture induced soil nitrogen changes. Int. Congr. Soil Sci. Trans. 7th (Madison, Wis.), II: 471-477.
3. Fritschen, L. J., and J. A. Hobbs. 1958. Effect of crop rotation and fertilizer treatment on the nitrogen and organic carbon contents of a prairie soil. Soil Sci. Soc. Amer. Proc. 22:439-441.
4. Gosdin, G. W., M. Stelly, and W. E. Adams. 1950. The organic matter and nitrogen content and carbon-nitrogen ratio of Cecil soil as influenced by different cropping systems on classes II, III, and IV land. Soil Sci. Soc. Amer. Proc. (1949). 14:203-208.
5. Haas, H. J., C. E. Evans, and E. F. Miles. 1957. Nitrogen and carbon changes in Great Plains soils as influenced by cropping and soil treatments. Technical Bulletin No. 164. USDA.
6. Hide, J. C., and W. H. Metzger. 1939. The effect of cultivation and erosion on the nitrogen and carbon of some Kansas soils. Agron. J. 31:625-632.
7. Hobbs, J. A., and P. L. Brown. 1957. Nitrogen and organic carbon changes in cultivated Western Kansas soils. Kansas Agr. Exp. Sta. Bull. 89.
8. Hobbs, J. A., and P. L. Brown. 1965. Effects of cropping and management on nitrogen and organic carbon contents of a western Kansas soil. Kansas Agr. Exp. Sta. Tech. Bull. 144.
9. Jenny, H. 1941. Factors of soil formation. McGraw-Hill Book Company, New York.

10. Jenny, H. 1960. Comparison of soil nitrogen and carbon in tropical and temperate regions. Missouri Agric. Exp. Sta. Res. Bull. 765:1-30.
11. Kai, H., Z. Ahmad, and T. Harada. 1973. Factors affecting immobilization and release of nitrogen in soil and chemical characteristics of the nitrogen newly immobilized. III. Transformation of the nitrogen immobilized in soil and its chemical characteristics. Soil Sci. Plant Nutr. 19:275-286.
12. Keeney, D. R., and J. M. Bremner. 1964. Effect of cultivation on the nitrogen distribution in soils. Soil Sci. Soc. Amer. Proc. 28:653-656.
13. Keeney, D. R., and J. M. Bremner. 1966. Characterization of mineralized nitrogen in soils. Soil Sci. Soc. Amer. Proc. 30:714-719.
14. Lee, C., and R. H. Bray. 1949. Organic matter and nitrogen contents of soils as influenced by management. Soil Sci. 68:203-212.
15. Mazurak, A. P., and E. C. Conrad. 1966. Changes in content of total nitrogen and organic matter in three Nebraska soils after seven years of cropping treatments. Agron. J. 58:85-88.
16. Meints, V. W., L. T. Kurtz, S. W. Melsted, and T. R. Peck. 1977. Long-term trends in total soil N as influenced by certain management practices. Soil Sci. 124:110-116.
17. Metger, W. H. 1939. Nitrogen and organic carbon of soils as influenced by cropping systems and soil treatments. Kansas Agr. Exp. Sta. Tech. Bull. 56.
18. Myers, H. E., A. L. Hallsted, J. B. Kuska, and H. J. Haas. 1943. Nitrogen and carbon changes in soils under low rainfall as influenced by cropping systems and soil treatment. Kansas Agr. Exp. Sta. Tech. Bull. 45.
19. Stewart, B. A., L. K. Porter, and D. D. Johnson. 1963. Immobilization and mineralization of nitrogen in several organic fractions of soil. Soil Sci. Soc. Amer. Proc. 27:302-304.
20. Van Bavel, C. H. M., and F. W. Schaller. 1951. Soil aggregations, organic matter and yields in a long-term experiment as affected by crop management. Soil Sci. Soc. Amer. Proc. (1950). 15:399-404.

## CHAPTER II

### EFFECT OF CULTIVATION ON THE CONTENT AND DISTRIBUTION OF NITROGEN FORMS IN SOME MICHIGAN SOILS

The role of organic matter and nitrogen in soil formation, fertility, and crop production has been treated extensively in published literature.

Surface organic matter and nitrogen distribution vary tremendously among and within the major soil orders of the world. The magnitude of variation depends to a great extent on soil forming factors such as climate, vegetation, topography, parent material and age. According to Jenny (22, 23), the importance of the factors determining the organic matter and nitrogen contents of medium textured soils of the United States decreased in the order:

climate > vegetation > topography = parent material > age

#### Effect of Cultivation on Organic Matter and Total N

Within a soil order, management factors, such as cultivation and fertilization bring about significant changes in organic matter and nitrogen distribution in surface and profile soils. Cultivation affects the distribution of organic matter and nitrogen through its influence on the organic carbon equilibrium in soils.

Some work has been done on the effect of cultivation on the organic matter and nitrogen contents of soils in the temperate, tropical, and subtropical regions. In their long-term study on the effect of cropping on the surface soil nitrogen and organic carbon content of the soils at 14 locations in the Great Plains, Haas and Evans (15) reported that nitrogen declined by 39% on the average over a 36-year period. This represents 1.07% loss of soil nitrogen for each year of crop production. The average organic carbon loss over a 37-year cropping period was 42% with an annual loss of 1.15%.

In a similar study in western Kansas soils under low rainfall conditions, Hobbs and Brown (18) reported that cropping had marked effect on nitrogen and organic carbon losses. The N losses were rapid after cultivation of the virgin soil began and the rate gradually decreased with time. Nitrogen and organic C losses averaged 23.3% and 36.2%, respectively, from 1916 to 1958. However, losses slowed down to 2.2% for nitrogen and 2.1% for organic C in the last eight years (19). In their preliminary studies on the status of organic matter and nitrogen in soils under shifting cultivation in the tropics, Isirimah et al. (20) found that cultivation decreased organic matter by 55% and total N content by 60% in all soil types. They also observed that the long fallow period had not increased the level of nitrogen and organic matter markedly. On a Greary silt loam Prairie soil in Kansas, Fritschen and Hobbs (13) worked on the effect of crop rotation on the N and organic carbon contents and found losses of both over the period. Similarly, Hide and Metzger (16) reported a decline in carbon and nitrogen of Kansas surface soils of



37% and 32%, respectively, due to cultivation. Working with surface soils in the Great Plains, Porter et al. (33) reported that cropping of virgin soils decreased the total N and the other forms of N. In another study, Smith and Young (36) showed that the total N and organic C of surface soils declined on the average by 42% and 33%, respectively, due to cultivation.

There is little information on the effect of cultivation on the mineral N forms. It was observed in some studies that exchangeable  $\text{NH}_4$  and nitrate N contents were normally small, and both fractions may not account for more than 2% of the total soil N. Nitrites do not accumulate in soils to a great extent, except in alkaline conditions, hence, large amounts are rarely detected in soil analysis. Mineral nitrogen also occurs as fixed  $\text{NH}_4^+$  and this fraction is very significant in some soil profiles. The average amount of fixed ammonium N remained unchanged, indicating that cultivation had made no effect on the fixed ammonium content of the surface soils of Canada (17).

The studies cited above have generally indicated a loss of organic matter and total N with cultivation. Some investigations have reported that cultivation increased organic matter (1, 14, 27). In their studies, Grigor'yev (14) and Konovalonva (27) reported that humus and N content increased with cultivation on sod-podzolic forest soils in the order:

well  
cultivated > moderately  
cultivated > slightly  
cultivated > forest soils

It is appropriate to indicate that most of these studies discussed the effect of cultivation on organic matter and total N contents of surface soils. Effect of cultivation is not restricted to surface horizons alone. The impact gradually moves to subsurface horizons. Furthermore, it is important to compare cultivated and virgin soils to appreciate the impact of cultivation in agricultural soils.

Several studies have shown that organic matter and total nitrogen declined with depth in both virgin and cultivated soils (29, 36). The magnitude and rate of decline was generally greater in the cultivated than in the virgin soil.

#### Cultivation and Content of Organic-N Forms

Cultivation decreased the content of all N forms markedly, except nonexchangeable (fixed)  $\text{NH}_4^+$  N in surface soils. The proportion of total N as nonexchangeable (fixed)  $\text{NH}_4^+$  N increased slightly, as did total hydrolyzable N and other hydrolyzable fractions such as ammonium N, hexosamine N, and unidentified N. The percentage of hydrolyzable amino acid N and nonhydrolyzable N decreased due to cultivation. The average percent loss of different forms of N on cultivation decreased in the order (24):

amino acid N (43.0%) > nonhydrolyzable N (39.4% >  
Total N (36.2%) > total hydrolyzable N (35.2%) >  
unidentified hydrolyzable N (34.5%) > hydrolyzable  
ammonium N (28.6%) > hexosamine N (27.6%) > nonexchang-  
able ammonium N (0.2%).

In another study, nondistillable acid-soluble N showed the greatest decline with cropping, followed by distillable acid-soluble ammonium N and acid-insoluble N (12).

These studies tend to show that the proportion of individual organic N fractions in the surface horizon may not be greatly changed by cultivation, but there normally is quantitative reduction in amounts of most fractional forms.

#### Cultivation and Profile Distribution of Organic N Forms

In many temperate soils, the proportion of the total N present as amino acid N, amino sugar N, and acid insoluble N range from 30-50%, 5-24%, and 20-30%, respectively. Hydrolyzable ammonium N and hydrolyzable unknown N (HUN) occur as 20-35% and 10-20%, respectively, of the total N. With depth, the contents and percentages of the soil N may increase, decrease, or remain the same, depending on the management or cultural practices, biotic, climatic, or edaphic factors or the status of decomposition of certain organic compounds in the soil environment.

Reports have indicated that the proportion of soil N as amino acid N decreased with depth in different soils (26, 30, 37, 41). The decrease of amino acid N with depth may be related to the decline with depth of the microbial population whose cells contain amino acids.

Several studies have reported that the percentage of amino sugar N decreased with depth (26, 35, 39, 40, 42). Other studies

showed that amino sugar N increased with depth (30, 41, 50). It is not clear why amino sugar N would increase with depth. This pattern may be related to the higher calcium content in the lower horizons. Some soils in subtropical regions showed a decline of amino sugar N with a decrease in percent calcium in the lower horizons (40). A fairly reasonable explanation for the increase in amino sugar N with depth may be due to extensive decomposition and turnover which may lead to selective preservation of amino sugar N (47, 50). The selective preservation may be due to protection by adsorption or complexation with organic and mineral colloids.

Although amino acid N and amino sugar N are the main identifiable organic N compounds in soil hydrolysates, it is important to know the distribution patterns of the other N forms. The proportion of soil N as hydrolyzable ammonium N increased with depth in soil profiles of the Ustoll suborder in western Nebraska (29) and a podzolic soil in central Sweden (30). An earlier study indicated the same trend in a wide variety of soils in the north-central U.S. (41). The rate of hydrolyzable ammonium N increase with depth varied with the soil type. The increase of hydrolyzable ammonium N with depth could be due, in part, to the liberation of  $\text{NH}_3$  from clay-fixed  $\text{NH}_4^+$  by acid hydrolysis, rather than from organic compounds (4, 26, 39, 41, 44, 48).

The distribution patterns of organic N forms can vary considerably with the soil type. In mineral soils of the tropical and subtropical region, total hydrolyzable N and unidentified N increased

with depth. Acid insoluble N decreased with depth. There was no consistent pattern in profile distribution in other organic N forms. Another study showed that total hydrolyzable N, amino acid N, and ammonium N decreased, but amino sugar N increased with depth in all but one profile (12).

Few studies have compared soil profile distribution patterns of organic N forms in cultivated and their virgin analogues. In their studies on some soil profiles, Meints and Peterson (29) reported that the concentration of the organic fractions in both cultivated and virgin soil profiles declined with depth. However, cultivation decreased the proportion of total N as nonhydrolyzable N and amino acid N. It increased the proportion of hydrolyzable ammonium N, compared to the virgin soil profiles. This indicates that regular additions of organic materials without soil disturbance over a period of time, as in virgin conditions, results in a characteristic distribution of organic N fractions, and that this distribution can be altered by differential decomposition when cultivated conditions are imposed. The rate and magnitude of change will be influenced by the type, quantity, and frequency of organic amendments added or crop residue returned and the length of time that a given system of management is imposed.

#### Objectives of Present Research

The nature and pattern of profile distribution of organic N components in Michigan soils has not been considered in published literature. The present investigation was undertaken as part of a cropping systems study to:

1. determine the effect of cultivation on the content and proportion of hydrolyzable and nonhydrolyzable forms of N
2. determine the pattern of profile distribution of organic matter, total N, and fractional forms of N in some soil types.

## MATERIALS AND METHODS

### Experimental Sites

Three pairs of soil profiles from cultivated soils and their virgin analogues were sampled. Each pair of profiles was located side by side on the same soil type. The cultivated soil profiles had been under one type of management or another continuously for at least ten years. The virgin-forested soil profiles had mixed vegetation for upwards of 50 years. Location and description of profile pairs are given in Table 1.

### Soil Sampling

Twenty cores were composited for the surface horizons (0-0.15m) from cultivated and virgin profiles. Twelve cores were composited for each subsoil horizon. Virgin and cultivated members of each pair were sampled on the same day. Depths sampled are shown in Table 1. All samples were screened to remove most undecayed and partly decayed plant residues, air-dried, ground, and stored for analysis.

### Laboratory Analyses

Soil pH was measured with pH meter using a glass electrode on a 1:1 soil-to-water suspension.

Table 1. Location and management of soils, description of profiles, and pH and carbon content of sampled soil depths.

Location	Soil Type	Management	Depth	pH	Organic C
			m		g/kg
Saginaw County	Charity clay	Cultivated (corn-bean- sugar beet rotation)	0.00-0.15	7.8	14
			0.15-0.23	7.8	6.7
			0.23-0.38	7.8	8.4
		Virgin (Forest)	0.00-0.08	6.5	49
			0.08-0.15	6.6	24
			0.15-0.23	6.5	20
			0.23-0.30	6.5	17
			0.30-0.38	6.8	12
Barry County	Kalamazoo sandy loam	Cultivated (Alfalfa-grass sod)	0.00-0.15	5.6	26
			0.15-0.23	6.8	20
		Virgin (Forest)	0.00-0.08	5.3	28
			0.08-0.15	5.0	30
			0.15-0.23	4.9	25
			0.23-0.30	6.8	23
Ingham County	Hodunk sandy loam	Cultivated (Potato- corn- corn)	0.00-0.15	6.5	5.6
			0.15-0.23	6.4	1.7
		Virgin (Forest)	0.00-0.15	5.2	29
			0.15-0.23	4.8	9.9
			0.23-0.41	4.8	4.3



Total Kjeldahl N was determined by the semimicro Kjeldahl methods described by Bremner (6), Bundy and Bremner (4), and Bremner and Mulvaney (7).

Easily oxidized organic C was determined by colorimetric method described by Schulte (34). This method involves chromic acid oxidation for determination of easily oxidized material through spontaneous heat. The method was standardized against the Walkley-Black method (52, 53). C/N ratio was taken as the ratio of total N to organic C.

Total hydrolyzable N, nonhydrolyzable N, and hydrolyzable N fractions, to include ammonium N,  $\alpha$ -amino acid N, hydroxyamino acid (serine + threonine) N and hydrolyzable unknown N were determined by the methods described by Bremner (5) and Stevenson (42, 45, 46, 47, 49).

All analyses were done in duplicate and the values reported are the means. Analyses were repeated where the duplicates varied more than 5%.

## RESULTS AND DISCUSSION

### Distributions of N in Virgin and Cultivated Profiles

#### Total Kjeldahl N and Organic Carbon

Organic carbon and total Kjeldahl N contents and their distributions in three Michigan soil profiles are shown in Table 2. At all three locations, quantities present at each sampling depth were substantially lower in cultivated than in virgin soil.

The declines in total N and organic carbon were relatively greater in the Charity and Hodunk soils than in the Kalamazoo. These differences would appear to reflect differences in management, rather than differences in genetic properties of soils (Table 1). The Kalamazoo had been protected by a cover of alfalfa and grass pasture for 7 years plus manure in the recent past--1980, whereas the Charity was subject to tillage each year of the rotation and also the Hodunk during the three years of the rotation.

The pH data in Table 1 indicate that the cultivated Hodunk soil may have been limed more heavily or recently than the Kalamazoo soil. The higher pH of cultivated Charity and Hodunk soils would have been more favorable for microbial populations that decompose crop residues. A larger proportion of annual carbon additions would have been lost as  $\text{CO}_2$ , and the net mineralization of N would have been greater. Losses of N from the soils would have occurred mainly through

Table 2. Organic carbon and total Kjeldahl nitrogen in cultivated and virgin soil profiles.

Depth	Charity clay			Kalamazoo sandy loam			Hodunk sandy loam		
	N <sup>†</sup>	OC	C/N	N	OC	C/N	N	OC	C/N
m	---g/kg ---			---g/kg---			---g/kg---		
Cultivated									
0.00-0.15	1.3	14	11	2.4	26	11	0.84	5.6	7
0.15-0.23	0.87	6.7	8	1.6	20	13	0.46	1.7	4
0.23-0.38	0.53	8.4	16	--	--	--	--	--	--
Virgin									
0.00-0.08	4.9	49	10	3.4	29	9	2.4	28	12
0.08-0.15	2.7	24	9	2.9	30	10	0.74	9.9	13
0.15-0.23	1.9	20	11	2.4	25	10	0.42	4.3	10
0.23-0.30	1.5	17	11	1.9	23	12	--	--	--
0.30-0.38	1.4	12	9	--	--	--	--	--	--

<sup>†</sup>N = Total Kjeldahl nitrogen; OC = Organic carbon; C/N = Carbon-nitrogen ratio

removal in harvested crops, although losses by volatilization, denitrification, erosion or leaching may have occurred also.

The C/N ratio of the cultivated Hodunk 0-0.15m and 0.15-0.23m depth was much lower than at the same depths in its virgin counterpart. This difference may reflect the fact that the profiles were sampled in late fall after harvest of corn and before incorporation of any surface residues.

Changes in C/N with depth suggest that different genetic horizons may have intercepted different proportions of nitrogenous to carbonaceous compounds or complexes moving downward in percolating water. There are not enough data to generalize on this point, however.

#### Fractional Forms of N

Fractional distributions of N in virgin and cultivated profiles are presented in Tables 3 through 9. In all cases, the quantities found at all depths were markedly lower in cultivated than in virgin soils. In all profiles, the quantities decreased with each increment of depth, except for the deepest samples in the virgin Charity clay. At this site, similar quantities of  $\alpha$ -amino acid N (Table 5), amino sugar N (Table 7), and nonhydrolyzable N (Table 9) were found in the 0.23-0.30m and 0.30-0.38m depths.

Thus, the depleting effects of cultivation extended downward for considerable depths in these profiles and affected all N fractions. However, different fractional forms decreased at different rates, resulting in wide variation in percentage distribution of N forms in the different depths.

Table 3. Content and distribution of total hydrolyzable N in cultivated and virgin soil profiles.

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	$\mu\text{gN/g}^\dagger$	% $^\ddagger$	$\mu\text{gN/g}$	%	$\mu\text{gN/g}$	%
Cultivated						
0.00-0.15	1111	87.9	2167	89.9	699	83.1
0.15-0.23	674	77.5	1273	80.6	366	79.0
0.23-0.38	531	82.4	--	--	--	--
Virgin						
0.00-0.08	3728	74.8	2735	80.4	1895	77.9
0.08-0.15	2307	87.0	2253	77.7	541	72.8
0.15-0.23	1663	86.3	1898	80.4	306	71.3
0.23-0.30	1359	88.8	1549	81.5	--	--
0.30-0.38	1159	85.8	--	--	--	--

$^\dagger \mu\text{gN/g}$  soil.

$^\ddagger$  Percent of total Kjeldahl N.

Table 4. Content and distribution of hydrolyzable ammonium N in cultivated and virgin soil profiles

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	$\mu\text{gN/g}^\dagger$	% $^\ddagger$	$\mu\text{gN/g}$	%	$\mu\text{gN/g}$	%
Cultivated						
0.00-0.15	343	27.1	517	21.4	188	22.3
0.15-0.23	248	28.5	335	21.2	97	20.9
0.23-0.38	216	33.5	--	--	--	--
Virgin						
0.00-0.08	811	16.2	597	17.5	375	15.4
0.08-0.15	668	25.2	577	19.9	149	20.0
0.15-0.23	525	27.2	521	22.0	57	13.3
0.23-0.30	462	30.2	383	20.1	--	--
0.30-0.38	426	31.5	--	--	--	--

$^\dagger$   $\mu\text{gN/g}$  soil.

$^\ddagger$  Percent of total Kjeldahl N

Table 5. Content and distribution of  $\alpha$ -amino acid N in cultivated and virgin soil profiles

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	$\mu\text{gN/g}^\dagger$	% $\ddagger$	$\mu\text{gN/g}$	%	$\mu\text{gN/g}$	%
Cultivated						
0.00-0.15	349	27.6	832	34.5	182	21.6
0.15-0.23	230	26.4	484	30.6	150	32.3
0.23-0.38	214	33.2	--	--	--	--
Virgin						
0.00-0.08	1586	31.8	1149	33.7	785	32.3
0.08-0.15	904	34.1	809	27.9	246	33.1
0.15-0.23	682	35.3	634	26.9	127	29.6
0.23-0.30	452	29.5	555	29.2	--	--
0.30-0.38	507	37.5	--	--	--	--

$^\dagger \mu\text{gN/g}$  soil.

$\ddagger$  Percent of total Kjeldahl N.

Table 6. Content and distribution of serine and threonine (hydroxyamino acid) N in cultivated and virgin soil profiles

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	$\mu\text{gN/g}^\dagger$	% $\ddagger$	$\mu\text{gN/g}$	%	$\mu\text{gN/g}$	%
Cultivated						
0.00-0.15	156	12.3	170	7.0	59	7.0
0.15-0.23	55	6.3	95	6.0	40	8.6
0.23-0.38	59	9.2	--	--	--	--
Virgin						
0.00-0.08	324	6.5	246	7.2	151	6.2
0.08-0.15	202	7.6	198	6.8	59	7.9
0.15-0.23	143	7.4	147	6.2	44	10.2
0.23-0.30	107	6.9	127	6.6	--	--
0.30-0.38	79	5.8	--	--	--	--

$^\dagger \mu\text{gN/g}$  soil.

$\ddagger$  Percent of total Kjeldahl N.



Table 7. Content and distribution of amino sugar N in cultivated and virgin soil profiles

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	$\mu\text{gN/g}^\dagger$	% $\ddagger$	$\mu\text{gN/g}$	%	$\mu\text{gN/g}$	%
Cultivated						
0.00-0.15	144	11.4	233	9.7	67	7.9
0.15-0.23	94	10.8	134	8.5	55	11.8
0.23-0.38	94	14.6	--	--	--	--
Virgin						
0.00-0.08	444	8.9	383	11.3	194	7.9
0.08-0.15	228	8.6	272	9.3	50	6.7
0.15-0.23	178	9.2	255	10.8	55	12.8
0.23-0.30	144	9.4	211	11.1	--	--
0.30-0.38	155	11.5	--	--	--	--

$^\dagger \mu\text{gN/g}$  soil.

$\ddagger$  Percent of total Kjeldahl N.

Table 8. Content and distribution of hydrolyzable unknown N(HUN)<sup>†</sup> in cultivated and virgin soil profiles

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	µgN/g <sup>‡</sup>	% §	µgN/g	%	µgN/g	%
Cultivated						
0.00-0.15	275	21.7	585	24.3	262	31.1
0.15-0.23	102	11.7	320	20.2	64	12.8
0.23-0.38	7	1.1	--	--	--	--
Virgin						
0.00-0.08	887	17.8	606	17.8	541	22.2
0.08-0.15	507	19.1	595	20.5	96	12.9
0.15-0.23	278	14.4	488	20.6	67	15.6
0.23-0.30	301	19.6	400	21.0	--	--
0.30-0.38	71	5.2	--	--	--	--

<sup>†</sup>HUN = Total hydrolyzable N minus (ammonium N + α-amino acid + hydroxyamino acid N + amino sugar N).

<sup>‡</sup>µgN/g soil.

§ Percent of total Kjeldahl N.

