Fate of ^{15}N-depleted Fertilizer N in a Corn-Rye Cropping Sequence: Plant Uptake and Soil Distribution

by

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(ABSTRACT)

A field experiment was conducted in the Ridge and Valley region of Virginia near Blacksburg during the 1989 through 1991 corn-rye growing seasons. The treatments in this experiment consisted of varying amounts of ^{15}N-depleted fertilizer N applied to corn (*Zea mays* L.) at planting followed by a winter rye (*Secale cereale* L.) cover crop treatment. The research was divided into four studies. The first study was conducted to evaluate an analytical procedure that could be used for the diffusion of low masses of ^{15}N-labeled NH_4 in 2M KCl and subsequent analysis for N recovery and ^{15}N concentrations in soil by direct combustion mass spectrometry. Diffusion was found to be a suitable technique for preparing low-mass N samples for automated ^{15}N analysis by Automated Nitrogen-Carbon Analysis/Mass Spectrometry (ANCA/MS). Recoveries of low masses of added N were quantitative, and accurate ^{15}N concentrations were obtained when the results were corrected for isotope dilution due to background or contaminant N.

The second study was conducted to determine if ^{15}N-depleted fertilizer N could be satisfactorily used as a tracer of residual fertilizer N in plant tissue and various soil N fractions through a corn-winter rye crop rotation. Fertilizer-derived N in the soil NO_3^--N fraction following corn harvest was clearly detectible and distinguishable from natural abundance to a 90-cm depth. Detection of fertilizer N in the total N pool below the 30-cm depth was not reliable, particularly at the lower N rates. Clay-fixation of fertilizer N measured at corn harvest was not detected by ^{15}N analysis. Inconclusive results indicate that further research is needed to determine the feasibility of using depleted material for measuring clay-fixation of fertilizer-derived NH_4^+-N. Nitrogen uptake by a winter rye cover crop reduced soil NO_3^--N levels below that required for accurate isotope-ratio analysis. Following winter fallow (approx. 1 yr after fertilizer application) residual ^{15}N-depleted fertilizer N was still detectable in plant tissue and the soil NO_3^--N fraction.

The objectives of the third study were to measure plant uptake and soil distribution of fertilizer N applied to corn at varying N rates and to determine the relationships between economic optimum N rate, fertilizer-use efficiency, and potential leaching loss of residual fertilizer N to ground water. Plant recovery of fertilizer N in 1989 ranged from 33 to 47% even though no grain yield and fertilizer N uptake response resulted from N fertilization. Greatest accumulation of residual fertilizer N was found in the surface 30-cm both years following corn harvest. The economic optimum N rate for 1990 corn planted into a rye mulch (218 kg N ha^{-1})

corresponded closely with the rate (224 kg N ha^{-1}) resulting in the highest fertilizer-use efficiency. Low levels of residual fertilizer-derived NO_3^- in the 60-90-cm depth following the 1990 corn harvest provides evidence to support the use of the economic optimum N rate concept from both economic and environmental viewpoints.

The fourth study was designed to measure the effectiveness of a winter rye cover crop for recovering residual fertilizer N from the previous application of varying N rates to corn. Recovery of fertilizer N by winter rye increased with increasing N rate applied to the previous corn crop and ranged from 3.5 to 35.9 kg N ha^{-1} in 1990 and 2.3 to 25.7 kg N ha^{-1} in 1991. Residual fertilizer N recovery in 1991 was higher in rye plots where the previous corn crop had been planted no-till into rye stubble as compared to corn planted no-till into rye mulch. Little or no fertilizer-derived mineral N was measured in the soil to a final depth of 90-cm following a winter rye cover crop. Amounts of fertilizer-derived mineral N increased with depth and previous fertilizer N rate applied to corn following winter fallow. These results provide evidence to support the use of a winter rye cover crop on a silt loam soil to recover residual fertilizer-derived mineral N that might otherwise be lost to ground water.

Dedication

To my wife Karen and my daughters, Lauren and Leah.

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Chapter I

Introduction

More fertilizer nitrogen (N) is applied to corn than on any other crop in the U.S.. Since 1964, fertilizer N use on corn has more than tripled to 8.6 million metric tons which accounts for 44 % of the U.S. total annual consumption (Natural Resource Economics Division USDA, 1985). Unfortunately, the recovery of added fertilizer N by the fertilized corn crop is seldom greater than 50 to 60% (Pearson et al., 1961; Jolley and Pierre, 1977; Gerwing et al., 1979; Legg et al., 1979; Bigeriego et al., 1979; Timmons and Cruse, 1990). The lack of a mechanism for long-term storage of plant available fertilizer N in soils suggest that N not utilized by the plant may pose a potential environmental hazard. Water quality, and especially the potential for contamination of ground water by fertilizer-derived nitrate-nitrogen (NO_3^--N) is of major concern to both agricultural and urban users of ground water.

The E.P.A. *Chesapeake Bay program: A Framework For Action* (Gillelan and Macknis, 1983) reported that 60 to 75% of the total nitrogen load to the Chesapeake Bay came from croplands of the watershed. Over-application of N-containing commercial fertilizers and animal wastes are identified as sources for NO_3^- enrichment of surface and subsurface waters.

Leaching is the predominant pathway for nitrogen loss from the root zone, particularly during the winter months following a growing season with low rainfall (Maclean, 1977). Accumulation of residual fertilizer N in the root zone following the harvest of a summer annual suggests that plant uptake by a winter annual may minimize the potential for fertilizer N to leach into ground water (Hahne et al., 1977; Linville and Smith, 1971; MacGregor et al., 1974). To adequately characterize the movement of fertilizer N in the soil profile, it is essential to determine the uptake of fertilizer N by crops and to measure the incorporation of fertilizer N into the various soil N fractions. Knowledge of these factors would enable more effective application of best management practices for increasing the efficiency of N fertilizer utilization and reducing NO_3^- contamination of ground water.

In 1989 the National Fertilizer and Environmental Research Center, Tennessee Valley Authority (TVA), initiated a regional project with a primary objective to assess the effectiveness of winter cover crops for reducing nitrate leaching of residual fertilizer N. Cooperative projects were located in Georgia, Nebraska, North Carolina, South Carolina, and Virginia utilizing ^{15}N-depleted fertilizers.

The present study includes the results obtained in fertilizer N experiments conducted from 1989 through 1991 corn-rye growing seasons. The objectives of the research presented in each chapter are as follows:

1. Chapter 2: to conduct a through review of the published literature and identify those management strategies that influence the economic and environmental use of nonleguminous winter cover crops.

2. Chapter 3: to evaluate a procedure for the diffusion of low masses of ^{15}N-labeled NH_4 in 2M KCl and subsequent analysis for N recovery and ^{15}N concentration in soil by direct combustion mass spectrometry.

3. Chapter 4: to determine the limits of ^{15}N-depleted fertilizer N detection as a tracer of residual fertilizer N in plant tissue and various soil N fractions through a corn-rye crop rotation.

4. Chapter 5: (1) to measure plant uptake and soil distribution of fertilizer N applied to corn at five N rates, (2) to measure the influence of fertilizer N rate on the recovery of fertilizer N in various soil N fractions following corn harvest, and (3) to establish the relationships between economic optimum N rate, fertilizer-use efficiency, and potential leaching loss of residual fertilizer-derived N to ground water.

5. Chapter 6: (1) to measure the effectiveness of winter rye to recover residual fertilizer N applied to the previous corn crop at five levels of N fertilization,

(2) to measure the influence of winter cover management on the distribution of residual fertilizer N in various soil N fractions, and (3) to estimate losses of fertilizer-derived mineral N to the environment in a corn-rye cropping sequence.

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Chapter II

Nonleguminous Cover Crop Management for Residual N Recovery and Subsequent Crop Yields

Abstract

When nonleguminous cover crops are part of a crop rotation, consideration should be given to those management practices that will reduce soil erosion, maximize recovery of residual mineral N, and optimize N-use efficiency by the following summer annual. In this paper, research is reviewed that identifies those management strategies that influence the economic and environmental use of nonleguminous winter cover crops. Nonlegume cover crops can play a major role in "trapping" residual NO_3^- from being leached during winter but the magnitude of such trapping will vary depending on i) cover crop planting date; ii) cover crop seeding rate and subsequent plant population; iii) amount of residual mineral N remaining after the harvest of the previous crop; and iv) cover crop growth stage at the time of termination. Cover crop removal from the soil surface (tillage incorporation or silage harvest vs surface mulch) appears to have the most negative effects on subsequent crop yield. Lower corn grain yields at low fertilizer N rate are common when planted no-tillage (NT) into nonlegume residues compared to winter fallow. However, at higher N

rates, corn grain yields tend to be higher for corn planted NT into nonlegume residues due to greater soil moisture availability resulting in greater fertilizer-use efficiency.

Introduction

The practice of sowing a winter annual crop following the harvest of a summer annual has long been recognized for its importance in conserving soil and water and maintaining or increasing soil organic matter levels (Pieters and McKee, 1938). In light of current governmental regulations pertaining to crop production on highly erodible soils and increasing interest in management practices that reduce the potential for nitrate pollution of surface and ground waters, there is need for information pertaining to both environmental and economic consequences of winter cover crop management.

Leguminous cover crops have generally received the most attention due to their N fixation potential and the escalating cost of nitrogen fertilizer. A significant amount of the cover crop research effort has been devoted to quantifying the N contribution of legumes to the following crop, and developing nitrogen management strategies that optimize grain yields (Hargrove, 1986). In contrast, information on the role of nonlegumes in crop production systems is limited and often incomplete. As Eckert (1988) points out, many farmers include small grain cover crops as part of their no-tillage grain production systems but limited research with the nonlegumes has made it difficult for farmers, consultants, and extension personnel to determine if the practice is economically and environmentally viable. However, one of the most useful sources of research information on the nonlegume cover crops are those studies that were designed to determine the N-supplying power of various legume cover crops. Typically, one or more nonlegumes in addition to a fallow or previous crop residue cover treatment were included in the experimental design for comparison purposes. Unfortunately, nonlegume effects, which might other wise have been manifest, were restricted by cover crop management practices that were best suited for the legumes.

The objectives of this paper are to review research that describes 1) the environmental role nonlegumes may play in the recovery of residual mineral N; and 2) the influence of cover crop management on subsequent summer crop N availability and grain crop yields.

Nonleguminous Cover Crops

The small grains which include rye (*Secale cereale* L.), wheat (*Triticum aestivum* L.), oats (*Avena sativa* L.), and barley (*Hordeum vulgare* L.) are the most popular species of nonleguminous cover crops. Compared to some of the perennial cover crops such as orchardgrass (*Dactylis glomerata* L.), tall fescue (*Festuca arundinacea* Schreb.), or mixtures of these grasses with red clover (*Trifolium pratense* L.), the small grains offer a number of valuable benefits and options to the farmer. Depending on need for forage and potential grain yield and price, the small grain cover crop may be harvested as livestock feed or as a cash grain crop. The small grain cover crops generally produce a mulch cover earlier and are less likely to contain undesirable perennial weeds than the perennial grasses (Moschler et al., 1967). Further use of the term "cover crop" will pertain to the small grains unless otherwise stated.

Rye has long been regarded as one of the most suited small grains for cover crop use because of its ability to survive low fertility and extreme winter temperatures (Pieters and McKee, 1938). Moschler et al. (1967) highly recommended rye as a cover crop for no-till corn because of its superior winter hardiness, susceptibility to herbicide kill and the production of relatively large amounts of persistent mulch. Wheat and oats were found to be comparable as mulches in Virginia except at higher elevations where oats winter-killed. Barley's winter kill susceptibility and resistance to paraquat (1,1'-dimethly-4,4'-bipyridinium ion) made it the least satisfactory as a winter cover crop for no-till corn (Moschler et al., 1967). Triplett (1986) and Gallaher (1977) recognized the importance of persistent cover crop residue in conserving enough soil water to withstand short-term drought during growth of both corn and soybean (*Glycine max* L.).

Cover Crop Recovery of Residual Mineral N

When high nitrogen fertilization rates are applied to a summer annual and/or unusually low crop yields result due to drought, NO_3^--N has been found to accumulate in the rooting zone at concentrations ranging from a few to several hundred mg kg^{-1} (Hahne et al., 1977; Linville and Smith, 1971; Macgregor et al., 1974). Maclean (1977) studied the movement of NO_3^--N on loam and sandy loam soils and found N losses from plots receiving 448 kg N ha^{-1} tended to be low during the summer annual cropping season. However, these same soils were found to be susceptible to considerable loss of N between early fall and the following spring. Studies in Virginia (Alley and Scharf, 1988 unpublished data) have found mineral N, predominantly NO_3^-, concentrations ranging up to 105 mg kg^{-1} during October in fields to be planted to winter wheat. This mineral

N is subject to leaching into the groundwater and/or uptake by a winter cover crop. Using an elaborate tile drainage system, Bergstrom and Brink (1986) applied up to 200 kg N ha^{-1} to spring rape and were able to measure significant nitrate leaching losses through a heavy clay soil between early fall and the following spring. These researchers also reported that the nitrate concentrations of the drainage water were reduced to almost the same level as that at the start of the experiment when winter wheat followed the spring rape crop. These studies clearly identify the period of time immediately following summer annual crop harvest as the most critical period for recovery of residual mineral N. Thus, nonlegume cover crops have the potential to play an important role in minimizing the effects of over fertilization and/or low N uptake and crop removal on the quality of ground and surface waters provided that there is enough warm weather after summer annual harvest for significant growth of the cover crop before winter dormancy.

The effectiveness of a winter cover crop to intercept or trap residual mineral N that might otherwise be lost through leaching, has been reported to range from 12 to 91 kg N ha^{-1} where wheat or rye followed corn (Wagger and Mengel, 1988). The amount of N recovered by the cover crop has been found to be a function of the following management practices:

1. cover crop planting date;

2. cover crop seeding rate and subsequent plant population;
3. amount of residual mineral N remaining after the harvest of the previous crop; and
4. cover crop growth stage at the time of termination (early vs late kill).

Planting Date

The most critical period for recovery of residual mineral N following a summer annual is from immediately after harvest until the cover crop reaches winter dormancy. Therefore, early sowing is essential for maximizing N recovery. Early sowing provides an opportunity for more rapid root extension resulting in greater soil exploration and increased plant N uptake (Valovich and Grif, 1974). Warmer soil temperatures and longer daylength associated with early sowing of winter annual crops stimulates tillering and ensures greater protection against soil erosion (Thorne and Wood, 1982). However, in cases where the cover crop is also intended for grain or forage harvest, extremely early planting may be detrimental if followed by long periods of warm weather in the fall. Temperatures in the 10 to 16° C range encourage populations of aphid species such as the corn leaf aphid (*Rhopalasiphum maidis* Fitch) to increase and spread barley yellow dwarf virus (Wiese, 1977). According to Brann and McPherson (1980), early planting also increases the likelihood for diseases to develop, however, early planting may still be beneficial to grain yields because development of greater numbers of tillers per unit area and higher total biomass production may increase yield potential.

Seeding Rates

Little information is available in the literature regarding optimum plant populations for small grains particularly when the objective is to trap residual mineral N and prevent soil erosion losses. Unfortunately, little insight was gained by our review of the cover crop literature because most investigators report cover crop seeding rates in kg ha^{-1}. Since the number of seeds per unit weight varies with seed size, plant population comparisons were virtually impossible to make. For this reason seeding rates should be expressed in seeds per m^2. Seeding rates for rye cover crops were found to have ranged from 78 to 190 kg ha^{-1} while methods of establishment varied from no-till drilling, drilling in conventional seedbed, and overseeding into standing corn.

Seeding recommendations for optimizing small grain yields are better established. Joseph et al. (1985) found that a seeding rate of 370 seeds per m^2 in 10-cm wide rows was sufficient to produce high yields with soft red winter wheat ('Tyler' cv.). Sim et al. (1982) emphasized the importance of adjustments in seeding rates for small and large seed to obtain populations of 204 to 257 plants per m^2 for winter wheat and 2 row barley. It appears reasonable to assume that seeding rates to produce high grain yields should also provide plant populations necessary for greatest N recovery. However, more information is needed to verify optimum cover crop populations that maximize recovery of residual mineral N immediately following the harvest of a heavily N fertilized summer annual.

Residual Mineral N

Using ^{15}N tracer techniques, researchers have found recoveries of fertilizer N in the above-ground portions of several nonleguminous summer annual plants to be only 50 to 60% of the amount applied (Herron et al., 1968; Hauck, 1971; Westerman et al., 1972). Therefore, when N leaching and denitrification losses are insignificant during the growing season it is common to find a direct relationship between winter annual cover crop dry matter yield, N uptake, and the amount of N applied to the previous crop.

Pelchat (1986) reported that wheat cover crop N uptake increased 17 kg N ha^{-1} when N applications to the previous no-till corn increased from 0 to 180 kg of N ha^{-1} (Table 1). Similarly, Utomo (1986) reported increases in rye N uptake from 22 to 66 kg N ha^{-1} when N applications to the previous corn crop increased from 0 to 170 kg N ha^{-1}. Evanylo (personal communication) in Virginia, simulated various levels of residual mineral N by making N applications of 0 to

Table 1. Effect of previous N fertilization on cover crop N uptake and dry matter (DM) accumulation. (Adapted from Wagger and Mengel 1988).

COVER CROP	PREVIOUS N APPLICATION	N UPTAKE	DM	LOCATION	REFERENCE	SOIL SERIES
	kg ha^{-1}		Mg ha^{-1}			
Rye	0	11	0.5	Virginia	Evanylo (unpublished data)	Bojac sl (mixed thermic Typic Hapludults)
	112	94	2.9			
	224	152	3.6			
Wheat	0	18	1.6	Indiana	Pelchat (1986)	
	180	34	3.9			
Rye	0	26	2.6	Kentucky	Utomo (1986)	Maury sil (fine mixed mesic Typic Paleudalfs)
	170	66	6.1			

224 kg N ha^{-1} to a sandy loam soil 3 wk prior to sowing a rye cover crop. Evanylo found rye dry matter yield and N uptake to increase with increasing N rate. These studies provide further evidence that winter cover crops may be used as a tool for trapping residual N and preserve it for potential use by the following crop.

Early vs. Late Kill

Cover crop N uptake (N concentration x dry matter production) is also related to the length of time the crop is allowed to grow. In a Kentucky study, Munawar et al., (1990) found rye cover crop dry matter yields doubled between the early boot and grain filling stage. Although cover crop N uptake data was not reported, N uptake usually proceeds until flowering (Kende and Zeewhart, 1979) resulting in greater N recovery with late kill. Moschler et al. (1967) in Virginia, found that delaying the termination of rye, wheat, and barley growth approximately 3 wk resulted in dry matter increases of 60, 23, and 50% respectively. Likewise, Wagger (1987) reported that a 2 wk delay in desiccation of a rye cover crop resulted in a 45% increase in top growth dry matter and a corresponding 13% increase in N accumulation. If a cover crop is sown primarily to serve as a "catch crop", these studies would suggest that extending the cover crops vegetative growth period will maximize N uptake. However, N accumulated by the cover crop during the fall and early winter months is the most critical in terms of reducing NO_3^- movement into groundwaters (Bergstrom and Brink, 1986; Hubbard et al., 1986; Maclean, 1977). In every study reviewed, cover crop N uptake was measured prior to planting a summer annual. Nitrogen uptake measured at this late date can be expected to represent a combination of residual mineral N and newly mineralized N. A more valuable estimate of the effectiveness of a winter cover crop to trap residual N would be measurements of N uptake prior to winter dormancy or spring green-up.

Cover Crop Influence on N Availability

Cover Crop Persistence

In no-tillage crop production systems, the persistence of the residue cover has been shown to be important in conserving moisture, preventing soil loss, and inhibiting weed growth by shading the soil (Van Doren and Triplett, 1973; Blevins et al., 1983; Mannering and Fenster, 1983). Rye and wheat residues have been regarded as the most persistent due to their slower rate of decomposition because of their wide carbon:nitrogen (C/N) ratios (Pieters and McKee, 1938; Moschler, 1967; Triplett, 1986). Triplett (1986) examined the carbon fraction of rye and wheat residues and related their persistence to a higher cellulose and lignin content compared to legumes. Wagger (1987) found that a 2 wk delay in terminating rye growth increased the cellulose and lignin content of the residues while the hemicellulose fraction remained nearly constant. As a generally accepted rule of thumb, plant materials with C/N ratios of 25 or greater can be expected to decompose more slowly than those with C/N ratios less than 25, and result in the immobilization of some of the inorganic N in the soil system (Pinck et al., 1945; Allison, 1966). The rate of decomposition for wide C/N ratio residues can also be increased by the addition of N fertilizer. Utomo (1986) measured rye decomposition over a 14-

wk period where corn had received a surface application of 0 or 170 kg N kg ha^{-1}. An increased rate of residue disappearance was due to the addition of fertilizer N which provided more available N for microbial decomposition. Therefore, the combination of a persistent mulch for conserving soil water and the addition of fertilizer N to accelerate the rate of decomposition and release of N, may serve to increase N availability to the following crop.

Cover Crop vs. No Cover

Understanding the influence cover crops have on N availability to the following crop is important when making economic as well as environmentally sound N recommendations. Consideration should be given to factors such as 1) cover crop growth stage at time of termination and corresponding C/N ratio, 2) C/N ratio of any other crop residues present, and 3) the management of the cover crop (chemical kill, removal or incorporation). All these factors have been found to govern whether the cover crop residues provide N to, or competes with the following crop for N. Traditionally, cover crops have been allowed to grow until planting of the summer annual resulting in residues with wide C/N ratios. Consequently, the literature is dominated with research studies suggesting N immobilization as the major mechanism for lower N uptake and reduced grain yields following nonlegume cover crops compared to fallow (no previous crop residues) situations, particularly at low levels of N fertilization (Hargrove 1986;

Tyler et al., 1987; Wagger 1986; Decker et al., 1987). At higher rates of N fertilization, grain yields tend to be greater with nonlegume cover crop mulches compared to no cover. Based on work by Utomo (1986) the addition of N fertilizer may enhance the rate of rye decomposition and accelerate the turnover of N by decreasing the soil C/N ratio. Rice and Smith (1984) at Kentucky used ^{15}N labelled ammonium sulfate to measure the amount of fertilizer N immobilized when surface applied at a rate of 168 kg N ha^{-1} to corn no-till planted into a rye cover crop. They found the amount of immobilized N in the no-till soil steadily increased to 21% of the fertilizer N at 35 d after application. These findings provide evidence that N immobilization processes are still significant at higher rates of N fertilization. Therefore, this work would suggest that higher grain yields for corn planted into cover crop is principally a function of greater soil moisture availability resulting in greater fertilizer N-utilization (Wagger, 1986; Mitchell and Teel, 1977). Cochran et al., (1980) and Elliot et al., (1981) have suggested the placement of fertilizer N below the soil surface decreases the potential for immobilization and improves the recovery of fertilizer N. However, little information has been published regarding the release of N "trapped" by the cover crop and availability to the following crop. A clearer understanding of these processes could perhaps translate into management practices that better synchronize release of cover crop N with N uptake patterns of the summer annual.

Cover Crop plus Previous Crop Residues vs. Previous Crop Residues

The important role crop residues play in protecting the soil from wind and water erosion, conserving moisture and maintaining soil productivity has been well documented in the literature. Factors such as climate, topography, soil type, and management systems influence the quantity and/or percent residue coverage needed to adequately protect the soil. Linstrom et al. (1981) calculated that an average of 58% of the total crop residues produced could be removed from the land in 10 major corn producing states without exceeding allowable soil loss for continued long-term soil productivity. Evidence supporting the validity of these calculations was provided by Doran et al., (1984) reporting that removal of 50% of surface crop residues had little or no effect on grain yields compared to no removal for corn, sorghum and soybeans. Yet, many farmers include a cover crop as a part of their no-tillage grain production systems regardless of the quantity of residue provided by the previous crop (Eckert, 1988). In such a case, the cover crop may play a more vital role as a catch crop for residual mineral N rather than a winter cover for added soil and water conservation. Eckert (1988) in Ohio, examined any potential benefits to corn yields when planting a rye cover into corn residue. He found that rye (growth terminated at corn planting) plus previous corn residues reduced no-till corn yields in 4 of 12 comparisons due to poorer stands. Corn yields were not reduced if rye cover did not reduce stands. Eckert (1988) related these stand reductions to 1) poor seed:soil contact due to pressing the rye into the seed furrow by the planter, 2) depletion of soil moisture by the growing rye resulting in seedling desiccation and mortality, and 3) seedling rot due to excessively wet conditions where heavy residues reduced soil drying. Mitchell and Teel (1977) also observed irregular no-till corn seedling emergence in a study where rye was allowed to grow until corn planting. Like Eckert (1988), they found a tendency for rye straw to be forced into the soil opening rather than to be sheared cleanly by the coulter as could be more easily accomplished with the legumes also evaluated in their study.

