REDISTRIBUTION AND FATE OF APPLIED ^{15}N-ENRICHED UREA UNDER IRRIGATED CONTINUOUS CORN PRODUCTION

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Redistribution and Fate of Applied 15N-enriched Urea

Under Irrigated Continuous Corn Production

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ABSTRACT

Schindler, Frank Vincent, M.S., Department of Soil Science, College of Agriculture, North Dakota State University, May 1996. Redistribution and Fate of Applied ^{15}N-enriched Urea Under Irrigated Continuous Corn Production. Major Professor: Dr. Raymond E. Knighton.

Understanding the redistribution and fate of N is essential for justification of Best Management Practices (BMP). This project was conducted on a Hecla fine sandy loam (sandy, mixed, Aquic Haploboroll) soil at the BMP field site near Oakes, North Dakota. One objective of this investigation was to evaluate the residence times of NO_3^--N in 20 undisturbed lysimeters and its infiltration time through the soil profile to tile drains. Corn (Zea mays L.) was fertilized with 135 kg N ha^{-1} as ^{15}N-enriched urea plus 13.5 and 48.1 kg N ha^{-1} preplant for 1993 and 1994, respectively. Urea-N was band applied to 20 and 10 undisturbed lysimeters at 2.0 and 5.93 atom percent (at. %) ^{15}N in 1993 and 1994, respectively. Average resident times of NO_3^--N in the lysimeters was 11.7 months. Lysimeter and tile drainage indicate the presence of preferential pathways. Residence times of NO_3^--N depend on frequency and intensity of precipitation events. Another objective was to determine what portion of the total N in the crop was from applied urea-N and what portion was from the native soil-N. Nitrogen plots received ^{15}N enrichments of 4.25 and 5.93 at. % ^{15}N in 1993 and 1994, respectively. At the end of the 1993 and 1994 growing season, 41.5% and 35.7% of the labeled fertilizer N remained in the soil profile, while the total recovery of applied ^{15}N in the soil-plant system was 86.2% and 75.4%, respectively. Low recoveries of applied N may have been the result of soil or aboveground plant biomass volatilization, or denitrification or preferential flow processes. Further research needs to be conducted with strict accountability of gaseous loss and the mechanism(s) responsible.

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Frank V. Schindler

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INTRODUCTION

Nitrogen (N) is commonly the most important fertilizer element applied to soil (Allison, 1966) and, therefore, is probably the most studied. Since the U.S. Public Health Administration established an upper limit of 10 mg of NO_3^--N per liter of drinking water as a safe concentration, it has become increasingly important to understand the fate of fertilizer N and its effect on ground water quality.

Tracer techniques, involving the use of ^{15}N, have evolved which allow the investigator to study the fate of the applied N as it enters, becomes transformed within, and leaves the soil-plant system (Hauck and Bremner, 1976). This approach gives more quantitative information that is useful in identifying ways to maximize yields, while minimizing potential ground water contamination.

Researchers in N management studies have used the heavy isotope of nitrogen (^{15}N) extensively as a tracer. For instance, to identify nitrate (NO_3^-) sources of ground waters, researchers have used natural abundance ^{15}N (delta ^{15}N) measurements. This method is based on the fact that commercial fertilizers, soil N, and various N-containing organic fertilizers vary slightly in their natural ^{15}N concentrations (Prunty and Montgomery, 1991). Moreover, with the use of ^{15}N-enriched fertilizers, researchers are better able to study the fate of applied N as well as the extent to which biological transformations occur within the N cycle.

Preferential or bypass flow has been observed in soil possessing little or no structure (Rice et al., 1991; DeSmedt et al., 1986; DeSmedt and Wierenga, 1984) and generally exhibits a high degree of spatial variability within the sampling framework (Richard and Steenhuis, 1988). Research at the Best

Management Practices (BMP) site near Oakes, North Dakota, indicates the possibility of preferential flow paths within the undisturbed lysimeters and to the tile drainage. By applying ^{15}N-labeled urea-N to the undisturbed lysimeters and newly established N plots, our objectives were to confirm the presence (or absence) of preferential pathways and to gain a better understanding of the fate and redistribution of applied N. These findings, when used in conjunction with other BMP data, will enable us to make more definitive inferences regarding the best N management practices.