Table 9. Content and distribution of nonhydrolyzable N<sup>†</sup> in cultivated and virgin soil profiles

Depth	Charity clay		Kalamazoo sandy loam		Hodunk sandy loam	
m	μgN/g <sup>‡</sup>	% <sup>§</sup>	μgN/g	%	μgN/g	%
Cultivated						
0.00-0.15	153	12.1	243	10.0	142	16.8
0.15-0.23	196	22.5	307	19.4	97	20.9
0.23-0.38	113	17.5	--	--	--	--
Virgin						
0.00-0.08	1256	25.2	665	19.5	537	22.0
0.08-0.15	343	12.9	647	22.3	202	27.2
0.15-0.23	264	13.7	462	19.6	123	28.7
0.23-0.30	171	11.2	351	18.6	--	--
0.30-0.38	191	14.1	--	--	--	--

<sup>†</sup>Nonhydrolyzable N - Total Kjeldahl N minus total hydrolyzable N.

<sup>‡</sup> μgN/g soil.

<sup>§</sup> Percent of total Kjeldahl N.

In the cultivated profiles, total hydrolyzable N as percent of total Kjeldahl N in each depth decreased below the 0.0-0.15m layer (Table 3). A similar reduction occurred below the 0-0.08m layer in the virgin Kalamazoo and Hodunk soils, whereas an increase occurred below the 0.08-0.15m layer in the Charity.

Changes in the proportion of nonhydrolyzable N (Table 9) were, of course, related inversely to these changes in the total for hydrolyzable forms. Sharp increase in illuvial (subsurface) layer probably represent nitrogenous materials intercepted and retained as resistant polymers and complexes.

The proportion of hydrolyzable  $\text{NH}_4^+$  (Table 4) increased with depth in the Charity profiles and the virgin Kalamazoo. Such increases have been reported frequently (29, 30) and often attributed to release during acid hydrolysis of clay-fixed  $\text{NH}_4^+$  (4, 17, 26, 29, 30, 38, 41, 44, 48). Release of  $\text{NH}_4^+$  during hydrolysis from labile amides, imino compounds, and certain  $\alpha$ -amino acids as tryptophane might also be expected to increase with depth (2, 6, 26, 38).

Except in the virgin Charity soil, hydrolyzable  $\text{NH}_4^+$  tended to vary directly with C/N ratio. This result would agree with reports that fixed  $\text{NH}_4^+$  and C/N both increase with depth (17), but is at variance with others where the percentage of total N as hydrolyzable  $\text{NH}_4^+$  varied inversely with C/N ratio (10).

No consistent patterns of change with depth were observed for  $\alpha$ -amino acids (Table 5) or hydroxyamino acids (Table 6). There was some tendency for amino sugars to increase relative to TKN in the

deeper horizons, as has been reported by others (30, 41, 50). The proportion of hydrolyzable unknown N (HUN) (Table 8) tended to decrease with depth in all but the virgin Kalamazoo profile. This decrease was sharp in the lower depths of the Charity clay.

It would appear that the level of TKN, as well as the distribution of fractional forms in these profiles represents a dynamic equilibrium at each depth between the rate of addition of C and N (as plant debris or mobile materials eluviated from above) and the rate of removal (by mineralization and leaching or by conversion of one fractional form to another).

#### Effects of Cultivation on Distribution of N in Surface Soil Layers

##### Changes in Total Kjeldahl N

Disturbance of soils by tillage increased porosity and aeration, thereby increasing the rate of decomposition of plant residues. Breakdown of aggregates by soil-working equipment also exposes previously protected matrix surfaces to interaction with the microbial biomass and with chemical systems in percolating soil water. As a result, a larger proportion of the native soil organic matter can enter into active cycles of mobilization-immobilization turnover (21, 28, 32). The rate of recycling and extent to which the release of mineralized N can occur may be enhanced further when microbial activity is stimulated by additions of lime to unfavorably acid soils.

The above impacts of cultivation are expressed directly on surface layers that are actually disturbed by tillage operations.

In Table 10, recoveries of N and percentage distributions of fractional forms, as the means for surface layers to 0.15m in virgin soils, are compared with values found in the plow layer (0-0.15m) of their cultivated counterparts.

It can be calculated from these data that the magnitude of total Kjeldahl N losses attributable to cultivation was above 67% in the Charity clay and 65% in the Hodunk sandy loam. These values compare with declines of 60 to 70% observed after 80 to 100 years under moderately intensive to intensive management systems in the prairies and great plains of midwestern U.S.A. (13, 15, 16, 18).

In the cited studies, organic matter and N in surface soils decreased at a declining rate over a period of 60 to 80 years, after which a new equilibrium was established between annual inputs and losses of C and N. The percentage depletion of soil organic matter and N (to the point where reduced levels became stable) varied directly with cultivation intensity and inversely with such factors as the proportion of legumes in the rotation, the level of amendment with animal manures and fertilizers and the level of crop yields maintained.

The cultivated soils at all three sites in the present study had probably been cleared and brought under cultivation at least 75 years ago. The fact that two-thirds of the N initially present had apparently disappeared from the plow layers of Charity and Hodunk soils indicate that these two soils had attained stable equilibrium under depletive rotations involving mainly cultivated

Table 10. Distribution of organic N fractions in cultivated and virgin surface (0.00-0.15m) soils

Soil Type & Management	TKN†	Hydrolyzable N										NHN		THN/ NHN
		THN		AN		AAN		ASN		HUN				
	μg/g‡	μg/g	%	μg/g	%	μg/g	%	μg/g	%	μg/g	%	μg/g	%	
Charity clay														
Virgin§	3817	3016	79.0	738	19.3	1245	32.6	336	8.8	697	18.4	801	20.9	3.8
Cultivated	1264	1111	87.9	343	27.1	349	27.6	144	11.4	275	21.7	153	12.1	7.3
Kalamazoo sandy loam														
Virgin	3150	2493	79.1	587	18.6	979	31.0	327	10.3	600	19.0	657	20.9	3.8
Cultivated	2410	2167	89.9	517	21.4	832	34.5	233	9.7	585	24.3	243	10.0	8.9
Hodunk sandy loam														
Virgin	2432	1895	77.9	375	15.4	785	32.3	194	7.9	541	22.2	537	22.0	3.5
Cultivated	841	679	80.7	188	22.3	162	19.3	67	7.9	262	31.1	162	19.3	4.2
Means Virgin	3133	2468	78.8	567	17.8	1003	32.0	286	9.0	613	19.6	665	21.2	3.7
Means Cultivated	1505	1319	87.6	349	23.6	448	27.1	148	9.7	374	25.7	186	13.8	7.1

<sup>†</sup> TKN = Total Kjeldahl N; THN = Total hydrolyzable N; AN = Ammonium N; AAN = α-amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = Nonhydrolyzable N; THN/NHN = Total hydrolyzable N:nonhydrolyzable N ratio.

<sup>‡</sup> μg/g = μgN/g soil; % = percent of total Kjeldahl N.

<sup>§</sup> Virgin soil, average of 0.00-0.08m and 0.08-0.15m; Cultivated soil, 0.00-0.15m.

crops (Table 1). The calculated loss for the Kalamazoo soil was only 23%. Management here would appear to have been much less depletive, at least in recent years.

It is not known what cropping systems may have been used at these sites over the decades since they were first cleared. The alfalfa-grass cover had been in place on the Kalamzaoo soil for 8 years plus manure in the recent past. Normally, annual equilibria under forage legumes and grasses are shifted in the direction of net increases in soil organic matter and N. It may be inferred that the cultivated Kalamazoo was in a "soil building" rather than a "soil depleting" cycle at the time these samples were taken.

#### Changes in Fractional Forms of N

The quantities of total Kjeldahl N and all fractional forms in surface layers (Table 10) were very much lower in the cultivated than virgin soils. However, the decreases within fractional forms were not proportional to the decreases in total Kjeldahl N. This may be seen in Figs. 1, 2, and 3, where the percent decrease within fractions is entered beside each pair of bars depicting content.

In all three soils, the percent decrease in the NHN fraction (not hydrolyzable in 6M HCl) was very much greater than the overall decrease in total Kjeldahl N, whereas the decrease in total hydrolyzable N (THN) was less. These differential decreases in Figs. 1 to 3 are reflected in the percentage distributions in Table 10. The proportion of total Kjeldahl N susceptible to hydrolysis (THN)



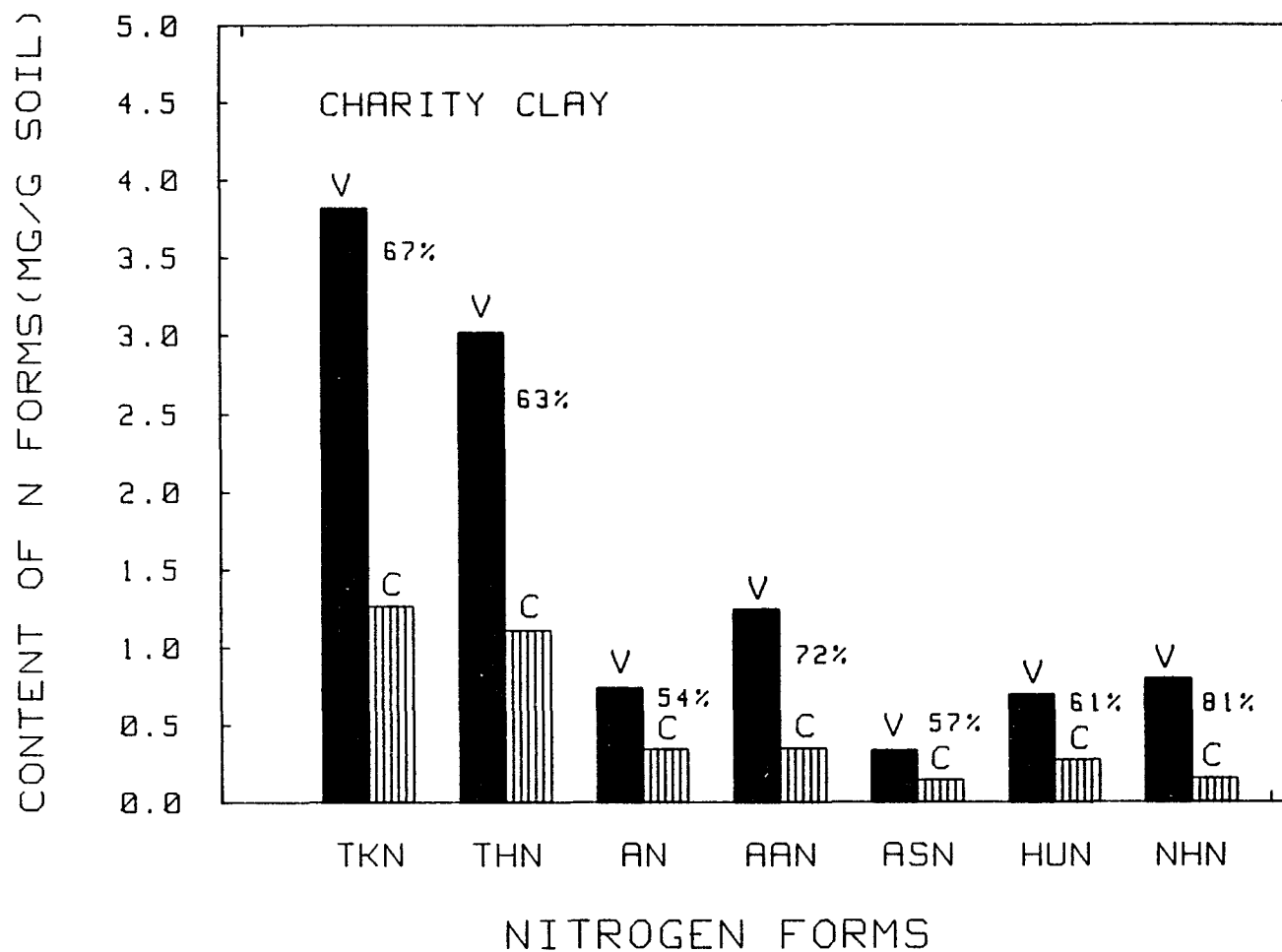


Fig. 1. Content of organic N fractions in cultivated (C) and virgin (V) surface (0-0.15m) in a Charity clay soil. Numbers beside each pair of bars indicates % decrease due to cultivation. TKN = total Kjeldahl N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N.

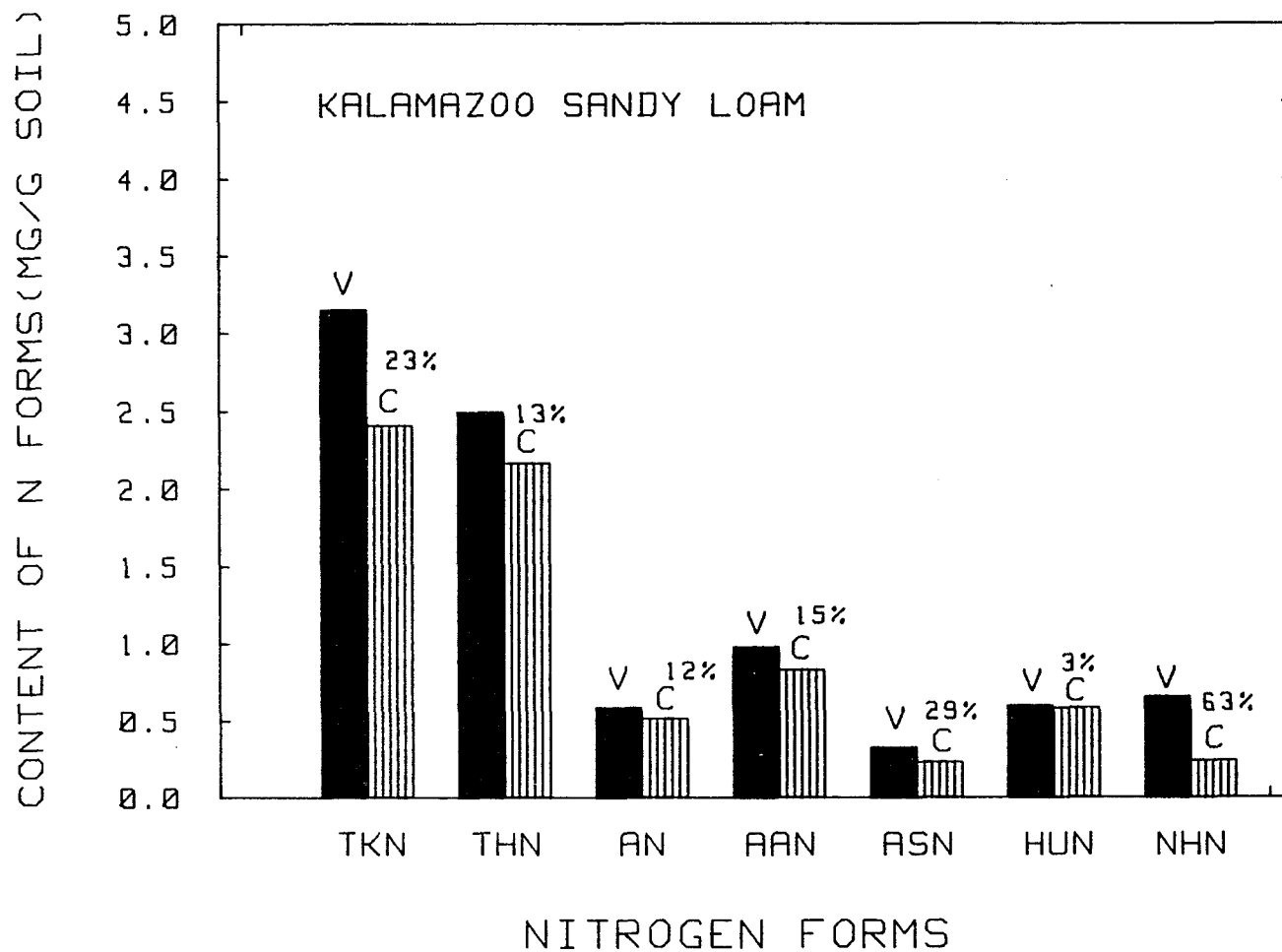


Fig. 2. Content of organic N fractions in cultivated (C) and virgin (V) surface (0-0.15m) in a Kalamazoo sandy loam soil. Numbers beside each pair of bars indicate % decrease due to cultivation. TKN = total Kjeldahl N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N.

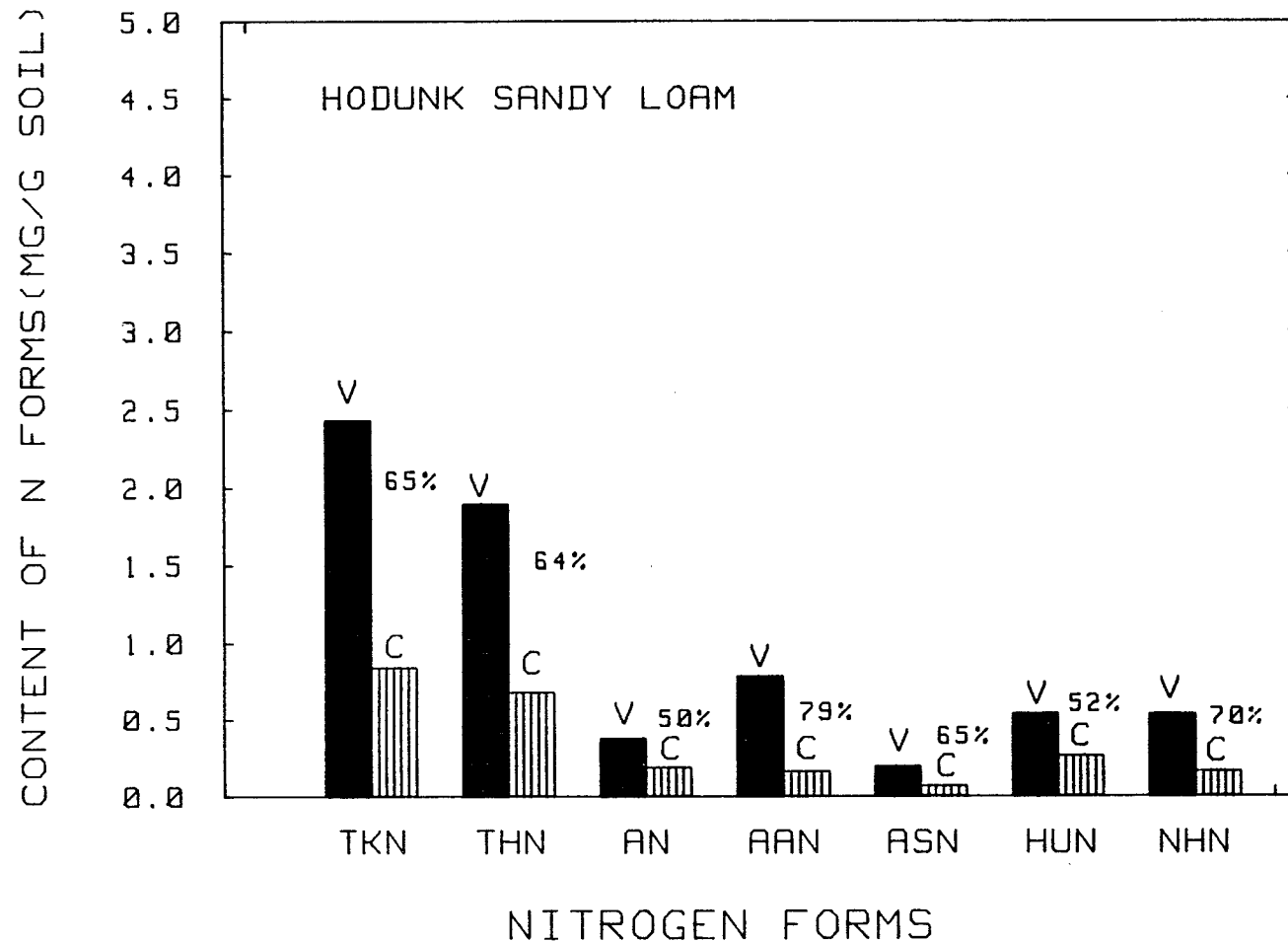


Fig. 3. Content of organic N fractions in cultivated (C) and virgin (V) surface (0-0.15m) in a Hodunk sandy loam soil. Numbers beside each pair of bars indicate % decrease due to cultivation. TKN = total Kjeldahl N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N.

increased, while the percentage not hydrolyzed (NHN) decreased. As a result, the ratio THN/NHN increased from 3.8 in the virgin Charity clay to 7.3 in the cultivated counterpart, and from 3.8 to 8.9 in the Kalamazoo soil. The increase from the Hodunk sandy loam was less, from 3.5 for virgin to 4.2 in cultivated soil.

Among the hydrolyzable forms in Table 10, the percentage distribution of hydrolyzable  $\text{NH}_4^+$  (AN) and the hydrolyzable unknown (HUN) fraction increased in all three cultivated surface soils. The proportion of total Kjeldahl N present as  $\alpha$ -amino acids (AAN) in the cultivated Kalamazoo had increased also, but had declined sharply with tillage in the Charity and Hodunk soils. Decreased proportions of amino sugar N (ASN) and serine + threonine N (STN) were found in the cultivated Charity, but their contribution to total Kjeldahl N in the other two soils was essentially unchanged to tillage.

An important effect of cultivation is the disruption of aggregated structures and the exposure of previously protected humic substances to the action of soil microbes and chemical systems in the soil solution (28). Modeling studies indicate that 50% of the humus in virgin soils may be protected by adsorption or entrapment in the soil matrix, whereas the degree of protection in soils under cultivation may be as low as 10% (32).

The large decreases (63 to 81%) in the NHN content of all three soils (Figs. 1 to 3) undoubtedly reflect the increased exposure and decreased stability of humic substances previously stabilized by adsorption, polymerization, condensation or entrapment.

These decreases in NHN were accompanied by relatively much smaller decreases in hydrolyzable  $\text{NH}_4^+$  (AN) and the unknown (HUN) fraction (Figs. 1 to 3). As the result of these differential decreases in content, the AN and HUN fractions actually increased as percent of total Kjeldahl N in cultivated soils (Table 10).

It is generally agreed that the N that is not hydrolyzed by 6M HCl (NHN fraction) exists mainly in the form of stable humic acids and humin; whereas, the hydrolyzable AN and HUN fractions originate in fulvic acids and less tightly bound peripheral groupings in humic acids and humin (32, 47, 51). As an average for all three soils, the ratios AN/NHN and HUN/NHN increased by a factor of 2 (Table 11). This again reflects increased exposure and decreased stability of humic substances due to cultivation. Similar relationships have not been pointed out by other authors, although instances can be found in published data where large losses of total N have occurred due to cultivation (24).

#### Fractional Contributions to Total Kjeldahl N Loss

In Fig. 4, fractional decreases have been represented as percent of total Kjeldahl N loss. In the Charity and Hodunk soils, the apparent contribution of the various fractions to loss was roughly proportional to the quantities and proportions present before cultivation (Table 10 and Figs. 1 and 3). This result is similar to the experience of other investigations (24, 29).

The results with the Kalamazoo soil were strikingly different (Fig. 4). The decrease in the NHN fraction accounted for

Table 11. Effect of cultivation on  $\text{NH}_4$  and unidentified N in acid hydrolysates in relation to nonhydrolyzable N.

Soil Type	AN/NHN <sup>†</sup>		HUN/NHN	
	Virgin	Cultivated	Virgin	Cultivated
Charity clay	0.9	2.2	0.9	1.8
Kalamazoo sandy loam	0.9	2.1	0.9	2.4
Hodunk sandy loam	0.7	1.3	1.9	1.8
Means	0.8	1.9	0.9	2.0

<sup>†</sup>AN = hydrolyzable  $\text{NH}_4^+$  N, HUN = hydrolyzable unknown N,

NHN = nonhydrolyzable N.