Difference in N availability to the summer annual manifested by rye cover in the presence of previous crop residues is particularly important in continuous no-tillage production systems (Table 2). Surprisingly little N recovery data by a summer annual following a nonlegume cover crop has been reported in the literature, although it is likely these measurements have been made. In most cases, grain yield data was the only indicator of differences in N availability. Ebelhar et al., (1984) in Kentucky, found no difference in corn yields between rye plus corn residue and corn residue only when fertilizer N was applied at 0 to 101 kg N ha^{-1}. Similar results were reported in another Kentucky study by Blevins et al., (1990) where corn yields were not different between these two cover treatments with N fertilizer applications up to 170 kg N ha^{-1}. Blevins

Table 2. Effect of nonlegume cover crop on following crop N uptake and grain yield.

COVER CROP	N UPTAKE kg N ha^{-1}		GRAIN YIELD Mg ha^{-1}		SOIL SERIES	REFERENCES
	0-N[†]	90-N	0-N	90-N		
Wheat	41	113	1.2 a[‡]	5.0 a	Matapeake sil (fine-loamy, mixed mesic, Typic Hapludults)	Decker et al., (1987)
No cover	47	125	1.8 a	5.5 a		
Wheat	70	118	4.4 b	8.2 b	Delanco sil (fine-loamy, mixed mesic, Aquic Hapludult)	Decker et al., (1987)
No cover	144	182	9.0 a	10.5 a		
	0-N	112-N	0-N	112-N		
Rye + Grain Sorghum	---	---	2.6 a	3.9 a	Cecil sl (clayey, kaolinitic, thermic typic Hapludults)	Hargrove (1986)
Grain Sorghum	---	---	2.9 a	3.9 a		
			0-N	170-N		
Rye + Corn	---	---	1.1 a	5.9 a	Zanesville sil (fine-silty, mixed mesic, Typic Fragiudalfs)	Blevins et al., (1990)
Corn	---	---	1.1 a	6.3 a		
	Earleaf % N					
	0-N	101-N	0-N	101-N		
Rye + Corn	1.43 a	2.18 a	4.0 a	7.6 a	Maury sil (fine-silty, mixed mesic, Typic Paleudalfs)	Ebelhar et al., (1984)
Corn	1.49 a	2.25 a	3.8 a	6.8 a		

[†] kg N ha^{-1}

[‡] Means within each column for each study followed by the same letter do not differ significantly at the 5% level of probability.

noted that corn residues from the previous year provided substantial cover and water conservation.

Work reported by Tyler et al., (1987) in Tennessee, further illustrates the influence cover crop management can have on fertilizer N response in no-till corn. During the first year of their study, corn was no-till planted into wheat residue or no cover (no previous crop residues). Corn yields were substantially reduced in the wheat cover at lower rates of N. As N rates increased the difference in corn yields between these two cover treatments continued to decrease up to 175 kg N ha^{-1} (Figure 1). During the second year, yield comparisons were made between corn residue and wheat plus corn residue covers (Figure 2). Little or no difference in corn yields were measured between these two cover treatments particularly at the lower N rates and at much reduced yield levels caused by drought conditions. Similar results for no-till corn were also reported by Neely et al., (1987) in Georgia and Decker et al. (1987) in Maryland.

When corn residues are present, N availability to the following corn crop may not be further reduced by sowing a winter cover. However, when no previous crop residues are present (example: corn silage production) N availability at low rates of N application to the summer annual, is likely to decrease if a winter

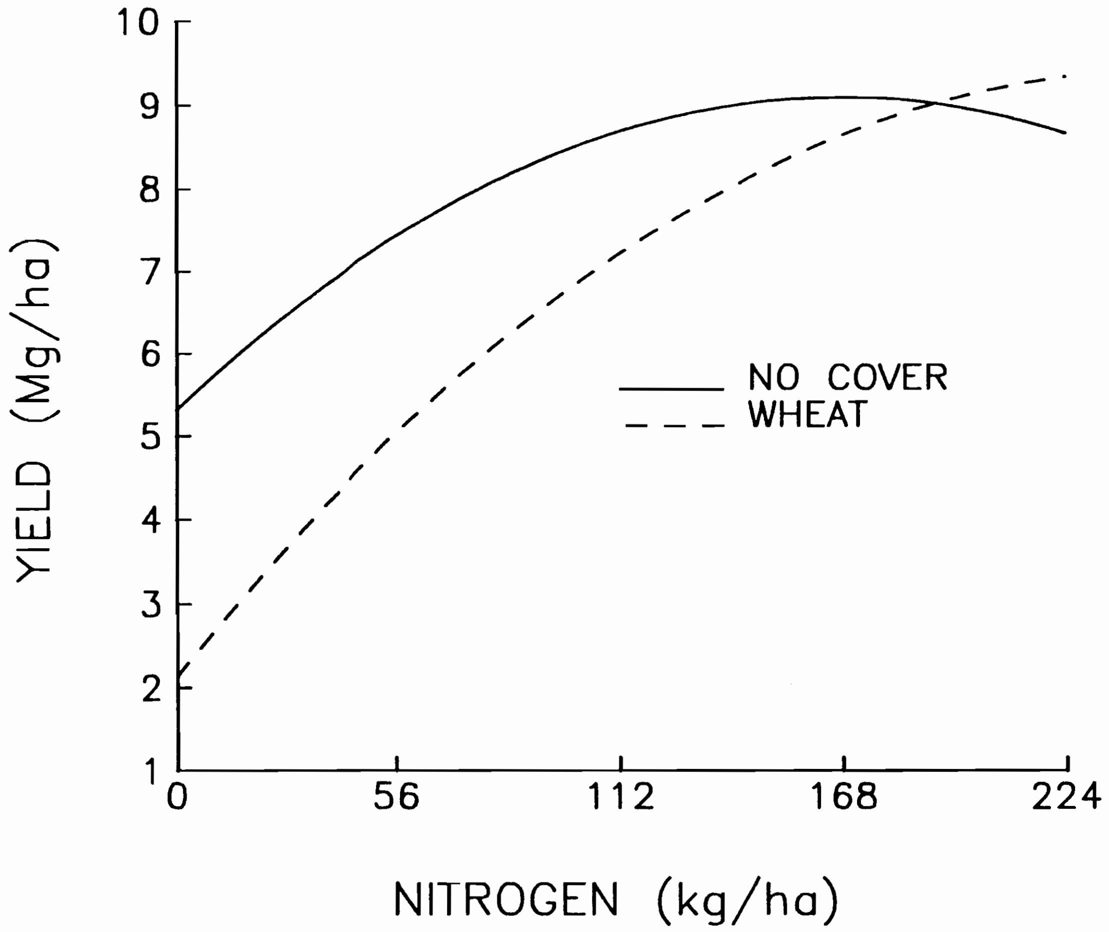

Figure 1. Influence of wheat cover crop on corn yield response to increasing N applications (Adapted from Tyler et al., 1987).

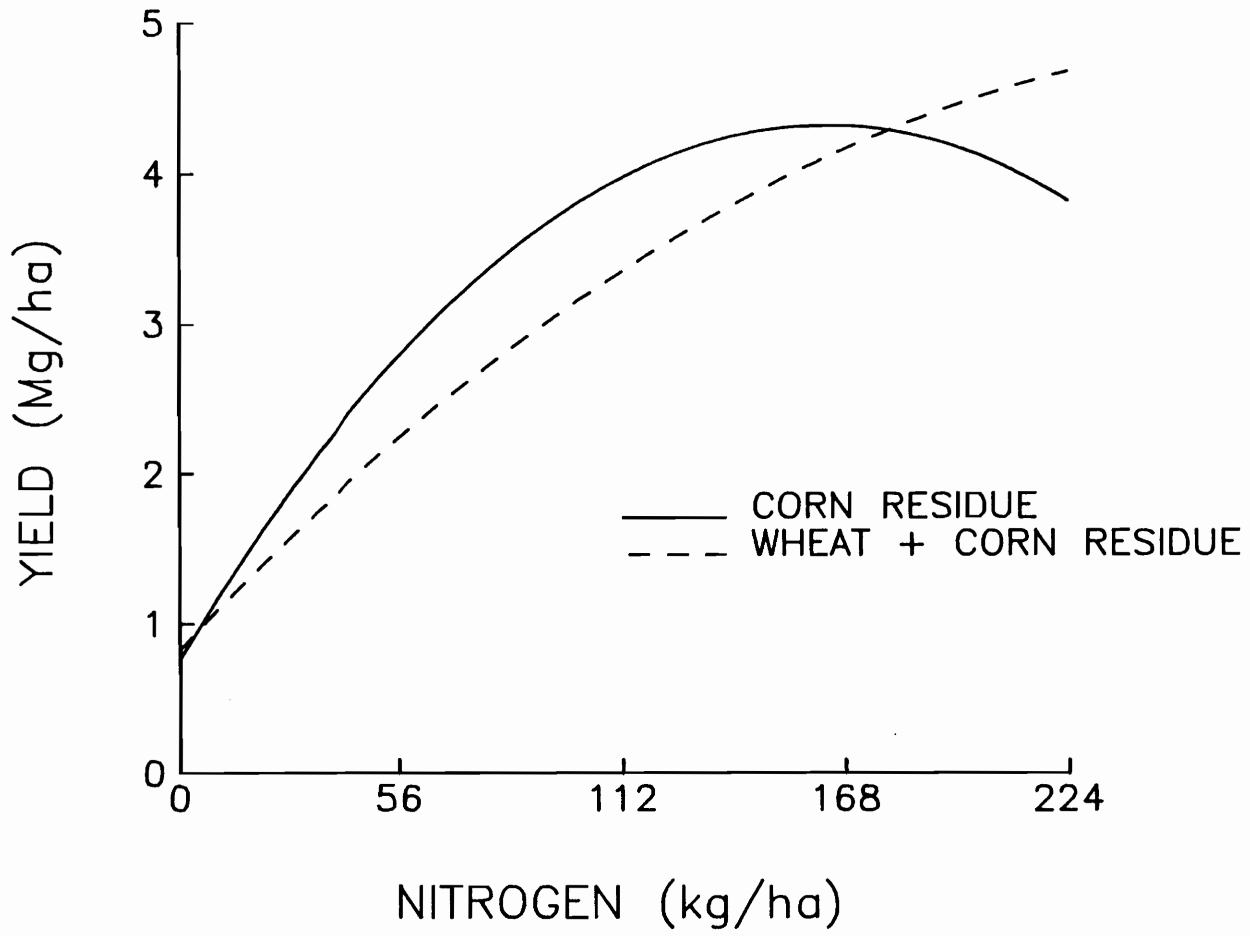

Figure 2. Influence of cover treatment on corn yield response to increasing N applications (Adapted from Tyler et al., 1987).

cover crop is sown and allowed to grow until planting of the summer annual (Table 2). In this case, application of higher rates of N fertilizer may be required to offset soil mineral N immobilized during decomposition of cover crop residues with wide C/N ratios.

Cover Crop Removal

A cover crop may also be managed for silage or hay production. In either case, removal of plant material leaves the soil surface essentially bare. Compared to the previously discussed cover crop scenarios where residues remain on the surface, consideration must be given to season long soil water availability and removal of plant nutrients from the soil system when making N fertilizer recommendations for the following summer annual. As Wagger and Mengel (1988) point out, environmental conditions can present problems in separating N dynamics from soil moisture effects. Moschler et al. (1967) and Gallaher (1977) each concluded that periodic moisture stress during the corn growing season lowered grain yield when rye was removed to simulate forage harvest or incorporated for conventional corn planting (Table 3).

Table 3. Effects of rye cover crop management on corn grain yields.

Location	Cover Crop Management	Grain Yield	Reference
		Mg ha^{-1}	
Georgia	Removed	8.9 b†	Gallaher, 1977
	Killed	13.1 a	
Virginia	Removed	2.4 b	Moschler et al., 1967
	Killed	6.6 a	
	Incorporated	3.7 b	

†Means within each column for each study followed by the same letter do not differ significantly at the 5% level of probability.

Conclusions

Limited information is available on residual N recovery by a nonlegume cover crop immediately following harvest of the summer annual until it's winter dormancy. However, numerous studies have demonstrated the potential nonlegumes have for increasing N uptake as residual N levels increase. Early seeding and insuring optimum plant populations are perhaps two of the most important management practices influencing the recovery of residual N that might otherwise be lost to the environment. Seeding rates should be made on a seeds/area basis with consideration given to field conditions that might prevent adequate seed:soil contact.

A number of best management practices for cropping systems including cover crops have been identified that should improve N-use efficiency and optimize crop yield of the primary summer crop. Aside from the moisture conserving attributes of a cover crop mulch and it's influence on N utilization, the C/N ratio of these residues will dictate to a large extent, N availability to the following crop. Terminating cover crop growth early, narrows the C/N ratio reducing the potential for N immobilization and conserves soil moisture otherwise lost by prolonging cover crop growth. Delaying the termination of cover crop growth can widen residue C/N ratios and increase the likelihood of N immobilization and need for higher rates of N fertilization. In either case, consideration should be given to the N source, timing and method of application that will maximize N availability.

Cover crop removal from the soil surface (tillage incorporation or silage production vs. surface mulch) appears to have the most negative effects on subsequent crop yields. Obviously the loss of surface mulches will change the crop-soil water relations which influence N-use efficiency. Although many nonlegume cover crop research needs still exist, a better understanding of the soil and climatic conditions affecting the release of residual N trapped by the cover crop is the most significant, especially in regard to N uptake by the following summer annual. Non-legume cover crops can play a major role in "trapping" residual soil NO_3^- from being leached during winter, but the magnitude of such "trapping" will vary depending on 1) cover crop planting date; 2) cover crop seeding rate and subsequent plant population; 3) amount of residual mineral N remaining after the harvest of the previous crop; and 4) cover crop growth stage at the time of termination.

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Chapter III

Diffusion and Automated Nitrogen-15 Analysis of Low-Mass Ammonium Samples

Abstract

Conventional steam distillation techniques for concentrating inorganic N in soil extracts prior to ^{15}N analysis are time consuming and labor-intensive procedures. Diffusion procedures have been proposed as alternatives to steam distillation, but incomplete recovery and dilution in ^{15}N concentration of diffused samples have been reported. A procedure for diffusing low masses of $^{15}NH_4$-N from 2 *M* KCl solution prior to isotope ratio analyses by continuous-flow direct combustion mass spectrometry was evaluated. The study was conducted to determine the effects of NH_4 and ^{15}N concentrations on recovery and isotope-ratio analysis of diffused N. Standard $(NH_4)_2SO_4$ salt containing 1.1461 atom % ^{15}N was used to prepare a series of solutions containing from 0.5 to 2.5 mg N L^{-1}. Forty-mL aliquots were placed in plastic specimen containers equipped with acidified glass fiber disks and were allowed to diffuse for either 6 d at room temperature or for 5 d at 55 °C. Nitrogen recovery in glass fiber disks after diffusion averaged 100.05% of the N added and was not affected by level of added N or temperature of incubation. Quantitative recovery of added N was also obtained in a second study in which 30-

concentrations varying from 0.1030 to 1.1461 atom % ^{15}N were diffused in diffusion containers for 10 d at 55 °C. Significant dilution of ^{15}N concentrations between diffused and non-diffused samples were attributed to background or contaminant N at an ^{15}N concentration of natural abundance. Close agreement was obtained between diffused and non-diffused samples when a simple isotope dilution equation was used to calculate the atom % ^{15}N concentration of the sample N. These studies indicate that the diffusion method is suitable for preparing low-mass N samples for automated ^{15}N analysis if the appropriate blanks are determined and used to correct for background N.

Introduction

Conventional steam distillation techniques for measurement and concentration of inorganic N in soil extracts or Kjeldahl digests are time-consuming and labor-intensive procedures. In addition, suitable precautions must be taken to minimize contamination of ^{15}N-labeled samples during processing. Diffusion procedures have been evaluated as alternatives to steam distillation procedures for Kjeldahl digests (MacKown et al., 1987; O'Deen and Porter, 1979; Russelle and Lory, 1988; Turner and Bergersen, 1980) and soil extracts (Brooks et al., 1989; Burke et al., 1990). Advantages reported for diffusion techniques over distillation procedures include the potential to simplify sample preparation, eliminate cross contamination, and reduce contamination during sample drying prior to ^{15}N analysis. Samples prepared by diffusion techniques can be analyzed for ^{15}N content by Rittenberg or direct combustion techniques.

Brooks et al. (1989) compared diffusion and distillation techniques for soil extracts and found that a diffusion method saved considerable time without loss of accuracy. They obtained quantitative recovery of NH_4 and NO_3 from KCl solutions containing from 80 to 800 μg N by diffusion for 6 d at room temperature. In contrast, Russelle and Lory (1988) evaluated the method described by Brooks et al. (1989) and concluded that the technique is not suitable for samples containing less than 1 mg N. Russelle and Lory (1988) reported that N recovery from simulated Kjeldahl digests was not quantitative and that the atom % ^{15}N concentrations of the diffused samples were consistently closer to natural abundance than those for non-diffused samples.

This paper presents the results of an evaluation of the procedure described by Brooks et al. (1989) for diffusion of low masses of ^{15}N-labeled NH_4 in 2 *M* KCl and subsequent analysis for N recovery and ^{15}N concentration by direct combustion mass spectrometry. A technique is presented to correct atom % ^{15}N concentrations of diffused N for isotope dilutions from background or contaminant N.

Materials and Methods

Diffusion Procedure

Standard salt solutions containing NH_4 at different N and ^{15}N concentrations were used to evaluate two modified versions of the diffusion method described by Brooks et al. (1989). In the first modification, aliquots of a standard solution were placed into 140-mL plastic specimen containers, 0.2 g of MgO was added, and an acidified glass fiber disk was suspended above the solution to trap diffused NH_3. A suitable length of stainless steel wire was placed across the inside of the opening of the plastic specimen container. A second piece (4 to 5-cm in length) of stainless steel wire was cut and formed into a small, "S"-shaped hook. Glass fiber disks (7-mm diam.) were prepared by cutting acid-washed Whatman GF/D glass fiber filter paper with a standard paper punch. Ten μL of 2.5 M $KHSO_4$ was pipetted onto each glass fiber disk for absorption of diffused NH_3. The acidified disk was impaled onto a stainless steel "S"-shaped hook and attached to the center of the 62-mm section of stainless steel wire to position the disk about 2.0-cm above the solution surface. An acid-washed glass bead was added to the sample solutions (to facilitate mixing), and the specimen container cap was immediately screwed tight. Sample contents were mixed by gentle swirling for approximately 15 s, and the samples were allowed to incubate. Upon completion of the diffusion period, the wire hook was removed, placed on a rack inside a desiccator containing $CaSO_4$, and the glass fiber disk was allowed to dry for 1 d. Individual disks then were placed into 4 by 6-mm Sn foil cups and analyzed for N recovery and ^{15}N concentration.

In the second modification, glass containers were used as diffusion chambers instead of plastic specimen cups. The glass containers were constructed from standard 28/15 O-ring spherical ball and socket joints. The ball joint was sealed 4.0-cm above the opening of the joint, and a 7.5-cm section of 7-mm Pyrex rod was attached to the upper inside surface. With this arrangement, the rod extended about 3.5-cm below the opening of the ball joint. The lower end of the rod was flattened and a 2-mm hole was formed for attachment of a stainless steel, "S"-shaped hook. The socket joint was attached to a 24-cm section of 2.5-cm diam. Pyrex tubing. The tubing was widened to a diameter of about 4.0-cm at a distance of 4.5-cm below the opening of the socket joint. With this configuration, each diffusion container had a volume of about 100-mL.

The acidified glass fiber disk was placed on a stainless steel hook and suspended into the center of the expanded portion of the tubing to prevent contact and solution transfer between the disk and the sides of the diffusion container. A standard pinch clamp was used to ensure an air-tight, leak-free seal between the ball and socket joints.

The glass diffusion system provided reusable, leak-free containers that can be utilized for diffusion at temperatures up to 130 °C (Burke et al., 1990). Although the initial cost is greater than for the plastic containers and additional cleaning is required, the glass containers eliminate the need to keep and adequate inventory of disposable supplies and avoid the economic and enviromental costs associated with the disposal of plastic container wastes.

Influence of NH_4 Concentration and Incubation Temperature on Recovery and N Concentration of Diffused N

A standard ^{15}N-enriched $(NH_4)_2SO_4$ salt was used to prepare a series of standard solutions containing 0.0, 0.5, 1.0, 1.5, 2.0, or 2.5 μg N mL^{-1} in 2 M KCl. Ten replicate samples for each solution were prepared by pipetting 40-mL aliquots into acid-washed, 140-mL plastic specimen containers. Five replicates at each concentration level were allowed to diffuse for 6 d at room temperature; the remaining five replicates were placed in a 55 °C oven and allowed to diffuse for 5 d. All of the samples in this study were prepared at the Virginia Polytechnic Institute and State University (VPI) and shipped to TVA's National Fertilizer and Environmental Research Center (NFERC) in Alabama for total N and ^{15}N analysis.

The ^{15}N concentration of the standard salt was estimated by direct analysis of appropriate weights of the $(NH_4)_2SO_4$ to provide 20, 40, 60, 80, and 100 μg N; mean atom % ^{15}N concentrations for four replicated samples at each N level ranged from 1.1433 to 1.1489 and were not affected by the level of added N. The mean ^{15}N concentration over all levels of the standard salt was 1.1461 atom % ^{15}N.

Influence of ^{15}N Concentration on Recovery and Isotope-Ratio Analysis of Diffused N

Standard $(NH_4)_2SO_4$ salts containing 0.1030, 0.2020, 0.5130, and 1.1461 atom % ^{15}N were used to prepare four standard solutions containing 25 μg N mL^{-1}. Six replicate samples containing 25, 50, or 100 μg N were prepared for each level of ^{15}N concentration by pipetting 1, 2, or 4-mL aliquots of each standard solution into glass containers for diffusion. The final volume of all samples was made to 30-mL with 2 M KCl. Ten replicate samples were prepared without added N to determine background N levels. Magnesium oxide and Devarda's alloy were added to each flask, and the samples were allowed to diffuse for 10 d at 55 °C. The ^{15}N concentrations of the added N were determined by direct analysis of appropriate weights of the standard salts to provide 100 μg N. All of the samples in this study were prepared and analyzed at the NFERC.

Recovery and Isotope-Ratio Analysis of Diffused N

Analyses for N recovery and ^{15}N concentration of the diffused N in the glass fiber disks were determined with an automated C-N analyzer/mass spectrometer (ANCA/MS) system consisting of an automated C-N analyzer (Roboprep C/N, Europa Scientific, Crewe, England) interfaced to a dual collector ratio mass spectrometer (Micromass VG 602, VG Micromass LTD, Cheshire, England). The ANCA/MS system, operated in an accelerated mode (Barrie et al., 1990), was capable of determining total N and atom % ^{15}N at a rate of 3 min per sample with a precision of 0.0005 atom % ^{15}N at natural abundance.

The glass fiber disks were placed into Sn foil cups, crimped into a spherical shape, placed into an autosampler, and sequentially introduced into an oxidation tube, consisting of Cr_2O_3, CuO wire and Ag wire at 1000 °C. Ten mL of ultra-high purity O_2 was admitted to the oxidation column promoting oxidation of the Sn foil and sample. A carrier gas (high purity He at a flow rate of 16-mL min^{-1}) swept combustion products through the oxidation column, a reduction tube containing reduced Cu wire at 550 °C, a $MgClO_4$ trap to remove H_2O, a Carbosorb trap to remove CO_2, and finally through a GC column at 28 °C. Approximately 1% of the HE/N_2 effluent was then admitted into the analyzer of the mass spectometer for total N and N isotope-ratio analysis.

Background Correction for Atom ^{15}N Concentrations of Diffused N

Equation [1] was used to calculate atom % ^{15}N concentration of diffused sample N corrected for dilution from contaminant N.

$$A_1 = [A_m (M_1 + M_2) - (M_2 A_2)]/((M_1 + M_2) - M_2) \qquad [1]$$

where:

A_1 = Atom % ^{15}N of sample N (corrected atom % ^{15}N)

A_m = Atom % ^{15}N of diffused N (uncorrected atom % ^{15}N)

A_2 = Atom % ^{15}N of background N (0.3663)

M_1 = μmol of sample N diffused into fiber disk

M_2 = μmol of background N diffused into fiber disk

$(M_1 + M_2)$ = Total μmol of diffused N

The atom % ^{15}N of the diffused N (A_m) is a combination of sample N plus background or contaminant N. The atom % ^{15}N of the background N (A_2) is assumed to be at natural abundance (0.3663). The total μmol of N diffused (sample + background) into the filter disk is identified as $(M_1 + M_2)$ in Eq. [1], and the μmol of N measured in the analytical blank (M_2) can be used to calculate the μmol of sample N diffused (M_1).

Results and Discussion

Influence of NH_4 concentration and incubation temperature on recovery and ^{15}N concentration of diffused N

Mean N recoveries in the glass fiber disks after diffusion ranged from 92.3 to 108.7% of the added N and were not affected by temperature of incubation (Table 4). Mean recoveries of added N were 99.8 and 101.0% for the samples incubated for 6 d at 25 °C or 5 d at 55 °C, respectively.