The objectives of this investigation were to 1) examine the temporal and spatial variations in NO_3^--N movement among 20 undisturbed lysimeters under irrigated corn production, 2) determine the concentration of and the time it takes NO_3^--N to move through the soil profile and reach the tile lines under irrigated conditions, 3) determine the fraction of total N in the crop derived from applied fertilizer and that derived from native soil N, and 4) determine an appropriate sample preparation method for total N and isotope-ratio analyses by the Dumas Combustion Separation Procedure.

Characteristics of Nitrogen-15

Definition. The two stable isotopes of N are ^{14}N and ^{15}N. According to Hill and Feigl (1987), an isotope is an atom of the same element with different atomic mass. This difference in mass is due to a varied number of neutrons present in the atom. For instance, ^{15}N has an atomic mass of 15, i.e., it has 7 protons and eight neutrons whereas the isotope ^{14}N has an atomic mass of 14 (7 protons and 7 neutrons). Together they occur naturally in a relatively secure abundance with about 273 atoms of mass 14 to every one atom of mass 15 (Hauck, 1973). Consequently, the average natural abundance of ^{15}N in air is approximately 0.3663 atom percent (at. %) ^{15}N or 3663 mg kg^{-1} ^{15}N (Hauck and Bremner, 1976).

Advantages and disadvantages of using nitrogen-15 as a tracer. One of the major advantages of using ^{15}N as a tracer in N research is that it is nonradioactive. Because this isotope is stable, there is no decay with time, it does not pose a health threat to the investigator or to the soil-plant system, and the researcher does not have to secure a permit to use the isotope (Hauck and Bremner, 1976).

Some researchers feel that another advantage of using ^{15}N in nitrogen studies is that the experiment can be conducted without the use of check treatments, thus "obviating the need to make certain assumptions regarding the similarity of transformation processes in treated and control systems" (Hauck and Bremner, 1976). However, other researchers do not share the same sentiment. For example, Jansson (1958) feels that in studies involving fertilizer use efficiencies, the indirect method (which incorporates check treatments) and

the direct isotope methods are complementary to each other and should be used in conjunction. By using both methods in the same experiment, there is less chance of making erroneous interpretations due to the mineralization-immobilization turnover (MIT) processes.

The one major disadvantage to using ^{15}N-enriched fertilizer as a tracer in nitrogen studies is its cost. The high cost of ^{15}N-enriched fertilizer has confined its use to laboratory and small-scale experiments. Also, to maximize the size of the experiment, many researchers dilute the labeled material and apply it in enrichments so low that after further dilution with native soil N, it becomes impossible to detect (Hauck and Bremner, 1976).

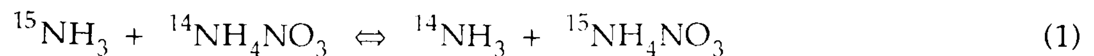
Assumptions. There are three primary assumptions associated with N isotopes when used as tracers in biological systems: 1) N isotopes in the natural state have a constant isotope composition, 2) plants cannot distinguish one isotope from another, and 3) the chemical properties of ^{14}N and ^{15}N are identical, and any differences that may occur in their behavior are attributed to their differences in mass or physical properties (Hauck and Bremner, 1976). These assumptions are not entirely valid for all tracer investigations. Studies involving minimum enrichment, i.e., regions of natural abundance where isotope effects become more of a concern, should be handled and evaluated with caution (Hauck and Bremner, 1976).

Biological interchange. Biological interchange is a very important process associated with ^{15}N tracer investigations. According to Hauck and Bremner (1976), biological interchange is a term related to isotope chemistry that is not always used correctly or properly understood. It is imperative that the researcher has a clear understanding of the internal N-cycle and the effects of biological interchange on data interpretation. If biological interchange is not clearly understood and considered from the outset of the tracer investigation,

research results may be meaningless, i.e., the real at. % ^{15}N values may be significantly higher or lower than the obtained values.

Biological interchange is the process in which labeled ions or molecules are replaced with unlabeled ions or molecules (or vice versa) by means of microbial synthesis or decomposition. In other words, a labeled molecule of the inorganic phase may be transpositioned into the organic phase as an unlabeled molecule through immobilization; and conversely, an unlabeled molecule of the organic phase may be transpositioned into the inorganic phase as a labeled molecule through mineralization. This tranpositioning process extends into the nitrification and denitrification transformations as well; and, therefore, just because nitrogen enters the soil system in one form does not mean it will leave the system in that form.