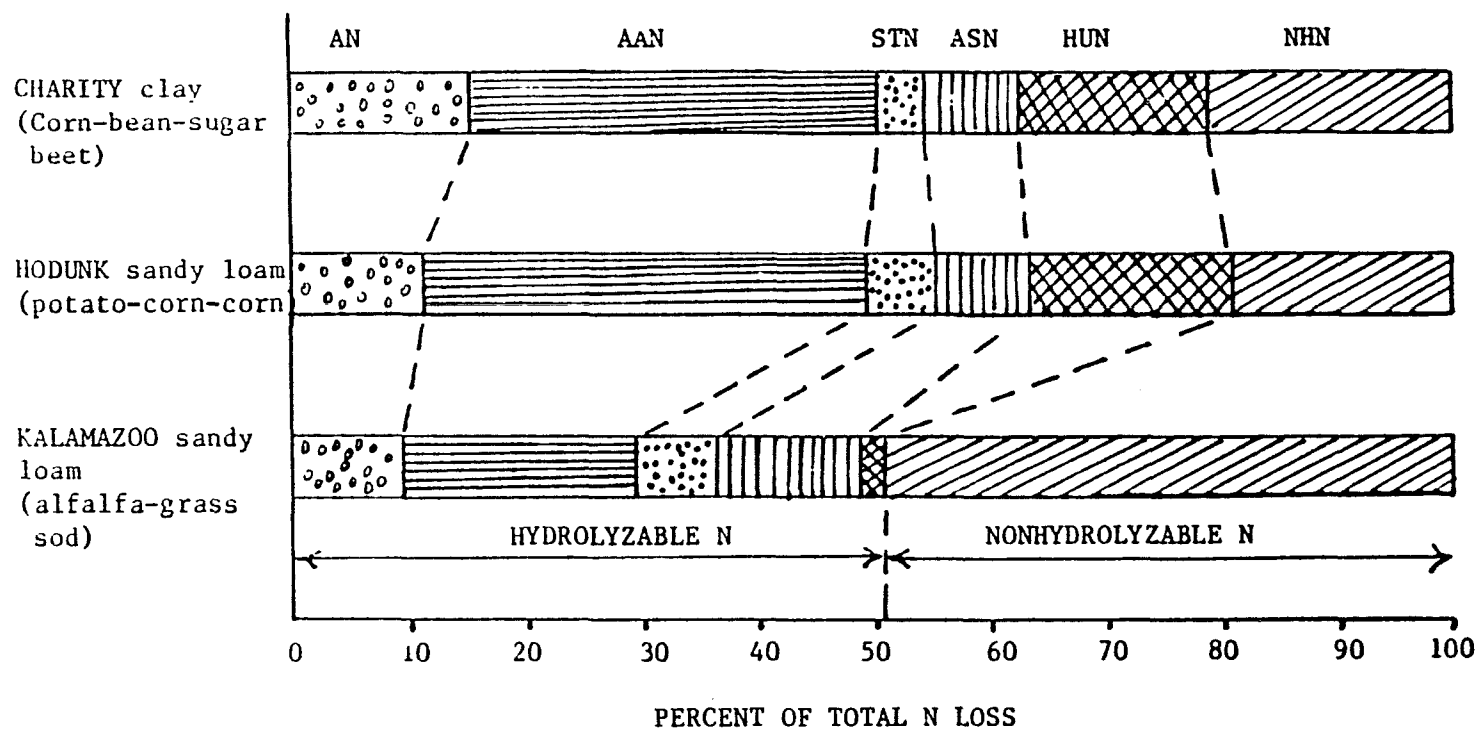


Fig. 4. Decrease in content of organic N fractions expressed as percent of total N loss due to cultivation.

AN = hydrolyzable N, AAN =  $\alpha$ -amino acid N, STN = serine + threonine N,  
ASN = amino sugar N, HUN = hydrolyzable unknown N, NHN = nonhydrolyzable N.

one-half of the total Kjeldahl N lost from the virgin soil. The apparent percent contributions of AN, AAN, and HUN were much less than in the other two soils and were also much less than their original proportion of total Kjeldahl N (Table 10). Decreases in ASN and STN, as percent of total loss in the Kalamazoo (Fig. 4), were similar to their percentage of total Kjeldahl N before cultivation.

Patterns of loss at the three locations are clearly related to differences in current management and, perhaps, also the soil pH (Table 1).

It is not known how long the cultivated Kalamazoo soil had been in alfalfa-grass at the time of sampling. It is apparent in Fig. 2 that under the protection afforded by sod cover residues and exudates from the legume-grass mixture were supporting a spectrum of N in hydrolyzable forms that was very similar to that in the virgin soil. The annual rate of return of N was such that the degree of depletion of all hydrolyzable forms was very much less than in the Charity clay (Fig. 1) or the Hodunk sandy loam (Fig. 3).

The degree of depletion of the NHN fraction in the cultivated Kalamazoo sandy loam was much greater than for the hydrolyzable fraction (Fig. 2). This may be residual evidence of more depletive management in the past, in which case the levels found in hydrolyzable forms would represent recoveries from more depleted levels prior to the establishment of the alfalfa-grass stand. It would appear that inputs of N due to  $N_2$ -fixation by the alfalfa may have equilibrated quickly with hydrolyzable fractions, whereas



further conversion to stable humic complexes may not have had time to proceed to equilibrium at a level of NHN approaching more closely that in the virgin soil.

The apparent fractional contributions to total Kjeldahl N loss as calculated for Fig. 4 serve to focus on changes that can be interpreted usefully in terms of equilibrium shifts due to depletive vs. conservative management practices. Obviously, they do not provide any basis for judging whether one form of N is more susceptible to mineralization than another, and therefore, more significant as a source of "available N" for crops. Comparison of Fig. 4 with Figs. 1, 2, and 3 does indicate that the hydrolyzable fractions respond more quickly to changes in management and are therefore more "active" than materials that are not hydrolyzed by acid.

## SUMMARY AND CONCLUSIONS

Effects of cultivation on organic matter content and on distributions of N in hydrolyzable and nonhydrolyzable forms were assessed by comparing data for paired virgin and cultivated profiles at three locations.

Decreases in organic carbon and total Kjeldahl N in cultivated surface soils and underlying subsoil layers were related to the intensity of current management. In a corn-navy bean-sugar beet rotation on Charity clay, organic C in the plow layer was reduced 62% from that in the wooded virgin soil to the same depth. The reduction for a potato-corn-corn sequence on Hodunk was 80%. By contrast, organic C in Kalamazoo sandy loam under alfalfa-grass sod was only 13% less than under forest cover.

Corresponding decreases in total Kjeldahl N were 67% and 65% for the Charity and Hodunk soils and 23% for the Kalamazoo. Decreases in the nonhydrolyzable fraction were substantially greater: 81% and 70% for the two currently tilled sites and 63% for the sodded Kalamazoo.

As a result, the proportion of nonhydrolyzable N to total Kjeldahl N in cultivated soils was reduced by approximately 40%. This reduction and a corresponding relative increase in the proportions of hydrolyzable  $\text{NH}_4^+$  and unidentified N were taken as evidence that

the stability of humic acids and humin had been weakened (their hydrolyzability increased) by increased exposure at matrix surfaces resulting from disturbance by tillage operations in all three locations.

Effects of current management became strikingly apparent when fractional declines were expressed as percentages of total Kjeldahl N loss. Under depletive cash crop systems on Charity and Hodunk soils, apparent contributions of the various fractional forms to total loss were roughly proportional to quantities and proportions present before cultivation, with the major proportion coming from the  $\alpha$ -amino acid fraction.

By contrast, inputs of N fixed by alfalfa in the Kalamazoo soil had supported a spectrum of N in hydrolyzable fractions that was similar to that in the virgin soils. The apparent percent contributions of  $\alpha$ -amino acids, hydrolyzable  $\text{NH}_4^+$  and unidentified N were much less than in the other two soils and less also than their original proportion of total Kjeldahl N.

It is concluded that acid hydrolyzable fractions include "active" forms that respond quickly to changes in current management. Changes involving stable humic substances in the nonhydrolyzable fraction apparently proceed much less rapidly and may reflect past management. It is unlikely, however, that susceptibility to acid hydrolysis can provide a basis for estimating the availability of N forms to crops without some basis in known management history for judging whether soils are in a depletive or conservative phase of management.

#### LITERATURE CITED

1. Aderikhin, P. G., Ye P. Tikhova, V. P. Kulahov, and N. Ya Degtyareva. 1960. Changes in the podzolic soils of the Murmansk Region under cultivation. *Soviet Soil Sci.* 4:379-383.
2. Bremner, J. M. 1949. Studies on soil organic matter. Part I. The chemical nature of soil organic nitrogen. *J. Agric. Sci.* 39:183-193.
3. Bremner, J. M. 1958. Amino sugars in soils. *J. Sci. Food Agric.* 9:528-532.
4. Bremner, J. M. 1959. Determination of fixed ammonium in soil. *J. Agric. Sci.* 52:147-160.
5. Bremner, J. M. 1965. Organic forms of nitrogen. In C. A. Black, et al. (eds.). *Methods of Soil Analysis, Part 2.* Agronomy 9:1238-1255.
6. Bremner, J. M. 1965. Total nitrogen. In C. A. Black, et al. (eds.). *Methods of Soil Analysis, Part 2.* Agronomy 9:1149-1178.
7. Bremner, J. M., and C. S. Mulvaney. 1983. Nitrogen--Total. In A. L. Page et al. (eds.). *Methods of Soil Analysis, (2nd ed.)*. 9:595-624.
8. Bremner, J. M., and K. Shaw. 1954. Studies on the estimation and decomposition of amino sugars in soil. *J. Agric. Sci.* 44:152-159.
9. Bundy, L. G., and J. M. Bremner. 1972. A simple titrimetric method for determination of inorganic carbon in soils. *Soil Sci. Soc. Amer. Proc.* 36:273-275.
10. Cheng, J. H., and J. Van Hove. 1964. Characterization of organic matter in European soils by nitrogen fractionation. *Pedologie.* 14:8-23.
11. Cornforth, I. S. 1968. The potential availability of organic nitrogen fractions in some Western Indian soils. *Exp. Agric.* 4:193-201.

12. Dalal, R. C. 1978. Distribution of organic nitrogen in organic volcanic and nonvolcanic tropical soils. *Soil Sci.* 125: 178-180.
13. Fritschen, L. J., and J. A. Hobbs. 1958. Effect of crop rotation and fertilizer treatment on the nitrogen and organic carbon contents of a prairie soil. *Soil Sci. Soc. Amer. Proc.* 22:439-441.
14. Grigor'yev, G. I. 1960. Diagnostic indices of sod-podzolic soils at various levels of cultivation. *Soviet Soil Sci.* 6:619-629.
15. Haas, H. J., C. E. Evans, and E. F. Miles. 1957. Nitrogen and carbon changes in Great Plains soils as influenced by cropping and soil treatments. Technical Bulletin No. 1164. USDA.
16. Hide, J. C., and W. H. Metzger. 1939. The effect of cultivation and erosion on the nitrogen and carbon of some Kansas soils. *Agron. J.* 31:625-632.
17. Hinman, W. C. 1964. Fixed ammonium in some Saskatchewan soils. *Can. J. Soil Sci.* 44:151-157.
18. Hobbs, J. A., and P. L. Brown. 1957. Nitrogen and organic carbon changes in cultivated western Kansas soils. *Kansas Agr. Exp. Sta. Bull.* 89.
19. Hobbs, J. A., and P. L. Brown. 1965. Effects of cropping and management on nitrogen and organic carbon contents of a western Kansas soil. *Kansas Agr. Exp. Sta. Tech. Bull.* 144.
20. Isirimah, N. O., E. F. A. Burutolu, D. A. Nwanchuku, and J. E. K. Aroh. 1981. Preliminary studies on the organic matter and nitrogen status of some soils of Rivers State. Paper presented at the National Conference in Agriculture, Rivers State Univ. of Sci. and Tech., Port Harcourt, Nigeria.
21. Jansson, S. L., and J. Persson. 1982. Mineralization and immobilization of soil nitrogen. In F. J. Stevenson, (ed.). *Nitrogen in Agricultural Soils.* *Agronomy* 22: 229-252.
22. Jenny, H. 1950. Causes of the high nitrogen and organic matter of certain tropical forest soils. *Soil Sci.* 69:63-69.
23. Jenny, H. 1960. Comparison of soil nitrogen and carbon in tropical and temperate regions. *Missouri Agric. Exp. Sta. Res. Bull.* 765:1-30.

24. Kenney, D. R., and J. M. Bremner. 1964. Effect of cultivation on the nitrogen distribution in soils. Soil Sci. Soc. Amer. Proc. 28:653-656.
25. Kahn, S. U. 1971. Nitrogen fractions in a gray wooded soil as influenced by long-term cropping systems and fertilizers. Can. J. Soil Sci. 51:431-437.
26. Khan, S. U., and F. J. Sowden. 1971. Distribution of nitrogen in the black Solonetzic and black Chernozemic soils of Alberta. Can. J. Soil Sci. 51:185-193.
27. Konovalonva, A. S. 1961. Comparative characteristics of sod-podzolic forest soils in various stages of cultivation. Soviet Soil Sci. 3:293-299.
28. Martel, Y. A., and E. A. Paul. 1974. Effects of cultivation on the organic matter of grassland soils as determined by fractionation and radiocarbon dating. Can. J. Soil Sci. 54:419-426.
29. Meints, V. W., and G. A. Peterson. 1977. The influence of cultivation on the distribution of nitrogen in soils of the Ustoll suborder. Soil Sci. 124:334-342.
30. Nommik, H. 1967. Distribution of forms of nitrogen in a podzolic soil profile from Garpenberg, Central Sweden. J. Soil Sci. 18:301-308.
31. Parker, D. I., F. J. Sowden, and J. J. Atkinson. 1952. The nitrogen distribution and amino acid content of certain soil organic matter fractions. Sci. Agric. 32:163-169.
32. Paul, E. A., and J. A. van Veen. 1979. The use of tracers to determine the dynamic nature of organic matter. p. 75-132. In J. K. R. Gasser (ed.). Modelling nitrogen from farm wastes. Applied Science Publishers, Ltd., London.
33. Porter, L. K., B. A. Stewart, and H. J. Haas. 1964. Effects of long-time cropping on hydrolyzable organic nitrogen fractions in some Great Plains soils. Soil Sci. Soc. Amer. Proc. 28:368-370.
34. Schulte, E. E. 1980. Recommended soil organic matter tests. In W. C. Dahnke, (ed.). Recommended chemical soil test procedures for the North Central Region. North Dakota Agr. Exp. Sta. Bull. 499 (Revised). N. D. State Univ., Fargo, N.D.

35. Singh, B. R., A. P. Uriyo, and B. J. Lontu. 1978. Distribution and stability of organic forms of nitrogen in forest soil profiles in Tanzania. *Soil Biol. Biochem.* 10:105-108.
36. Smith, S. J., and I. B. Young. 1975. Distribution of nitrogen forms in virgin and cultivated soils. *Soil Sci.* 120: 354-360.
37. Sowden, F. J. 1956. Distribution of amino acids in selected horizons of soil profiles. *Soil Sci.* 82:491-196.
38. Sowden, F. J. 1958. The forms of nitrogen in the organic matter of different horizons of soil profiles. *Can. J. Soil Sci.* 38:147-154.
39. Sowden, F. J. 1977. Distribution of nitrogen in representative Canadian soils. *Can. J. Soil Sci.* 57:445-456.
40. Sowden, F. J., S. M. Griffith and M. Schnitzer. 1976. The distribution of nitrogen in some highly organic tropical volcanic soils. *Soil Biol. Biochem.* 8:55-60.
41. Stevenson, F. J. 1957. Distribution of the forms of nitrogen in some soil profiles. *Soil Sci. Soc. Amer. Proc.* 21: 283-287.
42. Stevenson, F. J. 1957. Investigations of aminopolysaccharides in soils: I. Colorimetric determination of hexosamines in soil hydrolysates. *Soil Sci.* 83:113-122.
43. Stevenson, F. J. 1957. Investigations of aminopolysaccharides in soils: 2. Distribution of hexosamines in some soil profiles. *Soil Sci.* 84:99-106.
44. Stevenson, F. J. 1959. Carbon-nitrogen relationships in soil. *Soil Sci.* 88:201-208.
45. Stevenson, F. J. 1965a. Amino acids. *In* C. A. Black et al. (eds.). *Methods of Soil Analysis, Part 2.* Agronomy 9:1437-1451.
46. Stevenson, F. J. 1965b. Amino sugars. *In* C. A. Black et al. (eds.). *Methods of Soil Analysis, Part 2.* Agronomy 9:1429-1436.
47. Stevenson, F. J. 1982. *Humus Chemistry.* John Wiley and Sons, New York.
48. Stevenson, F. J. 1982. Organic forms of soil nitrogen. *In* F. J. Stevenson, (ed.). *Nitrogen in Agricultural Soils* Agronomy 22:67-122.

49. Stevenson, F. J. 1983. Nitrogen--Organic forms. In A. L. Page et al, (ed.). Methods of Soil Analysis, Part 2. Agronomy (2nd ed.). 9:625-641.
50. Stevenson, F. J., and D. C. Braids. 1968. Variation in the relative distribution of amino sugars with depth in some soil profiles. Soil Sci. Soc. Amer. Proc. 32:598-600.
51. Stout, J. D., K. M. Goh, and T. A. Rafter. 1981. Chemistry and turnover of naturally occurring resistant organic compounds in soil. In E. A. Paul and J. N. Ladd (eds.). Soil Biochemistry, Vol. 5 Marcel Dekker, Inc., N.J.
52. Walkley, A. 1935. An examination of methods for determining organic carbon and nitrogen in soils. J. Agr. Sci. 25: 598-609.
53. Walkley, A., and I. A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-37.



### CHAPTER III

#### INFLUENCE OF CROPPING SYSTEMS ON FORMS OF NITROGEN IN A CLAY SOIL

Organic matter and nitrogen continue to play significant roles in soil fertility and crop production. Maintaining and improving the fertile and productive status of agricultural soils require steady, but adequate, return of organic matter as crop residues to the soil through a planned intensive management practice. But intensive cultivation results in deterioration of soil properties which are costly and difficult to repair. The degradation of soil is often attributed to a gradual decline in organic matter which tends towards equilibrium with time. Moreover, crops are actual nutrient "miners" and "depositors." They are also potential toxin "excretors." Therefore, a planned selection and sequencing of crops is desirable in terms of adequate mineral nutrition, allelopathic effects of one crop species on another and yields.

The effectiveness of a cropping system in maintaining organic matter and N depends on the crop species in the rotation, the C/N ratio of the residues, duration of residue application, and incorporation method. Effects of crop species and cropping sequence on organic matter and N are due to differences in rooting habits and in quantity and quality of residues returned. For example, carbonaceous

residues low in N are decomposed by microorganisms at the expense of available soil N (24).

Studies of the effect of rotations indicated that organic matter and total N losses were least in rotations that included small grains and legumes with large or frequent amendments with livestock manures and/or fertilizers plus lime as needed (10, 12, 22, 23). Losses were greatest in continuous row cropping with little or no application of soil amendments (1, 8, 16, 27). In another study, continuous wheat, bluegrass and ladino clover-orchard grass pasture increased organic matter while continuous soybeans and corn reduced it over time (42). All treatments showed N loss except where peas were rotated with winter wheat. In the same study all treatments resulted in organic matter gains except plots in permanent fallow and those cropped 2 years with one intervening fallow in a 25-year rotation on a clay loam soil in Utah (11). Studies on the dryland soils of Kansas, from 1916 to 1956 (9) demonstrated that small grains grown continuously or alternating with fallow caused the smallest N and organic matter losses compared to continuous row crop, alternate row crop, and fallow which showed the greatest (15). Little information is available on rotations that include corn, navy beans, sugar beets in various combinations.

The types of crops grown do affect the degree of organic matter and N maintenance. However, investigators have also reported that specific management practices, such as fertilization, tillage practices, and residue application, may be more significant in maintaining organic matter and total N than the crop species.

In their 54- to 72-year study, White et al. (46) reported that NPK application was more effective in maintaining organic matter and N levels over time in the continuously cultivated than in the adjacent grassland soils. In a later 10-year study, Lee and Bray (18) reported that the overall trend of absolute N loss with time was evident in all treatments, although PK fertilization appeared to maintain the organic matter and N contents at higher levels relative to the untreated plots. They concluded that applications of more fertilizer might have increased the organic matter and N contents. These findings appear to have been confirmed by the work of Mazurak and Conrad (20). They found that application of N fertilizers on grasses, alfalfa, and small-grains increased the total N content of Brunizem, Chernozem, and Chestnut surface soils over a 7-year cropping history. However, large applications of NPK and lime, in another long-term study on 3 soil types, showed continuing decline in total N with time (21). In another study, Young et al. (47) found that total N and OM content declined regardless of the fertilizer treatment, but the rate of decline was greater in the check plots than in those that received the fertilizer treatment.

In general, these studies indicate that the effectiveness of fertilization in maintaining levels of N and organic matter over time may vary widely with cropping system, soil type, and climatic conditions.

Other investigations have examined the role of tillage practices in maintaining organic matter and total N. In general, losses of organic matter and N are reported for tillage practices that greatly

disturb soil structure or leave the soil unprotected by vegetation or residues for periods of time (12, 14, 23, 43). The degree of depletion increases with increasing intensity and frequency of tillage and with decreasing proportion of sod crops, notably legumes, in the rotations. Current practices are re-emphasizing the need to adopt no-till or minimum tillage practices as a measure for organic matter and N maintenance.

In crop rotations, each crop in the sequence affects the physical, chemical, and biological properties of the soil in varying degrees. Changes in soil properties affect the growth and yield of succeeding crops. An important way that crops affect soil properties is the return of organic matter as crop residues after harvest of the crops. In the rotation, the type and amount of crop residues returned annually affect the content and proportion of the various organic N fractions due to differences in crop composition, decomposition rates and suitability as substrates for the microbial population.

Cropping sequences and management practices that maintain high turnover rates through frequent return of carbonaceous residues tend to increase the contents of soil organic matter and nitrogen and change the relative proportions and composition of their various fractions. In general, changes in organic N fractions are proportional to significant changes in soil organic matter and total N. However, variations in fractional distribution can be observed in the absence of significant differences in organic matter and total soil N. This is important in short-term studies where remarkable

differences in total soil N due to cropping sequence and residue additions may not be noticed, but the proportions of the various organic forms may vary significantly.

Absolute contents of these organic forms vary widely in soils and variations are not only due to the quality and quantity of crop residues, but also due to differences in extraction, fractionation, and purification procedures. Of the total soil N, 30 to 50% occur as amino acid N, 5 to 24% as amino sugars, and 20 to 35% as acid-insoluble N (2, 6, 30, 34, 35, 36, 41).

In a long-time rotation study on a Flanagan silt loam (Brunizem), the corn-oats-clover rotation with annual applications of farmyard manure and crop residues had a higher proportion of the total N as amino acid N than the continuous corn and corn-oats rotations without manure and residue additions (33). The relative distribution of amino acids varied with rotations. However, it was not apparent from this study whether the observed differences were due to the inclusion of clover in the rotation, the addition of manure and crop residues, or a combination of both.

The proportions of total N as amino acid N and amino sugar N in soils from a 5-year rotation of grains and legumes were significantly greater than those from a wheat-fallow system even though there were no remarkable differences in total soil N (17). This study indicated that legumes in a rotation make a significant contribution to the formation of nitrogenous compounds in soils. Cropping systems can also have a significant effect on the kinds of amino acids in the amino acid fraction of the soil (31). On the

other hand, it has been reported that the incorporation of leguminous residues tended to lower the  $\alpha$ -amino acid N due to more complete degradation of the amino acids in the crop residues compared to carbonaceous residues such as corn (13).

Under field conditions, independent effects of crop residues are difficult to separate from the effects of several other environmental variables. In rotation studies, the effects attributed to crop residues are cumulative for previous treatments in the particular cropping sequence. Furthermore, accurate measurements of amounts returned annually by each crop type in the sequence are hard to come by. Only estimates are used to interpret results in most residue studies in cropping systems under field conditions.

In this study, the cropping systems involve alfalfa, navy beans, corn, and sugar beets, occurring from 25 to 75% of the time in the rotation. The objectives of this investigation were:

1. To determine the influence of cropping systems on the changes in soil organic matter and total N with time in a Charity clay.
2. To determine the content, proportion, and relative change of organic N fractions as influenced by various cropping systems.

## MATERIALS AND METHODS

### Field Experiment

A cropping system research project was initiated in 1972 on the Bean and Beet Research Farm in the Saginaw Valley of Michigan.