Averaged over all N levels and temperatures, NH_4-N in the fiber disks accounted for 100.5% of the N added, indicating that recovery of the added N was quantitative. Analytical precision for N recovery was not affected by level of added N over the measured range (CVs ranged from 4.1 to 5.5% for the 20 and 100 μg N (data not shown). The mean and standard error of the mean for diffused N in the analytical blanks were 3.6 and 0.5, respectively.

All atom % ^{15}N values for diffused N (uncorrected atom % ^{15}N) were significantly lower than those obtained by direct analysis of the standard $(NH_4)_2SO_4$ salt (Table 4). The atom % ^{15}N concentration of the diffused N increased with increasing level of added N, ranging from 1.0186 to 1.1183 atom % ^{15}N for 20 and 100 μg N levels,

Table 4. Percentage recovery and ^{15}N concentration of diffused N as affected by level of added N and incubation conditions.

Treatment				Diffused N	
N added[†]	Temp.	Period	Recovery	Uncorrected	Corrected[‡]
µg	°C	d	%	.... atom % ^{15}N	
20	25	6	106.9	1.0336	1.1654
	55	5	108.7	1.0096	1.1337
		Mean[§]	108.0 (1.6)	1.0186 (0.009)	1.1456 (0.011)
40	25	6	101.5	1.0823	1.1511
	55	5	99.9	1.0753	1.1404
		Mean	100.8 (1.4)	1.0788 (0.005)	1.1478 (0.006)
60	25	6	104.0	1.0901	1.1341
	55	5	101.8	1.0952	1.1404
		Mean	102.8 (1.5)	1.0929 (0.006)	1.1376 (0.007)
80	25	6	92.3	1.1174	1.1556
	55	5	96.5	1.1048	1.1406
		Mean	94.4 (1.5)	1.1111 (0.004)	1.1481 (0.004)
100	25	6	97.7	1.1210	1.1498
	55	5	98.0	1.1162	1.1446
		Mean	97.9 (1.8)	1.1183 (0.003)	1.1469 (0.003)
		¶ LSD	6.2	0.0149	ns
Source of Variation[#]					
N added			0.001	0.001	0.719
Temperature			0.431	0.015	0.075
N added X Temperature			0.691	0.999	0.342

† ^{15}N concentration of added N by direct analysis = 1.1461 atom % ^{15}N (SE = 0.002).

‡ Atom % ^{15}N concentration corrected for N in analytical blank (3.6 µg).

§ Standard error of the mean given in parenthesis.

¶ LSD for treatment means (ns = not significant at $P = 0.05$ level).

Significance of F tests for treatment and interaction effects.

respectively. The ANOVA tests indicate that the uncorrected atom % ^{15}N concentrations were significantly affected by the level of added N and temperature of incubation. Analytical precision for atom % ^{15}N decreased with decreasing level of added N (CVs ranged from 0.7 to 2.7 for 100 and 20 μg N levels, respectively).

The atom % ^{15}N concentrations of the sample N (corrected atom % ^{15}N) were calculated using Eq. [1] and the mean value for N recovered in the analytical blanks (3.6 μg N). In contrast to the uncorrected results, corrected atom % ^{15}N concentrations were not significantly affected by level of added N or temperature of incubation (Table 4). The mean corrected atom % ^{15}N, averaged over N levels and incubation temperatures, was 1.1453, which is in excellent agreement with the value obtained by direct analysis of the standard salt (i.e., 1.1461 atom % ^{15}N).

Influence of ^{15}N concentration on recovery and isotope-ratio analysis of diffused N

The rate of NH_3 diffusion increases with increasing surface area and decreases with increasing volume or depth of sample solution (Conway, 1957). The surface area-to-volume ratio was much lower for samples in the glass diffusion containers in comparison to the plastic containers used in the first study. Consequently, a diffusion period of 10 d was used to ensure complete recovery of added N and avoid errors arising from incomplete diffusion and isotopic fractionation of N

(O'Deen and Porter, 1979; Turner and Bergersen, 1980). The samples were incubated at 55 °C to ficilitate diffusion and to minimize moisture condensation on the sides of the glass caused by temperature fluctuations during incubation.

Recoveries of added N ranged from 98.7 to 105.5% and were not significantly affected by the level or ^{15}N concentration of the added N. These results indicate that diffusion and recovery of the added N were quantitative with the glass diffusion containers.

In agreement with the previous study and the findings of Russelle and Lory (1988), the atom % ^{15}N concentrations of the diffused N were different from the non-diffused samples. The atom % ^{15}N concentrations for the diffused N from samples that received ^{15}N-depleted standards (i.e., 0.1030 and 0.2020 atom % ^{15}N) were higher, and the samples that received ^{15}N-enriched standards (0.5130 and 1.1461 atom % ^{15}N) were lower than the corresponding values obtained through direct analysis. Furthermore, differences between the ^{15}N concentrations of diffused and non-diffused N increased with decreasing level of added N at each level of ^{15}N concentration.

Results for diffused N were corrected using blank N values obtained by two techniques. In the first case, the analytical blank was determined by analysis of glass fiber disks from the samples which did not receive added N. The N recovered from the analytical blanks ranged from 2.6 to 5.5 μg with a mean of 3.9 (SE = 0.24, data not shown). In the second case, the N contribution of the blank was estimated by the mass of N at 0.3663 atom % ^{15}N required to cause the observed deviation in atom % ^{15}N between the diffused and non-diffused samples that received 1.1461 atom % ^{15}N $(NH_4)_2SO_4$. Equation [1] was rearranged to determine the calculated blank for each level of added N (Eq. [2]).

$$M_2 = (M_1 + M_2)(A_m - A_1)/(A_2 - A_1) \qquad [2]$$

The calculated blanks were 4.5, 4.7, and 5.1 μg N for 25, 50, and 100 μg N levels, respectivley. The mean calculated blank, averaged over N levels, was used in Eq. [1] to determine the calculated blank-corrected ^{15}N concentrations for diffused N.

Results for the uncorrected data and analytical blank-corrected data are shown in Fig. 3. Differences between ^{15}N concentrations of the added N and uncorrected diffused N increased as the ^{15}N concentration of the added N increased or decreased from natural abundance levels. At a given ^{15}N concentration, the differences between the atom % ^{15}N concentrations of the added and diffused N were greatest at the lowest N level and decreased with increasing level of added N.

Close agreement was obtained between the ^{15}N concentrations of added N and diffused N after a correction for N in the analytical or calculated blank. Relative errors in atom % ^{15}N determination, calculated as the percentage differences between the added N and diffused N, ranged from 4.7 to 55.2% for the uncorrected results. The relative errors were much lower after correction for contaiminant N, ranging from 0.8 to 5.4% and from 0.4 to 3.2 for the analytical-blank and calculated-blank corrected results, respectively.

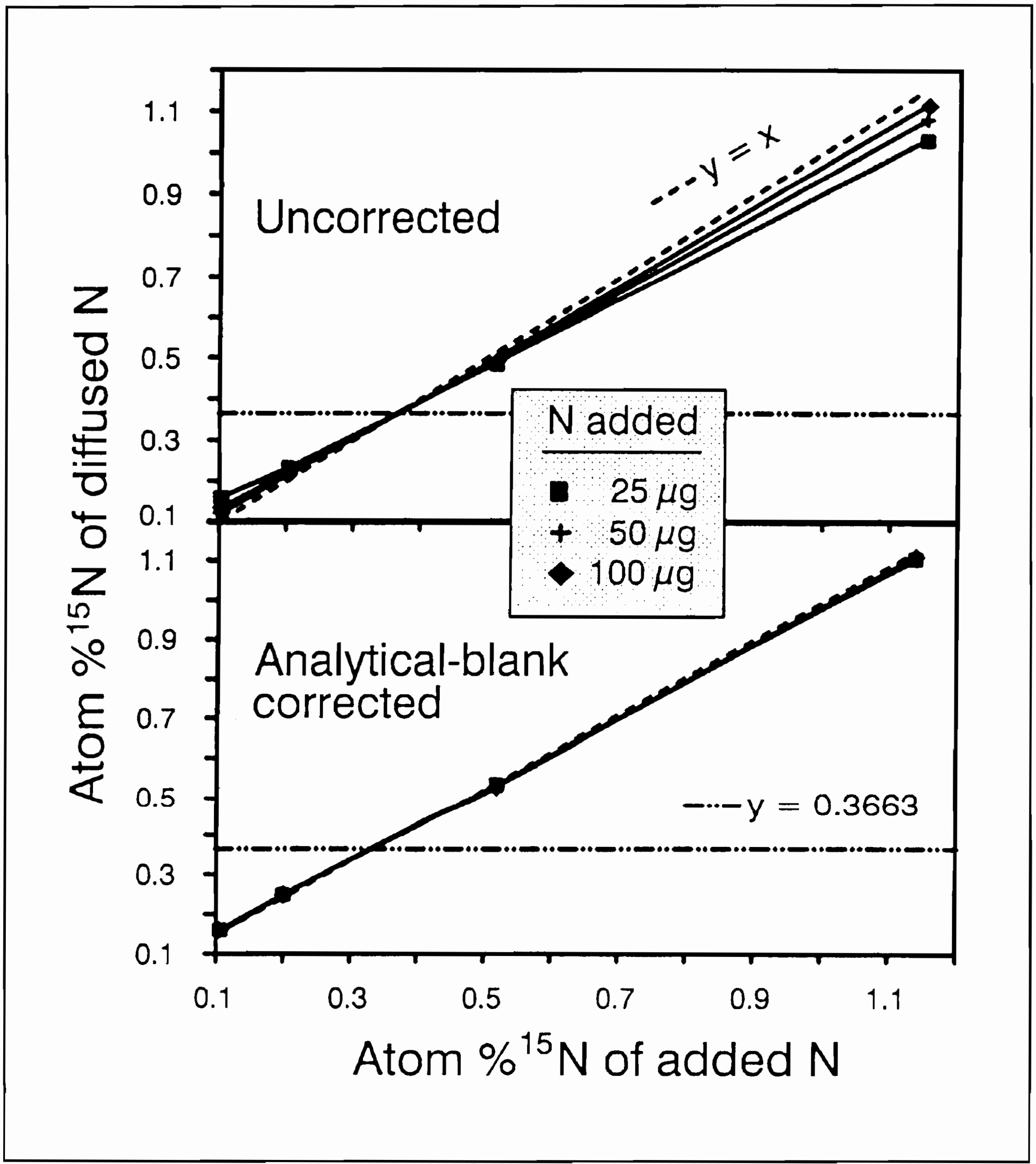

Figure 3. Effect of NH_4 and ^{15}N concentration of added N on the uncorrected and analytical-blank corrected ^{15}N concentration of added N.

Conclusions

These results indicate that significant dilution of ^{15}N concentration for low mass N samples can occur with the diffusion methods described by Brooks et al. (1989). These findings agree with those of Russelle and Lory (1988) who reported that ^{15}N concentrations of diffused samples were consistently closer to natural abundance than those of non-diffused samples. Differences between diffused and non-diffused samples were attributed to isotopic fractionation during diffusion and/or contamination during sample preparation. Our results indicate that differences in atom % ^{15}N between diffused and non-diffused samples can be attributed to contamination from N at natural abundance. Close agreement in atom % ^{15}N concentration was obtained between diffused and non-diffused samples when an isotope dilution equation was used to calculate the ^{15}N concentration of the sample N.

Analysis of the Sn foil and acid-washed glass fiber disk with the ANCA/MS indicated that these sources supplied about 1 μg of the 3.6 to 3.9 μg N found in the analytical blanks. Other possible sources of contaminant N include MgO, Devarda's alloy, KCl, water, glassware, and air (absorption of NH_3 during drying). These studies indicate that the level of contaminant N can be determined directly by analysis of the analytical blanks or indirectly by calculating the mass of N at 0.3663 atom % ^{15}N required to cause the observed deviation in the atom % ^{15}N between diffused and non-diffused standard samples. It is important that the analytical and/or calculated blank be determined for each batch of samples; it's also recommended that samples of known ^{15}N concentration be diffused and analyzed as internal checks.

The analytical blank was used in our laboratory to correct for contaminant N because this technique provides a direct measure of contaminant N levels and conserves ^{15}N-labeled materials. An evaluation of the calculated blank is presented because this technique can be used in those situations where quantitative determination of N in the analytical blank is not possible or impractical. Isotope-ratio analysis by manual or automated Rittenberg procedures, for example, does not provide for quantitative determination of N in the sample or blank, requiring a separate analysis of the analytical blank following extraction of the NH_4 from the glass fiber disk.

These results indicate that the diffusion procedure described by Brooks et al. (1989) is suitable for preparing low-mass N samples for automated ^{15}N analysis by ANCA/MS techniques. In contrast to the work of Russelle and Lory (1988), recoveries of low masses of added N were quantitative, and accurate ^{15}N

concentrations were obtained when the results were corrected for isotope dilution due to background or contaminant N.

Implementation of this diffusion procedure for routine analysis of 2 M KCL soil extracts in our laboratories indicates that approximately 70 samples per day can be processed. This includes preparing soil samples for 2 M KCl extraction, removing aliquots for analysis, and initiating the diffusion procedure.

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Chapter IV

Detectibility of ^{15}N-Depleted Fertilizer N in Soil and Plant Tissue During a Corn-Rye Crop Rotation

Abstract

Use of ^{15}N-depleted fertilizer materials have been primarily limited to fertilizer recovery studies of short duration. The objective of this study was to determine if ^{15}N-depleted fertilizer N could be satisfactorily used as a tracer of residual fertilizer N in plant tissue and various soil N fractions through a corn (*Zea mays* L.) -winter rye (*Secale cereale* L.) crop rotation. Nitrogen as ^{15}N-depleted $(NH_4)_2SO_4$ was applied at five rates (0, 84, 168, 252, and 336 kg N ha^{-1}) to corn. Immediately following corn harvest a winter rye cover crop treatment was initiated. Residual fertilizer N was easily detected in the soil NO_3^--N fraction following corn harvest (140-d after application). Low levels of exchangeable NH_4^+-N ($<$2.5 mg kg^{-1}) did not permit accurate isotope-ratio analysis. Fertilizer-derived N recovered in the soil total N fraction following corn harvest was detectable in the 0 to 30-cm depth at each N rate and in the 30 to 60 and 60 to 90-cm depths at the 336 kg ha^{-1} N rate. Atom % ^{15}N concentrations in the nonexchangeable NH_4^+-N fraction did not differ from the control at each N rate. Nitrogen recovery by the winter rye cover crop reduced residual soil NO_3^--N levels below the 10 kg ha^{-1} level needed for accurate isotope-ratio analysis. Atom % ^{15}N concentrations of the NO_3^--N fraction in the

winter fallow soil did not differ from natural abundance in the top 30-cm but decreased with increasing N rate in the 30 to 60 and 60 to 90-cm depths. Atom % ^{15}N concentrations in the soil total N fraction (approximately one yr after application) were indistinguishable from the control plots below the 168, 252, and 336 kg ha^{-1} N rate at the 0 to 30, 30 to 60, and 60 to 90-cm depths respectively. Recovery of residual fertilizer N by the winter rye cover crop was verified by measuring significant decreases in atom % ^{15}N concentrations in rye tissue with increasing N rates. The greatest limitation to the use of ^{15}N-depleted fertilizer N as a tracer of residual fertilizer N in a corn-rye crop rotation appears to be its detectibility from native soil N in the total N pool.

Introduction

The environmental consequences of fertilizer N applications in agricultural systems continue to be the major focus of many research programs. Researchers debate the best method for determining fertilizer N use efficiency in the context of crop production benefits and potential water quality hazards. The "Difference Method" for determining fertilizer N efficiency is simply the calculated difference between fertilized and nonfertilized treatments. This method tends to more accurately reflect the N treatment effect on N availability irrespective of mineralization-immobilization turnover (MIT) of fertilizer N (Jenkinson et al., 1985). However, in field studies where the direct measurement of fertilizer-derived N is of interest, the use of fertilizer material that is either enriched or depleted of the stable isotope ^{15}N is necessary.

The decision to use ^{15}N-enriched or ^{15}N-depleted materials has been largely based on i) the cost and availability of ^{15}N labelled materials, and ii) the fertilizer N dilution expected during the period of measurement. Studies have shown that ^{15}N-depleted nitrogen fertilizer added to soil can be measured in plants with similar accuracy and precision as fertilizer N containing a comparable level of ^{15}N enrichment (Edwards and Hauck, 1974; Starr et al., 1974). However, Hauck and Bremner (1976) suggest that the use of ^{15}N-depleted materials be limited to those studies where excessive N dilution is not likely to occur. Even though highly sensitive mass spectrometers are available to detect excessively dilute ^{15}N-depleted fertilizer N, variations in ^{15}N concentrations of naturally occurring nitrogen may make it difficult to distinguish fertilizer-derived N from native soil N. Limited data and the uncertainty of detection when using ^{15}N-depleted fertilizer N have minimized its use for studies of plant uptake and soil distribution of residual fertilizer N. For these type of studies, enriched nitrogen materials containing 3 to 10 at. % ^{15}N have been recommended (Hauck and Bremner, 1976; Stumpe et al., 1989).

The high cost of using ^{15}N-enriched materials for field plot size areas is often prohibitive. One method commonly used for reducing the cost of ^{15}N-enriched materials has been to apply labeled N only to a microplot within the field plot (Jokela and Randall, 1987; Sanchez et al., 1987; Stumpe et al., 1989). Physical problems such as the potential lateral movement of surface-applied fertilizer N for unconfined microplots, or restriction of plant lateral root growth as well as subsurface lateral movement of fertilizer N in confined microplots can affect plant uptake and soil distribution of fertilizer N. Also, even with the use of microplot experiments, the cost of ^{15}N-enriched fertilizer material still represent a major economic obstacle in much work. Depleted-^{15}N fertilizer materials offer an alternative to the more expensive enriched materials. However, more supporting data is needed to aid researchers in identifying those situtations where depleted material can be utilized without compromizing the detection objectives of the experiment.

The objective of this study was to determine if ^{15}N-depleted fertilizer N could be satisfactorily used as a tracer of residual fertilizer N in plant tissue and various soil N fractions through a corn (*Zea mays* L.) -winter rye (*Secale cereale* L.) crop rotation.

Materials and Methods

The field study was conducted during 1989 on a well drained Hayter silt loam soil (fine-loamy, mixed, mesic Ultic Hapludalf) near Blacksburg, Virginia. Selected soil physical and chemical properties are reported in Appendix M (Harris et al., 1980). The experimental site had been managed for alfalfa (*Medicago sativa* L.) hay production prior to initiating the study. A seed bed was prepared by moldboard plowing followed by disking and the use of a power driven harrow. Corn was planted in mid-May in 0.76-m row spacings and thinned to a final of population of 49 500 plants ha^{-1}. Nitrogen as ^{15}N-depleted $(NH_4)_2SO_4$ was surface applied to 4.6 by 4.6-m plots at five rates (0, 84, 168, 252, and 336 kg N ha^{-1}) in granular form in 1989 and as a liquid with the aid of a CO_2-pressurized backpack sprayer and metronome to ensure accurate and uniform application in 1990. The experimental design was a randomized complete block with 12 replications. Weed control was obtained through a combination of a pre-emergence herbicide application [paraquat (1,1-dimethyl-4,4'-bipyridinium dichloride) at 0.5 kg ha^{-1}, metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-mehtoxy-1-methylethyl) acetamide) at 2.25 kg ha^{-1} and, cyanazine (2-(4 chloro-6-(ethylamino)-s-triazine-2-*yl*) amino-2-methylpoprionitrile) at 2.25 kg ha^{-1}], mechanical cultivation, and handweeding for escapes. Rainfall was adequate and evenly distributed throughout the growing season (Table 5).

Immediately following the harvest of corn as silage, 2-cm soil cores were taken in 30-cm increments to a final depth of 90-cm from between the center two corn rows in each plot. Six cores at each depth were composited from each plot and immediately placed on dry ice and stored frozen prior to laboratory analyses.

Soil samples were thawed and extracted with 2M KCl (Keeney and Nelson, 1982) and NH_4^+ and NO_{3-} concentrations determined colormetrically with a QuikChem Automated Ion Analyzer (NO_3^- reduction by Cu-coated Cd column to NO_2^-). Residual fertilizer N in the soil NO_3^- and NH_4^+-N fractions was determined by preparing a 40-mL aliquot of each KCl extract for ^{15}N analysis by a diffusion procedure outlined by Brooks et al. (1989).

Non-exchangeable NH_4^+-N derived from residual fertilizer N was determined by the pretreatment of soil samples with KOBr-KOH, and destruction of clay minerals with (HF + HCL) solution (Keeney and Nelson, 1982). Ammonium-N was then prepared for N isotope-ratio analysis by a slight modification of the diffusion procedure outlined by Brooks et al. (1989). Atom % ^{15}N concentrations of the diffused N (exchangeable NH_4^+, NO_3^- and nonexchangeable NH_4^+) trapped in the acidified glass fiber filters were determined with an automated C-N analyzer/mass spectrometer (ANCA/MS) system consisting of an automated C-N analyzer (Roboprep C/N, Europa Scientific, Crewe, England) interfaced to a dual collector ratio mass spectrometer (Micromass VG 602C, VG Micromass LTD, Cheshire, England) at the TVA's National Fertilizer and Environmental Research Center (NFERC) in Muscle Shoals, Alabama. Atom % ^{15}N concentrations of diffused N were corrected for background N as described by Kelley et al. (1991).

Following corn harvest and soil sampling, a winter cover treatment was imposed on the experimental site to determine the effectiveness of a rye cover crop to recover residual fertilizer N. Experimental design was a split-plot where main plots were winter cover treatments (rye for no-till mulch, rye for silage, and fallow) and subplots were fertilizer N rates applied to corn with four replications. Rye was drilled into a conventional-tillage seedbed at a rate of 80 seeds m^{-1} of row into 18-cm wide rows. Rye managed as a no-till mulch was chemically killed in the early boot stage while rye managed for silage production was mechanically harvested at the early head stage. Reference to the rye cover crop treatment in this paper will pertain to the rye cover crop that was managed for a no-till mulch. A summary of field operations for the 1989-90 corn-rye growing season is presented in Table 5. Plant tissue samples were taken in the center

Table 5. Field operations summary for 1989-90 corn-rye growing season.

Field Operation	Date	Cummulative Precipitation (cm)	Days after N Application
Corn planting	17 May 1989	0	0
Corn harvest	28 Sept. 1989	63	135
Soil Sample	3 Oct. 1989	68	140
Plant Winter Rye	7 Oct. 1989	68	147
Chemical kill rye mulch trtmt.	2 Apr. 1990	107	325
Soil sample rye mulch and fallow trtmts.	4 Apr. 1990	107	327
Harvest rye silage trtmt. and soil sample	9 Apr. 1990	109	332

of each plot from adjacent one meter long rows for dry matter estimates and laboratory analyses. Soil samples were taken immediately following chemical kill and processed in the same manner described earlier. Aliquots of finely ground soil and plant tissue, containing 100 μg N, were placed in Sn foil cups and analyzed for total N content and atom % ^{15}N concentration by ANCA/MS (Kelley et al. 1991). Data for the experiment were analyzed statistically using procedures outlined by the SAS Institute (SAS, 1982). Least significant difference (LSD) values were calculated at the 0.05 level of probability.

Results and Discussion

Soil NO_3^- levels following corn harvest provided adequate N for accurate isotope ratio analysis. Atom % ^{15}N concentrations of the NO_3^--N fraction decreased with increasing N rate at each depth indicating the presence of ^{15}N-depleted fertilizer-derived N (Table 6). These data show that even small amounts of applied fertilizer N (84 kg ha^{-1}) as ^{15}N-depleted N, can be clearly detected in the soil NO_3^--N fraction 140-d after application and corn growth. This is likely due to i) the fact that NO_3^- constitutes only a very small percentage of the total N in soils at any specific moment (MacGregor et al., 1974; Robinson, 1975; Smith et al., 1977), ii) mineralization of decomposing alfalfa plant material resulted in high levels of plant available N which decreased fertilizer N uptake by corn, and iii) the microbial conversion of fertilizer NH_4^+ to NO_3^- can occur within a few weeks of application (Broadbent and Tyler, 1957; Justice and Smith, 1962) which increases the concentration of fertilizer-derived NO_3^- in the relatively small soil NO_3^--N pool.

Exchangeable NH_4^+-N levels following corn harvest were generally less than 2.5 mg kg^{-1} at each depth regardless of N rate following corn harvest (data not

Table 6. Atom % ^{15}N concentration of soil NO_3^--N fraction by depth as affected by ^{15}N-depleted fertilizer N application.

	Soil Depth					
	0-30 cm		30-60 cm		60-90 cm	
N Rate[†]	At. % ^{15}N	NO_3^--N[‡]	At. % ^{15}N	NO_3^--N	At. % ^{15}N	NO_3^--N
kg ha^{-1}		kg ha^{-1}		kg ha^{-1}		kg ha^{-1}
0	0.35956	18.9	0.36571	8.6	0.37550	5.4
84	0.33367	23.1	0.33929	15.4	0.33486	15.3
168	0.29308	27.8	0.28851	34.7	0.31447	20.9
252	0.25311	43.2	0.25065	49.5	0.28982	27.2
336	0.20498	71.7	0.21683	88.1	0.25293	38.0
LSD (0.05)	0.01515	15.3	0.01927	15.2	0.02916	7.0
CV (%)	6.4	56.2	7.2	51.5	9.5	43.9

[†] Fertilizer N applied 140-d prior to soil sampling.