Biological interchange is also known as mineralization-immobilization turnover (MIT) and constitutes a continual renewal of a material without observable changes in its net concentration (Hauck and Bremner, 1976). Biological interchange is closely related to isotope exchange, which, according to Hauck and Bremner (1976), is the "exchange of places by two atoms, but different isotopes, of the same element in different molecules" as seen in equation (1).



$$^{15}NH_3 + {}^{14}NH_4NO_3 \Leftrightarrow {}^{14}NH_3 + {}^{15}NH_4NO_3 \quad (1)$$

Hauck and Bremner (1976) continue that it is virtually impossible to distinguish between biological interchange and isotope exchange in most soil transformation studies. However, where it is possible to make the distinctions, it is often impossible to determine their relative contributions to the system's isotopic distribution. Consequently, biological interchange and isotope exchange can be considered as the same process.

Isotope-ratio analysis. Once ^{15}N is added to a soil system as an enrichment, it becomes mixed with the native soil nitrogen and assumes a new isotopic identity. A ratio of ^{14}N to ^{15}N is immediately established within the soil system, and it is the change in this ratio that allows the researcher to follow the labeled material as it passes through the system (Hauck, 1973). Isotope-ratio analysis is the process used to determine the ratio of ^{14}N to ^{15}N and, ultimately, the atom percentage ^{15}N of sample N.

Isotope-ratio analysis can be conducted by several methods, for instance: mass spectrometry, emission spectrometry, or nuclear magnetic resonance (NMR). Of these methods, mass and emission spectrometry has gained the most acceptance. Emmision spectrometry is the simpler of the two methods because it does not require a high vacuum and the instrument can be easily maintained by the laboratory technician. Mass spectrometry, however, is still the method of choice because it requires a larger concentration of N to accurately perform the analysis, thus reducing the risk of air or other chemical contamination (Fiedler and Proksch, 1975). For this reason and because it is beyond the scope of this paper to discuss all three methods of isotope-ratio analysis, only mass spectrometry will be discussed here.

Isotope-ratio analysis by means of mass spectrometry is a process in which ions of a specific element are separated into a spectrum according to their mass-to-charge (m/e) ratio (Hauck and Bremner, 1976; Mulvaney, 1993). In the case of N, however, before any ionization can take place, all nitrogen forms in the sample must be converted to a suitable gas, generally dinitrogen (N_2), by oxidation with an alkali such as sodium or lithium hypobromite. At this point, the N_2 is exposed to an ion source and is bombarded by a flow of electrons emitted from a tungsten filament. Because of the chemical characteristics of N_2, this electron bombardment causes the nitrogen molecules

to lose an electron and form the cations $^{28}N_2^+$, $^{29}N_2^+$, and $^{30}N_2^+$. After ionization, the cations are separated into a spectrum according to their masses by a magnetic field, collected on insulated electrodes, and their ion currents measured at m/e 28, m/e 29, and m/e 30 (Mulvaney, 1993).

The atom percentage ^{15}N is a ratio of ^{15}N containing molecules to all N containing molecules and is expressed as

$$\text{atom \% } ^{15}N = \frac{^{15}N}{\left(^{15}N + {}^{14}N\right)} \times 100 \qquad (2)$$

Assuming, however, that an equilibrium exist among the ^{28}N, ^{29}N, and ^{30}N molecules of N_2, i.e., $^{28}N + {}^{30}N$ is in equilibrium with two ^{29}N, then atom percentage ^{15}N can be calculated as

$$\text{atom \% } ^{15}N = \frac{\left[^{15}N_2 + \left(0.5\ {}^{15}N\ {}^{14}N\right)\right]}{\left(^{15}N_2 + {}^{15}N\ {}^{14}N + {}^{14}N_2\right)} \qquad (3)$$

and subsequently, the percentage ^{15}N excess can be calculated as

$$\%\ ^{15}N \text{ excess} = \text{atom \% } ^{15}N - \left(\text{natural } ^{15}N \text{ abundance of material}\right) \qquad (4)$$

and used to determine the amount, e.g., kg ha^{-1}, of labeled fertilizer N present in the plants and soil after harvest (Fiedler and Proksch, 1975). According to Fiedler and Proksch (1975), equation (3) must be used with mass spectrometry if the equilibrium rate is unknown and if the concentration of ionic molecules can be measured accurately.