The objectives of the study were:

1. To determine the effect of rotation length, cropping system, and cropping sequence on production, yield, and quality of navy beans and sugar beets
2. To evaluate the effect of these systems on specific soil properties related to yield.

The seven cropping systems in this investigation were selected from twelve cropping systems in the whole research project. They included the following crops: corn (Zea mays L.), sugar beets (Beta vulgaris L.), navy beans (Phaseolus vulgaris L.), oats (Avena sativa L.), and alfalfa (Medicago sativa L.). The selected systems were:

1. C-Bn-Bn-SB
2. C-C-Bn-SB
3. C-C-C-SB
4. C-SB
5. Bn-SB
6. O-A-Bn-SB
7. O-Bn-SB

C = Corn; Bn = Navy beans;  
SB = Sugar beets; O = oats;  
A = Alfalfa

The complete sequence of crops in each rotation was grown each year.

All crops received adequate  $P_2O_5$  and micronutrients based on soil test levels. No additional fertilizer K was applied due to an adequate soil test K level. Annual N applications and crops for each year in the rotation are indicated on Table 1.

The plots (5.73 x 20.12m) were laid out on a Charity clay in a randomized complete block design with 4 replications.

#### Soil Type

The soil type was a Charity clay (Aeric, Hapleaquept, fine, illitic, calcareous, mesic) (Appendix B3). The soil test results for the general research area were: pH, 7.7; Bray  $P_1$  phosphorus, 38 kg/ha; exchangeable K, 506 kg/ha; exchangeable Ca, 11,267 kg/ha; exchangeable Mg, 1,852 kg/ha and percent organic matter, 4.3 (26).

#### Soil Sampling

In June, 1972, 20 core samples were randomly taken from the plow layer (0-0.23 m) of each plot. All plots which had been in the crops listed for 1983 Table 1 were sampled again in November, 1983. A composite sample for each plot was obtained after passing the core samples through a 5 mm screen. Surface residues were removed from the samples. The air-dried samples were first ground to pass through a 2 mm sieve and aliquots were then ground to pass an 0.18 mm sieve before being used for the various analyses.



Table 1. Crops grown and supplemental N applied to cropping systems from 1972 to 1983<sup>†</sup>

Year	C-Bn-Bn-Sb <sup>‡</sup>		C-C-Bn-SB		C-C-C-SB		C-SB		Bn-SB		O-A-Bn-SB		O-Bn-SB	
	Crop	Suppl. N <sup>§</sup>	Crop	Suppl. N	Crop	Suppl. N	Crop	Suppl. N	Crop	Suppl. N	Crop	Suppl. N	Crop	Suppl. N
		kg/ha		kg/ha		kg/ha		kg/ha		kg/ha		kg/ha		kg/ha
1972	C	150	Bn	30	C	150	C	150	Bn	30	O	56	O	56
1973	Bn	28	SB	50	C	168	SB	50	SB	84	A	0	Bn	28
1974	Bn	28	C	224	C	106	C	224	Bn	28	Bn	28	SB	50
1975	SB	50	C	140	Sb	50	SB	50	SB	84	SB	50	O	56
1976	C	168	Bn	28	C	224	C	224	Bn	28	O	56	Bn	28
1977	Bn	28	SB	56	C	168	SB	56	SB	84	A	0	SB	56
1978	Bn	28	C	168	C	168	C	224	Bn	28	Bn	28	O	56
1979	SB	56	C	168	SB	56	SB	56	SB	84	SB	56	Bn	28
1980	C	168	Bn	128	C	168	C	224	Bn	28	O	56	SB	56
1981	Bn	28	SB	56	C	168	SB	56	SB	84	A	0	O	56
1982	Bn	28	C	168	C	168	C	224	Bn	28	Bn	28	Bn	28
1983	SB	56	C	168	SB	56	SB	56	SB	84	SB	56	SB	56

<sup>†</sup> Each crop in each cropping system was grown each year. Samples for this study were taken in June 1972 and November 1983.

<sup>‡</sup> C = Corn; Bn = Navy beans; SB - sugar beets; O = Oats; A = Alfalfa

<sup>§</sup> N in basal fertilizer at planting: Corn, 40; beans, 60; beets, 30; oats, 30; alfalfa, none

SOURCE: Research Reports. 1972 to 1983. Saginaw Valley bean-beet-research farm and related bean-beet research, MSU, Agr.- Exp. Stn.

### Laboratory Analyses

Total Kjeldahl N was determined by semimicro Kjeldahl methods described by Bremner (3), Bundy and Bremner (7), and Bremner and Mulvaney (5).

Easily oxidized organic C was determined by colorimetric method described by Schulte (28). This method involves chromic acid oxidation for determination of easily oxidized material through spontaneous heat. The method was standardized against the Walkely-Black method (44, 45). Organic matter was taken by multiplying %C by 1.724.

C/N ratio was taken as the ratio of total N to C.

Total hydrolyzable N(THN), hydrolyzable ammonium N (AN), amino acid N (AAN), amino sugar N (ASN), hydrolyzable unknown N (HUN), and nonhydrolyzable N (NHN) were determined by methods described by Bremner (4) and Stevenson (37, 38, 40).

### Statistical Analyses

Data were subjected to analysis of variance and other essential analyses using methods described by Snedecor and Cochran (29), Steel and Torrie (32) and Little and Hills (19).

## RESULTS AND DISCUSSION

### Effect of Cropping System on the Distribution of N Over Time

#### Changes in Total Kjeldahl N and Organic Carbon

The contents of organic carbon and total Kjeldahl N in 1972 and after 11 years of rotational cropping are shown in Table 2. The quantities were lower in 1983 than in 1972 in all cropping systems. The decline of total Kjeldahl N and organic carbon due to cropping ranged from 5.9 to 10.5% and 12.3 to 17.0%, respectively. This represents 0.5 to 1.0% loss of N and 1.1 to 1.5% loss of organic carbon annually over the 11-year cropping period. This compares with 1.07% and 1.15% annual loss of soil N and organic C, respectively, over a 37-year cropping period in the Great Plains (12). Information concerning cropping practices prior to 1972 is not available. The small decline of soil N and organic carbon appears to indicate the establishment of equilibrium between the rate of annual inputs and losses. The C/N ratios declined in all cropping systems over time. The average C/N change ratio of 0.90 was very similar to the values for the individual cropping systems (Table 2).

Although organic carbon and soil N decreased over time, the percentage depletion did not appear to vary significantly among the cropping systems. This appeared to indicate that all the cropping

Table 2. Effect of cropping system on total Kjeldahl N and organic carbon levels and carbon-nitrogen ratio in a Charity clay soil.

Cropping System	O.C <sup>†</sup>		% <sup>‡</sup> Change	C:N		% Change	C:N	
	1972	1983		1972	1983		Ratio 83/72	
C-Bn-Bn-SB	16.8	14.7	-12.5	9.33	8.49	- 9.00	0.90	
C-C-Bn-SB	16.5	14.4	-12.7	9.21	8.62	- 6.40	0.93	
C-C-C-SB	17.6	14.7	-16.5	9.46	8.54	- 9.72	0.90	
C-SB	16.6	14.2	-14.5	9.54	8.40	-11.90	0.88	
Bn-SB	16.4	13.6	-17.1	8.86	8.29	- 6.43	0.93	58
O-A-Bn-SB	17.6	14.7	-16.5	9.83	8.85	- 9.96	0.90	
O-Bn-SB	16.2	13.9	-14.2	9.36	8.22	-12.20	0.87	
Means	16.8	14.3	-14.9	9.38	8.46	- 9.80	0.90	
LSD <sub>0.05</sub>	NS <sup>§</sup>	NS	--	NS	NS	--	--	

<sup>†</sup>O.C = Easily oxidizable organic carbon

<sup>‡</sup>% Change = The percentage of mean values with cropping, based on initial values

<sup>§</sup>NS = Not significant at 95% probability level

systems, regardless of the proportion of corn or legume in the rotations, contributed to a "soil depleting," rather than a "soil building" cycle. The eleven-year cropping period seemed short for significant differences to occur among the cropping systems, though real differences occurred. In the virgin-cultivated comparisons of Chapter II, declines in organic carbon and soil N were large and these reflected differences in intensity of current management among the sampling sites.

#### Changes in Fractional Forms of N

The quantities and distribution of fractional N forms are presented in Table 3. The fractional forms of N increased or decreased after eleven years of cropping.

The mean values show that the present decrease of total Kjeldahl N not hydrolyzed by 6M HCl (NHN) was about three times as great as total Kjeldahl N. The percent decrease in total hydrolyzable N (THN) was less than that of total Kjeldahl N (Table 3). The proportion of TKN present as nonhydrolyzable N decreased by 15%, while that of THN increased by 4% (Table 4). That give an average increase in THN/NHN ratio from 4.0 in 1972 to 5.1 in 1983 (Table 5).

In general, the proportion of TKN as hydrolyzable  $\text{NH}_4$  (AN) and hydrolyzable unknown N (HUN) increased, while that of amino acid N (AAN) and amino sugar N (ASN) decreased in most cropping systems (Table 4). Furthermore, the concentration of NHN (Table 3) decreased by 20% on the average compared to decreases of 2% (THN) and 6% (TKN).

Table 3. Effect of cropping system on the concentration of nitrogen forms and percentage change.

Cropping System	Hydrolyzable N																				
	TKN †		% ‡	THN §		% ¶	AN		% ¨	AAN		% ¨	ASN		% ¨	HUN		% ¨	NHN		% ¨
	1972	1983		1972	1973		1972	1983		1972	1983		1972	1983		1972	1983		1972	1983	
	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change	Change				
	---mg/kg---			---mg/kg---			---mg/kg---			---mg/kg---			---mg/kg---			---mg/kg---			---mg/kg---		
C-Bn-Bn-SB	1802	1732	- 3.9	1470	1416	- 4.0	433	453	+ 4.6	634	449	-29.2	261	118	-54.8	147	396	+169	332	316	- 3.4
C-C-Bn-SB	1798	1677	- 6.7	1401	1390	- 0.8	455	424	- 6.8	550	492	-10.5	158	152	- 3.9	238	322	+ 35.3	397	287	-27.7
C-C-C-SB	1863	1727	- 7.3	1468	1479	+ 0.7	479	477	- 0.4	603	497	-17.6	171	134	-21.6	215	371	+72.6	395	248	-37.2
C-SB	1746	1695	- 2.9	1423	1394	- 2.0	421	410	- 2.6	555	467	-15.8	189	184	- 2.6	258	333	+29.0	323	301	- 6.8
Bn-SB	1851	1648	-10.9	1398	1429	+ 2.2	428	410	- 4.2	586	555	- 5.3	189	155	-18.0	195	309	+58.5	453	219	-51.6
O-A-Bn-SB	1793	1666	- 7.0	1484	1377	- 7.2	404	435	+ 7.7	577	488	-15.4	188	140	-25.5	315	314	- 0.3	309	289	- 6.5
O-Bn-SB	1733	1696	- 2.1	1425	1401	- 1.6	453	399	-11.9	528	510	- 3.4	189	134	-29.1	255	358	+40.4	307	295	- 4.5
Means	1798	1691	- 5.8	1439	1412	- 1.8	439	430	- 1.9	576	494	-13.9	192	145	-22.2	232	343	+57.8	359	279	-19.6
LSD <sub>0.05</sub>	NS	NS	--	NS	NS	--	43.5	32.2	--	39.7	NS	--	45.5	NS	--	84.4	NS	--	NS	NS	--

† TKN = Total Kjeldahl nitrogen

‡ % Change = Percentage change of mean values with cropping, based on initial values.

§ THN = Total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N.

Table 4. Effect of cropping system on the distribution of total Kjeldahl N among organic N fractions and percent change.

Cropping System	Hydrolyzable N															Non-hydrolyzable N (NHN)		
	THN†			AN			AAN			ASN			HUN					
	% ‡			% ‡			% ‡			% ‡			% ‡			% ‡		
	1972	1983	Change	1972	1983	Change	1972	1983	Change	1972	1983	Change	1972	1983	Change	1972	1983	Change
C-Bn-Bn-SB	81.6	81.8	+ 0.2	24.0	26.1	+ 8.8	35.2	25.9	-26.4	14.5	6.8	-53.1	8.2	22.8	+178.0	18.4	18.2	- 1.1
C-C-Bn-SB	77.9	82.8	+ 6.3	25.3	25.3	0.0	30.6	29.3	- 4.2	8.8	9.1	+ 3.4	13.2	19.2	+ 45.4	22.0	17.1	-22.3
C-C-C-SB	78.8	85.6	+ 8.6	25.7	27.6	+ 7.4	32.4	28.8	-11.1	9.2	7.7	-16.3	11.5	21.5	+ 86.9	21.2	14.4	-32.1
C-SB	81.5	82.2	+ 0.8	24.1	24.2	+ 0.4	31.8	27.5	-13.5	10.8	10.8	0.0	14.7	19.6	+ 33.3	18.5	17.8	- 3.8
Bn-SB	75.5	86.7	+14.8	23.1	24.9	+ 7.8	31.6	33.6	+ 6.3	10.2	9.4	-7.8	10.5	18.8	- 79.0	24.5	13.3	-45.7
O-A-Bn-SB	82.7	82.6	- 0.1	22.5	26.1	+16.0	32.2	29.3	- 9.0	10.4	8.4	-19.2	17.5	18.8	+ 7.4	17.2	17.1	- 0.6
O-Bn-SB	82.2	82.6	- 0.5	26.1	23.5	- 9.9	30.5	30.1	- 1.3	10.9	7.9	-27.5	14.7	21.1	+ 43.5	17.7	17.3	- 2.3
Means	80.0	83.5	+ 4.3	24.4	25.4	+ 4.3	32.0	29.2	8.6	10.7	8.6	-17.2	12.9	20.2	+ 67.6	19.9	16.5	-15.4
LSD <sub>0.05</sub>	NS	NS	--	NS	2.08	--	NS	2.54	--	2.73	NS	--	3.85	NS	--	NS	NS	--

† THN = Total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = non-hydrolyzable N; TKN = total Kjeldahl N.

‡ % change in percentage distribution of TKN.

Table 5. Effect of cropping system on total hydrolyzable N (THN), hydrolyzable ammonium (AN), and hydrolyzable unknown N (HUN) in relation to nonhydrolyzable N (NHN)

	THN/NHN			AN/NHN			HUN/NHN		
	1972	1983	Ratio 83/72	1972	1983	Ratio 83/72	1972	1983	Ratio 83/72
C-Bn-Bn-SB	4.51	4.45	0.98	1.32	1.42	1.07	0.45	1.24	1.75
C-C-Bn-SB	3.52	4.84	1.37	1.14	1.47	1.28	0.59	1.12	1.89
C-C-C-SB	3.71	6.05	1.63	1.21	1.95	1.61	0.54	1.51	2.79
C-SB	4.40	4.62	1.05	1.30	1.36	1.04	0.79	1.10	1.39
Bn-SB	3.08	6.54	2.12	0.94	1.87	1.98	0.42	1.41	3.35
O-A-Bn-SB	4.78	4.73	0.98	1.30	1.49	1.14	1.01	1.07	1.05
O-Bn-SB	4.62	4.73	1.02	1.46	1.35	0.92	0.82	1.21	1.47
Means	4.01	5.06	1.26	1.22	1.54	1.26	0.65	1.23	1.89



These trends were reflected by increases in overall mean AN/NHN ratio from 1.22 in 1972 to 1.54 in 1983, and HUN/NHN ratio from 0.65 in 1972 to 1.23 in 1983 (Table 5). These changes indicate that cropping tended to increase exposure to the action of the soil biomass and decrease stability of previously protected humic substances. The increase in concentration of AN and HUN were due to the fact that these fractions may have originated in fulvic acids and less tightly bound peripheral groupings on humic acids and humic (25, 39).

With most rotations, the distribution among hydrolyzable fractions shifted sharply towards larger ratios for HUN/THN, whereas the AAN/THN and ASN/THN ratios decreased (Table 6). These changing ratios indicate the "active nature of the hydrolyzable N fractions and their responsiveness to management." However, the percent distribution of the organic N fractions was not appreciably different for the different cropping systems.

The lack of significant differences in concentrations and proportions of the organic N forms among cropping systems may be due to the fact that the samples were taken in 1983 followed sugar beets in all but one treatment (Table 1). The eleven-year cropping period may have been too short a time to produce significant differences. However, the trends in N cycling between the NHN and THN and the fractions within THN were similar to the findings in Chapter II, but less dramatic.

Table 6. Effect of cropping system on hydrolyzable  $\text{NH}_4^+$  (AN), amino acid N (AAN), amino sugar N (ASN) and hydrolyzable unknown N (HUN) in relation to the total hydrolyzable N (THN)

	AN/THN			AAN/THN			ASN/THN			HUN/THN		
	1972	1983	Ratio 83/72	1972	1983	Ratio 83/72	1972	1983	Ratio 83/72	1972	1983	Ratio 83/72
C-Bn-Bn-SB	0.29	0.32	1.10	0.43	0.32	0.74	0.18	0.08	0.44	0.10	0.23	1.77
C-C-Bn-SB	0.32	0.30	0.94	0.39	0.35	0.90	0.11	0.11	1.00	0.17	0.23	1.35
C-C-C-SB	0.33	0.32	0.97	0.41	0.34	0.82	0.12	0.09	0.75	0.15	0.25	1.67
C-SB	0.30	0.29	0.97	0.39	0.34	0.87	0.13	0.13	1.00	0.18	0.24	1.33
Bn-SB	0.31	0.29	0.94	0.42	0.39	0.93	0.14	0.11	0.79	0.13	0.22	1.38
O-A-Bn-SB	0.27	0.32	1.19	0.38	0.35	0.92	0.12	0.10	0.83	0.21	0.23	1.00
O-Bn-SB	0.31	0.28	0.90	0.36	0.36	1.00	0.13	0.10	0.77	0.17	0.26	1.37
Means	0.30	0.30	1.00	0.40	0.35	0.88	0.13	0.10	0.77	0.16	0.24	1.50

## SUMMARY AND CONCLUSIONS

The effects of cropping systems on the content of organic carbon and distribution of nitrogen forms over an eleven-year period were evaluated.

Organic carbon and total Kjeldahl N decreased with cropping for all cropping systems. Total Kjeldahl N losses ranged from 2.1% for the O-Bn-SB rotation to 11.4% for the Bn-SB rotation. Organic C losses ranged from 13% for C-Bn-Bn-SB and C-C-Bn-SB rotations to 17% for the Bn-SB rotation. The overall average decrease for organic C was 14.9%, for TKN it was 5.8%.

The 5.8% decrease in TKN was comprised of a 19.6% decrease in quantity of nonhydrolyzable N (NHN) and a 1.8% decrease in the quantity of hydrolysable N (THN). These decreases can be compared with data for Charity clay in Fig. 1 of Chapter II (p. 31) where decreases due to cultivation were 67% for TKN, 81% for NHN and 63% for THN.

Thus, it appeared that management under all seven cropping systems continues to be depletive. The annual disturbance of the soil matrix, due to tillage, serves to expose structurally protected colloidal surfaces to microbial and chemical activities that decrease the stability of humic complexes. An expected consequence would be the differentially greater decline in NHN relative to THN observed here, as well as in the profile study of Chapter II.

The average change in composition for the seven cropping systems was not great (from THN/NHN = 4.01 in 1972 to 5.06 in 1983). This change may be compared with the profile study, where THN/NHN increased from 3.8 in virgin Charity clay to 7.3 in the cultivated soil. Nevertheless, the relatively greater retention of N in active forms suggests an increased rate of annual turnover. This may be due, perhaps, to higher levels of yield and residues returned since 1972.

Among the hydrolyzable N fractions, hydrolyzable ammonium (AN) remained constant at about 25% of TKN, whereas it had increased from 18% of TKN in the virgin soil to 24% in the cultivated analog. Unidentified N (HUN) increased relative to TKN in both studies, but the final proportions were similar (20 to 22%). The proportion of amino acids (AAN) decreased in both studies, but over a similar range (28 to 32% of TKN). Amino sugar composition decreased from 11% to 9% of TKN, as a mean for the rotations, but remained constant at about 9% in the profile study. These values are within the range reported by others, but they do not point to any clear trends.

No significant differences for cropping systems had developed during the 11-year period between 1972 and 1983. Differences may develop over a longer period of time as new equilibria between inputs and removals of N and C are approached.

## LITERATURE CITED

1. Bartholomew, W. V., and D. Kirkham. 1960. Mathematical descriptions and interpretations of culture induced soil nitrogen changes. Int. Congr. Soil Sci. Trans. 7th (Madison, Wis.), II: 471-477.
2. Bremner, J. M. 1958. Amino sugars in soils. J. Sci. Food Agric. 9:528-532.
3. Bremner, J. M. 1965. Total nitrogen. In C. W. Black (ed.), Methods of Soil Analysis, Part 2. Agronomy. 9:1149-1178.
4. Bremner, J. M. 1965. Organic forms of nitrogen. In C. A. Black, (Ed.). Methods of Soil Analysis, Part 2. Agronomy. 9:1238-1255.
5. Bremner, J. M., and C. S. Mulvaney. 1983. Nitrogen--Total. In A. L. Page et al, (ed.). Methods of Soil Analysis, Part 2. Agronomy (2nd ed.). 9:595-624.
6. Bremner, J. M., and K. Shaw. 1954. Studies on the estimation and decomposition of amino sugars in soil. J. Agric. Sci. 44:152-159.
7. Bundy, L. G., and J. M. Bremner. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Amer. Proc. 36:273-275.
8. Campbell, C. A. 1978. Soil organic carbon, nitrogen, and fertility, pp. 173-271. In M. Schnitzer and S. U. Khan (eds.). Soil Organic Matter. Elsevier North-Holland, New York.
9. Fahad, A. A., L. N. Mielke, A. D. Flowerday, and D. Swartzendruber. 1977. Soil physical properties as affected by soybean and other cropping sequences. Soil Sci. Soc. Amer. J. 46:377-381.
10. Gosdin, G. W., M. Stelly, and W. E. Adams. 1950. The organic matter and nitrogen content and carbon-nitrogen ratio of Cesil Soil as influenced by different cropping systems on Classes II, III, and IV land. Soil Sci. Soc. Amer. Proc. 14:203-208.

11. Greaves, J. E., and A. F. Bracken. 1946. Effect of cropping on the nitrogen, phosphorus, and organic carbon content of a dry-farm soil and on the yield of wheat. *Soil Sci.* 62:355-364.
12. Haas, H. J., C. E. Evans, and E. F. Miles. 1957. Nitrogen and carbon changes in Great Plains soils as influenced by cropping and soil treatments. *Tech. Bull.* 1164 USDA.
13. Harrison, R. M. 1963. Quantitative and qualitative changes in soil organic matter as related to residue additions, cropping sequence and management. Ph.D. Dissertation, Michigan State University, East Lansing, Michigan.
14. Hobbs, J. A., and P. L. Brown. 1957. Nitrogen and organic carbon changes in cultivated western Kansas soils. *Kansas Agr. Exp. Sta. Bull.* 89.
15. Hobbs, J. A., and P. L. Brown. 1965. Effects of cropping and management on nitrogen and organic carbon contents of a western Kansas soil. *Kansas Agr. Exp. Stn. Tech. Bull.* 144.
16. Johnston, J. R., G. M. Browning, and M. B. Russell. 1942. The effect of cropping practices of aggregation, organic matter content, and loss of soil and water in the Marshall silt loam. *Soil Sci. Soc. Amer. Proc.* 7:105-107.
17. Khan, S. U. 1971. Nitrogen fractions in a grey wooded soil as influenced by long-term cropping systems and fertilizers. *Can. J. Soil Sci.* 51:431-437.
18. Lee, C. K., and R. H. Bray. 1949. Organic matter and nitrogen contents of soils as influenced by management. *Soil Sci.* 68:203-212.
19. Little, T. M., and F. J. Hills. 1978. *Agricultural Experimentation Design and Analysis.* John Wiley and Sons, New York.
20. Mazurak, A. P., and E. C. Conard. 1966. Changes in content of total nitrogen and organic matter in three Nebraska soils after seven years of cropping treatments. *Agron. J.* 58:85-88.
21. Meints, V. W., L. T. Kurtz, S. W. Melsted, and T. R. Peck. 1977. Long-term trends in total soil N as influenced by certain management practices. *Soil Sci.* 124:110-116.