[‡] Bulk density = 1.47 g cm^{-3} used to calculate NO_3^--N on kg ha^{-1} basis.

shown). Such low levels of NH_4^+-N, extracted at a 10:1 ratio of 2M KCl:soil, did not provide enough N following diffusion to meet the 10 μg N sample^{-1} minimum required for accurate isotope ratio analysis. Modification of the extraction and diffusion procedure to concentrate more NH_4^+-N for isotope ratio analysis is possible, however, the additional time and expense required to trace fertilizer-derived N in a pool that represented less than 10 kg N ha^{-1} could not be justified.

Fertilizer-derived N recovered in the total N fraction was clearly detected in the 0 to 30-cm depth following corn harvest as indicated by decreasing atom % ^{15}N concentrations with increasing N rate (Table 7). The size of the total N pool in the soil was not affected by N rate. Atom % ^{15}N concentrations in the total N pool also tended to decrease with N rate in the 30 to 60 and 60 to 90-cm depths but was only significantly lower than natural abundance (measured in the control plots) at the 336 kg ha^{-1} N fertilizer rate. This suggests that fertilizer-derived N was primarily confined to the top 30-cm for N rates less than 336 kg ha^{-1}.

The clay minerology of this site is dominated by hydroxy interlayer vermiculite, hydrous mica, and montmorillonite (Parker et al., 1979). Soils rich in these minerals can contain large amounts of NH_4^+ ions trapped in the interlayer

Table 7. Atom % ^{15}N concentration of total N pool by depth as affected by addition of ^{15}N-depleted fertilizer N.

	Soil Depth					
	0-30 cm		30-60 cm		60-90 cm	
N Rate[†]	At. % ^{15}N	Total N[‡]	At. % ^{15}N	Total N	At. % ^{15}N	Total N
kg ha^{-1}		Mg ha^{-1}		Mg ha^{-1}		Mg ha^{-1}
0	0.36811	3.99	0.37432	1.38	0.37472	1.07
84	0.36677	4.33	0.37151	1.42	0.37105	0.98
168	0.36560	4.21	0.36856	1.29	0.37368	0.97
252	0.36395	4.37	0.36912	1.41	0.37221	1.07
336	0.36161	4.21	0.36532	1.41	0.36909	1.01
LSD (0.05)	0.00156	0.51	0.00539	0.15	0.00341	0.17
CV (%)	0.5	14.6	1.8	13.3	1.1	19.6

[†] Fertilizer N applied 140-d prior to soil sampling.

[‡] Bulk density = 1.47 g cm^{-3} used to calculate total N on Mg ha^{-1} basis.

spaces. According to Nommik and Vahtras, (1982), the dynamics of nonexchangeable NH_4^+-N is regulated by the equilibrium between the different forms of NH_4^+ in the soil system.

$$NH_4^+ \text{ solution} \rightleftharpoons NH_4^+ \text{ exchangeable} \rightleftharpoons NH_4^+ \text{ fixed.}$$

Therefore, the addition of large amounts of fertilizer N would be expected to increase the amount of nonexchangeable NH_4^+. The absence of a grain yield and N uptake response to fertilizer N application (data not shown) indicate that plant available N levels were high during this growing season and a shift in the soil N equilibrium towards fixation of fertilizer-derived NH_4^+-N was possible. Atom % ^{15}N concentrations in the nonexchangeable NH_4^+ fraction, however, did not differ from the control plots to 90-cm depth with fertilizer N applications up to 336 kg N ha^{-1} which suggest the fertilizer N was not clay-fixed (data not shown). Dilution of fertilizer N in a large available N pool resulting from the mineraliztion of decomposing alfalfa material may have limited its detectibility in the nonexchangeable NH_4^+-N fraction. Also, the nontreatment application of K to the experimental site may have caused the interlayers of these 2:1 clay minerals, particularly in the surface 30-cm of incorporation, to collapse and prevent the fixation of fertilizer-derived NH_4^+.

Uptake of residual soil NO_3^--N by the winter rye cover crop (data not shown) reduced NO_3^- levels below that needed for accurate isotope-ratio analysis. In the top 30-cm, atom % ^{15}N concentrations of the NO_3^--N in the winter fallow soil were lower than natural abundance at the 252 kg N ha^{-1} rate only (Table 8). In the 30 to 60 and 60 to 90-cm depths, atom % ^{15}N concentrations decreased with increasing N rate, indicating significant movement of residual fertilizer-derived NO_3^--N into the deeper depths of the profile. The ability to trace fertilizer-derived N from ^{15}N-depleted material in the soil NO_3^- fraction approximately one year after application can be attributed to the fact that soil NO_3^- represents a small fraction of the soil total N pool thus preventing excessive dilution of the fertilizer N.

Detection of fertilizer-derived N in the soil total N pool approximately one year after application was related to N rate applied to the previous corn crop and sample depth (Table 9). Atom % ^{15}N concentrations (averaged across cover crop treatment) in the soil total N pool at the 0 to 30, 30 to 60, and 60 to 90-cm depths differed from the control plots with the N application rates of 168, 252, and 336 kg ha^{-1} respectively, even though the amount of total N in the 0 to 30-cm depth was approximately 3 times higher than that measured in the two lower sampling depths (Table 9). Variability in the size of the total N pool (CV's of 25.8, 20.5, and 20.9 for the 0 to 30, 30 to 60, and 60 to 90-cm depths

Table 8. Atom % ^{15}N concentration in soil NO_3^--N fraction by depth following winter fallow.

	Soil Depth					
	0-30 cm		30-60 cm		60-90 cm	
N Rate†	At. % ^{15}N	NO_3^--N	At. % ^{15}N	NO_3^--N	At. % ^{15}N	NO_3^--N
kg ha^{-1}		kg ha^{-1}		kg ha^{-1}		kg ha^{-1}
0	0.35951	14.5	0.36463	23.1	0.36722	20.6
84	0.34225	15.7	0.34236	28.7	0.34387	31.0
168	0.34764	15.5	0.32635	30.3	0.32531	38.8
252	0.28326	18.7	0.27195	46.2	0.25843	50.1
336	0.31218	26.7	0.23768	52.5	0.22469	87.5
LSD (0.05)	0.0567	10.3	0.0363	15.8	0.0351	24.2
CV (%)	11.2	36.6	7.6	28.4	7.6	34.5

† Previous N application to corn 327-d prior to soil sampling.

Table 9. Atom % ^{15}N concentration in soil total N pool following winter cover crop treatments.

		Soil Depth					
	Cover Crop Treatment	0-30 cm		30-60 cm		60-90 cm	
N Rate†		At. % ^{15}N	Total N	At. % ^{15}N	Total N	At. % ^{15}N	Total N
kg ha^{-1}			Mg ha^{-1}		Mg ha^{-1}		Mg ha^{-1}
0	Fallow	0.36780	4.46	0.36968	1.34	0.36693	1.06
	Rye Cover	0.36850	3.61	0.36853	1.19	0.36848	0.67
	Mean	0.36815		0.36910		0.36771	
84	Fallow	0.36659	3.89	0.36281	1.29	0.37015	1.12
	Rye Cover	0.36705	4.25	0.36754	1.32	0.36872	0.91
	Mean	0.36682		0.36771		0.36796	
168	Fallow	0.36349	4.32	0.36601	1.41	0.36551	0.99
	Rye Cover	0.36621	3.69	0.36795	1.13	0.37040	0.87
	Mean	0.36485		0.36698		0.36796	
252	Fallow	0.36546	5.18	0.36355	1.25	0.36421	0.99
	Rye Cover	0.36450	5.57	0.36600	1.36	0.36834	1.03
	Mean	0.36498		0.36478		0.36628	
336	Fallow	0.36333	4.09	0.36264	1.39	0.35622	1.05
	Rye Cover	0.36270	3.97	0.36650	1.21	0.36685	0.89
	Mean	0.36301		0.36457		0.36153	
‡ LSD (0.05)		0.0017		0.0032		0.0044	
§ Significance of Trtmt.							
N Rate		**	NS	*	NS	*	NS
Cover Crop		NS	NS	NS	NS	NS	*
N Rate x Cover Crop		NS	NS	NS	NS	*	NS

† Previous N application to corn 327-d prior to soil sampling.

‡ LSD for N treatment means.

§ Significance of F test for treatment and interaction effects: NS = not significant at P = 0.05 level.
*, ** significant at the 0.05 and 0.01 levels of probability respectively.

respectively) and/or excessive dilution of residual fertilizer N is probably responsible for limiting the detection of fertilizer N in the soil total N pool at deeper depths at low N rates.

The absence of a N rate x cover crop interaction on the atom % ^{15}N concentrations of the total N pool within each depth possibly suggests that cover crop N removal had no measurable impact on the size of the total N pool or the amount of residual fertilizer N remaining in the soil at each N rate (Table 9). Such conclusions are incorrect since soil NO_3^--N levels were found to be less than 10 kg N ha^{-1} at each N rate following a rye cover crop and as high as 88 kg N ha^{-1} after winter fallow (data not shown). Thus, the measured influence of a winter cover crop on the soil NO_3^- pool is apparently undetectable in the total N pool due to the relatively small size of the NO_3^- pool and the high degree of spacial variability associated with soil total N levels.

Recovery of residual ^{15}N-depleted fertilizer N by the winter rye cover crop was verified by measuring significant decreases in the atom % ^{15}N concentration in the rye tissue with increasing N rate (data not shown). The ^{15}N dilution from natural abundance ranged from 0.35631 to 0.25699 at the 0 and 336 kg ha^{-1} N rates, respectively. These data provide evidence that ^{15}N-depleted fertilizer N can be successfully used as a tracer for residual fertilizer N plant recovery under the conditions of this study.

Conclusions

The use of ^{15}N-depleted preplant applied fertilizer N to determine the contribution of fertilizer-derived N in the soil NO_3^- fraction following corn was clearly detectible and distinguishable from native soil NO_3^- to a 90-cm depth. Nitrogen uptake by a winter rye cover crop reduced soil NO_3^--N levels below that required for accurate isotope-ratio analysis (<10 kg ha^{-1}). Therefore, if the fate of residual fertilizer-derived NO_{3-}-N is to be traced in the soil following a winter cover crop, soil extraction procedures must be modified to concentrate N prior to diffusion for accurate isotope-ratio analysis.

The greatest limitations to the use of ^{15}N-depleted fertilizer N as a tracer of residual fertilizer N in a corn-rye crop rotation appears to be its detectability from native soil N in the soil total N pool. Detection below 30-cm depth was not reliable, particularly at the lower N rates, due to excessive dilution. Therefore, ^{15}N-depleted fertilizer N cannot be recommended as a means of tracing mineralization-immobilization turnover of fertilizer-derived N, especially for soils with a large total N pool. Inconclusive results indicate that further research is needed to determine the feasiblity of using depleted material for measuring clay-fixation of fertilizer derived NH_4^+-N.

Following winter fallow (approx. 1 yr after fertilizer application) residual ^{15}N-depleted fertilizer N was still detectable in the NO_3^--N fraction as indicated by significantly lower atom % ^{15}N concentrations as N rate increased. Greater variability in atom % ^{15}N concentrations are likely to occur closer to the soil surface due to downward movement of fertilizer-derived soil NO_3^- throughout the winter months.

The results of this study suggest that under conditions, of adequate rainfall (107 cm), high soil N availability, and N rates ranging from 0 to 336 kg ha^{-1}, ^{15}N-depleted fertilizer N material can be reliably used as a tracer of residual fertilizer N in the soil NO_3^-N fraction and plant tissue up to one yr after N application.

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Chapter V

Fate of ^{15}N-Depleted $(NH_4)_2SO_4$ Applied to Corn at the Economic Optimum N Rate

ABSTRACT

Nitrate contamination of ground water is a major environmental concern in agricultural regions. The objectives of this study were to (i) measure plant uptake and soil distribution of fertilizer N applied at 84, 168, 252, and 336 kg N ha^{-1} as ^{15}N-depleted $(NH_4)_2SO_4$ to corn (*Zea mays* L.), and (ii) determine the relationships between economic optimum N rate, fertilizer-use efficiency, and potential leaching loss of residual fertilizer-derived N to ground water. Plant recovery of fertilizer N in 1989 ranged from 33 to 47% of applied even though no grain yield response to N fertilization was measured. Approximately 60 % of the fertilizer N remaining in the soil after harvest was in the top 30-cm at each N rate. In 1990, corn planted with no-tillage into a rye mulch (NT-mulch) produced greater grain yield and fertilizer N uptake response to fertilizer N application compared to corn planted with no-tillage into rye stubble (NT-stubble) and a winter fallow (WF) seedbed. Approximately 90% of the fertilizer-derived N remaining in the soil after 1990 corn harvest was in the top 30-cm. The economic optimum N rate for 1990 NT-mulch corn (218 kg N ha^{-1}) corresponded closely with the rate (224 kg N ha^{-1}) resulting in the highest fertilizer-

use efficiency. Residual fertilizer-derived NO_3^- in the 60-90-cm depth following the 1990 corn harvest ranged from 0.5 to 3.5 kg N ha^{-1}. Higher levels of fertilizer-derived NO_3^- in the 60 to 90-cm depth in 1989, when the economic optimum N rate was zero, indicates the environmental importance of knowing when soil nitrogen supplies are adequate to support crop growth. However, when soil N supplies are inadequate to support crop growth, this study provides evidence to support the use of the economic optimum N rate concept from both economic and environmental viewpoints.

INTRODUCTION

Corn growers face three inherent N management problems; (i) determining the plant available N supplying potential of the soil, (ii) predicting the amount of fertilizer N needed to optimize economic return and (iii) managing N inputs in a manner that is environmentally safe. Although the understanding of N dynamics in the biological system continues to improve, the enigma of N management is complicated by various tillage systems, crop rotations, soil N amendments, and their varying effects on soil water and N availability. The determination of optimum N fertilizer rates for corn amid increasing environmental concerns is a major unsolved problem in most humid regions of the United States.

Numerous investigators have focused their N research programs on identifying grower accepted diagnostic tools such as timely tissue testing and soil NO_3^--N sampling, that can ultimately provide a more quantitative approach to predicting economic optimum fertilizer N rates for corn (Dahnke and Vasey, 1973; Stanford, 1982; Keeney,1982; Magdoff et al., 1984; Fox and Piekielek, 1984; Fox et al., 1989; Bindford et al., 1990). In addition to increasing the probability of maximizing profit, the attractiveness of predicting economic optimum N rates has also been its somewhat intuitive relationship with maximum fertilizer-use efficiency. Parr (1973) defined fertilizer-use efficiency as "the percentage recovery of fertilizer N by the crop". The movement of NO_3^- below the root zone has been shown to be related to fertilizer N applications at rates higher than the optimum in numerous corn studies (Linville and Smith, 1971; Macgregor et al., 1974; Jolley and Pierre, 1977). Others have concluded that if fertilizer N applications do not exceed crop needs, then NO_{3-} leaching losses are not an environmental problem (Pratt et al., 1972; Power, 1970). This concept was further developed by Fried et al. (1976) who suggested that as long as fertilizer N use efficiency (fertilizer N uptake: fertilizer N applied) is maintained at a high level, only small amounts of N will be subject to leaching.

The influence of tillage on economic optimum N rates and subsequent fertilizer use efficiency is of particular interest in light of current government regulations pertaining to crop production on highly erodible land. In Kentucky and other regions with similar climates and topography, long-term comparisons of tillage systems have demonstrated that corn yields with no-tillage (NT) at low fertilizer N rates are usually lower than corn yields with conventional tillage (CT). However, at higher N rates, fertilizer N recovery and yields are generally higher with NT (Blevins et al., 1977; Bandel et al., 1975; Moschler et al., 1972; Moschler and Martens, 1975; Triplett and Van Doren, 1969; Legg et al., 1979). According to Kitur et al. (1984) such observations can be interpreted as indicating greater fertilizer use efficiency in NT because an added increment of fertilizer usually increases yield more with NT than with CT.

Limited studies have attempted to examine the fate of residual fertilizer-derived N resulting from fertilizer N applied to corn at the economic optimum N rate because the relationship between economic optimum N rate and fertilizer use efficiency appears to be so intuitive. Fertilizer-use efficiency is commonly reported as a percentage and is thus easily misinterpreted as a gauge of potential environmental impact of treatments.

This study was conducted using ^{15}N-depleted $(NH_4)_2SO_4$ to (i) measure plant uptake and soil distribution of varying rates of fertilizer N applied to corn, and (ii) establish the relationships between economic optimum N rate, fertilizer-use efficiency, and potential leaching loss of residual fertilizer-derived N to ground water.

Materials and Methods

The field study was conducted during 1989 and 1990 on a well drained Hayter silt loam soil (fine-loamy, mixed, mesic Ultic Hapludalf) in the Valley region of Virginia near Blacksburg. The experimental site had been managed for alfalfa (*Medicago sativa* L.) hay production prior to initiating the study. An alfalfa-corn rotation is common throughout the region. A seed bed was prepared by moldboard plowing followed by disking and the use of a power driven harrow. Corn was planted in mid-May in 0.76-m row spacings and thinned to a final of population of 49 500 plants ha^{-1}.

Nitrogen as $(NH_4)_2SO_4$ was surface applied immediately after planting at five rates (0, 84, 168, 252, and 336 kg N ha^{-1}) in a granular form in 1989 and as a liquid in 1990. The $(NH_4)_2SO_4$ solution in 1990 was applied with a CO_2-pressurized backpack sprayer and metronome to ensure accurate and uniform application. Within each N rate plot, two subplot areas (4.6 by 4.6-m) were established for the application of ^{15}N-depleted $(NH_4)_2SO_4$; one area for 1989 and one for 1990. Non-labeled $(NH_4)_2SO_4$ was applied on the opposite subplot at the corresponding N rate.

The experimental design in 1989 was a randomized complete block with 12 replications. Following harvest of the 1989 corn crop, a winter cover crop management treatment was imposed. This facilitated the addition of a cover treatment to the 1990 corn crop study. The experimental site was thus transformed into a split-plot design where main plots were tillage treatments (no-tillage into rye mulch, no-tillage into rye stubble, and conventional tillage) and sub-plots were N rates (same plots in 1989). Weed control was obtained through a combination of a pre-emergence herbicide application, mechanical cultivation, and hand weeding for escapes. Rainfall during the 1989 corn growing season was adequate (64-cm) and evenly distributed. In comparison, rainfall during the 1990 corn growing season was less plentiful, (46-cm) poorly distributed and resulted in short periods of drought stress.

Six whole plants were uniformly sampled from the center two rows of each plot at harvest for total N and ^{15}N analyses by direct combustion mass spectrometry. Corn grain and silage yields were calculated from weights of plant material harvested from a 1.5 by 3-m area in the center of each plot. Corn cobs were ground and analyzed with the stover. Grain was weighed and analyzed separately.

Immediately following the harvest of corn as silage, soil samples were taken in 30-cm increments to a final depth of 90-cm from between the center two corn rows in each plot. Six cores at each depth were composited from each plot and immediately placed on dry ice and stored in a frozen condition until laboratory analyses.

Soil nitrate (NO_3^-) and exchangeable ammonium (NH_4^+) were extracted from thawed, moist soil samples with 2M KCl (Kenny and Nelson, 1982) and their concentrations determined colormetrically with a QuikChem Automated Ion Analyzer (NO_3^- reduction by Cu-coated Cd column to NO_2^-). Residual fertilizer N in the soil NO_3^- and NH_4^+-N fractions was determined by preparing a 40-mL aliquot of each KCl extract for ^{15}N analysis by a diffusion procedure outlined by Brooks et al. (1989). The atom % ^{15}N concentration of the diffused N trapped in the acidified glass fiber filter was determined with an automated C-N analyzer/mass spectrometer (ANCA/MS) system consisting of an automated C-N analyzer (Roboprep C/N, Europa Scientific, Crewe, England) interfaced to a dual collector ratio mass spectrometer (Micromass VG 602C, VG Micromass LTD, Cheshire, England) at the TVA's National Fertilizer and Environmental Research Center (NFERC) in Muscle Shoals, Alabama. Atom % ^{15}N concentrations of diffused N were corrected for background N as described by Kelley et al. (1991). Soil samples were analyzed for total N content and atom % ^{15}N concentration by direct combustion mass spectrometry (Kelley and Mulvaney, 1991).

A winter cover management treatment for determining the effectiveness of a rye cover crop to recover residual fertilizer N was imposed on the experimental site following 1989 corn harvest and soil sampling. Experimental design was a split-plot where main plots were winter cover treatments (rye for no-till mulch, rye for silage, and fallow) and subplots were fertilizer N rates applied to the previous corn crop with four replications. Rye was drilled into a conventional seedbed at a rate of 80 seeds m^{-1} of row into 18-cm wide rows. Rye managed for a no-till mulch was chemically killed in the early boot stage while rye managed for silage production was mechanically harvested at the early head stage. Corn was planted approximately two wk after rye silage harvest. A summary of field operations for the 1989-90 corn-rye growing season is presented in table 10.

Economic optimum N rates were calculated as the fertilizer N rate that makes the first derivative of the response function equal to the price ratio of fertilizer N to corn ($/kg N to $/kg corn) (Heady et al., 1955). Response curves to N fertilizer applied were studied with regression analysis. Best fit was selected as the model with the largest R^2 value and the smallest standard error of the estimated regression coefficients (Montgomery and Peck, 1982). Data for the experiment were analyzed statistically using procedures outlined by the SAS Institute (SAS, 1982). Least significant difference (LSD) values were calculated at the 0.05 level of probability.

Table 10. Field operations summary for 1989-90 corn-rye growing season.

Field Operation	Date	Days after N Application
Corn planting	17 May 1989	0
Corn harvest	28 Sept. 1989	135
Soil sample	3 Oct. 1989	140
Plant winter rye	7 Oct. 1989	147
Chemical kill rye mulch trtmt.	2 Apr. 1990	325
Soil sample rye mulch and fallow trtmts.	4 Apr. 1990	327
Harvest rye silage trtmt. and soil sample	9 Apr. 1990	332
Corn planting	27 Apr. 1990	0
Corn harvest	17 Sept. 1990	143
Soil sample	18 Sept. 1990	144

RESULTS AND DISCUSSION

Grain Yields

The absence of a grain yield response to fertilizer N applied in 1989 (mean yield=11.1 Mg ha^{-1}) indicates that significant amounts of biologically fixed N were provided by the incorporated alfalfa crop (data not shown). Grain yield response to fertilizer N applied in 1990 followed the classical N rate by tillage interaction (Fig. 4). At low N rates (<90 kg N ha^{-1}), grain yields were highest with WF where no response to applied N was measured. As N rates increased, grain yields increased with NT-mulch and NT-stubble systems reaching a maximum of 9.1 and 7.5 Mg ha^{-1} at 273 and 184 kg N ha^{-1} respectively (Fig. 4). Higher grain yields with the NT-mulch system is most likely related to a more favorable soil moisture regime during a growing season where rainfall was limited (46-cm).

Economic optimum N rates were calculated at a price ratio ($/kg N : $/kg grain) of 5.64 from the NT-mulch and NT-stubble grain yield response functions shown in Table 11. The economic optimum N rate in 1989 was zero in the absence of a grain yield response to applied fertilizer N. In 1990, the economic optimum N rate was 218 and 139 kg N ha^{-1} for the NT-mulch and NT-stubble systems, respectively. The economic optimum N rate is important from a production point of view

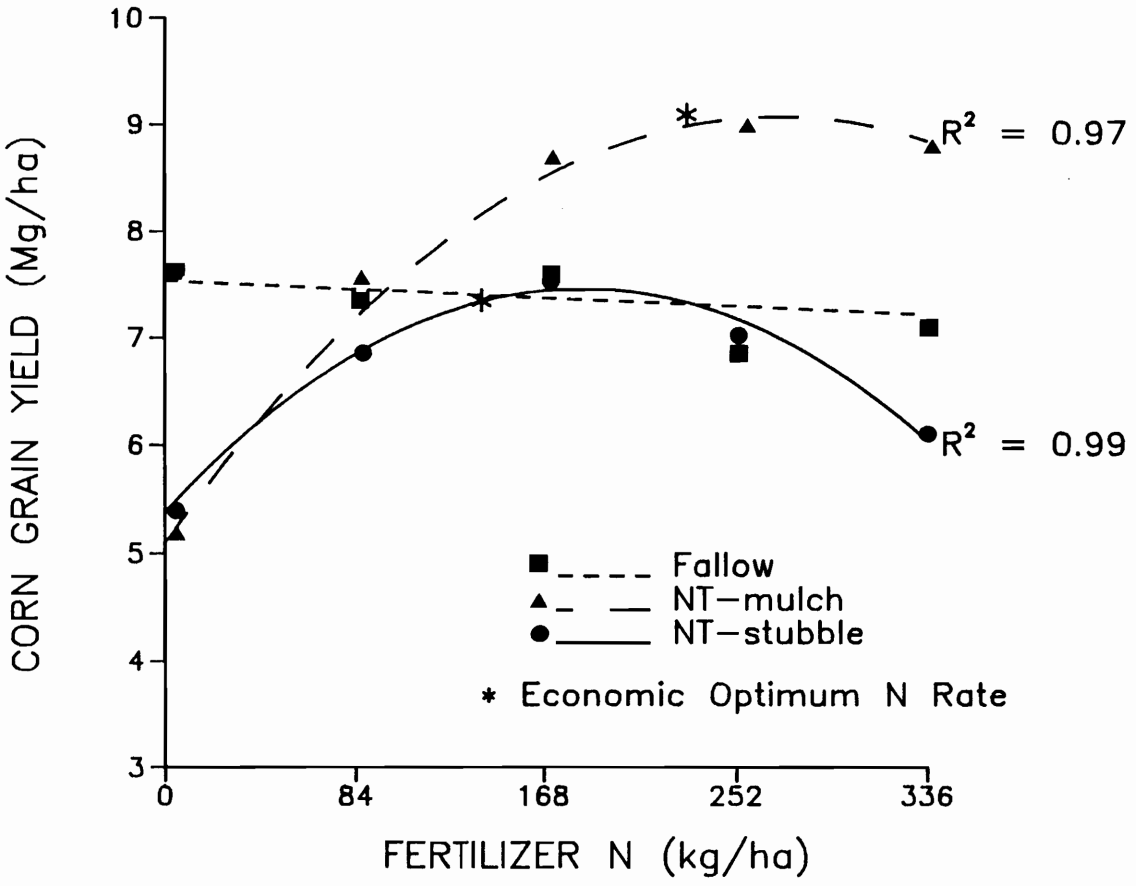

Figure 4. Influence of cover treatment on 1990 corn grain yield response to five levels of fertilizer N.

because it identifies the point where an increase in yield from an increment of added N will only cover the cost of the added N. According to Haby et al. (1983) these are the conditions necessary for maximizing profits from N fertilizer.

N Uptake

The presence of high levels of plant available N and adequate soil moisture in 1989 are evident by the plant N uptake (grain + stover) of 200 kg N ha^{-1} where no N was applied (Fig. 5). Although there was a slight trend for plant N uptake to increase with fertilizer N rate, only 25% ($R^2 = 0.25$) of the observed variation in this relationship could be attributed to changes in fertilizer N applied. These data indicate that the plant available N pool was adequate in meeting the N requirements of the corn crop without the addition of fertilizer N. However, fertilizer N uptake, measured by the isotope method, was found to increase with increasing N rate ($R^2 = 0.83$). The percentage of applied fertilizer N recovered in the corn crop ranged from 33 to 46% with the highest recovery occurring at the 84 kg N ha^{-1} rate (Fig. 5). This positive fertilizer N uptake response to applied N is likely a function of temporal and spatial distributions of the available N source. Fertilizer N applied on the surface at/or near planting is concentrated in a zone near the developing root system and in a form readily available for plant uptake. Mineral N derived from decomposing alfalfa material, is incorporated into a larger soil

Table 11. Regression equations for response to fertilizer N rate applied to corn.

Year	Dependent Variable	Cover[†]	Equation	R^2	CV (%)
1989	Fert. N Uptake	WF	$y = 17.368 + 0.278x$	0.83	15.9
1990	Grain Yield	WF	$y = 7.533 - 0.00089x$	0.01	13.2
		NT-mulch	$y = 5.094 + 0.0295x - 0.00005x^2$	0.97	11.9
		NT-stubble	$y = 5.377 + 0.0227x - 0.00006x^2$	0.99	11.6
1990	Fert.Use Effc.	WF	$y = 0.371 - 0.0005x$	0.93	17.4
		NT-mulch	$y = 0.0016 + 0.00309x - 0.0000069x^2$	0.92	16.5
		NT-stubble	$y = 0.296 + 0.00015x - 0.0000014x^2$	0.95	13.6
1990	N Uptake	WF	$y = 120.035 + 0.3887x - 0.0007x^2$	0.42	15.6
		NT-mulch	$y = 61.027 + 0748x - 0.001x^2$	0.90	16.1
		NT-stubble	$y = 66.154 + 0.576x - 0.001x^2$	0.90	8.7

† WF = winter fallow; NT-mulch = no-tillage rye mulch; NT-stubble = no-tillage rye stubble.

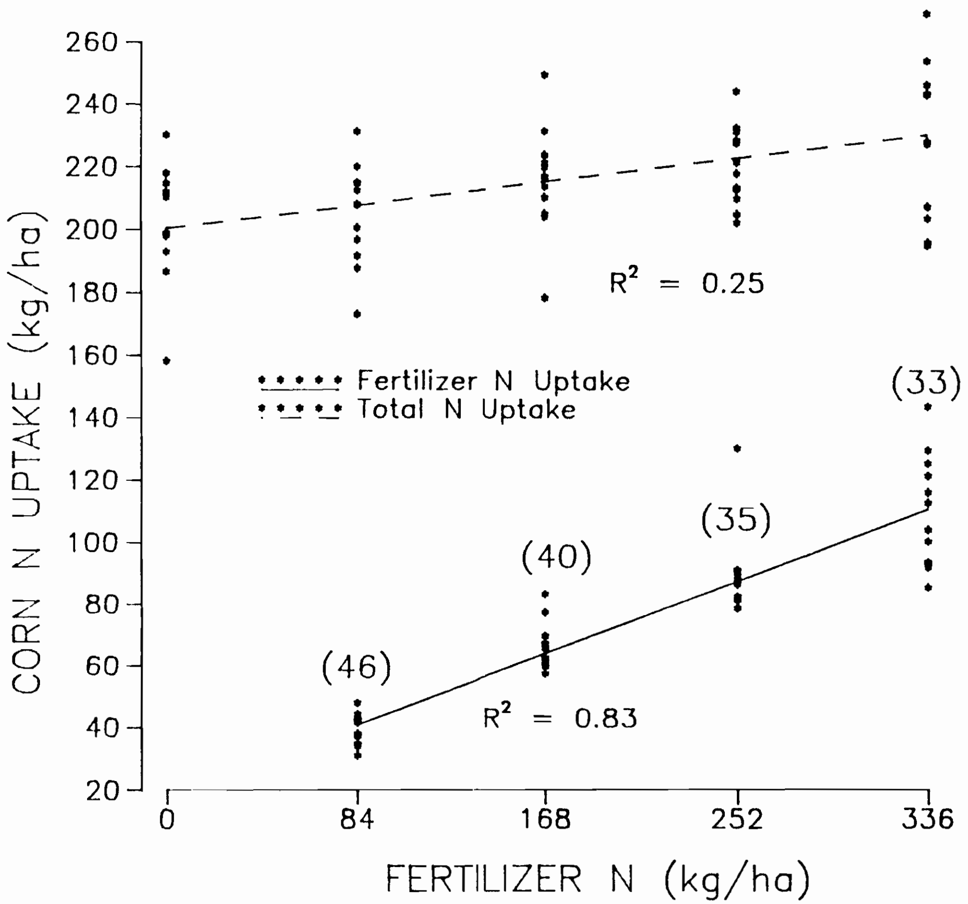

Figure 5. Influence of fertilizer N rate on total N and fertilizer N uptake by 1989 corn. Values in parenthesis indicate percentage of applied fertilizer N recovered in plant (fertilizer–use efficiency).

volume during tillage and is probably less available early in the growing season. In partial support of this explanation, Huntington et al. (1985), found that most of the N mineralized from hairy vetch (*Vicia villosa* Roth) became available to corn after the period of silking. These data demonstrate the importance of adjusting fertilizer N rates for N supplied by the previous legume crop.

Fertilizer N effects on plant N uptake were similar to those observed for grain yield in 1990 (Fig. 6). At low N rates, N uptake was greatest with WF compared to NT-mulch and NT-stubble. Similar observations have been reported and attributed to greater immobilization of fertilizer N in no-till environments due to the presence of wide C:N ratio crop residues at the soil surface (Doran 1980; Mengel et al., 1982). Similar N uptake responses between NT-mulch and NT-stubble (heavy residue vs. minimal surface residues) treatments at low rates of applied N might imply that N immobilization was not the primary mechanism responsible for the observed differences in N availability. However, the combination of high C:N ratio rye residues and a depleted mineral N pool resulting from N recovery in rye biomass (mean = 82 kg N ha^{-1}) can be expected to have provided an excellent environment for net N immobilization to occur in the NT-mulch system. Under these conditions, greater soil moisture contents with NT-mulch probably permitted more efficient N uptake from a relatively smaller available N pool.

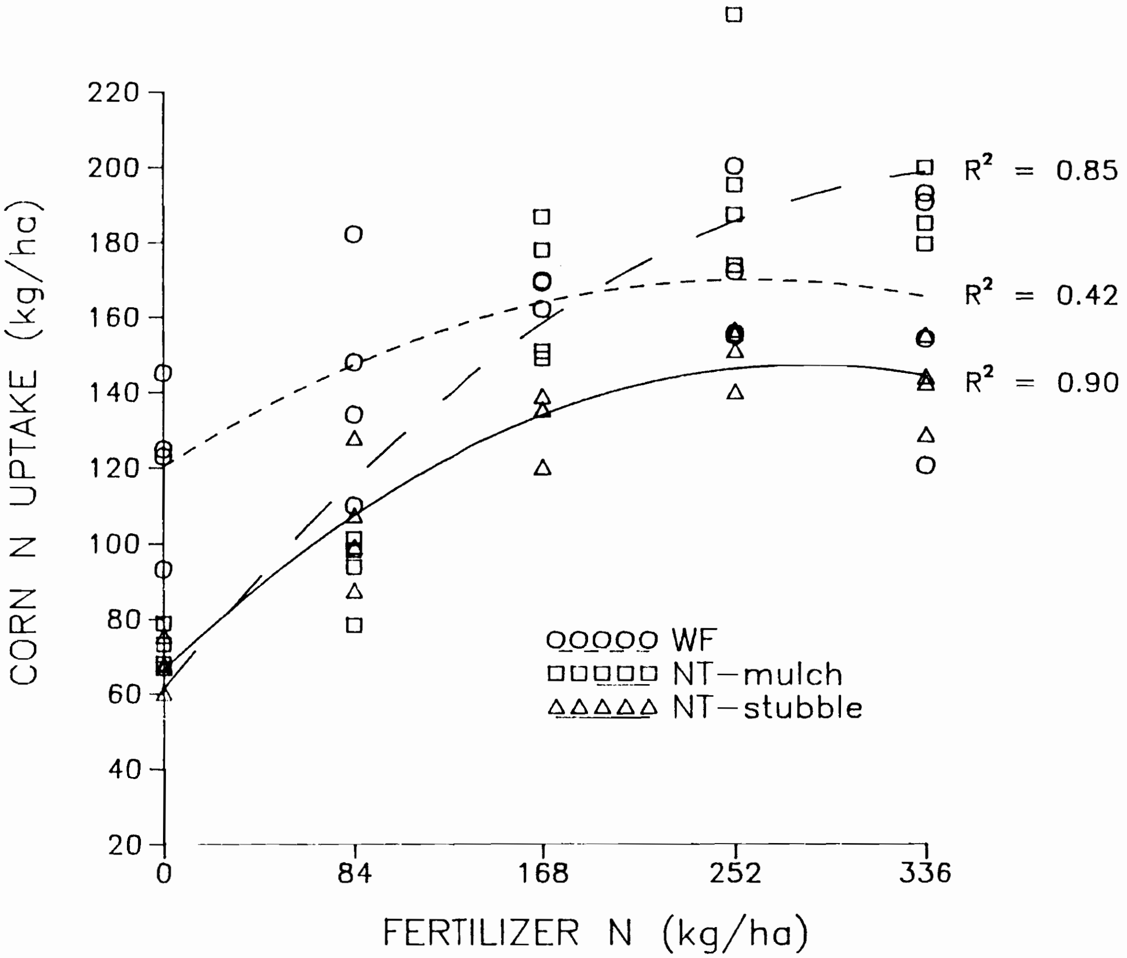

Figure 6. Influence of cover treatment and fertilizer N rate on 1990 corn N uptake.

At higher N rates, N uptake was greatest with NT-mulch and continued to increase above the economic optimum N rate of 218 kg N ha^{-1} with increasing N rate (Fig. 6). Maximum N uptake with NT-stubble and WF was obtained at the 288 and 278 kg N ha^{-1} rates, respectively. Nitrogen released from rye residues in the NT-mulch system are expected to be small especially during a comparatively dry growing season when decomposition rates would be reduced. Wagger (1989) found that 16 wk after planting corn into a rye mulch, only 41% of the initial residue N in rye residues had been released. Therefore, higher N recoveries with the NT-mulch system are most likely the result of a more favorable soil water regime compared to the NT-stubble and WF systems.

The 1990 fertilizer N uptake response to fertilizer N applied followed similar trends observed for N uptake and grain yield (Fig. 7). Fertilizer N uptake was lowest for NT-mulch compared to NT-stubble and WF at the 84 kg N ha^{-1} rate. Legg et al. (1979) related this type of behavior to early-season leaching losses. Previous work in Kentucky and elsewhere has shown that a greater potential for denitrification, as well as leaching losses of applied N, exist in NT environments due to higher soil water contents (Rice and Smith, 1982; Doran, 1980; McMahon and Thomas, 1979). Fertilizer N uptake was highest with NT-mulch as N rate increased above 168 kg N ha^{-1} indicating greater fertilizer-use efficiency compared to NT-stubble and WF at higher levels of applied N.

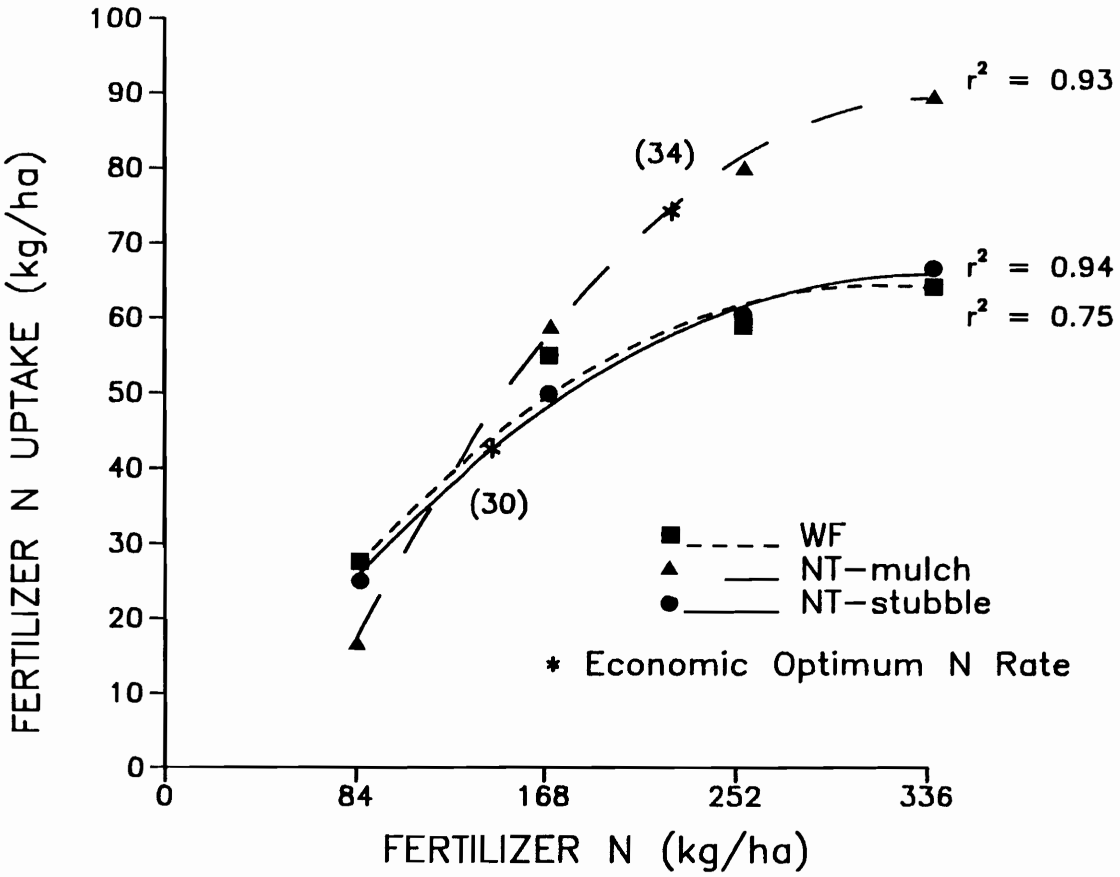

Figure 7. Influence of cover treatment and fertilizer N rate on uptake of fertilizer N by 1990 corn. Values in parenthesis indicate percentage of applied fertilizer N recovered in plant (fertilizer–use efficiency).

Fertilizer N uptake at the economic optimum N rates for the 1990 corn crop were calculated by substituting the economic optimum N rate into the fertilizer N uptake response function reported in Table 11 and expressed as a percentage of that applied (fertilizer-use efficiency). The economic optimum N rate of 218 kg N ha^{-1} for the NT-mulch and 139 kg N ha^{-1} for NT-stubble corresponded to fertilizer-use efficiencies of 34 and 30% respectively (Fig. 7). Fertilizer-use efficiency of 34% for the NT-mulch system at the economic optimum N rate of 218 kg N ha^{-1} corresponded very closely to the maximum fertilizer-use efficiency of 34.4% at a N rate of 224 kg ha^{-1} calculated from the response functions reported in Table 11 (Fig. 8). Lower plant available soil moisture in the NT-stubble and WF systems resulted in decreasing fertilizer use efficiency with increasing N rate.

Soil Recovery and Distribution of Fertilizer N

The amounts and soil distribution of residual fertilizer N following the 1989 and 1990 corn harvest are shown in Figures 9 and 10, respectively. Results from ^{15}N analysis of the soil total N fraction indicates that increasing fertilizer N rate increased the amount of residual fertilizer N remaining in the soil to the 90-cm depth both yrs. Cover treatments also affected the amount of residual fertilizer N remaining in the soil following harvest in 1990 (Fig. 10). More favorable soil moisture conditions with NT-mulch compared to NT-stubble and WF resulted in greater fertilizer N uptake and subsequently less residual fertilizer N in the soil

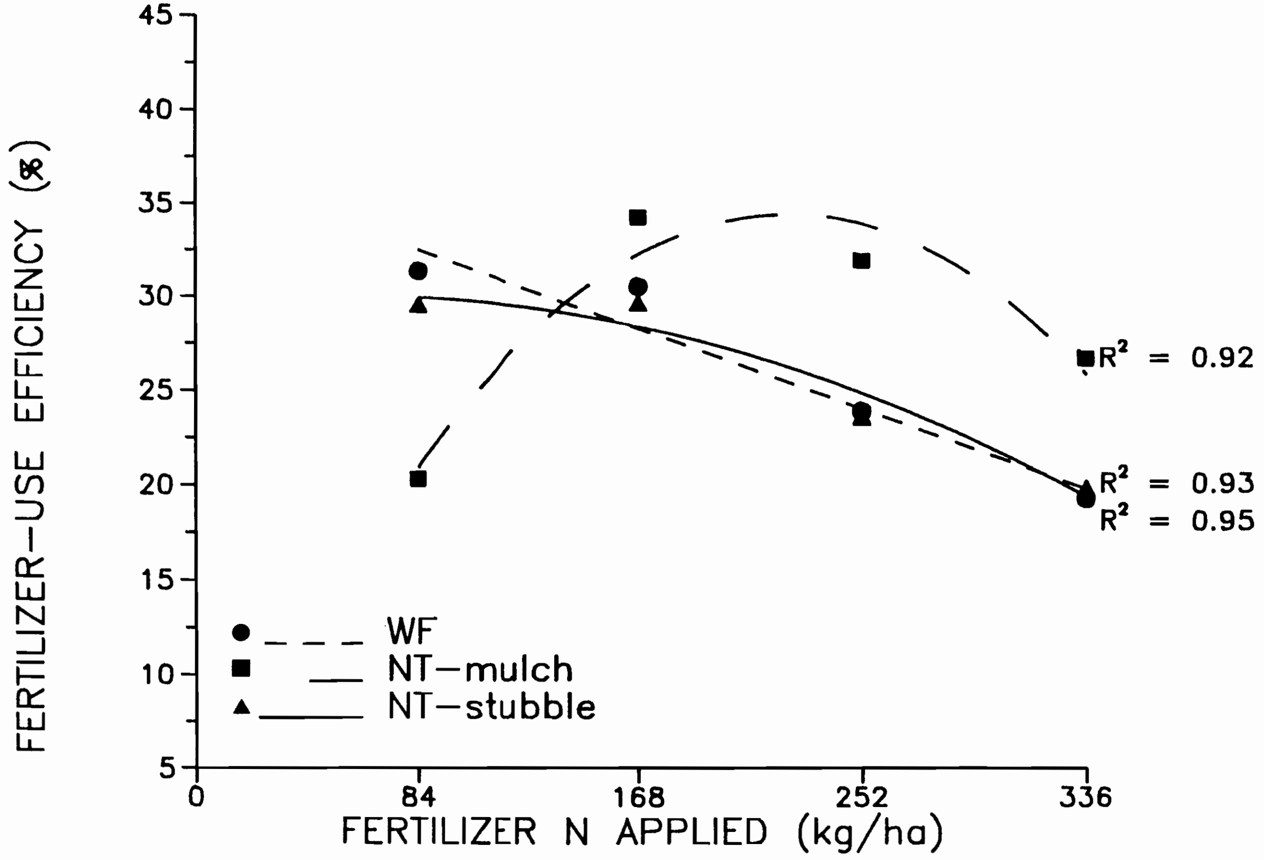

Figure 8. Influence of fertilizer N rate and cover treatment on fertilizer–use efficiency by the 1990 corn crop.

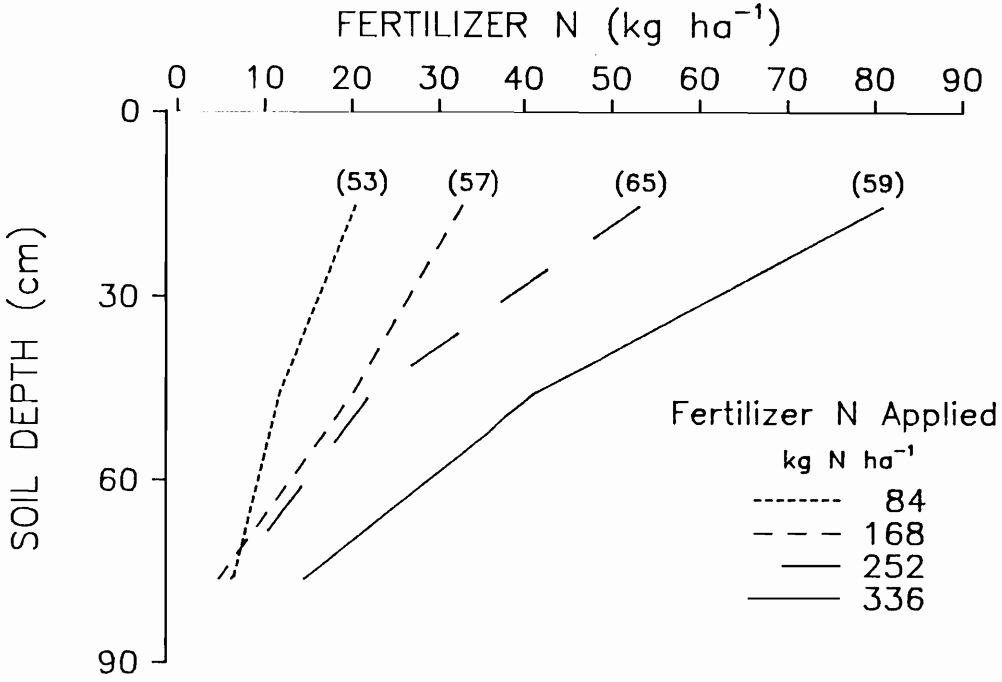

Figure 9. Distribution of fertilizer N recovered in each 30–cm increment of soil to 90–cm depth after 1989 corn harvest. Values in parenthesis indicate percentage of soil recovered fertilizer N in the surface 30–cm depth increment.