22. Metzger, W. H. 1939. Nitrogen and organic carbon of soils as influenced by cropping systems and soil treatments. Kansas Agr. Exp. Sta. Tech. Bull. 45.
23. Myers, H. E., A. L. Hallsted, J. B. Kuska, and H. J. Haas. 1943. Nitrogen and carbon changes in soils under low rainfall as influenced by cropping systems and soil treatment. Kansas Agr. Exp. Sta. Tech. Bull. 56.
24. Odland, T. E. and J. B. Smith. 1933. The effect of certain crops on succeeding crops. J. Amer. Soc. Agron. 25: 612-618.
25. Paul, E. A., and J. A. van Veen. 1979. The use of tracers to determine the dynamic nature of organic matter. p. 75-132. In J. K. G. Gasser (ed.). Modelling nitrogen from farm wastes. Applied Science Publishers, Ltd., London.
26. Research Report. 1980. Saginaw Valley bean-beet research farm and related bean-beet research. Michigan State Univ. Agr. Exp. Sta.
27. Salter, R. M., and T. C. Green. 1933. Factors affecting the accumulation and loss of nitrogen and organic carbon in cropped soils. J. Amer. Soc. Agron. 25:622-630.
28. Schulte, E. E. 1980. Recommended soil organic matter tests. In W. C. Dahnke, (ed.). Recommended chemical soil test procedures for the North Central Region. North Dakota Agr. Exp. Stn. Bull. 499 (Revised). N. D. State Univ., Fargo, N.D.
29. Snedecor, G. W., and W. G. Cochran. 1974. Statistical Methods (6th ed.). Iowa State University Press, Ames, Iowa.
30. Sowden, F. J. 1959. Investigations on the amounts of hexosamines found in various soils and methods for their determination. Soil Sci. 88:138-143.
31. Sowden, F. J. 1977. Distribution of nitrogen in representative Canadian soils. Can. J. Soil Sci. 57:445-456.
32. Steel, R. G. D., and J. H. Torrie. 1980. Principles and Procedures of Statistics. McGraw-Hill Book Company, New York.
33. Stevenson, F. J. 1956. Effect of some long-time rotations on the amino acid composition of the soil. Soil Sci. Soc. Amer. Proc. 20:204-208.
34. Stevenson, F. J. 1957. Distribution of the forms of nitrogen in some soil profiles. Soil Sci. Soc. Amer. Proc. 21: 283-287.

35. Stevenson, F. J. 1957. Investigations of aminopolysaccharides in soils: 1. Colorimetric determination of hexosamines in soil hydrolysates. *Soil Sci.* 83:113-122.
36. Stevenson, F. J. 1957. Investigations of aminopolysaccharides in soils: 2. Distribution of hexosamines in some soil profiles. *Soil Sci.* 84:99-106.
37. Stevenson, F. J. 1965a. Amino acids. In C. A. Black et al. (eds.). *Methods of Soil Analysis, Part 2. Agronomy* 9: 1437-1451.
38. Stevenson, F. J. 1965b. Amino sugars. In C. A. Black et al. (eds.). *Methods of Soil Analysis, Part 2. Agronomy* 9:1429-1436.
39. Stevenson, F. J. 1982. Organic forms in soil nitrogen. In F. J. Stevenson, (ed.). *Nitrogen in Agricultural Soils.* *Agronomy* 22:67-122.
40. Stevenson, F. J. 1983. Nitrogen--Organic forms. In A. L. Page et al, (eds.). *Methods of Soil Analysis. Part 2. Agronomy* (2nd ed.). 9:625-641.
41. Stevenson, F. J., and C. N. Cheng. 1970. Amino acids in sediments: recovery by acid hydrolysis and quantitative estimation by a colorimetric procedure. *Geochimica et Cosmochimica Acta.* 34:77-88.
42. Strickling, E. 1957. Effect of cropping systems and VAMA on soil aggregation, organic matter and crop yields. *Soil Sci.* 84:489-498.
43. Unger, P. W. 1968. Soil organic matter and nitrogen changes during 24 years of dryland wheat tillage and cropping practices. *Soil Sci. Soc. Amer. Proc.* 32:427-429.
44. Walkley, A. 1935. An examination of methods for determining organic carbon and nitrogen in soils. *J. Agr. Sci.* 25:598-609.
45. Walkley, A., and I. A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37:29-37.
46. White, J. W., F. J. Holden, and A. C. Richer. 1945. Maintenance level of nitrogen and organic matter in grassland and cultivated soils over periods of 54 and 72 years. *J. Amer. Soc. Agron.* 37:21-31.



47. Young, R. A., J. C. Zubriski, and E. B. Norum. 1960. Influence of long-time fertility management practices on chemical and physical properties of a Fargo Clay. Soil Sci. Soc. Amer. Proc. 24:124-128.

CHAPTER IV

EFFECT OF TYPE AND RATE OF CROP RESIDUES ON THE  
CONCENTRATION AND DISTRIBUTION OF NITROGEN  
FORMS DURING INCUBATION

An important way that crops affect soil properties is the return of organic matter as exudates and residues produced during growth, but mostly after harvest of the crops. The types and amount of crop residues affect the concentration and proportion of the various organic N fractions due to differences in crop composition, decomposition rates, and suitability as substrates for the microbial population.

Application of alfalfa, cornstalks, sawdust, oat straw and brome grass at rates of 0 to 16 tons/ha/year increased the organic C and nitrogen in proportion to the amount of residues added over a period of 11 years (12). These authors found no significant differences among the five residues except for sawdust which produced significantly lower values for nitrogen. In other studies, organic amendments such as green rye, straw, alfalfa hay, deciduous leaves, peat, muck, and manure were added to an Uplands sand and a Rideau clay under field conditions for a 20-year period. The practice maintained the levels of total N, organic matter and the distribution of the various nitrogenous compounds (23, 24).

Some investigators have noted a relative constancy in the proportions of organic N fractions with large decreases in total N content due to cultivation and cropping (5, 11, 15, 19, 28). In soils where large increases in total N have occurred under fertilized legume pastures in tropical and temperate areas in Australia, organic N fractions proportions have remained relatively constant (16). This appeared to suggest that organic N fractionation by hydrolysis using 6 M HCl produced a pattern that bore little relation to the biological labile of soil nitrogen.

Some other studies showed that the proportion of organic N fractions would not necessarily remain constant with large changes in total N. It was reported that the addition of fresh residues was accompanied initially by an increase in hydrolyzable  $\alpha$ -amino acid arising by proteolysis and microbial synthesis (6). Changes were also observed for other organic N fractions. The changes were related more closely to the degree of oxidation of the total organic fraction than to the composition of the materials that were added. Cornsforth (3) reported that considerable redistribution of N took place indicating changes in the proportions of the organic-N fractions with changes in the amounts of total N. Other workers showed that cultivation and cropping resulted in a marked decline in the proportions of total N as organic N fractions (8, 20). These investigators did not show the magnitude of change in proportions of total N as organic N fractions if various energy sources were added at varying rates with no additional application of fertilizer N.

The above reports have shown that the concentration and proportion of total N as organic N fractions may be significantly affected by management practices. That appears to indicate that any cultural practice that returns large quantities of some crop residues may increase or decrease the relative proportions of total N present as organic N fractions.

The redistribution of N can occur in several ways. In general, a decline in total N due to cultivation or cropping is associated with redistribution of hydrolyzable N and nonhydrolyzable N fractions. However, it has been reported that a large decrease of carbon and nitrogen during cultivation did not result in measurable changes in the distribution of the hydrolyzable and nonhydrolyzable fractions of N (14). The addition of crop residues with varying C/N ratios can also lead to the redistribution of N from the hydrolyzable N to the nonhydrolyzable N and vice versa, depending on the stage of humification. During the early stages of humication, the nonhydrolyzable N fraction tends to increase at the expense of the hydrolyzable N which comprise the "active" materials.

Within the hydrolyzable N fraction, hydrolyzable ammonium N, amino acid N, amino sugar N, and the hydrolyzable unknown N (HUN) change in concentration and proportion relative to change in the total hydrolyzable N. This depends on the stability of these fractions. Under incubated conditions, hydrolyzable fractions such as amino acid N, hydroxyamino acid N and HUN were found to be more susceptible to loss than total N (9). This means that these decreases would account for the overall decline of total hydrolyzable N which would account for

the decline in total N. In other studies, the decrease in total N was accounted for by a decrease in nonhydrolyzable N and other hydrolyzable fractions such as hydroxyamino acid N (3).

There is very little information about the effect of alfalfa tops, navy bean straw, corn stover, and sugar beet tops on the concentration and distribution of N forms in an acid soil low in soil organic matter. The results can be meaningfully related to the behavior and potential behavior of total N and organic N fractions under field conditions. The objective of the incubation study was:

To determine the influence of various types and rates of crop residues and time of incubation on the concentration and distribution of N forms.

## MATERIALS AND METHODS

Incubation studies were performed on a homogenous lot of Hodunk sandy loam soil collected in the fall of 1983 after harvest of second year of corn in a potato-corn-corn sequence. The soil was passed through a 4.8 mm screen to remove undecomposed plant materials, air-dried, and then stored in a plastic bag.

Bulk samples of corn stover, dry bean straw, sugar beet tops and alfalfa tops were taken from the field in October. The plant materials were dried and ground to pass a 2.0 mm sieve and stored in plastic bags. The ground materials were mixed with 500g aliquots of the soil at rates of 0, 2, 10, and 50 g/kg. The amended aliquots were placed in plastic ice cream cartons and moistened to field capacity (0.03 mPa) with deionized water. They were then placed in polyethylene bags to reduce evaporation during incubation at 27°C. Pin hole punctures were made in each bag for gas exchange. A total of 156 experimental units were prepared to permit sacrificing triplicate units of an unamended control and of each material/rate combination after 9, 21, 42, and 63 days. Water was added as needed to maintain a constant weight during incubation.

Sacrificed samples were frozen and stored at -4°C for analysis.

### Laboratory Analyses

Total N was determined by the salicyclic acid-thiosulfate modification of the Kjeldahl method described by Bremner and Mulvaney (2). Exchangeable  $\text{NH}_4^+$  N and  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  N were determined by the methods described by Keeney and Nelson (10).

Easily oxidized organic C was determined by the colorimetric method described by Schulte (21). This method involves chromic acid oxidation for determination of easily oxidized material through spontaneous heat. The method was standardized against the Walkley-Black method (31, 32).

Total hydrolyzable N (THN), hydrolyzable ammonium N (AN), amino acid N (AAN), amino sugar N (ASN), hydrolyzable unknown N (HUN) and nonhydrolyzable N (NHN) were determined by the methods described by Bremner (1) and Stevenson (26, 27, 29, 30).

### Statistical Analyses

The experiment was designed in a randomized complete block and the data were subjected to analyses of variance, using methods described by Snedecor and Cochran (22), Steel and Torrie (25), and Little and Hills (13).

## RESULTS AND DISCUSSION

Changes in concentration and distribution of N forms were followed over a 63-day incubation period in a sandy loam soil amended with residues of alfalfa, navy beans, corn, or sugar beets at rates up to 50 g/kg. A Hodunk sandy loam low in organic matter was used so that residue effects would be most pronounced for measurement.

Chemical analyses for the four crop materials used are given in Table 1.

Table 1. Composition of crop residues used in the incubation study

Residue type	Total N	P	K	Ca	C/N <sup>†</sup>
	----- % -----				
Alfalfa	3.45	0.24	1.53	0.23	14
Navy bean	0.77	0.07	1.49	0.38	65
Corn	0.79	0.09	0.38	0.20	63
Sugar beet	1.51	0.13	1.10	0.39	33

<sup>†</sup> Estimated C/N ratio, assuming 40% C.

### Apparent Gains and Losses of N

Simple effects and 2-way and 3-way interactions of residues, rates and times on total N were statistically significant



(Table 1, Appendix A). The data for the 3-way interactions are shown graphically in Figs. 1 to 4.

At zero time, the concentration of total N reflected the differences in N concentration of the residues (Table 1) and the rates of addition. Subsequent changes during incubation, however, were not parallel for the different materials nor different rates of the same material.

In the case of alfalfa at the highest rate, a striking decrease in total N occurred, during the 63-day incubation period. At the 10 g/kg rate, a similar decrease was preceded by a significant increase in the second sampling. At the lowest rate (2 g/kg), there was a continuing increase over the entire incubation period. With the other residues, patterns of change were different and varied with rate of addition.

The magnitude of several of the changes over time in Fig. 1 and their statistical significance, indicate that real increases and real decreases may have occurred at different times. Mechanisms for loss of N from soil systems included volatilization of  $\text{NH}_3$  and denitrification of nitrate and nitrite. Mechanisms for adding N include absorption of  $\text{NH}_3$  from the atmosphere and  $\text{N}_2$ -fixation by nitrogen-fixing bacteria.

Energy to support biological denitrification and/or  $\text{N}_2$ -fixation would have been supplied by the added residues. The more readily available carbon substrates were dissipated rather quickly (Table 2). Thus the probability that heterotrophic activities were

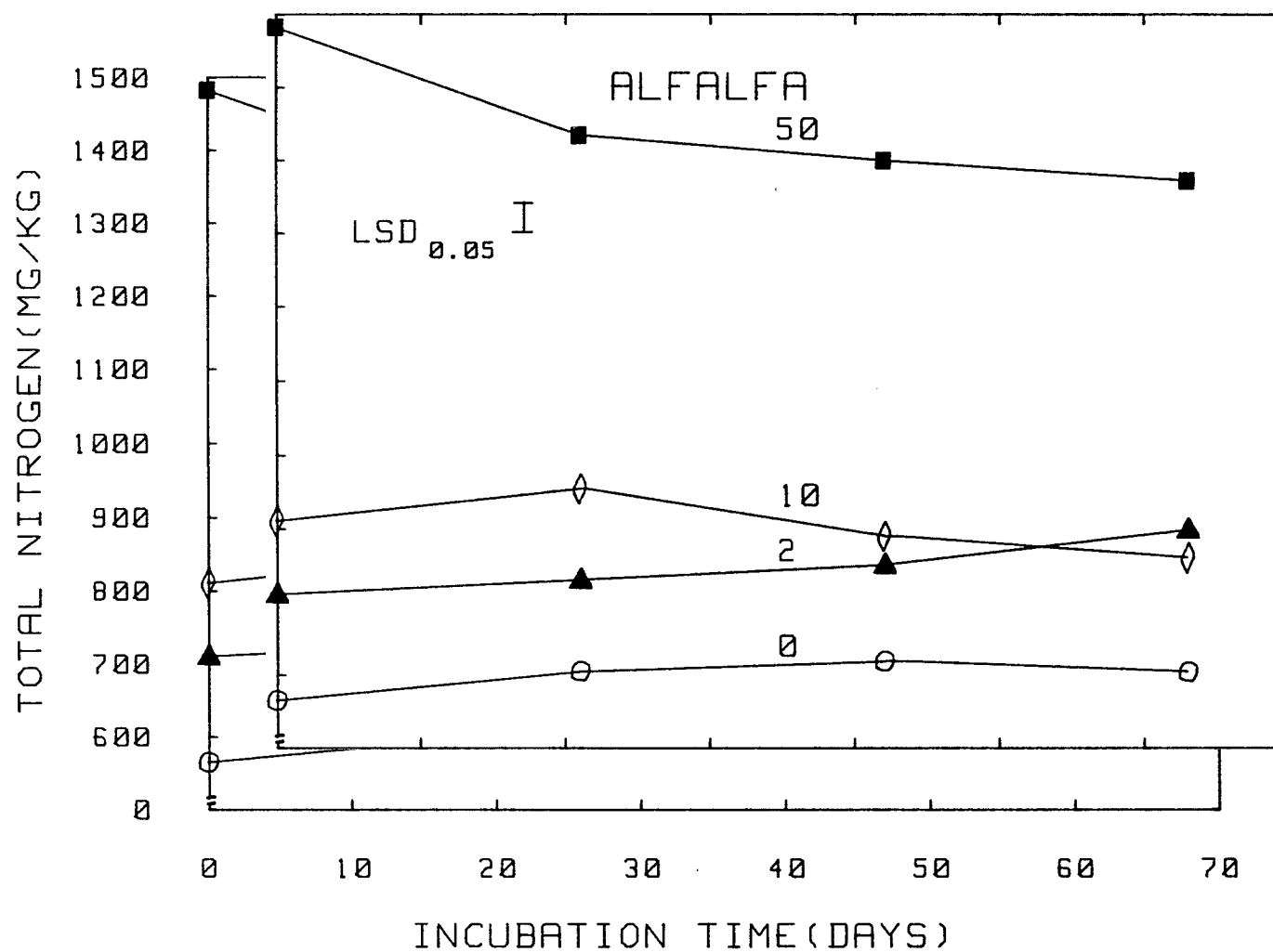


Fig. 1. Effect of type and rate of alfalfa residues and time of incubation on the concentration of total nitrogen (rates = 0, 2, 10, and 50 g/kg).

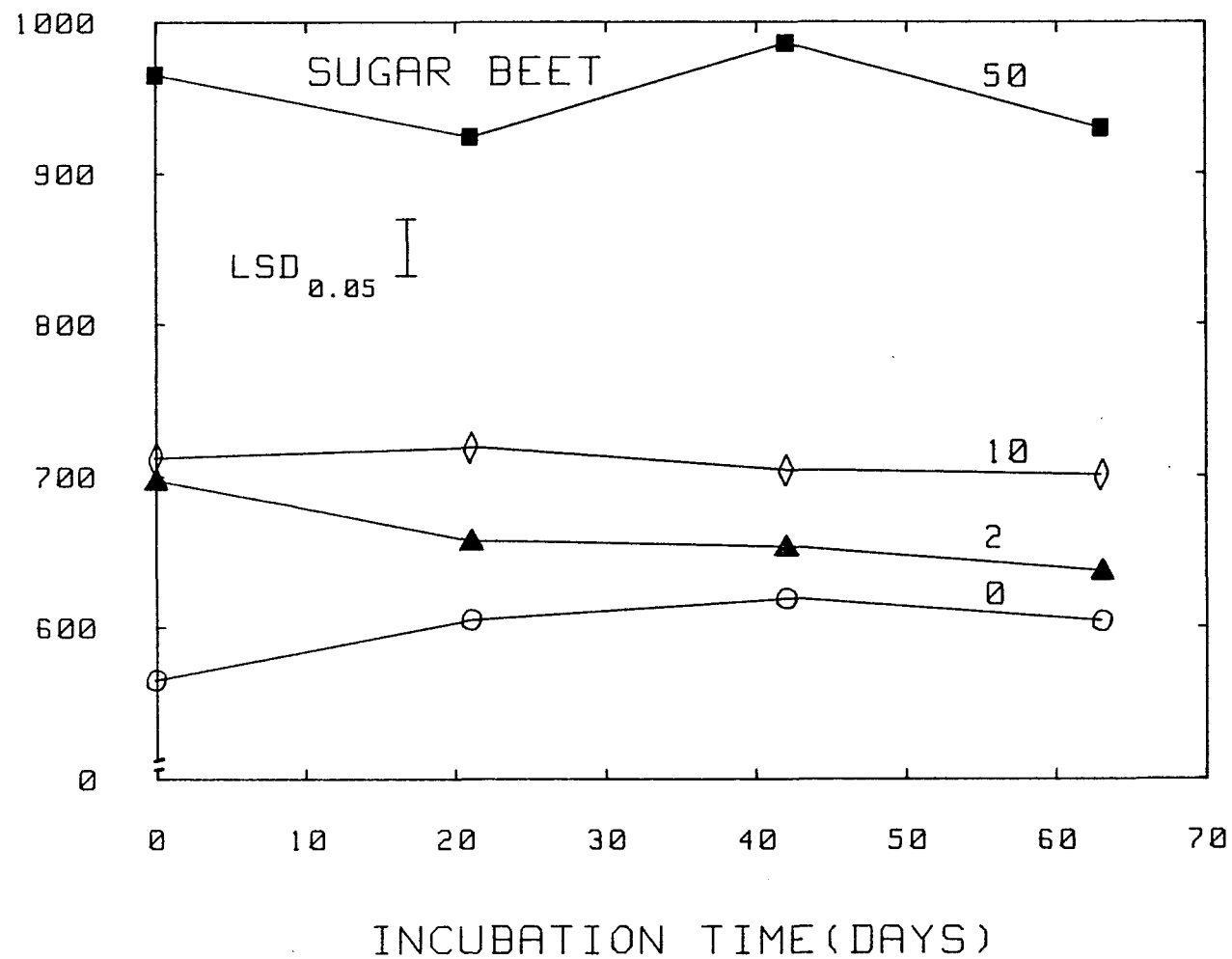


Fig. 2. Effect of type and rate of sugar beet residues and time of incubation on the concentration of total nitrogen (rates = 0, 2, 10, and 50 g/kg).

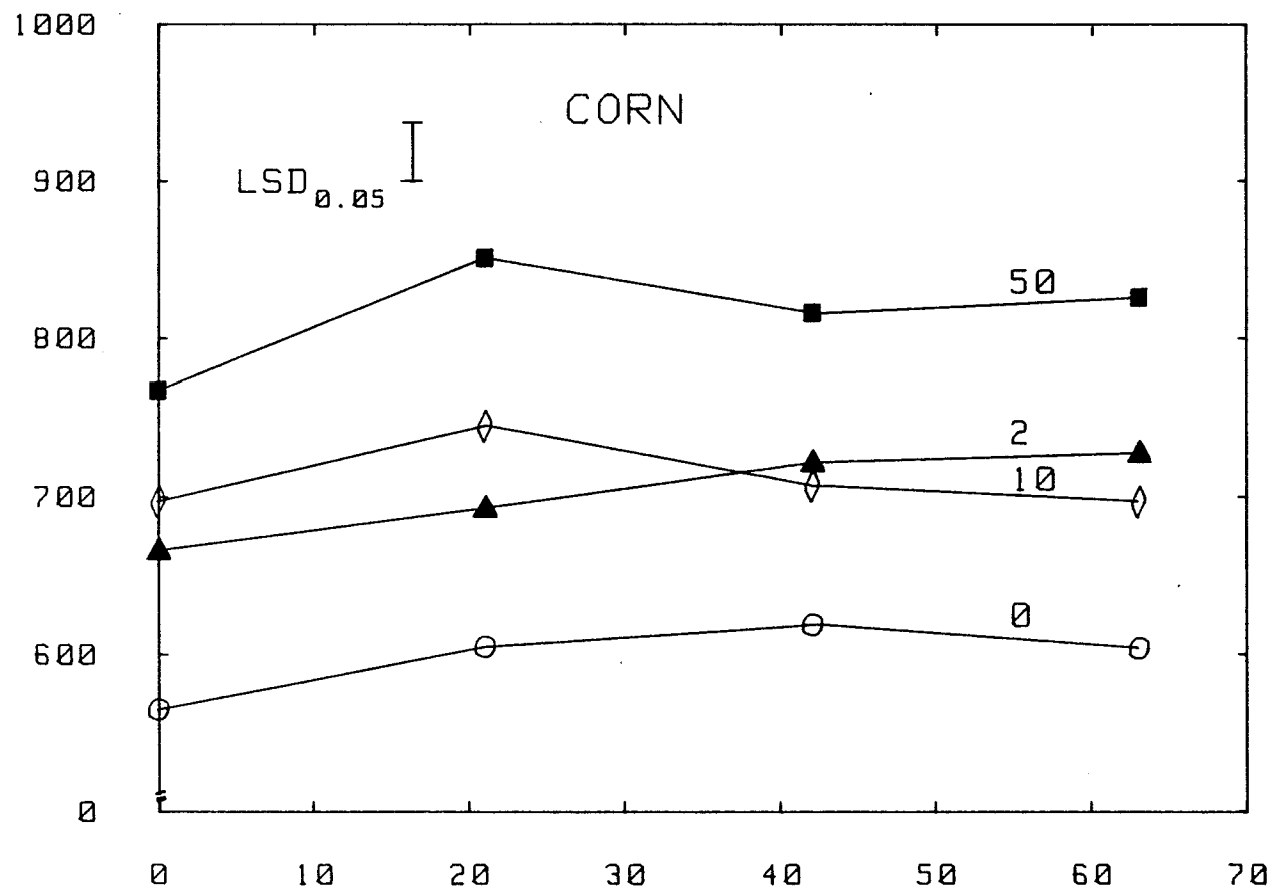


Fig. 3. Effect of type and rate of corn residues and time of incubation on the concentration of total nitrogen (rates = 0, 2, 10, and 50 g/kg).