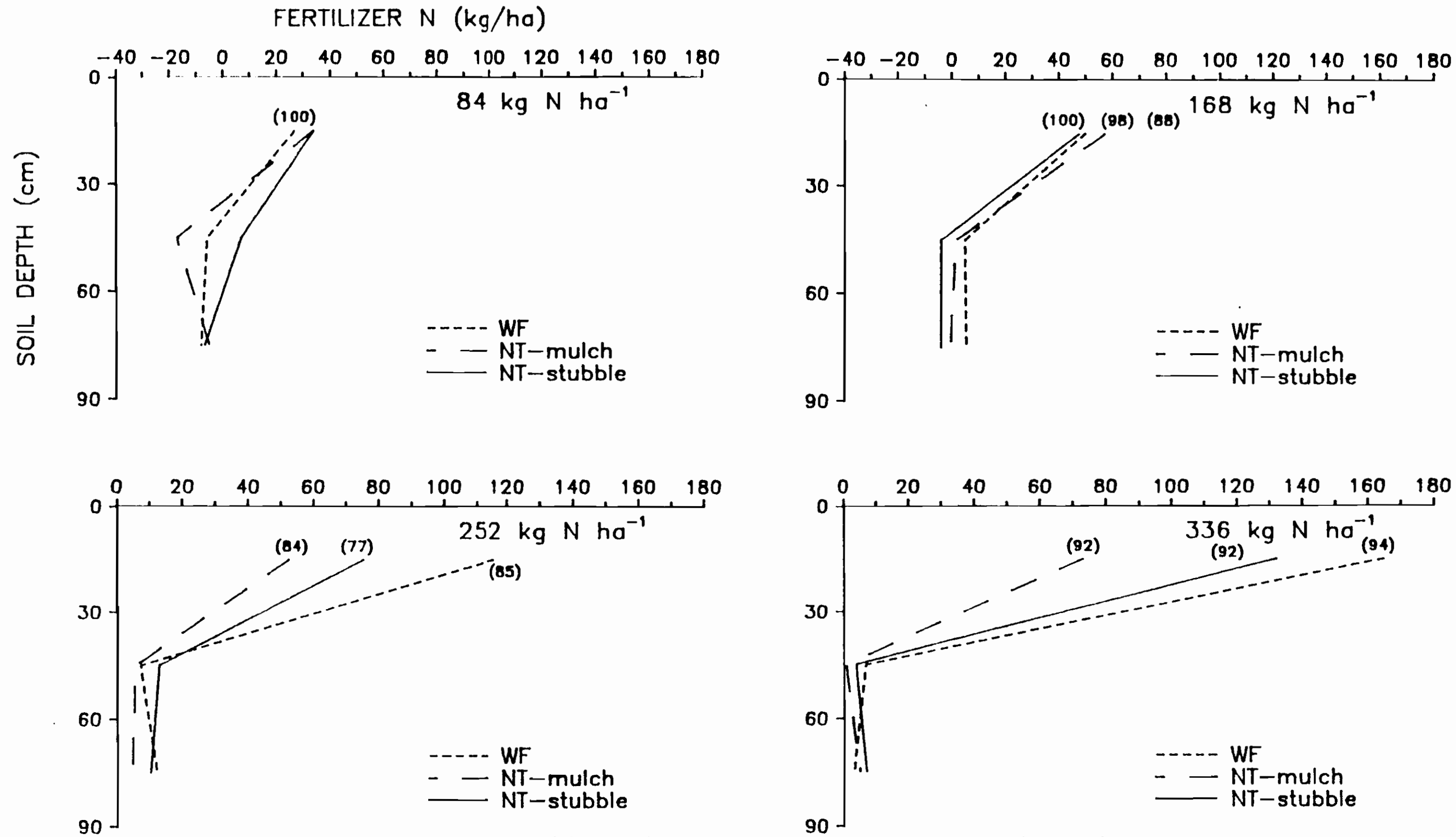

Figure 10. Influence of fertilizer N rate and cover treatment on distribution of soil residual fertilizer N in each 30–cm increment to 90–cm depth following 1990 corn harvest. Values in parenthesis indicate percentage of soil recovered fertilizer N in the surface 30–cm depth increment.

following corn harvest. The absence of a cover x N rate interaction show that the influence of cover on residual fertilizer N levels did not change with increasing N rates.

The greatest accumulation of residual fertilizer N detected in soil samples taken after harvest was found in the top 30-cm and decreased to 90-cm depth both yrs (Fig. 9 and 10). An average of 59 and 91% of the fertilizer N recovered in the soil to 90-cm depth was found in the top 30-cm following the 1989 and 1990 corn harvest, respectively. The retention of fertilizer N in the top 30-cm can be attributed to immobilization of fertilizer N into the organic N fraction and the presence of fertilizer-derived NO_3^- in soil micropores. The amount of fertilizer N immobilized in the top 30-cm increased with increasing N rate, however, the percentage of residual fertilizer N found in the organic N fraction decreased from 90 to 43% in 1989 and 89 to 51% in 1990 with increasing N rate (Table 12). Subsequently, the amount of fertilizer N retained in the surface 30-cm as NO_3^- increased with increasing N rate. Similar results reported by Tyler and Thomas (1977) showed that when NO_3^- was present in micropores, surface applied water caused little displacement of water in micropores resulting in a slow leaching of NO_3^-. However, during the winter months when macropores are saturated and where a positive potential is present, macropores may play a significant role in NO_3^- leaching by channelling solution from the micropores (Reneau et al., 1990).

Table 12. Influence of fertilizer N rate and cover treatment on fertilizer N in various soil N fractions in the 0 to 30-cm depth increment.

	Soil N Fraction[†]					
	1989			1990		
N Rate (N)	**Total N**	**Mineral N[‡]**	**Organic N[§]**	**Total N**	**Mineral N**	**Organic N**
			kg ha^{-1}			
84	21	3	18	32	4	28
168	33	7	26	60	21	39
252	54	18	36	70	13	57
336	81	38	43	100	49	51
Cover (C)						
WF	-	-	-	66	33	33
NT-mulch	-	-	-	54	10	44
NT-stubble	-	-	-	72	22	51
Statistics						
N (LSD 0.05)	23.8	11.7	19.5	22.3	16.4	19.7
C (LSD 0.05)	-	-	-	NS	NS	NS
N x C	-	-	-	NS	*	NS
CV (%)	61.2	86.1	77.2	40.0	90.4	52.5

* Indicates significance at the 0.05 level of probability. NS = not significant.

[†] Measured to 90-cm depth.

[‡] Mineral N = NH_4^+ + NO_3^- - N.

[§] Organic N = Total N - Mineral N.

One approach to assessing the potential loss of fertilizer N to ground water when applied at the economic optimum N rate was to measure the amount of fertilizer-derived NO_3^--N present in the lowest increment of soil examined (60 to 90-cm depth) following the corn harvest. Residual fertilizer-derived NO_3^--N detected in the 60 to 90-cm depth ranged from 0.7 to 11.6 kg N ha^{-1} in 1989 and 0.5 to 3.5 kg N ha^{-1} in 1990 (Table 13) at the 84 and 336 kg N ha^{-1} rates respectively. In spite of greater fertilizer-use efficiency at each N rate in 1989 (Fig. 5) compared to 1990 (Fig. 8), the potential for applied N to leach below the root zone during the corn growing season appears to also be higher in 1989. Perhaps the large available N pool following alfalfa sod narrowed the soil C:N ratio which minimized fertilizer N immobilization resulting in a greater percentage of residual fertilizer N residing in the easily leachable nitrate form. However, in 1990 the plant available N pool had reached a new equilibrium following two years of intensive row crop production. These results suggest that the potential for fertilizer N leaching to ground water is not very large when applied at the economic optimum N rate.

Table 13. Influence of fertilizer N rate on soil residual fertilizer-derived NO_3^--N levels in the 60 to 90-cm depth increment following corn.

	Fertilizer-Derived NO_3^--N	
N Rate	**1989**	**1990**
	kg ha^{-1}	
84	0.7	0.2
168	2.6	1.5
252	4.4	1.7
336	11.6	3.5
Cover Treatment		
Winter Fallow (WF)	-	1.1
NT-mulch -	-	2.8
NT-stubble	-	1.3
Statistics		
N (LSD 0.05)	3.7	1.2
Cover Treatment	-	NS
N x Cover Treatment	-	**

** indicates significance at the 0.01 level of probability.
NS = not significant. (P>0.05)

CONCLUSIONS

These results indicate that a close relationship between economic optimum N rate and fertilizer-use efficiency does exist in a silt loam soil when there is a plant response to fertilizer N application. However, the relationship between fertilizer-use efficiency and the potential for fertilizer N leaching to ground water appears to be inconsistent and unreliable as a means of estimating the environmental impact of applied N on ground water. Although the NT-mulch system in 1990 demonstrated the highest fertilizer use efficiency at the economic optimum N rate, little difference in potential loss of fertilizer N during the growing season was observed between all cover treatments. This study provides evidence to support the application of fertilizer N at the economic optimum N rate as an N management strategy that poses little treat to ground water resources.

Finally, it is important to recognize that the recovery of fertilizer-N in soil and plant tissue is a function of mineralization-immobilization-turnover (MIT) which subsequently influences the atom % ^{15}N concentrations of the various soil N pools.

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Chapter VI

Effectiveness of a Rye Cover Crop for Accumulating ^{15}N-Depleted Fertilizer N from Five Levels of N Fertilizer Applied to Corn

Abstract

Excessive nitrogen fertilization rates applied to a summer annual and/or unusually low crop yields due to drought, can result in accumulation of NO_3^--N in the rooting zone. The objectives of this study were to (i) measure the recovery of residual ^{15}N-depleted fertilizer N by a winter rye crop following corn having received fertilizer N at 84, 168, 252, and 336 kg N ha^{-1}, (ii) determine the influence of winter rye cover crop management on the distribution of residual fertilizer-derived N in the various soil N fractions, and (iii) estimate losses of fertilizer-derived mineral N to the environment following a corn-rye rotation. Recovery of fertilizer N by winter rye increased with increasing N rate applied to the previous corn crop and ranged from 3.5 to 35.9 kg N ha^{-1} in 1990 and 2.3 to 25.7 kg N ha^{-1} in 1991. Fertilizer N recovery in 1991 was higher in rye plots where the previous corn crop had been planted no-till (NT) into rye stubble. Little or no fertilizer-derived mineral N was measured to a final depth of 90-cm following a winter rye cover crop. In contrast, amounts of fertilizer-derived mineral N increased with depth and previous fertilizer N rate with winter fallow. These results provide evidence to support the use of a

winter rye cover crop on a silt loam soil to recover residual fertilizer-derived mineral N that might otherwise be lost to ground water.

Introduction

Sowing a winter annual crop following the harvest of a summer annual has long been recognized for its importance in conserving soil and water and maintaining or increasing soil organic matter levels (Pieters and McKee, 1938). Rye (*Secale cereale* L.) is regarded as one of the most suited small grains for winter cover crop use because of its wide adaptability, tolerance to extreme winter temperatures and ease of establishment. Moschler et al.(1967) highly recommended rye as a cover crop for no-till corn because of its superior winter hardiness, susceptibility to herbicide kill and the production of relatively large amounts of persistent mulch.

Recently, a tremendous increase in the concern for NO_3^- leaching into ground water where high nitrogen fertilization rates are applied to a summer annual and/or unusually low crop yields result due to drought has begun to redirect the emphasis of growing a small grain cover crop. Numerous studies have demonstrated the ability of the nonlegumes to recover soluble N even when high rates of N are applied to soils with high leaching potential (Morgan et al., 1942; Martinez and Girard, 1990; Karraker et al., 1950; Mesinger et al., 1990; Nielson and Jensen, 1985; Staver and Brinsfield, 1990). Nitrate accumulations in the rooting zone have been found to range from a few to several hundred mg kg^{-1} (Hahn et. al., 1977; Linville and Smith, 1971; MacGregor et al., 1974) Studies in Virginia (Alley and Scharf, 1987 and 1988, unpublished data) have found mineral N, predominantly NO_3^-, concentrations ranging up to 105 mg kg^{-1} during October in fields to be planted to winter wheat.

The effectiveness of a winter cover crop to intercept or trap residual mineral N that might otherwise be lost through leaching has been reported to range from 12 to 91 kg N ha^{-1} (Wagger and Mengel, 1988). Based on a review by Ditsch and Alley (1991), the amount of N recovered by the cover crop is largely a function of i) cover crop planting date, ii) cover crop seeding rate and subsequent plant population, iii) amount of residual mineral N remaining after the harvest of the previous crop, and iv) cover crop growth stage at the time of termination (early vs late kill). However, limited data is available to quantify the effectiveness of a rye cover crop to recover accumulated residual fertilizer-derived N from previous N fertilization.

The objectives of this study were to i) measure the recovery of residual ^{15}N-depleted fertilizer N by a winter rye cover crop, ii) determine the influence of winter cover crop management on the distribution of residual fertilizer-derived N in various soil N fractions, and iii) estimate losses of fertilizer-derived mineral N to the environment following a corn-rye cropping sequence.

Materials and Methods

The field study was conducted from 1989 through 1991 on a well drained Hayter silt loam soil (fine-loamy, mixed, mesic Ultic Hapludalf) near Blacksburg Virginia. The experimental site had been managed for alfalfa (*Medicago sativa* L.) hay production prior to initiating the study. Alfalfa-corn is a common rotation in the Valley region of Virginia. In 1989, a seedbed was prepared by moldboard plowing followed by disking and the use of a power driven harrow. Corn was planted in mid-May in 0.76-m row spacings and thinned to a final population of 49 500 plants ha^{-1}.

Nitrogen as $(NH_4)_2SO_4$ was surface applied immediately after corn planting in 1989 and 1990 at five rates (0, 84, 168, 252, and 336 kg N ha^{-1}) in a granular form in 1989 and as a liquid in 1990. The $(NH_4)_2SO_4$ solution in 1990 was applied with a CO_2-pressurized backpack sprayer and metronome to ensure accurate and uniform application. Within each N rate plot, two subplot areas (4.6 by 4.6-m) were established for the application of ^{15}N-depleted $(NH_4)_2SO_4$; one area for 1989 and one for 1990. Non-labeled $(NH_4)_2SO_4$ was applied on the opposite subplot at the corresponding N rate.

A winter rye cover crop management treatment was imposed on the experimental site following harvest of the 1989 corn crop as silage to determine the effectiveness of a rye cover crop to recover residual fertilizer N. This would also facilitate the addition of a cover treatment for the 1990 corn crop. The experimental site was thus transformed into a split-plot design where main plots were winter cover treatments (winter fallow, rye for no-tillage mulch, and rye harvested for silage) and subplots were residual N levels (resulting from N rates applied to previous corn crop) with four replications. A seedbed was prepared with an offset disk and power driven harrow. Rye was drilled into a conventional-tillage seedbed at a rate of 80 seeds m^{-1} row into 18-cm wide rows. In 1990, rye managed for a no-till mulch was chemically killed with paraquat (1,1-dimethyl-4,4'-bipyridinium dichloride at 0.5 kg ha^{-1}) in the early boot stage while rye managed for silage production was mechanically harvested at the early head stage 7-d later. Due to rapid plant growth during the spring of 1991, rye growth was terminated for both management treatments at the early head stage. Plant tissue samples for dry matter estimates and laboratory analyses were taken in the center of each plot from adjacent one meter long rows. Immediately following chemical kill (rye for mulch) and harvest (rye for silage), soil samples were taken in 30-cm increments to a final depth of 90-

cm from the center of each plot. Six cores at each depth were composited from each plot and immediately placed on dry ice and stored in a frozen condition until laboratory analyses. Winter cover crop management treatments were established following harvest of the 1990 corn crop managed as describe before.

Soil nitrate (NO_3^-) and exchangeable ammonium (NH_4^+) were extracted from thawed, moist soil samples with 2M KCl (Keeney and Nelson, 1982) and their concentrations determined colormetrically with a QuikChem Automated Ion Analyzer (NO_3^- reduction by Cu-coated Cd column to NO_2^-). Residual fertilizer N in the soil NO_3^- and NH_4^+-N fractions was determined by preparing a 40-mL aliquot of each KCl extract for ^{15}N analysis by a diffusion procedure outlined by Brooks et al. (1989). The atom % ^{15}N concentration of the diffused N trapped in the acidified glass fiber filter was determined with an automated C-N analyzer/mass spectrometer (ANCA/MS) system consisting of an automated C-N analyzer (Roboprep C/N, Europa Scientific, Crewe, England) interfaced to a dual collector ratio mass spectrometer (Micromass VG 602C, VG Micromass LTD, Cheshire, England) at the TVA's National Fertilizer and Environmental Research Center (NFERC) in Muscle Shoals, Alabama. Atom % ^{15}N concentrations of diffused N were also corrected for background N as described by Kelley et al. (1990). Aliquots of finely ground soil and plant tissue, containing 100 μg N were placed in Sn foil cups and analyzed for total N content and atom % ^{15}N concentration by ANCA/MS (Kelley and Mulvaney, 1991). A summary of field operations for the

1989-91 corn-rye growing season is presented in Table 14. Data for the experiment were analyzed statistically using procedures outlined by the SAS Institute (SAS, 1982). Least significant difference (LSD) values were calculated at the 0.05 level of probability.

Table 14. Field operations summary for 1989-91 corn-rye growing seasons.

Field Operation	Date	Cummulative Precipitation (cm)	Days after N Application
Corn planting	17 May 1989	0	0
Corn harvest	28 Sept. 1989	64	135
Soil Sample	3 Oct. 1989	68	140
Plant Winter Rye	7 Oct. 1989	68	147
Chemical kill rye mulch trtmt.	2 Apr. 1990	107	325
Soil sample rye mulch and fallow trtmts.	4 Apr. 1990	107	327
Harvest rye silage trtmt. and soil sample	9 Apr. 1990	109	332
Corn planting	27 Apr. 1990	0	0
Corn harvest and soil sample	17 Sept. 1990	46	143
Plant winter rye	20 Sept. 1990	46	146
Chemical kill rye mulch trtmt. Harvest rye silage trtmt. Soil Sample	10 Apr. 1991	107	348

Results and Discussion

Soil Distribution of Residual Fertilizer N Immediately Following 1989 and 1990 Corn Harvest

Recovery of applied fertilizer N by corn in 1989 and 1990 ranged from 33 to 47% and 21 to 27%, respectively. Fertilizer N uptake during these two corn growing seasons was most likely related to differences in plant available soil moisture. Rainfall during the 1989 corn growing season was adequate (64-cm) and evenly distributed. In comparison, rainfall during the 1990 corn growing season was less plentiful (46-cm), poorly distributed and resulted in short periods of drought stress. Following corn harvest both yr, soil residual fertilizer N levels to the 90-cm depth were found to increase with increasing N rate with the greatest accumulation of residual fertilizer N measured in the surface 30-cm for all cover treatments (Figure 9 and 10). Low levels of residual fertilizer-derived NO_3^--N measured in the soil 60 to 90-cm depth increment (< 12 kg N ha^{-1} in 1989 and < 4 kg N ha^{-1} in 1990) suggest that fertilizer N loss by leaching during the corn growing season was minimal (Table 13).

Rye N Uptake and Dry Matter Accumulation

Rye total N uptake and dry matter accumulation in 1990 and 1991 increased with increasing N rate applied to the previous corn crop in 1989 and 1990 respectively (Table 15). Greater rye N uptake in 1990 (mean = 82 kg N ha^{-1}) as compared to 1991 (mean = 49 kg N ha^{-1}) demonstrates the high level of residual N that prevailed following a corn growing season (corn following alfalfa) where no grain yield or N uptake response to applied N was measured (data not shown).

In 1990, a 7-d delay in terminating the growth of rye (early heading stage vs. early boot) resulted in a 21% increase in dry matter accumulation with no corresponding increase in total N uptake averaged over previous N applications (Table 15). In 1991, the growth of rye was terminated at the early heading stage for both cover management treatments (rye mulch and rye silage) thus eliminating the time of kill as a possible mechanism for differences in total N uptake and dry matter accumulation. Rye total N uptake and dry matter accumulation averaged over N rate were greatest with rye harvested for silage as compared to rye chemically killed for NT-mulch (Table 15). These differences are probably related to the previous cropping sequence and its influence on plant N uptake and soil residual N levels. Rye harvested for silage in 1991 followed corn planted NT into rye stubble

Table 15. Total N uptake and dry matter (DM) accumulation by rye as affected by previous N application to corn (1990-1991).

	1990		1991	
N Rate[†]	**N Uptake**	**DM**	**N Uptake**	**DM**
-----kg ha^{-1}-----		Mg ha^{-1}	kg ha^{-1}	Mg ha^{-1}
0	46.9	4.1	24.7	2.1
84	62.6	5.2	25.8	2.0
168	86.3	5.8	42.2	3.2
252	93.0	6.5	61.1	4.5
336	120.5	7.1	91.8	5.7
Cover Mgt (CM)				
Rye Mulch	82.4	5.2	43.3	3.2
Rye Silage	81.3	6.3	54.9	3.8
Statistics				
N LSD (0.05)	14.5	0.6	12.1	0.7
CM LSD (0.05)	NS	0.4	7.7	0.5
N x CM	NS	NS	NS	NS
CV (%)	17.1	9.2	23.9	19.7

[†] Fertilizer N applied to previous corn crop.
NS = not significant ($P > 0.05$).

(from 1990 rye silage harvest) while chemically killed rye followed corn planted NT into rye mulch (from the 1990 rye growing season). Lower plant available soil moisture with the corn NT-stubble treatment as compared to the corn NT-mulch treatment likely limited total N uptake (Figure 6) and consequently resulted in a higher level of soil residual N following corn harvest.

Rye Recovery of Fertilizer N

Recovery of residual fertilizer N by winter rye as determined from isotope-ratio analysis and calculated by the difference between total N uptake in fertilized and unfertilized plots (difference method) is shown in Table 16. Fertilizer N recovery as calculated by the difference method, was two to three times higher than that determined by isotope-ratio analysis. The discrepancy in these two methods of calculating residual fertilizer N recovery has often been attributed to a "priming effect" of fertilizer N on soil mineralization (Legg et al., 1971; Westerman and Kurtz, 1973). Isotope dilution as a result of mineralization-immobilization transformations could also result in an apparent increase in residual fertilizer N recovery (Jansson and Persson, 1982). According to Jenkinson et al. (1985), fertilizer N uptake calculated by the difference method more accurately reflects the treatment effect on N availability irrespective of mineralization-immobilization turnover (MIT) of applied fertilizer N.

Fertilizer N uptake by the ^{15}N method reflects the degree of isotope dilution resulting from the mixing of fertilizer N with indigenous soil N and its incorporation into the various soil N fractions. Therefore, the following discussion pertaining to fertilizer N recovery by winter rye will be based on isotope-ratio analysis which is

Table 16. Recovery of residual fertilizer-derived N by a winter rye cover crop.

	Fertilizer N Recovery			
	1990		1991	
N Rate[†]	^{15}N Method	Difference[‡]	^{15}N Method	Difference
	--------------------------kg N ha^{-1}--------------------------			
84	3.5	15.7	2.3	1.1
168	11.9	39.3	5.9	17.5
252	16.9	46.0	11.9	36.4
336	35.9	73.5	25.7	67.1
Cover Mgt (CM)				
Rye Mulch	15.7	49.8	7.4	18.3
Rye Silage	11.6	37.5	11.0	30.3
Statistics				
N LSD (0.05)	9.1	15.0	2.3	11.8
CM LSD (0.05)	5.7	10.6	1.5	7.5
N x CM	NS	NS	**	NS
CV (%)	18.1	32.8	24.8	47.1

† N applied to previous corn crop.
‡ N uptake (fertilized) - N uptake (unfertilized).
** indicates significance at the 0.01 level of probability. NS = not significant (P>0.05).

necessary for tracing the fate of residual fertilizer N.

Previous N application to corn strongly influenced fertilizer N recovery by winter rye both yr (Table 16). Recovery of fertilizer N by winter rye increased with increasing N rate applied to the previous corn crop and ranged from 3.5 to 35.9 kg N ha^{-1} in 1990 and 2.3 to 25.7 kg N ha^{-1} in 1991. Cover crop management had no affect on fertilizer N recovery in 1990. The presence of a N rate by cover crop management interaction on fertilizer N recovery in 1991 is illustrated in Figure 11. As fertilizer N rate applied to the previous corn crop increased, the recovery of fertilizer N by rye harvested for silage continued to increase at a greater rate than rye killed for NT-mulch. These data indicate that higher residual fertilizer N levels were present following corn planted NT into rye stubble. These results demonstrate the importance of sowing a rye cover crop to trap residual fertilizer N particularly following a growing season when fertilizer N uptake by corn is limited by drought.

Soil Distribution of Residual Fertilizer N Following a Winter Rye Cover Crop

The contribution of fertilizer-derived N to the mineral N pool was clearly detectible and distinguishable from native mineral N by isotope-ratio analysis to 90-cm depth provided enough mineral N was present for accurate isotope-ratio analysis (>10 kg NO_3^--N and/or NH_4^+-N ha^{-1}). Detection of residual fertilizer N in the total N pool

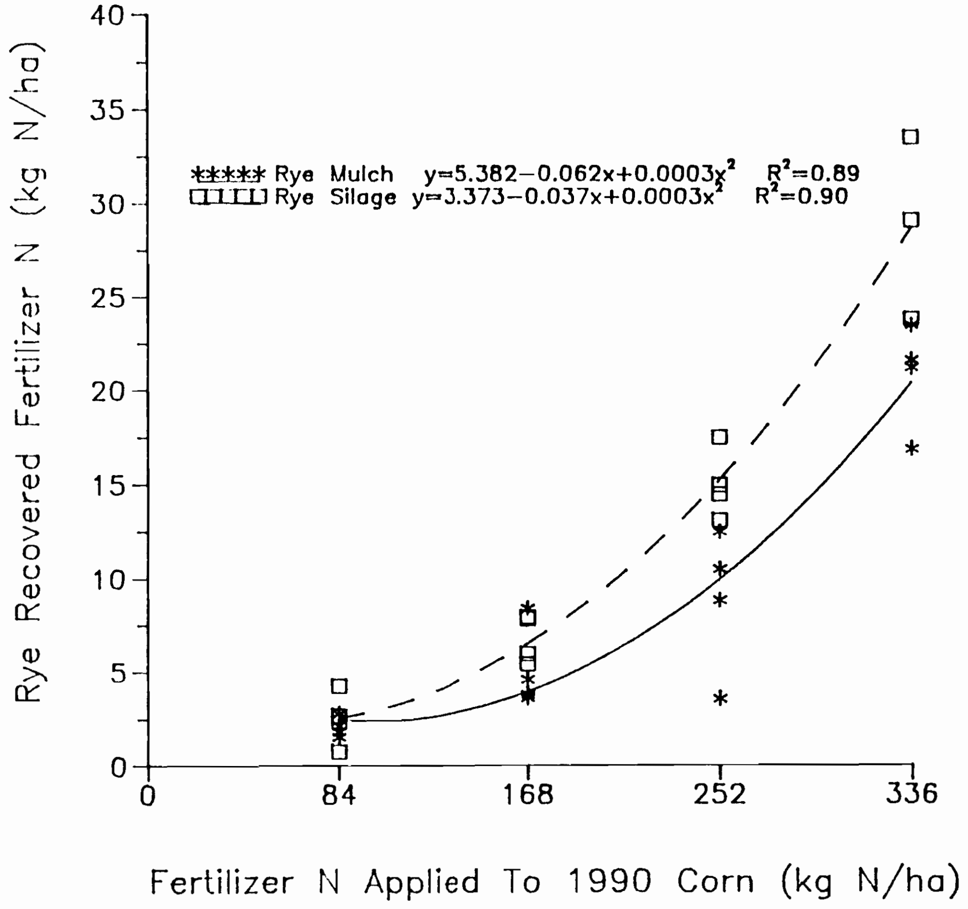

Figure 11. Influence of previous fertilizer N application to 1990 corn and cover crop management on residual fertilizer N recovery by 1991 winter rye.

below 30-cm depth was not successful due to excessive dilution of the ^{15}N-depleted fertilizer N. Therefore, a complete account of the fate of fertilizer N throughout a corn-rye rotation was not possible in the study.

Soil distribution of residual fertilizer-derived mineral N immediately following the termination of winter rye growth in 1990 and 1991 are shown in Figures 12 and 13 respectively. In 1990 and 1991, little or no fertilizer-derived mineral N was detected in each 30-cm increment of soil to 90-cm depth following a winter rye cover crop where the previous fertilizer N application to corn ranged from 84 to 336 kg N ha^{-1}. In the absence of a winter rye cover crop (fallow), the amount of residual fertilizer-derived mineral N in each 30-cm increment increased with depth and the fertilizer N rate applied to the previous corn crop both yr. These data provide evidence to support the use of a winter rye cover to recover residual fertilizer N that might otherwise be lost to ground water.

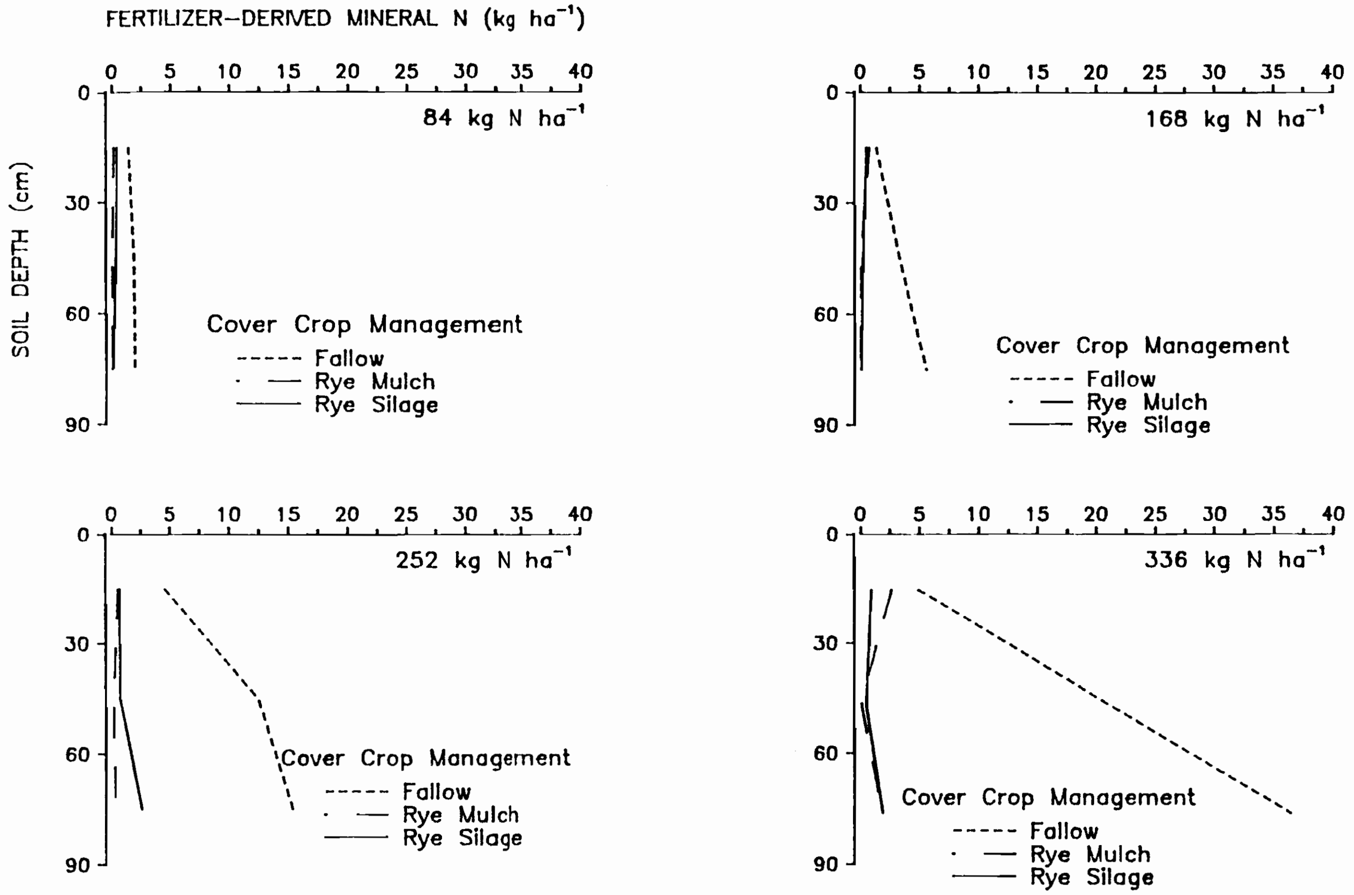

Figure 12. Distribution of residual fertilizer-derived mineral N in each 30-cm increment to 90-cm depth following 1990 winter cover crop.

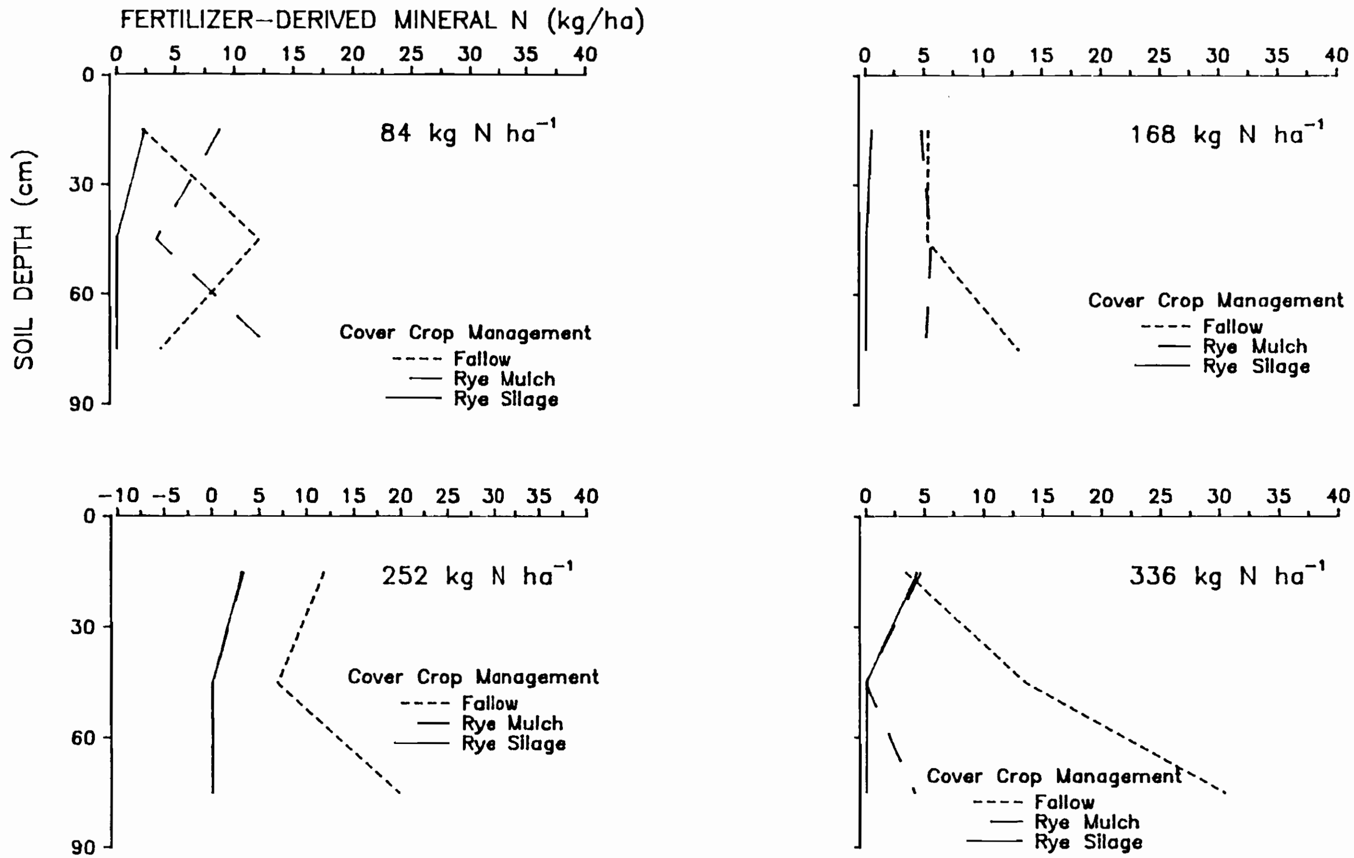

Figure 13. Influence of previous N fertilization to corn on distribution of fertilizer–derived mineral N in each 30–cm increment of soil to 90–cm depth following 1991 winter cover crop treatment.

Conclusions

These results indicate that the effectiveness of a winter rye cover crop to accumulate residual fertilizer N is related to previous fertilizer N application rate and summer annual cover treatment (rye-stubble vs. rye-mulch). Greater recovery of residual fertilizer N when rye followed corn planted NT into rye stubble demonstrates the importance of sowing a rye cover crop to trap residual fertilizer N particularly following a growing season when fertilizer N uptake is limited by drought. Little or no residual fertilizer-derived mineral N was measured in the soil to a final depth of 90-cm in plots where a winter rye cover crop was grown following corn receiving five rates of fertilizer N. These results indicate that on a silt loam soil a winter rye cover crop is extremely effective in trapping residual fertilizer-derived NO_3^- and NH_4^+ which constitute the N species of most interest in terms of plant uptake and contamination of groundwater.

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Chapter VII

Summary and Conclusions

When nonleguminous cover crops are part of a crop rotation, consideration should be given to those management practices that will reduce erosion, maximize recovery of residual mineral N and optimize N-use efficiency by the following summer annual. Previous studies have found that the amount of N recovered by the winter cover crop and subsequent influence on N availability to the following crop are a function of i) cover crop planting date, ii) cover crop seeding rate and subsequent plant population, iii) amount of residual mineral N remaining after the harvest of the previous crop, and iv) cover crop growth stage at the time of termination (early vs late kill). There is strong evidence in the literature to suggest that properly managed non-legume cover crops can play a major role in "trapping" residual fertilizer N that might otherwise be lost to the environment.

To facilitate the tracing of residual fertilizer N following corn harvest in the soil exchangeable NH_4^+-N and readily leachable NO_3^--N fractions a study was conducted to evaluate a diffusion technique that would permit accurate isotope-ratio analysis. Results indicate that recovery of added N by diffusion is quantitative and not affected by level of added N ($\leq$ 2.5 mg N L^{-1}) or temperature of mass N samples can occur with the diffusion technique. Differences in atom % ^{15}N between diffused and non-diffused samples can be attributed to contamination from N at natural abundance. Close agreement in atom % ^{15}N concentration was obtained between diffused and non-diffused samples when the following isotope dilution equation was used to calculate the ^{15}N concentrations of the sample N.

$$A_1 = [A_m (M_1 + M_2) - (M_2 A_2)]/((M_1 + M_2) - M_2)$$

where:

A_1 = Atom % of sample N (corrected atom % ^{15}N)

A_m = Atom % ^{15}N of diffused N (uncorrected atom % ^{15}N)

A_2 = Atom % ^{15}N of background N (0.3663)

M_1 = μmol of sample N diffused into fiber disk

M_2 = μmol of background N diffused into fiber disk

$(M_1 + M_2)$ = Total μmol of diffused N

These results indicate that the diffusion procedure described is suitable for preparing low-mass N samples for automated ^{15}N analysis by ANCA/MS techniques.

In field studies where the direct measurement of fertilizer-derived N is of interest, the use of fertilizer material that is either enriched or depleted of the stable isotope

^{15}N is necessary. The objective of this portion of the study was to determine if ^{15}N-depleted fertilizer N could be satisfactorily used as a tracer of residual fertilizer N in plant tissue and various soil N fractions through a corn-rye crop rotation.

The use of ^{15}N-depleted preplant applied fertilizer N to determine the contribution of fertilizer-derived N in the soil NO_3^--N fraction following corn was clearly detectible and distinguishable from the control plots to a 90-cm depth. Nitrogen uptake by a winter rye cover crop reduced soil NO_3^--N levels below that required for accurate isotope-ratio analysis ($<$10 kg ha^{-1}). Therefore, if the fate of residual fertilizer-derived NO_3^--N is to be traced in the soil following a winter cover crop, soil extraction procedures must be modified to concentrate N prior to diffusion for accurate isotope-ratio analysis.

The greatest limitation to the use of ^{15}N-depleted fertilizer N as a tracer of residual fertilizer N in a corn-rye crop rotation appears to be its detectability from native soil N in the soil total N pool. Therefore, ^{15}N-depleted fertilizer N can not be recommended as a means of tracing mineralization-immobilization turnover of fertilizer-derived N, especially for soils with a large total N pool.

The lack of a significant decrease in the clay-fixed NH_4 atom % ^{15}N concentration suggest that fertilizer-derived NH_4^+-N was not incorporated into the nonexchangeable NH_4^+-N fraction during the corn growing season in a soil environment conducive for clay-fixation. These inconclusive results indicate that further research utilizing equally enriched ^{15}N fertilizer N is needed to determine the feasibility of using depleted material for measuring clay-fixation of fertilizer-derived NH_4^+-N.

Following winter fallow (approx. 1 yr after fertilizer application) residual ^{15}N-depleted fertilizer N was still detectable in the NO_3^--N fraction as indicated by significantly lower atom % ^{15}N concentrations as N rate increased. Greater variability in atom % ^{15}N concentrations are likely to occur closer to the soil surface due to downward movement of fertilizer-derived soil NO_3^--N throughout the winter months.

The results of this study suggest that under conditions of adequate rainfall (107-cm), high soil N availability, and N rates ranging from 0 to 336 kg ha^{-1}, ^{15}N-depleted fertilizer N material can be reliably used as a tracer of residual fertilizer N in the soil NO_3^--N fraction and plant tissue up to one yr after application.

Limited studies have attempted to examine the fate of residual fertilizer-derived N resulting from fertilizer N applied to corn at the economic optimum N rate because the relationship between economic optimum N rate and fertilizer-use efficiency appears to be so intuitive. This study was conducted to i) measure plant uptake and soil distribution of varying rates of fertilizer N applied to corn, and ii) establish the relationships between economic optimum N rate, fertilizer-use efficiency, potential leaching loss of residual fertilizer-derived N to ground water.

Plant recovery of fertilizer N in 1989 ranged from 33 to 47% of applied even though no corn grain yield response resulted from N fertilization. In contrast, plant recovery of fertilizer N in 1990 ranged from 18 to 34% of applied even though a positive grain yield response to N fertilization was measured. Greater plant recovery of fertilizer N in 1989 in the presence of a larger available N pool compared to 1990 is primarily a function of a more favorable soil water regime and the temporal and spatial distributions of the available N source.

A close relationship between economic optimum N rate and fertilizer-use efficiency does exist in a silt loam soil when there is a plant response to fertilizer N application. However, the relationship between fertilizer-use efficiency and the potential for leaching to ground water appears to be inconsistent and unreliable as a means of estimating the environmental impact of applied N on ground water. Although the NT-mulch system in 1990 demonstrated the highest fertilizer-use efficiency at the economic optimum N rate, little difference in potential loss of fertilizer N during the growing season was observed for all cover treatments. This study provides evidence to support the application of fertilizer N at the economic optimum N rate as an N management strategy that poses little threat to ground water resources.

Numerous studies have demonstrated the ability of a small grain cover crop to recover soluble N even when high N rates are applied to soils with high leaching potential. However, limited data is available to determine the effectiveness of winter rye cover crop to recover accumulated residual fertilizer-derived N following a corn crop receiving varying rates of fertilizer N. The objectives of this study were to i) measure the recovery of residual ^{15}N-depleted fertilizer N by a winter rye cover crop, ii) determine the influence of winter cover crop management on the distribution of residual fertilizer-derived N in the various soil N fractions, and iii) estimate losses of fertilizer-derived mineral N to the environment following a corn-rye cropping sequence.

Recovery of residual fertilizer N by winter rye as determined from isotope-ratio analysis indicates that previous fertilizer N applications rates and fertilizer N uptake by corn strongly influence fertilizer N recover in a silt loam soil by a winter rye cover crop.

The contribution of fertilizer-derived N to the soil mineral N pool was clearly detectible and distinguishable from native mineral N by isotope-ratio analysis. Due to excessive dilution of the ^{15}N-depleted fertilizer N in the soil total N pool, detection of residual fertilizer N below 30-cm depth was not successful. Therefore, a complete account of the fate of fertilizer N throughout the corn-rye rotation was not possible. Our results indicate that little or no fertilizer-derived mineral N was detected in each 30-cm increment of soil to 90-cm depth following a winter rye cover crop where the previous fertilizer N application to corn ranged from 84 to 336 kg N ha^{-1}. In the absence of a winter rye cover crop, the amount of residual fertilizer-derived mineral N increased with depth and previous fertilizer N rate. These data provide evidence to support the use of a winter rye cover crop to recover residual fertilizer N that might otherwise be lost to ground water.

Further research is needed to determine the effectiveness of a winter rye cover crop to recover residual fertilizer N applied to sandy textured soils. Should significant leaching of fertilizer N occur during the corn growing season, the ability of winter rye to recover residual fertilizer N that may accumulate at greater depths before winter recharge is questionable.

Appendices

Appendix A. Dry matter (DM) production and distribution of N in corn crop as affected by N rate and cover treatment (1989-1990).

	Cover	1989				1990			
			N Uptake				N Uptake		
N Rate	Treatment	DM	Total	Grain	Stover	DM	Total	Grain	Stover
kg ha^{-1}		Mg ha^{-1}		-----------kg ha^{-1}-----------		Mg ha^{-1}		-----------kg ha^{-1}-----------	
0	Fallow	21	203	130	73	13	122	73	49
	NT-mulch	-	-	-	-	9	71	42	29
	NT-stubble	-	-	-	-	8	68	44	24
84	Fallow	20	204	128	76	13	144	83	61
	NT-mulch	-	-	-	-	12	93	53	40
	NT-stubble	-	-	-	-	11	106	64	42
168	Fallow	20	216	130	86	14	165	90	75
	NT-mulch	-	-	-	-	16	166	92	74
	NT-stubble	-	-	-	-	13	133	78	55
252	Fallow	21	221	135	86	13	170	84	87
	NT-mulch	-	-	-	-	17	200	103	97
	NT-stubble	-	-	-	-	13	151	82	69
336	Fallow	21	232	135	97	13	165	84	81
	NT-mulch	-	-	-	-	16	193	99	94
	NT-stubble	-	-	-	-	11	143	72	71
				Analysis of Variance					
N Rate		NS	**	NS	**	**	**	**	**
Cover Trtmt		-	-	-	-	*	+	+	**
N Rate x Cover Trtmt	-		-	-	-	**	**	**	+
CV (%)		7.3	8.5	10.5	14.4	9.0	17	13.3	19.6

**, *, + = significant at 0.01, 0.05, and 0.10 probability levels, respectively.
NS = not significant at P > 0.10.

Appendix B. Uptake and distribution of fertilizer-derived N in corn crop as affected by N rate and cover treatment (1989-1990).

	Cover	1989			1990		
N Rate	Treatment	Total	Grain	Stover	Total	Grain	Stover
kg ha^{-1}		kg ha^{-1}					
84	Fallow	39 (47)[†]	24 (29)	15 (18)	27 (32)	15 (18)	12 (14)
	NT-mulch	-	-	-	18 (20)	10 (11)	8 (9)
	NT-stubble	-	-	-	25 (30)	15 (18)	10 (12)
168	Fallow	67 (40)	40 (24)	27 (16)	45 (26)	21 (12)	24 (14)
	NT-mulch	-	-	-	60 (36)	31 (19)	29 (17)
	NT-stubble	-	-	-	50 (29)	29 (17)	21 (12)
252	Fallow	88 (35)	51 (20)	37 (15)	60 (21)	30 (12)	30 (9)
	NT-mulch	-	-	-	80 (32)	39 (16)	41 (16)
	NT-stubble	-	-	-	60 (24)	32 (13)	28 (11)
336	Fallow	110 (33)	64 (19)	46 (14)	65 (20)	33 (10)	32 (10)
	NT-mulch	-	-	-	81 (24)	47 (14)	34 (10)
	NT-stubble	-	-	-	67 (20)	34 (10)	33 (10)
Analysis of Variance							
N Rate		**	**	**	**	**	**
Cover Crop		-	-	-	NS	+	NS
N Rate x Cover Crop		-	-	-	+	*	NS
CV (%)		18.1	16.1	31.9	18.9	22.3	39.4

[†] percentage of applied fertilizer N.

**, *, + = significant at 0.01, 0.05, and 0.10 probability levels, respectively. NS = not significant at P > 0.10.

Appendix C. Percentage of plant N derived from fertilizer N as influenced by N rate and cover treatment.

	Cover	1989			1990		
N Rate	Treatment	Whole Plant	Grain	Stover	Whole Plant	Grain	Stover
kg ha^{-1}		%					
84	Fallow	19	19	19	18	18	19
	NT-mulch	-	-	-	18	18	19
	NT-stubble	-	-	-	24	23	24
168	Fallow	31	31	31	31	30	32
	NT-mulch	-	-	-	36	34	38
	NT-stubble	-	-	-	38	38	38
252	Fallow	40	38	44	35	36	35
	NT-mulch	-	-	-	41	39	42
	NT-stubble	-	-	-	40	39	41
336	Fallow	47	47	47	39	39	39
	NT-mulch	-	-	-	48	47	48
	NT-stubble	-	-	-	47	46	47
				Analysis of Variance			
N Rate		**	**	**	**	**	**
Cover Trtmt		-	-	-	**	*	**
N Rate x Cover Trtmt		-	-	-	*	NS	*
CV (%)		12.5	7.3	27.9	6.9	9.2	7.8

**, * = significant at 0.01 and 0.05 probability levels, respectively. NS = not significant at P > 0.05.

Appendix D. Source of N uptake by corn as affected by fertilizer N rate and cover treatment.

Year[†]	N Rate	Cover Trtmt	Total	Soil[‡]	Fertilizer N Uptake	
					^{15}N Method	Difference Method[§]
	kg ha^{-1}		----------------------------kg ha^{-1}----------------------------			
1989	84	Fallow	204	165	39	2
	168		215	148	67	13
	252		220	132	88	17
	336		232	122	110	30
1990	84	Fallow	144	118	26	22
		NT-mulch	93	76	17	21
		NT-stubble	105	80	25	38
	168	Fallow	142	98	44	21
		NT-mulch	166	108	58	95
		NT-stubble	132	82	50	65
	252	Fallow	170	110	60	49
		NT-mulch	199	118	81	128
		NT-stubble	151	91	60	83
	336	Fallow	165	100	65	40
		NT-mulch	193	112	81	98
		NT-stubble	143	78	67	75

[†] Year of fertilizer N application.
[‡] Total N uptake - fertilizer derived N uptake.
[§] N uptake (fertilized) - N uptake (unfertilized).