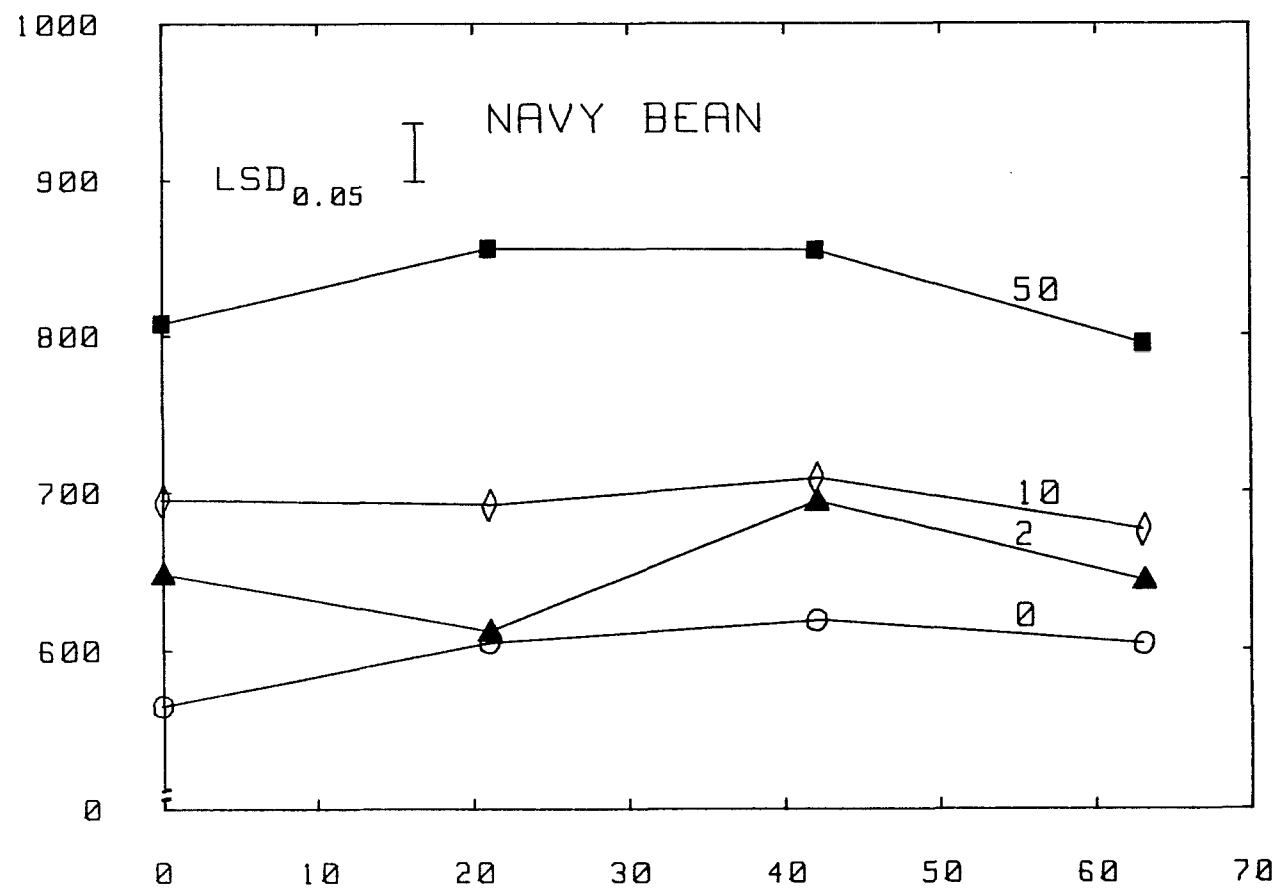


Fig. 4. Effect of type and rate of navy bean residues and time of incubation on the concentration of total nitrogen (rates = 0, 2, 10, and 50 g/kg).

Table 2. Effect of type and rate of crop residue and time of incubation on organic carbon.

Residue	Rate	Organic carbon			
		Incubation time (days)			
		0 <sup>†</sup>	21	42	63
	g/kg	----- g/kg -----			
Check	0 <sup>‡</sup>	8.1	8.1	7.7	6.2
Alfalfa	2	9.0	8.4	8.0	9.0
	10	12.0	9.3	7.8	8.9
	50	28.0	13.0	11.0	11.0
Navy bean	2	9.0	8.6	7.3	7.8
	10	12.0	9.9	7.3	8.4
	50	28.0	16.0	11.0	9.7
Corn	2	9.0	9.2	7.4	7.5
	10	12.0	10.0	8.5	8.6
	50	28.0	17.0	14.0	11.0
Sugar beet	2	9.0	8.4	7.8	7.3
	10	12.0	8.5	7.9	7.5
	50	28.0	12.0	9.7	8.6
LSD <sub>0.05</sub>	(3-way interaction)				

<sup>†</sup> Assuming 40% C in residues:

$$\text{Calculated} = \frac{8\text{g C in 1,000 g soil} + 0.4 \times \text{g/kg residue added}}{1,000 \text{ g soil} + \text{g kg residue added}}$$

<sup>‡</sup> Values at zero rate not included in ANOVA

responsible for losses or gains of N would have been greatest during early stages of incubation and would have declined with declining rate of carbon loss.

On the other hand, the likelihood that losses of N might occur by chemical denitrification would be expected to increase as oxidation progressed and phenol-quinone systems appeared that could react with nitrite under acid conditions to produce  $N_2$ ,  $N_2O$ , and other gases (17).

In the case of high N materials, rapid dissipation of carbon is accompanied by net mineralization and rapid release of  $NH_3$ . If  $NH_3$  is released more rapidly than it can be adsorbed or transformed by soil systems, volatilization losses will occur. This would appear the most likely explanation for the disappearance of N at the highest rate of addition of alfalfa.

In the case of carbonaceous materials, low in N, decomposition is accompanied by immobilization of mineral forms of N into microbial tissues. The presence of carbonaceous materials can increase the adsorptive capacity of the soil for  $NH_3$  in the ambient atmosphere.

In the present experiment, it is possible that  $NH_3$  lost by volatilization from high N treatments may have equilibrated, through the confined atmosphere of the growth chamber, with soil and residues in low N treatments. Thus a significant increase in total N occurred during the first 21 days at all rates of corn addition. At the 2 g/kg rate, the increasing trend was maintained through the 63rd day with both corn and alfalfa. Differences between 2 and 10 g/kg applications were not great, but it did appear that interacting systems which

affect the balance between gains and loss were influenced differently by the rate of addition.

#### Changes in Exchangeable Ammonium

Volatilization or adsorption of  $\text{NH}_3$  reflect shifts in dynamic equilibria that involve exchangeable  $\text{NH}_4^+$  (18). The immediate effect of added residues at time zero (Table 3) was to reduce exchangeable  $\text{NH}_4^+$  initially present in the soil to trace levels. Levels were sharply higher at 21 days in all samples. Addition of water at the beginning of incubation would have activated the soil microbial population. The quantities of  $\text{NH}_4^+$  found represent the balance at the time of sampling between the rate of release of  $\text{NH}_3$  by the activated population and the rate of its removal by several processes, including immobilization into microbial tissues and metabolic products, nitrification, volatilization, and chemical transformation leading to incorporation into humic complexes (7).

Differences in exchangeable  $\text{NH}_4^+$  levels in Table 3 are not related consistently to the N content of the residues. The 32 mg/kg present at 21 days with the highest rate of alfalfa is consistent with the earlier conclusion that large loss of N from this system may have been due to volatilization of  $\text{NH}_3$  released at rates exceeding the adsorptive capacity of the soil (Fig. 1).

Exchangeable  $\text{NH}_4^+$  levels were lower in the last sampling in the control than in most amended soils. This probably reflects a more rapid decrease in size and activity of the microbial population due to earlier depletion of available substrates.



Table 3. Effect of type and rate of residue and time of incubation on exchangeable ammonium N.

Residue	Rate	Exchangeable ammonium N			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0†	2.8	16.0	9.9	4.2
Alfalfa	2	Trace‡	19.0	16.0	7.1
	10	Trace	4.2	19.0	7.1
	50	Trace	32.0	7.1	9.9
Navy bean	2	Trace	7.1	9.9	7.1
	10	Trace	9.9	9.9	9.9
	50	Trace	11.0	7.2	7.2
Corn	2	Trace	19.0	9.9	10.0
	10	Trace	7.1	7.5	
	50	Trace	8.5	11.0	8.5
Sugar beet	2	Trace	18.0	9.9	5.7
	10	Trace	7.1	5.7	8.5
	50	Trace	18.0	23.0	9.9
LSD <sub>0.05</sub>	(3-way interaction)		3.2		

† Values at zero rate not included in ANOVA.

‡ Trace = A value of 1.0 mg/kg was assigned for statistical analysis.

## Changes in Nitrified N

Normally nitrification represents an important sink for  $\text{NH}_4^+$  in soils. Nitrification rates and the quantities of nitrate plus nitrite produced with alfalfa and sugar beet (Table 4) reflected both the differences in nitrogen content of these two residues and the rates of addition. The transformation was most rapid and extensive with alfalfa, which contained 3.45% N, followed by sugar beet tops which contained 1.51% N and least with corn and navy beans.

In the case of navy bean residues (0.77% N) and corn (0.80% N) the addition of 2 g/Kg had no effect on nitrification as compared with the control. At higher rates, nitrification was severely delayed. These delays occurred even though levels of exchangeable  $\text{NH}_4^+$  (Table 3) were no lower than many of those associated with high nitrification rates in soils amended with alfalfa or sugar beets.

Thus, the failure of nitrate to accumulate normally at higher rates of wide C/N ratio residues in this study does not appear to have been due to competitive immobilization of  $\text{NH}_4^+$ , the substrate for the first step in nitrification. Rather, it would appear that  $\text{NO}_2^-$  and/or  $\text{NO}_3^-$  were removed by other transformations as rapidly as formed. Processes that utilize  $\text{NO}_2^-$  and/or  $\text{NO}_3^-$  include microbial assimilation, microbial denitrification and reaction of  $\text{NO}_2^-$  with organic compounds at acid pH. These reactions of  $\text{NO}_2^-$  can result in both chemical immobilization and chemical denitrification (17).

Table 4. Effect of type and rate of crop residues and time of incubation on the concentration of nitrate plus nitrite

Residue	Rate	N added in residue	Nitrate plus nitrite nitrogen			
			Incubation time (days)			
			0	21	42	63
	g/kg		mg/kg			
Check	0 <sup>†</sup>	--	0.9	16.5	26.1	30.8
Alfalfa	2	69	1.5	26.2	39.5	50.6
	10	345	3.1	66.4	81.4	83.9
	50	1725	6.4	207.0	241.0	277.0
Navy bean	2	15	1.5	17.1	18.8	30.9
	10	79	1.5	1.3	1.3	8.6
	50	387	1.5	1.5	1.5	44.5
Corn	2	16	1.5	11.2	26.1	31.4
	10	80	1.5	1.3	6.7	11.0
	50	400	1.5	1.1	0.9	0.9
Sugar beet	2	30	1.3	15.5	30.9	37.1
	10	151	1.5	13.5	33.1	41.7
	50	755	1.5	19.0	95.8	99.8
LSD <sub>0.05</sub>	(3-way interaction)		11.6			

<sup>†</sup> Values at zero rate not included in ANOVA

### Changes in Organic N Fractions

In Figs. 5 to 8, data for nitrate plus nitrite are compared graphically with recoveries of N in organic forms at the 50 g/kg rate of addition. It should be noted that  $\text{NH}_3$  recovered in the hydrolyzable fraction (AN) would have included the exchangeable  $\text{NH}_4^+$  in Table 3. Because the values were low, exchangeable  $\text{NH}_4^+$  was not broken out separately in the figures. Patterns of change in the AN fraction or in total organic N (TON) would not have been altered appreciably if this mineral fraction had been excluded. If present,  $\text{NH}_4^+$  fixed by clay minerals would have also contributed to AN. However, it is unlikely that much fixed  $\text{NH}_4^+$  would have been present in this sandy loam soil.

Changing levels of organic N (TON) in Figs. 5 to 7 reflected net mineralization to  $\text{NO}_2^-$  and/or  $\text{NO}_3^-$ . In the case of corn (Fig. 8), TON accounted for total N (TN) in the system because net nitrification did not occur.

### Total Hydrolyzable N and Nonhydrolyzable N

In the case of alfalfa (Fig. 5) and sugar beet tops (Fig. 6), changes in TON were due mainly to changes in total hydrolyzable N (THN). Changes in the nonhydrolyzable fraction (NHN) were small.

By contrast, changes in TN and TON with the two low N residues (Figs. 7 and 8) reflected changes in both hydrolyzable and nonhydrolyzable forms. With both navy beans and corn, increases in NHN contributed to the early increases in TN and TON at 21 days.

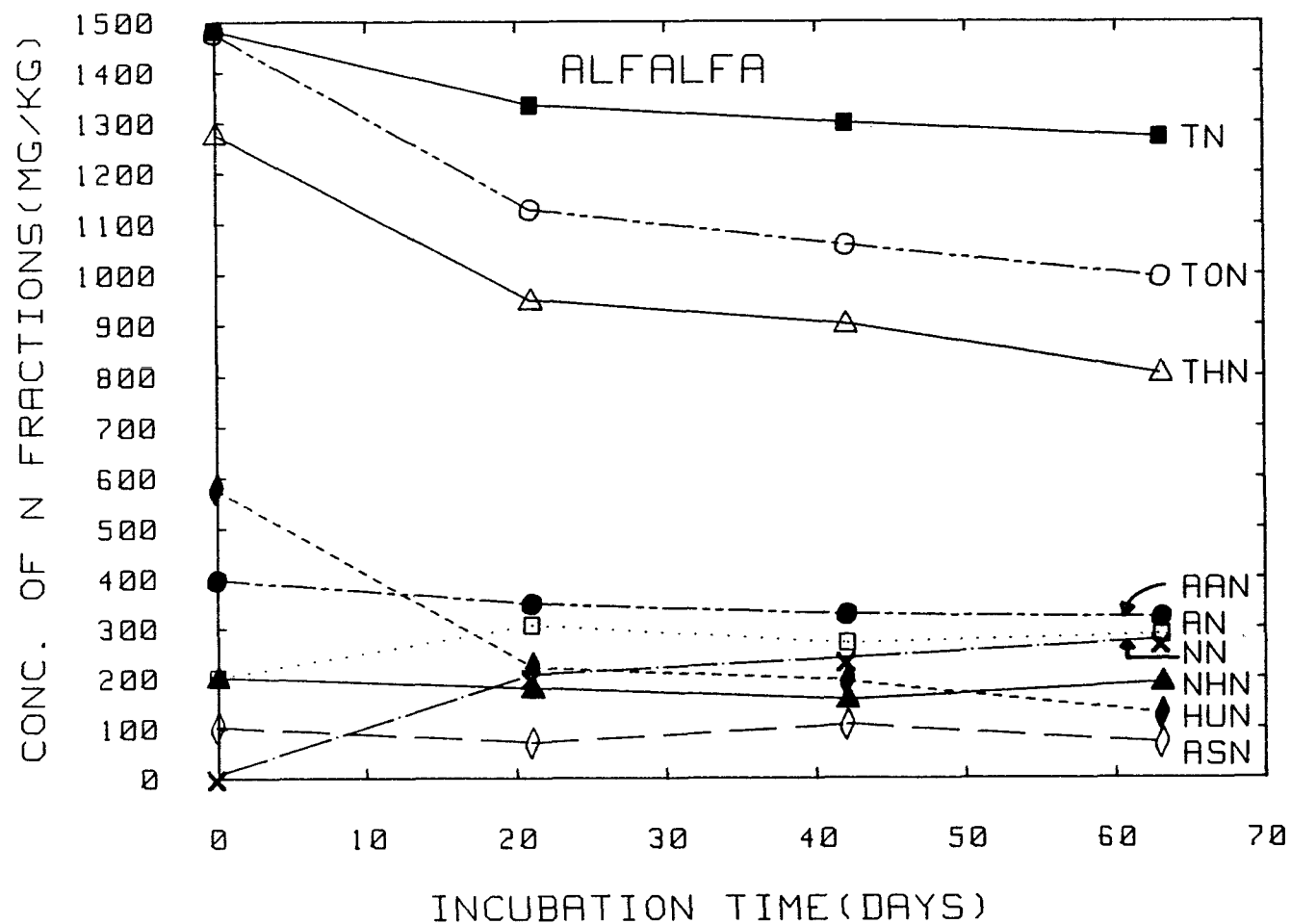


Fig. 5. Concentration of nitrogen fractions during incubation at 50 g/kg alfalfa residue addition. TN = total N; TON = total organic N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N; NN = nitrate + nitrite N. (Refer to Tables 4 to 11 for statistical tests.)

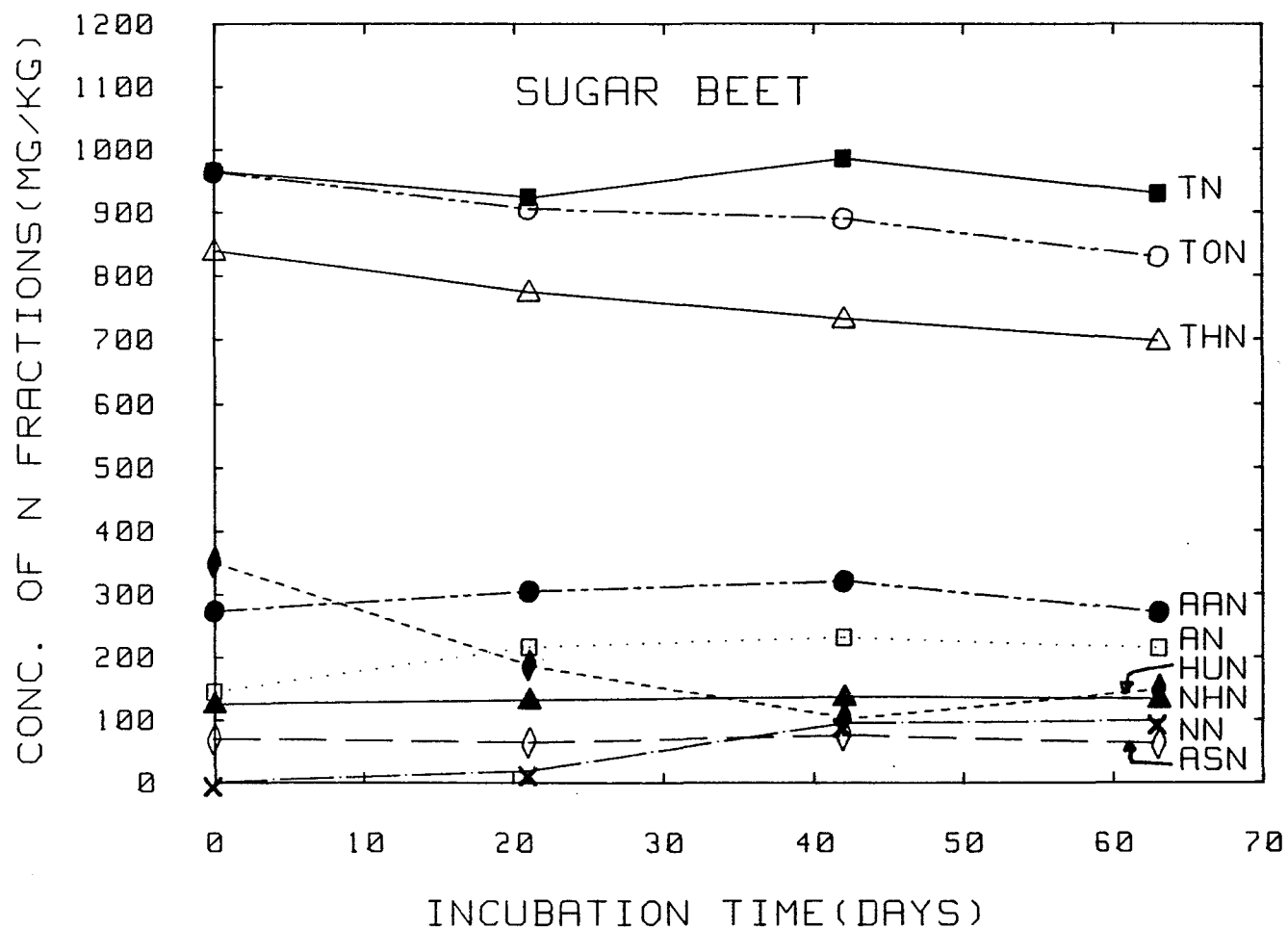


Fig. 6. Concentration of nitrogen fractions during incubation at 50 g/kg sugar beet residue addition. TN = total N; TON = total organic N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N; NN = nitrate + nitrite N. (Refer to Tables 4 to 11 for statistical tests.)

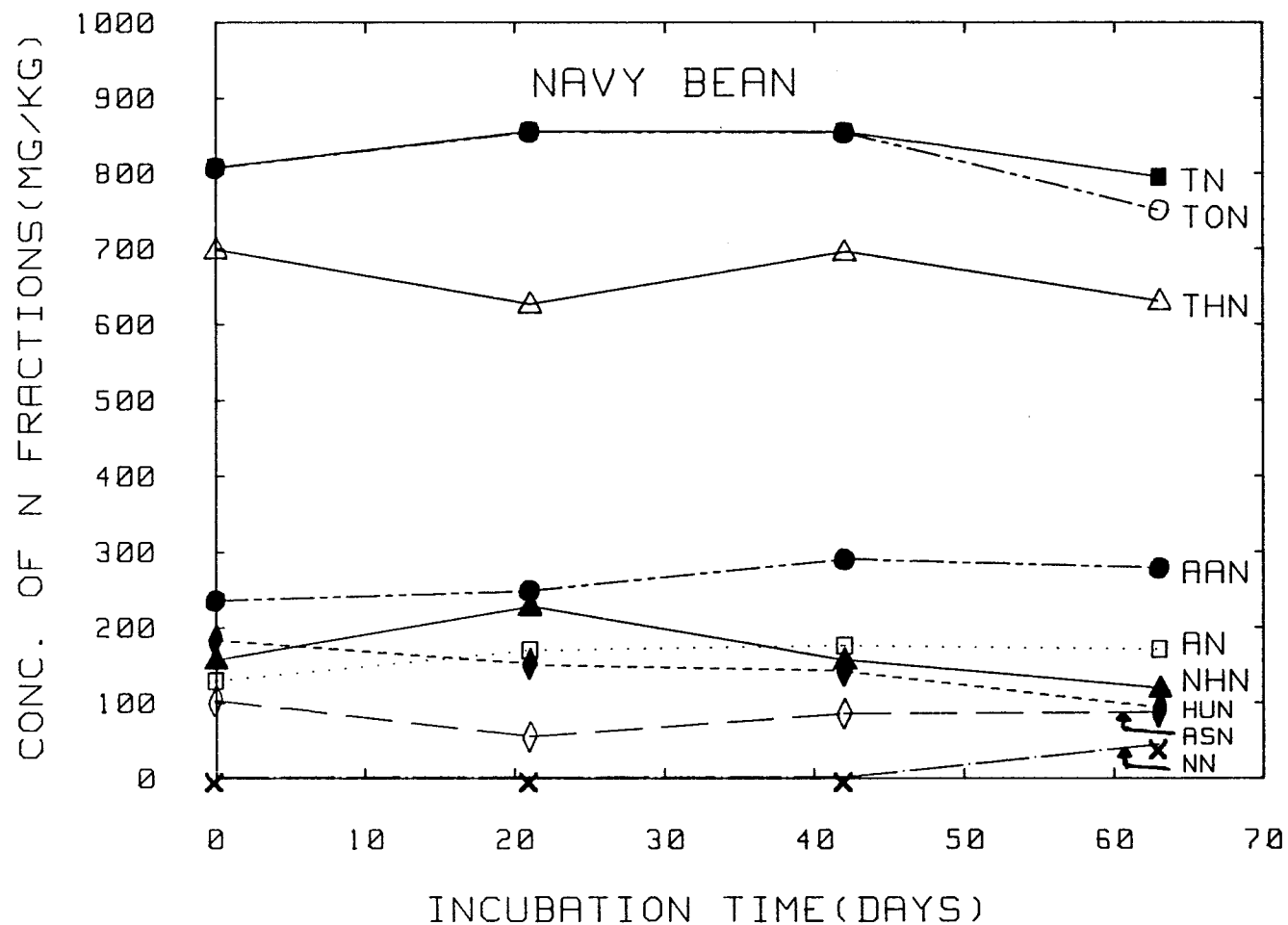


Fig. 7. Concentration of nitrogen fractions during incubation at 50 g/kg navy bean residue addition. TN = total N; TON = total organic N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N; NN = nitrate + nitrite N. (Refer to Tables 4 to 11 for statistical tests.)