Appendix E. Fertilizer nitrogen balance following 1989 and 1990 corn harvest.

	Cover	Fertilizer N Recovered							
		1989				1990			
N Rate	Treatment	Plant	Soil	Total	%†	Plant	Soil	Total	%
kg ha^{-1}		--------------kg ha^{-1}--------------				--------------kg ha^{-1}--------------			
84	Fallow	39	38	77	92	26	15	41	49
	NT-mulch	-	-	-	-	17	12	29	35
	NT-stubble	-	-	-	-	25	33	58	69
168	Fallow	67	57	124	74	44	87	131	78
	NT-mulch	-	-	-	-	58	58	116	69
	NT-stubble	-	-	-	-	50	39	89	53
252	Fallow	88	82	170	67	60	135	195	77
	NT-mulch	-	-	-	-	81	62	143	57
	NT-stubble	-	-	-	-	60	98	158	63
336	Fallow	110	137	247	74	65	174	239	71
	NT-mulch	-	-	-	-	81	79	160	48
	NT-stubble	-	-	-	-	67	143	210	63
		Analysis of Variance							
N Rate		**	**			**	**		
Cover Trtmt		-	-			+	**		
N Rate x Cover Trtmt		-	-			+	NS		
CV (%)		9.79	55.6			18.9	62.6		

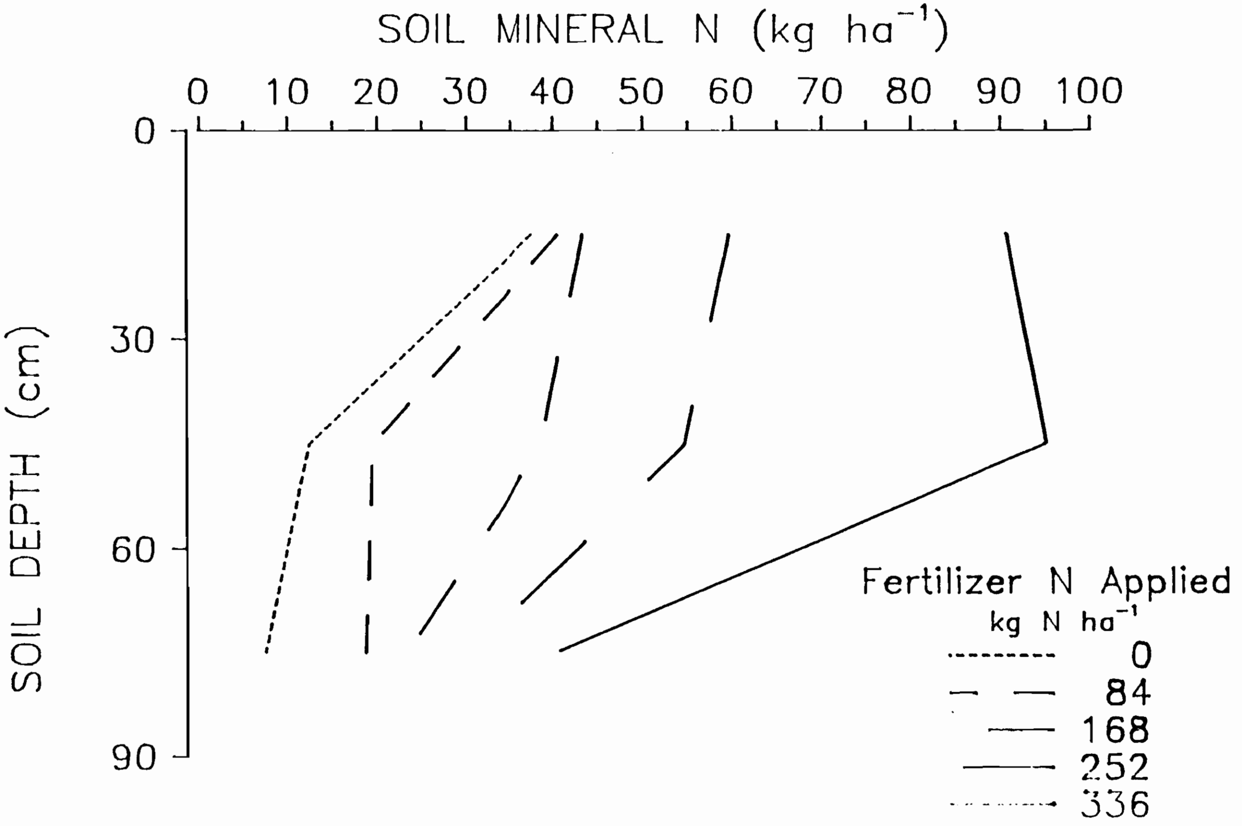
**, *, and + = significance at the 0.01, 0.05, and 0.10 level of probability respectively. NS = not significant at P > 0.10.

† Percentage of applied fertilizer N.

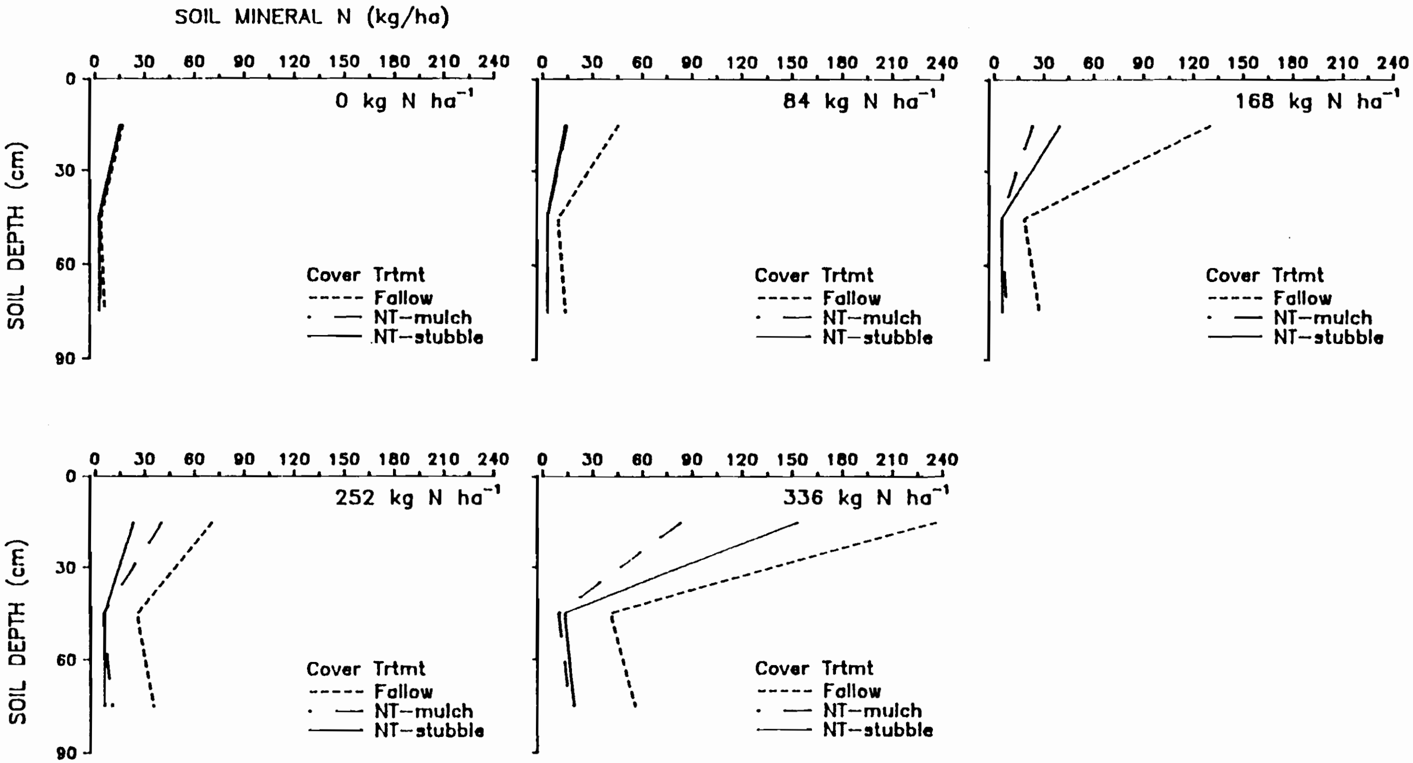
Appendix F. Atom % ^{15}N concentration of clay-fixed NH_4^+-N in each 30-cm increment of soil to 90-cm depth following corn.

	Soil Depth		
N Rate	0-30 cm	30-60 cm	60-90 cm
kg N ha^{-1}	--------------------------Atom % ^{15}N--------------------------		
0	0.3674	0.3684	0.3669
84	0.3610	0.3609	0.3622
168	0.3468	0.3672	0.3769
252	0.3566	0.3303	0.3660
336	0.3929	0.3673	0.3642
LSD (0.05)	NS	NS	NS
CV (%)	10.3	7.5	2.1

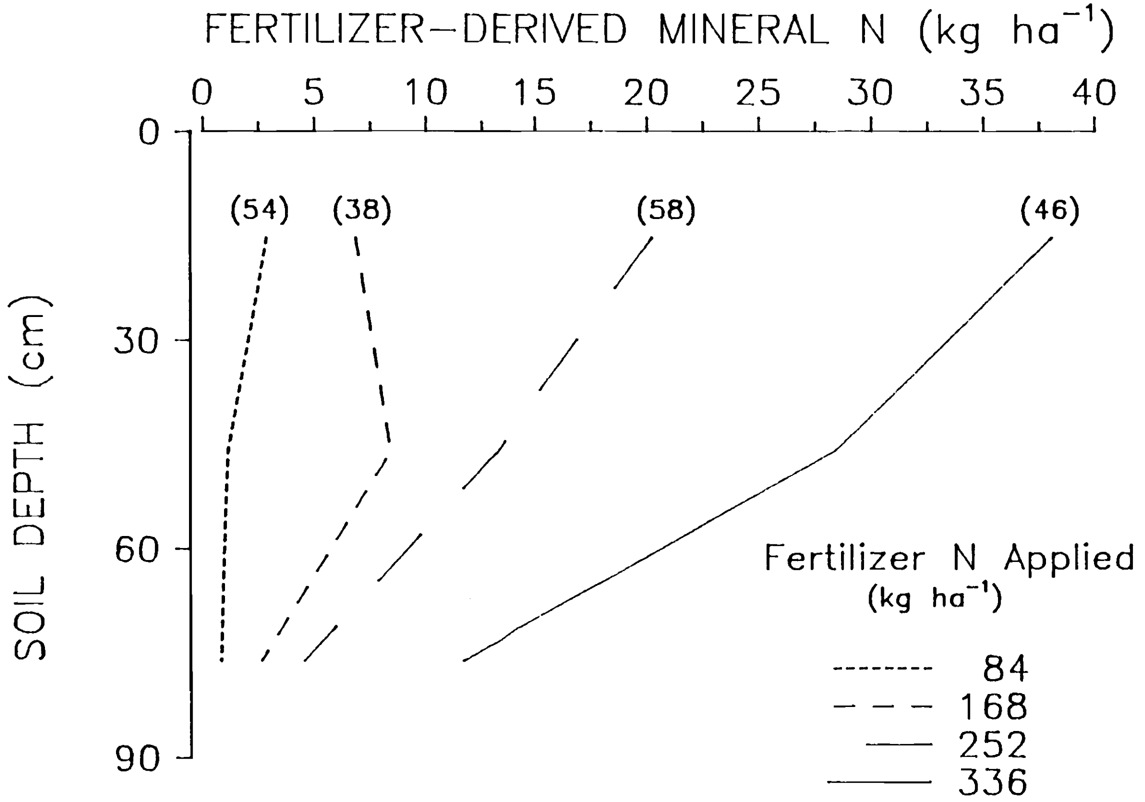
NS = not significant at the 0.05 level of probability.



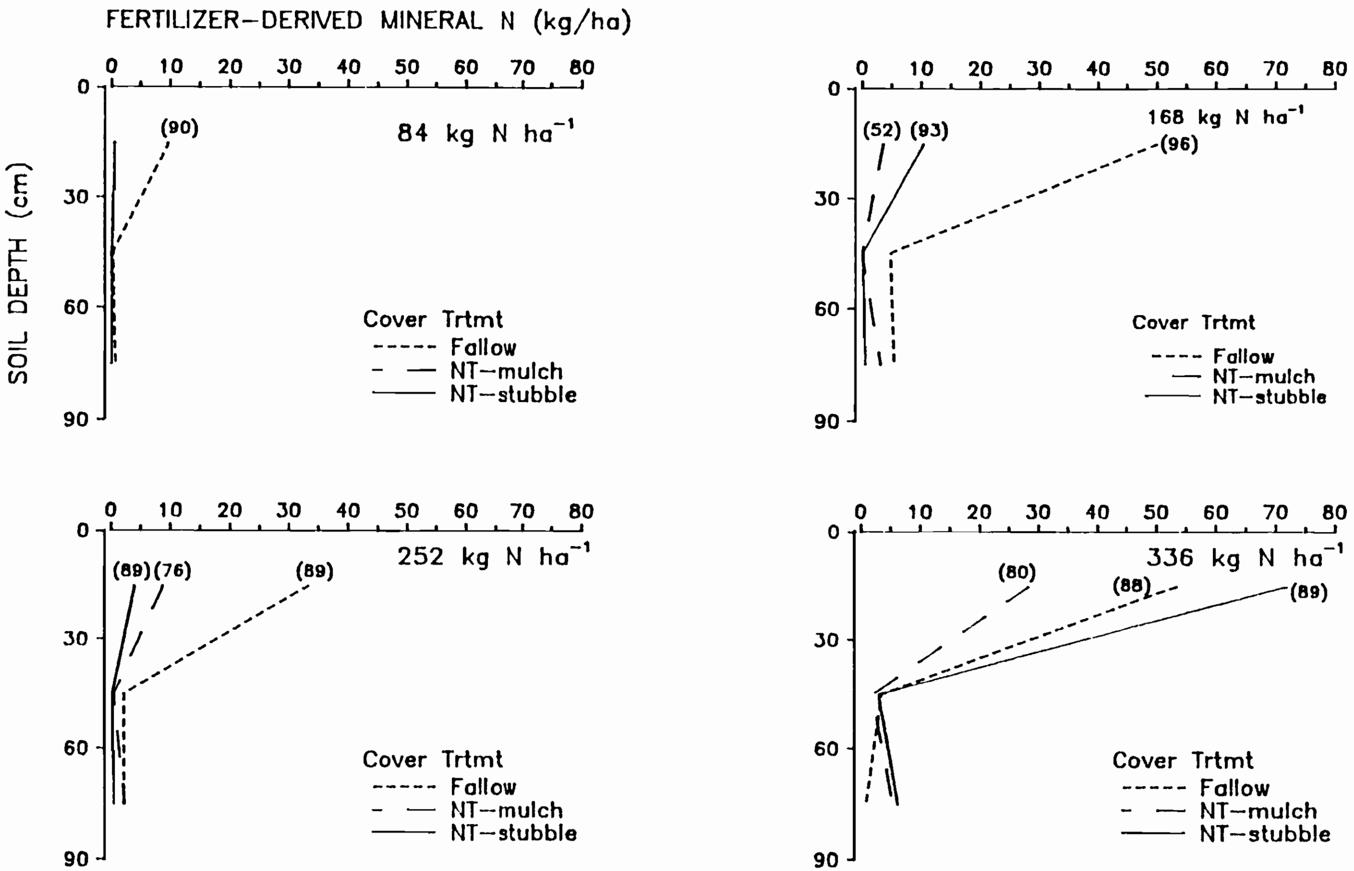
Appendix G. Influence of applied fertilizer N on distribution of soil mineral N (NH_4^+ + NO_3^-) in each 30–cm increment of soil to 90–cm depth following 1989 corn harvest.



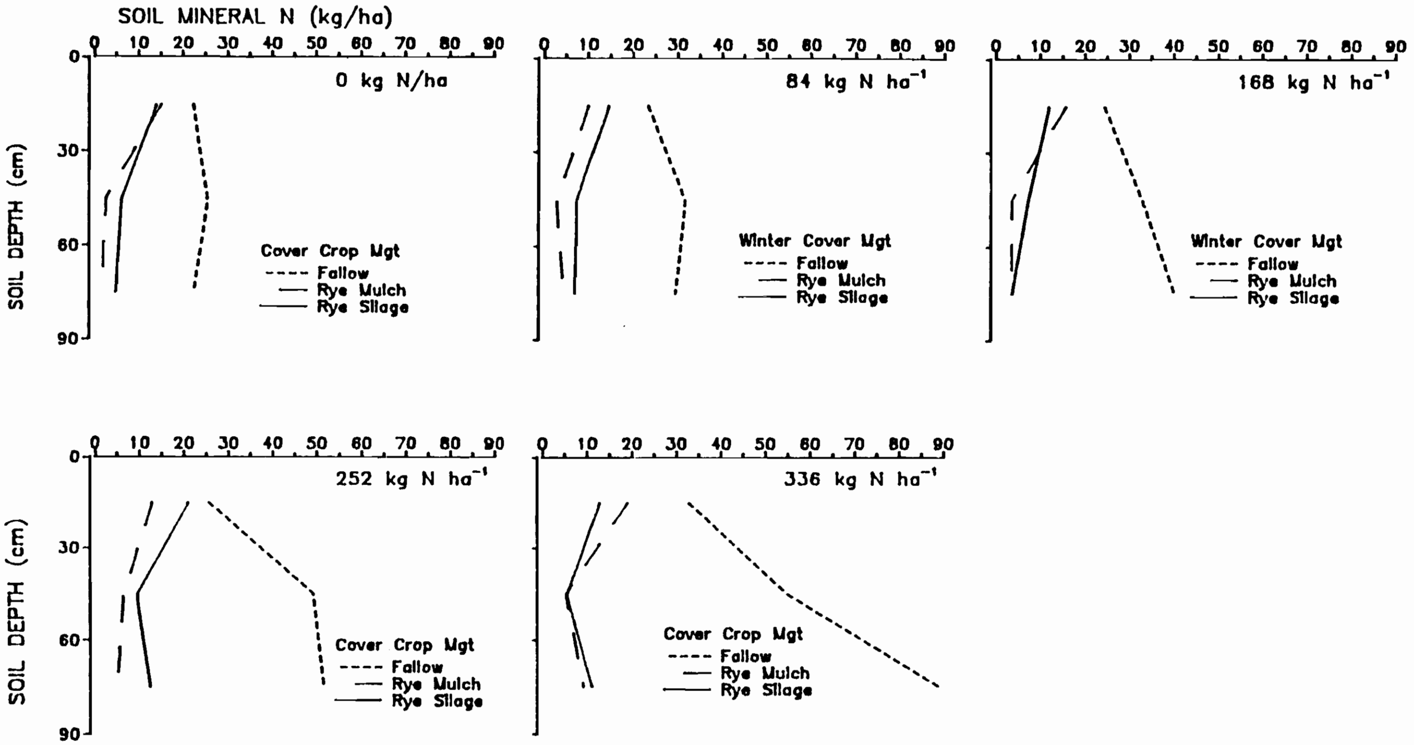
Appendix H. Influence of applied fertilizer N and cover treatment on distribution of soil mineral N in each 30–cm increment of soil to 90–cm depth following 1990 corn harvest.



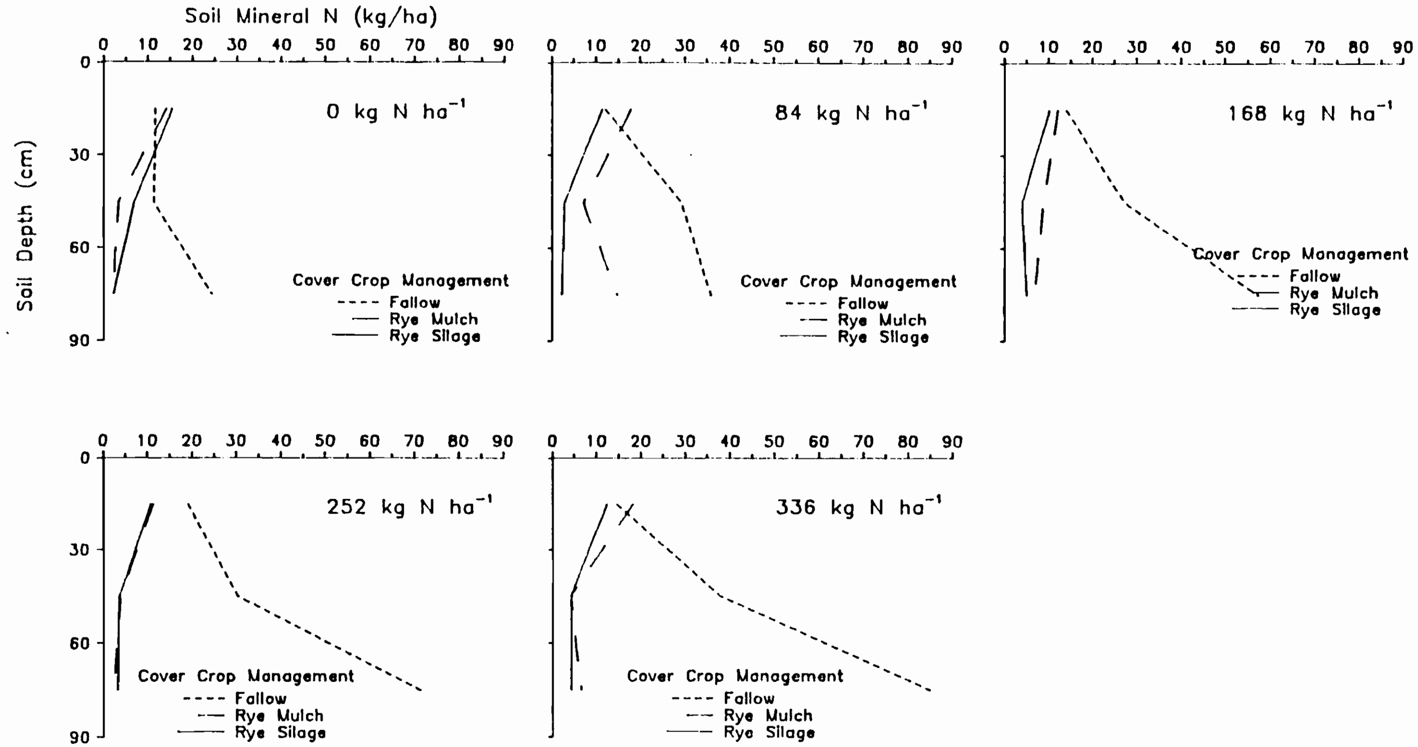
Appendix I. Distribution of fertilizer–derived mineral N (NH_4^+ + NO_3^-) recovered in each 30–cm increment of soil to 90–cm depth after 1989 corn harvest. Values in parenthesis indicate percentage of soil recovered fertilizer–derived mineral N in top 30–cm of profile.



Appendix J. Distribution of fertilizer–derived mineral N in each 30–cm increment of soil to 90–cm depth following 1990 corn harvest. Values in parenthesis indicate percentage of soil recovered fertilizer–derived mineral N in top 30–cm of profile.



Appendix K. Influence of previous N fertilization to corn on distribution of soil mineral N in each 30–cm increment to 90–cm depth following 1990 winter cover crop management.



Appendix L. Influence of previous N fertilization to corn on distribution of soil mineral N in each 30-cm increment to 90-cm depth following 1991 winter cover crop management.

Appendix M. Selected soil physical and chemical properties from experimental site area.

Horizon	Depth	Sand[†]	Silt	Clay	pH[‡]	Σ Exch. bases[§]	CEC[¶]	BaCl$_2$-TEA Acidity	KCl Acidity	CD-Fe[#]
	cm		---------%---------				----------cmol kg^{-1}----------			%
Ap	0-35	40.2	39.4	20.4	6.1	7.8	16.6	8.8	-	1.4
B21t	35-50	37.5	39.7	22.8	5.5	4.2	12.6	8.4	0.5	1.6
B22t	50-65	38.1	38.7	23.2	5.4	3.8	11.8	8.0	0.5	1.3
B23t	65-80	41.3	34.2	24.4	5.5	4.5	11.3	6.8	0.4	1.6
B24t	80-95	30.4	46.0	23.6	5.5	4.5	11.4	6.9	0.3	1.5
IIB25t	95-115	51.8	25.4	22.9	5.5	4.5	11.3	6.9	0.3	2.1
IIB3t	115-138	56.1	21.5	22.5	5.3	5	11.4	6.4	0.2	2.2
IIC	138-185	48.8	28.7	22.5	5.5	5.6	12.0	6.4	0.2	2.3

[†] Particle size determined by pipette analysis.
[‡] pH determined from 1:1 soil/water samples.
[§] Exchangeable bases by sum of Ca, Mg, and K extracted with 1 N NH_4OAc adjusted to pH 7.
[¶] Cation exchange capacity (CEC) computed as sum of exchageable bases and extractable acidity.
[#] Citrate-dithionite extractable Fe.

Vita

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