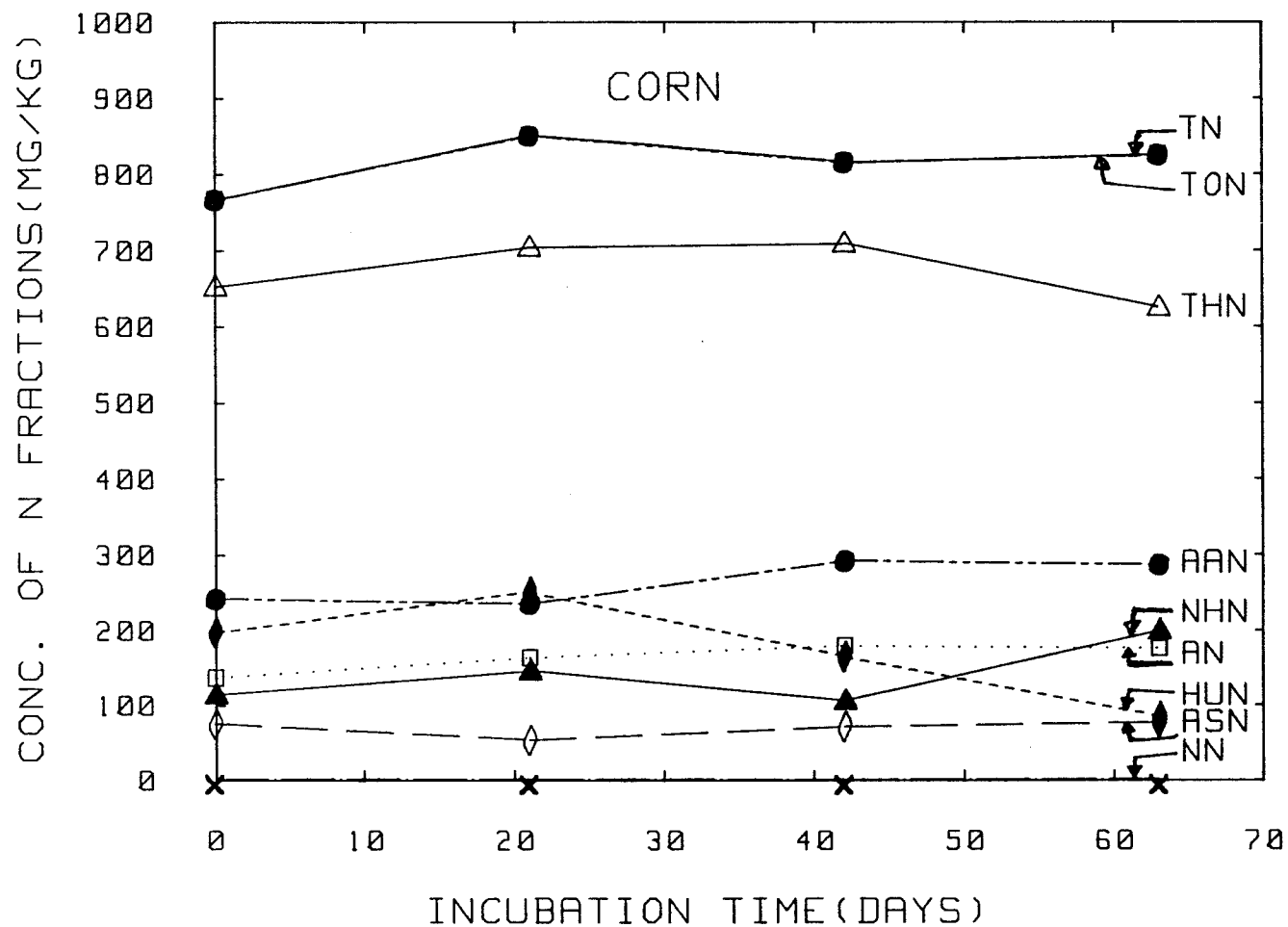


Fig. 8. Concentration of nitrogen fractions during incubation at 50 g/kg corn residue addition. TN = total N; TON = total organic N; THN = total hydrolyzable N; AN = hydrolyzable ammonium N; AAN = amino acid N; ASN = amino sugar N; HUN = hydrolyzable unknown N; NHN = nonhydrolyzable N; NN = nitrate + nitrite N. (Refer to Tables 4 to 11 for statistical tests.)



In the case of navy beans (Fig. 7) significant losses of N from the system during the last 21 days (Table 5) were due to decreases in both THN (Table 6) and NHN (Table 7). An additional decrease in organic N (TON) was due to net nitrification.

With corn (Fig. 8) no accumulation of nitrate or nitrite occurred. Instead, it appeared that a large transfer of N from hydrolyzable to nonhydrolyzable fraction occurred during the last 21 days. As a result, both TN and TON remained essentially unchanged.

#### Changes Among Hydrolyzable Forms of N

The 3-way interaction plotted in Figs. 5 to 8 for the different forms of N in the acid hydrolysate are tabulated in Table 8 to 11. Probabilities for main effects and interactions are given in Tables 1 and 2, Appendix A.

Alfalfa system: In Fig. 5, it appears that much of the N that was lost from alfalfa-amended soil at the highest rate must have originated in the hydrolyzable unknown fraction (HUN). Also, much of the N that appeared as  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  must have originated in the HUN fraction.

A large increase in the hydrolyzable ammonium fraction (AN) during the first 21 days indicates that unidentified HUN materials were first converted to hydrolyzable  $\text{NH}_4^+$  and/or exchangeable  $\text{NH}_4^+$  before entering into further transformation.

Gradual decreases in amino acids (AAN) may reflect the recycling of alfalfa proteins into a declining microbial population. A

Table 5. Effect of type and rate of crop residues and time of incubation on the concentration of total N

Residue	Rate	Total nitrogen (TN)			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0 <sup>†</sup>	565	605	619	604
Alfalfa	2	711	731	751	799
	10	811	855	790	760
	50	1483	1334	1299	1271
Navy bean	2	648	612	694	644
	10	695	692	709	676
	50	808	856	855	795
Corn	2	666	693	722	728
	10	697	745	707	697
	50	767	851	816	826
Sugar beet	2	697	657	653	637
	10	712	719	704	701
	50	965	924	986	930
LSD <sub>0.05</sub>	(3-way interaction)	38			

<sup>†</sup> Values at zero rate not included in ANOVA.

Table 6. Effect of type and rate of crop residues and the time of incubation on the concentration of total hydrolyzable nitrogen

Residue	Rate	Total hydrolyzable nitrogen (THN)			
		Incubation time (days)			
		0	21	42	63
	g/kg	-----mg/kg -----			
Check	0 <sup>†</sup>	498	531	552	521
Alfalfa	2	557	526	542	534
	10	699	607	628	594
	50	1276	948	901	804
Navy bean	2	550	540	523	488
	10	576	572	592	524
	50	698	627	696	631
Corn	2	471	505	521	504
	10	553	547	588	546
	50	652	704	709	625
Sugar beets	2	557	546	506	519
	10	591	577	577	570
	50	839	774	732	697
LSD <sub>0.05</sub>	(3-way interaction)	64			

<sup>†</sup> Values for zero rate not included in ANOVA.

Table 7. Effect of type and rate of crop residues and time of incubation on the concentration of nonhydrolyzable N

Residue	Rate	Nonhydrolyzable N (NHN) <sup>†</sup>			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0 <sup>‡</sup>	67	74	67	83
Alfalfa	2	153	179	169	214
	10	109	182	80	82
	50	200	179	157	191
Navy bean	2	97	55	152	126
	10	117	119	115	147
	50	157	228	158	119
Corn	2	194	177	175	192
	10	142	197	113	140
	50	114	146	106	200
Sugar beet	2	140	95	116	81
	10	119	128	114	89
	50	125	132	137	133
LSD <sub>0.05</sub>	(3-way interaction)	NS			

<sup>†</sup> NHN = Nonhydrolyzable N = TN - THN

<sup>‡</sup> Values at zero rate not included in ANOVA

Table 8. Effect of type and rate of crop residues and time of incubation on the concentration of hydrolyzable unknown N

Residue	Rate	Hydrolyzable unknown nitrogen (HUN) <sup>†</sup>			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0 <sup>‡</sup>	79	150	131	103
Alfalfa	2	181	114	84.0	67.2
	10	207	116	89.1	88.5
	50	578	233	195	128
Navy bean	2	151	135	73.8	62.9
	10	119	182	98.2	70.5
	50	184	152	143	93.4
Corn	2	152	110	51.2	92.0
	10	164	119	101	76.9
	50	198	251	166	84.4
Sugar beet	2	211	141	80.7	95.3
	10	243	132	82.3	100
	50	351	188	103.2	149
LSD <sub>0.05</sub>	(3-way interaction)	88.6			

<sup>†</sup> HUN = Hydrolyzable unknown N = Total hydrolyzable N  
(Ammonium N + amino acid N + amino sugar N)

<sup>‡</sup> Values at zero rate not included in ANOVA

Table 9. Effect of type and rate of crop residues and time of incubation on the concentration of hydrolyzable ammonium N

Residue	Rate	Hydrolyzable ammonium nitrogen (AN) <sup>†</sup>			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0 ‡	141	165	168	172
Alfalfa	2	113	168	162	166
	10	133	198	192	184
	50	201	306	271	287
Navy beans	2	121	156	167	162
	10	157	159	161	168
	50	129	170	176	171
Corn	2	97	160	180	159
	10	132	148	166	166
	50	137	164	180	176
Sugar beet	2	133	170	179	160
	10	137	167	188	183
	50	145	217	232	215
LSD <sub>0.05</sub>	(3-way interaction)	24.6			

† AN = hydrolyzable ammonium N including exchangeable  $\text{NH}_4^+$

‡ Values at zero rate not included in ANOVA

Table 10. Effect of type and rate of crop residues and time of incubation on the concentration of amino acid N.

Residue	Rate	Amino acid nitrogen (AAN)			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0†	186	153	186	136
Alfalfa	2	155	180	194	202
	10	274	225	242	218
	50	396	349	328	321
Navy beans	2	226	188	205	192
	10	242	185	234	200
	50	236	249	291	279
Corn	2	147	179	222	194
	10	194	226	236	242
	50	242	235	292	287
Sugar beets	2	155	184	202	192
	10	178	227	236	223
	50	274	305	321	272
LSD <sub>0.05</sub> (any comparison)			46.3		

† Values at zero rate not included in ANOVA.

Table 11. Effect of type and rate of crop residues and time of incubation on the concentration of amino sugar N.

Residue	Rate	Amino sugar nitrogen (ASN)			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0 <sup>†</sup>	119.0	58.0	67.0	60.0
Alfalfa	2	108	65.3	102	98.9
	10	86.0	68.1	105	104.0
	50	102	70.8	107	69.3
Navy bean	2	52.7	61.9	77.7	71.0
	10	58.2	46.5	99.8	85.1
	50	103	55.3	86.1	87.8
Corn	2	74.9	56.4	68.4	58.4
	10	63.8	54.2	85.0	61.9
	50	74.9	53.5	71.6	77.6
Sugar beet	2	58.2	51.9	44.3	71.2
	10	63.8	51.9	70.3	63.8
	50	69.4	64.3	75.8	61.9
LSD <sub>0.05</sub> (3-way interaction)			27.4		

<sup>†</sup>Values at zero rate not included in ANOVA.



significant increase in amino sugars (ASN) from 21 days to 42 days would be consistent with net synthesis by the microbial population.

Sugar beet system: It would appear that with sugar beets as with alfalfa, N lost during the first 21 days and N nitrified during the first 42 days must have originated in the HUN fraction (Fig. 6). Also, it would appear that HUN materials were first converted to hydrolyzable  $\text{NH}_4^+$  and/or exchangeable  $\text{NH}_4^+$  before being transformed further.

The evidence that N may have been added to the system between 21 and 42 days may reflect the lower N content and wider C/N ratio of sugar beets as compared with alfalfa. The apparent increase at this time and the apparent loss of N during the last 21 days affected all fractions except HUN.

The rate of nitrification leveled off after 42 days. This would be consistent with denitrification as the mechanism for N loss at this time.

Navy bean system: The initial increase in TN and TON in Fig. 7 was reflected mainly in NHN and the AN fractions. This would seem to support the view that additions of N to the system were due to adsorption of  $\text{NH}_3$  from the atmosphere. The added  $\text{NH}_3$  would be expected to accumulate first at active surface sites in the AN fraction before being fixed in more stable combinations in the NHN fraction. If biological  $\text{N}_2$ -fixation had occurred it would be expected to appear first in recognized metabolic products such as amino acids and amino sugars. In fact, increases in AAN and ASN occurred

later and at the expense of N that previously accumulated in the NHN fraction.

Apparent losses of N from the system during the last 21 days involved mainly decreases in NHN and HUN. However, it is likely that this nitrogen was first nitrified and then lost by either biological or chemical denitrification. The low pH of the soil (pH 5.5) would have favored chemical denitrification.

Corn system: Increases in TN during the first 21 days (Fig. 8) involved increases in both AN and NHN, but also in HUN. Increases in identifiable metabolic products (AAN and ASN) did not occur until later. Again, this is evidence that adsorption of  $\text{NH}_3$ , rather than  $\text{N}_2$ -fixation, was responsible for increased N in the system.

As in the other three systems, the hydrolyzable  $\text{NH}_4^+$  fraction (AN) appears to represent N held transitionally by active surface groups. Its equilibrium level did not fluctuate widely, but the flux of N through this stage was undoubtedly high.

The HUN fraction may represent another transitional phase through which N compounds and complexes of intermediate weight pass en route to and from larger and more stable complexes in the NHN fraction. Thus, during the last 21 days of incubation, it appears that NHN increased directly at the expense of the HUN fraction (Fig. 8). The same thing happened at this time in the alfalfa system (Fig. 5). Similar reciprocal changes between these two factions had occurred during the first 21 days with navy beans (Fig. 4) and during later stages of incubation with sugar beets (Fig. 3).

Nitrite or nitrate did not accumulate at any time in the corn system (Fig. 8). It must be assumed that active nitrifying populations were present because trace levels were maintained (Table 4). It is possible that nitrite may have been sidetracked into reactions leading to stable organic combinations and that these reactions may have been involved in the transfer of N from the HUN fraction to NHN during the last 21 days.

## SUMMARY

Alfalfa tops, navy bean straw, corn stover and sugar beet tops at 0, 2, 10, and 50 g/kg were incorporated in a Hodunk sandy loam soil. Changes in concentration and distribution of N forms were followed over a 63-day incubation period.

Patterns of nitrogen transformation and distributions of N in different forms were essentially unaffected by the additions of the different residues at the 2 g/kg rate. Nitrification rates and the quantities of  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  produced increased with the rate of addition of residues high in N (alfalfa tops, 3.45% N, and sugar beet tops, 1.51% N). In the case of low N materials (navy bean straw and corn stover, both about 0.8% N), net nitrification was delayed at higher rates of addition. At 50 g/kg, no more than trace quantities of  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  were encountered at any time with the corn amendment. Some recovering of nitrifying capacity in the high rate bean system was apparent in the last sampling (63 days).

These different patterns of nitrate accumulation demonstrate the effect of C/N ratio on the balance between net mineralization and net immobilization of N as plant residue carbon is converted to  $\text{CO}_2$  and microbial cells and products. Major losses of carbon occurred during the first 21 days of incubation, but continued at decreasing rates through the 63rd day. Changes in total N (TN) and differential

effects on fractional forms of N were most pronounced at the highest rate of residue addition (50 g/kg).

Large losses of N occurred during the first 42 days from the highest rate of alfalfa and sugar beet tops. Losses of N from these narrow C/N systems were ascribed to volatilization of  $\text{NH}_3$ . Increases in hydrolyzable ammonium (AN), including transiently high levels of exchangeable  $\text{NH}_4^+$  were consistent with the interpretation that rapid respiratory loss of C was accompanied by net mineralization of N, at rates that exceeded the soil's capacity to adsorb and stabilize the released  $\text{NH}_3$ . Denitrification did not appear to be responsible for losses of N during the first 42 days in these two systems, since  $\text{NO}_3^-$  accumulated at rapid and uniform rates over this period.

On the other hand, the addition of wide C/N materials (navy beans and corn) at high rates resulted in significant increases in total N during the first 21 days. These increases were ascribed to adsorption of  $\text{NH}_3$  volatilized from alfalfa and sugar beet systems and transferred by diffusion through the confined atmosphere of the growth chamber. The increases in TN were accounted for by increases in the nonhydrolyzable fraction (NHN), hydrolyzable ammonium (AN), and unidentified hydrolyzable forms (HUN). Increases in recognizable metabolic products--amino acids (AAN) and amino sugars (ASN)--did not occur until later. This was taken as evidence that the initial increases in TN were due to adsorption of  $\text{NH}_3$  rather than to biological  $\text{N}_2$  fixation.

Significant losses of N occurred during the last 21 to 42 days from the high rate systems. These appeared to have been due

to denitrification, since the rate of nitrate accumulation was sharply curtailed with alfalfa and sugar beets and continued to be strongly repressed in the presence of beans and corn. The low pH of the soil (pH 5.5) would have favored chemical denitrification by sidetracking reactions of nitrite. Also, the more readily available energy substrates to support biological denitrification would have been largely dissipated during the first several days of incubation.

Significant increases and decreases in amino acids and amino sugars suggest that microbial populations may have reached peak numbers sometime between the 21st and 42nd day of incubation. However, it appeared that much larger quantities of N were actively cycled over the entire incubation period by transformations involving the HUN and NHN fractions.

Reciprocal changes in the HUN and NHN fractions suggest that HUN materials represent a transitional phase through which N in compounds of intermediate molecular weight passes en route to and from larger and/or more stable complexes in the NHN fraction.

The AN fraction (which included exchangeable  $\text{NH}_4^+$ ) probably represents N held transiently by active surface groups. Its equilibrium level did not fluctuate widely, as is to be expected if quantities present depend primarily on active surface area. Nevertheless, the flux of N through this phase was undoubtedly high. Ammonia entering the system from the external atmosphere or released within the systems by mineralization would likely appear first at surface sites before entering into further transformations such as microbial immobilization, nitrification, volatilization and chemical condensation to form

humic complexes of varying stability to be found in the HUN and NHN fractions.

## CONCLUSIONS

The observed distributions of N may have resulted, in part, from artifacts of acid hydrolysis. Nevertheless, the data indicate that fractional analyses based on acid hydrolysis can be used to differentiate a number of chemically distinct categories of N compounds that appear to exist in dynamic sequential relationships, one to another.

The basic transformation leading to changing distributions of N was undoubtedly the respiratory disengagement of  $\text{CO}_2$  by the soil heterotrophic population. The most actively fluctuating fractions were recovered in the hydrolysate.

One-half or less of the hydrolyzable N was in recognizable products of microbial synthesis. Thus, much of the active cycling of N may have involved strictly chemical and/or physical transformations in the extracellular environment.

Nonenzymatic processes inferred from the data included volatilization and adsorption of  $\text{NH}_3$ , sequences of polymerization and depolymerization involving precursors and components of fulvic and humic acids, and reactions of nitrous acid leading to both chemical immobilization and chemical denitrification.

These conclusions were based mainly on results at the 50 g/kg rate of amendment. Sequential changes were not clearly expressed at



more practical lower rates. Nevertheless, similarly high concentrations of plant exudates and residues undoubtedly attain in microhabitats under normal management in the field and both biological and nonbiological processes are similarly involved.

## LITERATURE CITED

1. Bremner, J. M. 1965. Organic forms of nitrogen. In C. A. Black (ed.). Methods of Soil Analysis, Part 2. Agronomy. 9:1238-1255.
2. Bremner, J. M., and C. S. Mulvaney. 1983. Total nitrogen. In A. P. Page et al (eds.). Methods of Soil Analysis, Part 2. Agronomy (2nd ed.). 9:595-624.
3. Cornforth, I. S. 1968. The potential availability of organic nitrogen fractions in some West Indian soils. Expl. Agric. 4:193-201.
4. Dalal, R. C. 1978. Distribution of organic nitrogen in organic volcanic and nonvolcanic tropical soils. Soil Sci. 125: 178-180.
5. Fleige, H., and K. Baeumer. 1974. Effect of zero-tillage on organic carbon and total nitrogen content, and their distribution in different N fractions in loessial soils. Agro-Eco-systems. 1:19-29.
6. Harrison, R. M. 1963. Quantitative and qualitative changes in soil organic matter as related to residue additions, cropping sequence and management. Ph.D. Dissertation, Michigan State University, East Lansing, Michigan.
7. Jansson, S. L., and J. Persson. 1982. Mineralization and immobilization of soil nitrogen. In F. J. Stevenson (ed.). Nitrogen in Agricultural Soils. Agronomy 22:229-252.
8. Keeney, D. R., and J. M. Bremner. 1964. Effect of cultivation on the nitrogen distribution in soils. Soil Sci. Soc. Amer. Proc. 28:653-656.
9. Keeney, D. R., and J. M. Bremner. 1966. Characterization of mineralized nitrogen in soils. Soil Sci. Soc. Amer. Proc. 30:714-719.
10. Keeney, D. R., and D. W. Nelson. 1982. Nitrogen--Inorganic forms. In A. L. Page et al. (ed.). Methods of soil analysis, Part 2. Agron. 9:643-698.

11. Khan, S. U. 1971. Nitrogen fractions in a grey wooded soil as influenced by cropping systems and fertilizers. *Can. J. Soil Sci.* 51:431-437.
12. Larson, W. E., C. E. Clapp, W. H. Pierre, and Y. Morachan. 1972. Effects of increasing amounts of organic residues on continuous corn: II. Organic carbon, nitrogen, phosphorus, and sulfur. *Agron. J.* 64:204-208.
13. Little, T. M., and F. J. Hills. 1978. *Agricultural Experimentation Design and Analysis*. John Wiley and Sons, New York.
14. Martel, Y. A., and E. A. Paul. 1974. Effect of cultivation on the organic matter of grassland soils as determined by fractionation and radiocarbon dating. *Can. J. Soil Sci.* 54:419-426.
15. Meints, V. W., and G. A. Peterson. 1977. The influence of cultivation on the distribution of nitrogen in soils of the Ustoll suborder. *Soil Sci.* 124:334-342.
16. Moore, A. W., and J. S. Russell. 1968. Relative constancy of soil nitrogen fractions with varying total soil nitrogen. 9th Int. Cong. Soil Sci. Transactions Adelaide, Australia. 2:557-566.
17. Nelson, D. W. 1982. Gaseous losses of nitrogen other than through denitrification. In F. J. Stevenson (ed.). *Nitrogen in Agricultural Soils*. *Agronomy* 22:327-364.
18. Normmik, H., and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. In F. J. Stevenson (ed.). *Nitrogen in Agricultural Soils*. *Agron.* 22:123-171.
19. Osborne, G. J. 1977. Chemical fractionation of soil nitrogen in six soils from Southern New South Wales. *Aust. J. Soil Res.* 51:159-165.
20. Porter, L. K., B. A. Stewart, and H. J. Haas. 1964. Effects of long-time cropping on hydrolyzable organic nitrogen fractions in some Great Plains soils. *Soil Sci. Soc. Amer. Proc.* 28:368-370.
21. Schulte, E. E. 1980. Recommended soil organic matter tests. In W. C. Dahnke, (ed.). *Recommended chemical soil test procedures for the North Central Region*. North Dakota Agr. Exp. Stn. Bull. 499 (Revised. N. D. State Univ., Fargo, N.D.
22. Snedecor, G. W., and W. G. Cochran. 1974. *Statistical Methods* (6th ed.). Iowa State University Press, Ames, Iowa.

23. Sowden, F. J. 1968. Effect of long-term annual additions of various organic amendments on the nitrogenous components of a clay and a sand. *Can. J. Soil Sci.* 48:331-339.
24. Sowden, F. J., and H. J. Atkinson. 1968. Effects of long-term annual additions of various organic amendments on the organic matter of a clay and a sand. *Can. J. Soil Sci.* 48:323-330.
25. Steel, R. G. D., and J. H. Torrie. 1980. *Principles and Procedures of Statistics.* McGraw-Hill Book Company, New York.
26. Stevenson, F. J. 1965a. Amino acids. *In* C. A. Black et al, (eds.). *Methods of Soil Analysis, Part 2.* Agronomy 9:1437-1451.
27. Stevenson, F. J. 1965b. Amino sugars. *In* C. A. Black et al, (eds.). *Methods of soil analysis, Part 2.* Agronomy 9:1429-1436.
28. Stevenson, F. J. 1982. Organic forms of soil nitrogen. *In* F. J. Stevenson (ed.). *Nitrogen in Agricultural soils.* Agronomy 22:67-122.
29. Stevenson, F. J. 1982. Nitrogen--Organic forms. *In* A. L. Page et al, (eds.). *Methods of Soil Analysis. Part 2.* Agronomy (2nd ed.). 9:625-641.
30. Stevenson, F. J., and S. N. Tilo. 1966. Nitrogenous constituents of deep-sea sediments. *Adv. Organic Geochem.* 237-263.
31. Walkley, A. 1935. An examination of methods for determining organic carbon and nitrogen in soils. *J. Agr. Sci.* 25:598-609.
32. Walkley, A., and I. A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* 37:29-37.

## APPENDICES

APPENDIX A  
STATISTICAL DATA FOR  
CHAPTER IV

Table 1. Probabilities for significance of main effects and interactions of residues, rates, and times on analyses for carbon and forms of nitrogen.

Parameter Measured	Source of variance						
	Residence (R)	Rate (A)	Time (T)	R x A	R x T	A x T	R x A x T
Degrees of Freedom	3	2	3	6	9	6	18
n =	36	48	36	12	9	12	3
Total N	0.01	0.01	0.05	0.01	0.01	0.01	0.01
Total hydrolyzable N	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Hydrolyzable ammonium N	0.01	0.01	0.01	0.01	0.01	0.05	NS
Amino acid N	0.01	0.01	0.05	0.01	NS	NS	0.05
Amino sugar N	0.01	NS	0.01	NS	NS	NS	NS
Hydrolyzable unknown N	0.01	0.01	0.01	0.05	0.01	0.05	0.05
Nonhydrolyzable N	0.01	0.01	NS	0.01	NS	0.05	NS
Exchangeable $\text{NH}_4^+$	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Nitrate + nitrite N	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Organic C	0.01	0.01	0.01	NS	NS	0.01	NS

Table 2. Probabilities for significance of main effects and interactions of residues, rates, and times on the proportion (% of total N) of fractional forms of N.

Parameter measured	Source of variance						
	Residue (R)	Rate (A)	Time (T)	R x A	R x T	A x T	R x A x T
Degrees of Freedom	3	2	3	6	9	6	18
n =	36	48	36	12	9	12	3
Total hydrolyzable N	0.01	0.05	0.01	0.01	0.05	0.05	NS
Hydrolyzable ammonium N	0.01	0.01	0.01	0.05	0.05	0.05	NS
Amino acid N	0.01	0.01	0.01	0.05	0.05	NS	0.05
Amino sugar N	0.01	0.01	0.01	0.01	NS	NS	NS
Hydrolyzable unknown N	NS	NS	0.01	NS	NS	NS	NS
Nonhydrolyzable N	0.01	0.01	N.S.	0.01	N.S.	0.05	NS



Table 3. Effect of type and rate of crop residues and time of incubation on the concentration of total organic nitrogen.

Residue	Rate	Total organic nitrogen (TON) <sup>†</sup>			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- mg/kg -----			
Check	0 <sup>‡</sup>	564	589	593	573
Alfalfa	2	710	705	712	748
	10	808	789	709	676
	50	1477	1127	1058	994
Navy bean	2	647	595	675	613
	10	694	691	707	667
	50	807	855	854	751
Corn	2	665	682	696	697
	10	696	745	700	686
	50	766	850	815	825
Sugar beet	2	696	642	622	600
	10	711	706	671	659
	50	964	905	890	830
LSD <sub>0.05</sub>	(3-way interaction)	NS			

<sup>†</sup> TON = Total Organic N = Total N - C (Nitrate + nitrite N)

<sup>‡</sup> Values at zero time not included in ANOVA

Table 4. Effect of crop residue type and time of incubation on the proportion of total N as total hydrolyzable N.

Residue	Total hydrolyzable N (expressed as % of total N)				Residue Mean
	Incubation time (days)				
	0	21	42	63	
	-----	%	-----		
Alfalfa	83.6	71.3	73.7	69.5	74.5
Navy bean	84.6	81.5	80.2	71.5	80.9
Corn	78.3	76.7	80.6	74.5	77.5
Sugar beet	83.3	82.5	78.6	79.2	80.9
Time mean	82.5	77.9	78.3	75.2	
LSD <sub>0.05</sub>	(2-way interaction)			4.8	

Table 5. Effect of type and rate of crop residues on the proportion of total N as total hydrolyzable N.

	Total hydrolyzable N (expressed as % of total N)				
	Residue rate (g/kg)				
Residue	0†	2	10	50	Residue Mean
	----- % -----				
Alfalfa	87.7	72.4	78.7	72.4	77.8
Navy bean	87.7	81.1	81.7	80.1	82.6
Corn	87.7	71.6	78.7	82.4	80.1
Sugar beet	87.7	80.5	81.7	80.5	82.6
Rate mean	87.7	76.4	80.2	78.8	
LSD <sub>0.05</sub>	(2-way interaction)			4.2	

<sup>†</sup> Values at zero rate not included in ANOVA.

Table 6. Effect of crop residue rate and time of incubation on the proportion of total N as total hydrolyzable N.

	Total hydrolyzable N (expressed as % of total N)				
	Incubation time (days)				
Rate	0	21	42	63	Rate Mean
g/kg	----- % -----				
0†	77.4	76.6	75.6	74.7	76.1
2	78.4	79.4	74.3	73.4	76.4
10	82.9	76.6	82.1	78.8	80.2
50	86.0	77.7	78.3	73.3	78.8
Time mean	81.2	77.6	77.6	75.1	
LSD <sub>0.05</sub>	(2-way interaction)			4.2	

<sup>†</sup> Values at zero rate not included in ANOVA

Table 7. Effect of type and rate of crop residue on the concentration of nonhydrolyzable N.

Residue	Nonhydrolyzable N <sup>†</sup>				Residue Mean
	Residue rate (g/kg)				
	0 <sup>‡</sup>	2	10	50	
	----- mg/kg -----				
Alfalfa	70.0	178.8	113.2	181.7	135.9
Navy bean	70.0	107.2	124.6	153.7	113.9
Corn	70.0	184.4	147.7	141.7	135.9
Sugar beet	70.0	107.8	107.5	131.7	104.2
Rate mean	70.0	144.6	123.2	152.2	
LSD <sub>0.05</sub>	(2-way interaction)			34.7	

<sup>†</sup> Nonhydrolyzable N = Total N - Total hydrolyzable N

<sup>‡</sup> Values at zero rate not included in ANOVA

Table 8. Effect of residue rate and time of incubation on the concentration of nonhydrolyzable N.

	Nonhydrolyzable N <sup>†</sup>				
	Incubation time (days)				
Rate	0	21	42	63	Rate Mean
g/kg	----- mg/kg -----				
0‡	70.0	154.0	55.0	167.0	111.5
2	145.3	126.0	152.8	153.3	144.6
10	121.6	156.5	100.4	114.3	123.2
50	137.5	171.2	139.3	160.8	152.2
Time mean	118.7	152.0	111.9	148.9	
LSD <sub>0.05</sub>	(2-way interaction)			34.7	

<sup>†</sup> Nonhydrolyzable N = Total N - Total hydrolyzable N

<sup>‡</sup> Values at zero rate not included in ANOVA

Table 9. Effect of type and rate of crop residue on the proportion of total N as nonhydrolyzable N.

	Nonhydrolyzable N <sup>†</sup> (expressed as % of total N)				
	Residue rate (g/kg)				
Residue	0 <sup>‡</sup>	2	10	50	Residue Mean
	----- % -----				
Alfalfa	12.3	23.7	13.9	13.5	15.9
Navy bean	12.3	16.2	17.9	18.3	16.2
Corn	12.3	26.2	20.6	17.1	19.1
Sugar beet	12.3	16.1	15.1	13.8	14.3
Rate mean	12.3	20.6	16.9	15.7	
LSD <sub>0.05</sub>	(2-way interaction )			4.2	

<sup>†</sup> Nonhydrolyzable N = Total N - Total hydrolyzable N

<sup>‡</sup> Values at zero rate not included in ANOVA

Table 10. Effect of residue rate and time of incubation on the proportion of total N as nonhydrolyzable N.

	Nonhydrolyzable N <sup>†</sup> (expressed as % of total N)				
	Incubation time (days)				
Rate	0	21	42	63	Rate Mean
g/kg	----- % -----				
0 <sup>‡</sup>	12.3	22.5	19.1	24.3	19.6
2	21.3	18.2	21.5	21.3	20.6
10	16.8	20.6	13.8	16.3	16.9
50	13.7	17.8	14.2	17.1	15.7
Time mean	16.0	19.8	17.1	19.8	
LSD <sub>0.05</sub>	(2-way interaction)			4.2	

<sup>†</sup>Nonhydrolyzable N = Total N - Total hydrolyzable N

<sup>‡</sup>Values at zero rate not included in ANOVA



Table 11. Effect of residue type and time of incubation on the concentration of hydrolyzable ammonium N.

Residue	Hydrolyzable ammonium N (AN) <sup>†</sup>				Residue Mean
	Incubation time (days)				
	0	21	42	63	
	----- mg/kg -----				
Alfalfa	148.6	223.8	208.2	211.8	198.1
Navy bean	135.4	161.7	167.9	166.9	158.0
Corn	121.8	157.2	175.1	161.1	155.3
Sugar beet	138.0	184.4	199.6	186.0	177.0
Time mean	135.9	181.8	187.7	182.9	172.1
LSD <sub>0.05</sub>	(2-way interaction)			14.2	

<sup>†</sup> AN = Hydrolyzable ammonium N including exch.  $\text{NH}_4^+$

Table 12. Effect of type and rate of crop residues on the concentration of hydrolyzable ammonium N.

	Hydrolyzable ammonium N (AN) <sup>†</sup>				
	Residue rate (g/kg)				
Residue	0 <sup>‡</sup>	2	10	50	Residue Mean
	----- mg/kg -----				
Alfalfa	141.0	151.9	176.6	265.6	183.8
Navy bean	141.0	151.5	161.0	161.6	153.8
Corn	141.0	149.2	152.7	164.1	151.8
Sugar beet	141.0	160.5	168.6	201.9	168.0
Rate mean	141.0	153.3	164.7	198.3	
LSD <sub>0.05</sub>	(2-way interaction)			12.3	

<sup>†</sup>AN = Hydrolyzable ammonium N including exch.  $\text{NH}_4^+$

<sup>‡</sup>Values at zero rate not included in ANOVA

Table 13. Effect of residue rate and time of incubation on the concentration of hydrolyzable ammonium N.

	Hydrolyzable ammonium N (AN) <sup>†</sup>				
	Incubation time (days)				
Rate	0	21	42	63	Rate Mean
g/kg	----- mg/kg -----				
0 ‡	141.0	165.0	168.0	172.0	161.5
2	115.9	163.4	171.9	161.9	153.3
10	139.4	167.9	176.6	175.0	164.7
50	152.6	214.0	214.7	212.0	198.3
Time mean	137.2	177.6	182.8	180.2	
LSD <sub>0.05</sub>	(2-way interaction)			12.3	

<sup>†</sup> AN = Hydrolyzable ammonium N including exch.  $\text{NH}_4^+$

‡ Values at zero rate not included in ANOVA

Table 14. Effect of residue type and time of incubation on the proportion of total N as hydrolyzable ammonium N.

Residue	Hydrolyzable ammonium N (AN) <sup>†</sup>				Residue Mean
	Incubation time (days)				
	0	21	42	63	
	----- % ‡ -----				
Alfalfa	15.2	22.9	22.2	22.4	20.7
Navy bean	19.0	22.8	22.5	23.8	22.0
Corn	17.2	20.7	23.5	22.3	20.9
Sugar beet	17.8	24.2	25.7	24.8	23.1
Time mean	17.3	22.7	23.5	23.3	
LSD <sub>0.05</sub>	(2-way interaction)			1.7	

<sup>†</sup> AN = Hydrolyzable ammonium including exch.  $\text{NH}_4^+$

<sup>‡</sup> Expressed as % of total N

Table 15. Effect of type and rate of crop residues on the proportion of total N as hydrolyzable ammonium N.

	Hydrolyzable ammonium N (AN) <sup>†</sup>				
	Residue rate (g/kg)				
Residue	0 <sup>‡</sup>	2	10	50	Residue Mean
	----- % § -----				
Alfalfa	24.8	20.3	22.0	19.9	21.8
Navy bean	24.8	23.3	23.3	19.5	22.7
Corn	24.8	21.2	21.5	20.2	21.9
Sugar beet	24.8	24.4	23.8	21.3	23.6
Rate mean	24.8	22.3	22.6	20.2	
LSD <sub>0.05</sub>	(2-way interaction)			1.5	

<sup>†</sup> AN = Hydrolyzable ammonium N including exch.  $\text{NH}_4^+$

<sup>‡</sup> Value at zero rate not included in ANOVA

§ Expressed as % of total N

Table 16. Effect of residue rate and time of incubation on the proportion of total N as hydrolyzable ammonium N.

	Hydrolyzable ammonium N (AN) <sup>†</sup>				
	Incubation (days)				Rate Mean
	0	21	42	63	
g/kg	----- % <sup>‡</sup> -----				
0 §	24.8	26.4	27.6	25.0	25.9
2	17.0	24.4	24.5	23.3	22.3
10	19.3	22.3	24.3	24.7	22.6
50	15.6	21.4	21.8	22.1	20.2
Time mean	19.2	23.6	24.6	23.8	22.8
LSD <sub>0.05</sub>	(2-way interaction)			1.5	

<sup>†</sup> AN = Hydrolyzable ammonium N including exch.  $\text{NH}_4$

<sup>‡</sup> Expressed as % of total N

§ Values at zero rate not included in ANOVA

Table 17. Effect of type and rate of crop residues and time of incubation on the proportion of total N as amino acid N.

Residue	Rate	Amino acid nitrogen (AAN)			
		Incubation time (days)			
		0	21	42	63
	g/kg	----- % <sup>†</sup> -----			
Check	0 <sup>‡</sup>	32.9	26.1	30.0	30.8
Alfalfa	2	21.7	24.5	25.9	25.3
	10	33.7	26.3	30.5	28.6
	50	26.7	26.0	25.2	25.2
Navy bean	2	34.8	30.6	29.5	29.7
	10	34.8	26.6	33.0	29.6
	50	29.2	28.9	34.1	35.1
Corn	2	22.1	25.7	30.7	26.8
	10	27.9	30.3	33.4	34.6
	50	31.6	27.8	35.7	34.7
Sugar beet	2	22.1	27.9	30.9	30.1
	10	25.0	25.8	33.5	31.8
	50	28.3	28.5	32.5	29.2
LSD <sub>0.05</sub>	(3-way interaction)	4.7			

<sup>†</sup> Expressed as % of total N

<sup>‡</sup> Values at zero rate not included in ANOVA

Table 18. Simple effect of type of crop residues and time of incubation on the concentration and proportion of total N as amino sugar N.

Residue	Amino sugar N	Time of incubation	Amino sugar N (ASN)	
	mg/kg	day	mg/kg	% <sup>†</sup>
Alfalfa	90.5	0	76.2	9.7
Beans	73.7	21	58.4	7.4
Corn	66.7	42	82.8	10.4
Sugar beet	62.2	63	75.9	9.9
LSD <sub>0.05</sub>	7.9		7.9	1.1

<sup>†</sup> Expressed as % of total N



Table 19. Effect of type and rate of residue on the proportion of total N as amino sugar N.

	Amino sugar N (ASN)				
	Residue rate (g/kg)				
Residue	0†	2	10	50	Residue Mean
	----- ‡-----				
Alfalfa	16.2	12.5	11.4	6.5	11.6
Navy bean	16.2	10.1	10.5	10.1	11.7
Corn	16.2	9.2	9.3	8.6	10.8
Sugar beet	16.2	8.6	8.8	7.1	10.2
Rate mean	16.2	10.1	9.9	8.1	
LSD <sub>0.05</sub>	(2-way interaction)			1.8	

† Values at zero rate not included in ANOVA

‡ Expressed as % of total N

Table 20. Simple effect of time of incubation on the proportion of total N as hydrolyzable unknown N.

Incubation time	Hydrolyzable unknown N (HUN) <sup>†</sup>
Day	% ‡
0	27.2
21	20.5
42	13.1
63	13.4
LSD <sub>0.05</sub>	1.1

<sup>†</sup> HUN = Hydrolyzable unknown N = Total hydrolyzable N  
 - (ammonium N + amino acid N + amino sugar N)

<sup>‡</sup> Expressed as % of total N

APPENDIX B

SOIL SERIES

## APPENDIX B1

### HODUNK SERIES

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

Soil Profile: Hodunk sandy loam

AP	0-0.18m	Dark grayish brown (10 YR 4/2) to very dark grayish brown (10 YR 3/2); sandy loam; moderately fine, granular structure; friable when moist and soft when dry; medium content of organic matter; medium to slightly acid; abrupt smooth boundary. 0.10 to 0.28m thick
A <sub>2</sub>	0.18-0.41m	Yellowish brown (10 YR 5/4); pale brown (10 YR 6/3) or light yellowish brown (10 YR 6/4); sandy loam; weak, fine, granular to weak, fine subangular blocky structure; very friable when moist and soft when dry; medium acid; abrupt wavy boundary. 0.15 to 0.51 m thick.
B <sub>im</sub>	0.41-0.64m	Brown (10 YR 5/3) to pale brown (10 YR 6/3); sandy loam to light sandy clay loam; massive to weak, thick, platy structure; firm when moist and brittle when dry; weak to moderately developed fragipan; few thin clay flows; medium to strongly acid; clear wavy boundary. 0.10 to 0.30 m thick.

B <sub>2g</sub>	0.64-1.17m	Brown (10 YR 5/3) to yellowish brown (10 YR 5/4) mottled with yellowish brown (10 YR 5/8) and dark brown (7.5 YR 4.4), mottles are common, medium, distinct; sandy clay loam, heavy sandy loam, or light clay loam; few thin clay flows; weak, medium, subangular blocky structure; firm when moist, strongly to medium acid in the upper part and slightly acid in the lower part; abrupt irregular boundary. 0.38 to 0.76 m thick.
Cg	1.18 m +	Light yellowish brown (10 YR 6/4) to brown (10 YR 5/3) mottled with yellowish brown (10 YR 5/6-5/8), mottles are common, medium, distinct; sandy loam; massive to very weak, coarse, subangular blocky structure; friable when moist and hard when dry; calcareous.
<u>Topography:</u>		Gently to moderately sloping till plains and moraines.
<u>Drainage and Permeability:</u>		Moderately well drained. Surface runoff is slow to moderate. Permeability is moderate to slow depending upon the degree of development of the fragipan.
<u>Natural Vegetation:</u>		Deciduous forest consisting of sugar maple, beech, oak, and hickories.
Source:		Schneider, I. F., R. W. Johnson, and E. P. Whiteside. 1967. Tentative placement of Michigan series in the new soil classification system. Dept. of Crop and Soil Sci., Michigan State University, East Lansing, Michigan.

## APPENDIX B2

### KALAMAZOO SERIES

The Kalamazoo series consists of deep, well drained soils, formed in loamy outwash overlying sand, loamy sand, or sand and gravel on outwash plains, terraces, valley trains, and low lying moraines. These soils have moderate permeability in the A and B horizons and rapid permeability in the 11B and 11C horizons. Slopes range from 0 to 12 percent. Mean annual precipitation is about 34 inches, and mean annual temperature is about 49 degrees F.

#### TAXONOMIC

CLASS: Fine-loamy, mixed, mesic Typic Hapludalfs.

Typical Pedon: Kalamazoo loam--on a 1 percent slope in a cultivated field. (Colors are for moist soil unless otherwise stated.)

#### Soil Profile

Ap	0-0.28m	Dark grayish brown (10 YR 4/2) loam; weak medium granular structure; friable; common fine roots; neutral; abrupt smooth boundary. 0.15 to 0.28 m thick.
B1	0.28-0.41m	Dark yellowish brown (10 YR 4/4) loam; weak medium subangular blocky structure; friable; common fine roots; worm channels filled with Ap material; neutral; gradual wavy boundary. 0 to 0.15 m thick.
B21t	0.41-0.51m	Dark yellowish brown (10 YR 4/4) clay loam; moderate medium subangular blocky structure; firm; thin continuous dark yellowish brown (10 YR 3/4) clay films on faces of peds; few fine roots; 1 percent pebbles; neutral; gradual wavy boundary.
B22t	0.51-0.76m	Dark brown (7.5 YR 4/4) clay loam; moderate medium subangular blocky structure; firm; thin continuous dark yellowish brown (10 YR 3/4) clay films on faces of peds; few fine roots; 1 percent pebbles; neutral; gradual wavy boundary. The combined thickness of the B21t and B22t horizons 0.20 to 0.76 m.

B23t	0.76-0.96m	Dark yellowish brown (10 YR 4/4) sandy loam; weak medium subangular blocky structure; friable; thin discontinuous dark yellowish brown (10 YR 3/4) clay films on faces of peds; 5 percent pebbles; medium acid; gradual wavy boundary. 0.15 to 0.38 m thick.
I Ib31	0.96-1.07m	Dark yellowish brown (10 YR 4/6) loamy coarse sand; massive; friable; 10 percent pebbles; medium acid; gradual wavy boundary. t to 0.51 m thick.
I Ib32	1.1-1.39m	Dark yellowish brown (10 YR 4/4) gravelly loamy sand; massive; friable; 20 percent pebbles; neutral; gradual wavy boundary. 0 to 0.38 thick.
I IC	1.4-1.63m	Dark yellowish brown (19 YR 4/4) gravelly coarse sand; single grained; loose; 20 percent pebbles; slight effervescence; mildly alkaline.
Drainage and Permeability:		Well drained. Runoff is slow on the level areas and rapid on the steeper slopes. Permeability is moderate in the A and B horizons and rapid in the I IB3 and I IC horizons.
Use and Vegetation:		A large part is cropped to corn, wheat, soybeans, and hay. A small part is in pasture. Some areas adjacent to the larger cities are idle cropland. The native vegetation was oak and hickory forest.
Source:		National Cooperative Soil Survey, U.S.A., 1978.

## APPENDIX B3

### CHARITY SERIES

The charity series consists of poorly drained to very poorly drained and limy soils which developed from highly calcareous stratified lacustrine clay and silty clay materials (management group 1c-c). They are generally located in nearly level till and lake plain areas.

Representation profile of Charity silty clay loam in a cultivated field:

0.0-0.15m	Very dark gray, friable, limy silty clay loam; strong granular structure.
0.15-0.28m	Grayish-brown, firm, limy silty clay.
0.28-0.51m	Light brownish-gray, very firm, limy silty clay; faintly mottled with pale brown.
0.51-1.07m +	Light brownish-gray, very firm, limy clay.

Taxonomic class for the Charity Clay: Aeric, Hapleaquept, fine, illitic (calcareous, mesic)

Source: Soil Survey Arenac County, Michigan. USDA Soil Conservation Service in Cooperation with Michigan Agric. Exp. Sta. and Michigan Dept. of Conservation, May 1967.