Sample preparation for isotope-ratio analysis. Before the atom percentage of sample N can be determined, all N forms must be converted to N_2 gas. Dinitrogen gas is the most appropriate N form for isotopic composition determinations because of its low molecular weight and its ease in preparation from both organic and inorganic compounds and because it does not react with

the other compounds of the analyzing system (Hauck, 1982). Most commonly, isotope-ratio analysis of sample N involves a three step process: 1) conversion of sample N to NH_4^+-N by acid digestion, 2) oxidation of NH_4^+-N to N_2 via alkaline sodium or lithium hypobromite, and 3) determination of the isotopic composition of the N_2 (Hauck, 1982). However, with dry combustion, sample N can be converted directly to dinitrogen, eliminating the need for traditional Kjeldahl digestions.

The Kjeldahl or wet oxidation procedure is still the most common method used to determine total N. In this method, all organic N is converted to NH_4^+-N by digestion with concentrated H_2SO_4. After digestion is complete, NH_4^+-N is determined by distilling the digest with a strong alkali and collecting the liberated NH_3 in a H_3BO_3 solution. If, however, the distillate is to be analyzed for its isotopic compostion, it is necessary that the distillate be acidulated and concentrated by evaporation. It is recommended that H_2SO_4 be used as the acidulating agent because the $(NH_4)_2SO_4$ that is formed remains stable up to 235°C, whereas there can be considerable N loss when $NH_4H_2BO_3$ is taken to complete dryness (Hauck, 1982). Unless the temperature of the evaporating solution is diligently controlled, i.e., under 90°C, Hauck does not recommend HCl as the acidulating agent because solid NH_4Cl can sublime causing serious N loss and possible isotopic fractionation.

There are several modifications for the Kjeldahl method that were created to include the NO_2^- and NO_3^- fractions in the total N analysis. One of these modifications is the salicylic acid-thiosulfate modification in which the sample is pretreated with a salicylic acid/sulfuric acid solution. The salicylic acid, under these acidic conditions, reacts with the NO_3^-, forming nitro compounds which are reduced to amino compounds with the addition of sodium thiosulfate (Bremner and Mulvaney, 1982). The second modification is

the permanganate-reduced Fe modification in which sample N is pretreated with $KMnO_4$ and H_2SO_4, producing an oxidation of NO_2^- to NO_3^-. Elemental Fe is subsequently added to the sample to reduce the NO_3^- to NH_4^+ (Bremner and Mulvaney, 1982). The latter modification is the preferred method when sample N is to be isotopically analyzed. According to Hauck (1982), the former method fails to recover all the NO_2^--N which may lead to erroneous ^{15}N recovery data since the nitrite fraction may have been enriched with the heavier isotope through biological interchange. It should also be mentioned that that there are differing opinions regarding the quantitative recovery of NO_2^- and NO_3^- with soil samples containing large quantities of water. Piper (1947) found that the salicylic acid-thiosulfate modification failed to give quantitative recovery of NO_2^- and NO_3^- with field-moist soil samples; however, Cheng and Bremner (1964) reported good recovery of NO_2^--N and NO_3^--N with soil samples containing 0.6 ml of water g^{-1} of soil (Bremner and Mulvaney, 1982).

The Dumas combustion (oxidation) separation procedure has become increasingly popular for total N and isotope-ratio analyses. With this method, sample N is converted directly to N_2 by oxidation and reduction of the organic N compounds and nitrogen oxides, respectively. Oxidation of organic N is accomplished by heating the sample with copper monoxide (CuO) at a temperature greater than 600°C. The liberated nitrogen oxides are then carried by a gas, generally purified carbon dioxide (CO_2) or helium (He), over hot elemental Cu, becoming reduced to N_2. At this point, a gaseous mixture of N_2-CO_2-CO exists which is reacted with CuO to convert the carbon monoxide (CO) to CO_2. The CO_2 is absorbed by a strong alkali, either potassium hydroxide (KOH) or calcium monoxide (CaO), leaving only the N_2 gas to be measured (Bremner and Mulvaney, 1982).

There are several advantages to using the Dumas procedure for isotopically analyzing N samples. This procedure gives the investigator ^{15}N information and simultaneously provides total N values as well. Because of this fact, the investigator is exempt from having to perform traditional Kjeldahl digestions, hence reducing laboratory time and needed personnel. Moreover, because total N values can be obtained directly, the need for steam distillations is unnecessary. By eliminating the distilling process, one eliminates the risks of isotopic fractionation that is often associated with improper distillation (Hauck, 1982). Because fewer steps are required to prepare samples for the Dumas procedure, the risk of cross contamination is also reduced.

There are, however, disadvantages associated with using the Dumas method for total N and ^{15}N analyses. First, since solid samples are analyzed directly for N_2, homogeneity becomes a very important factor. To insure adequately homogenized samples, Smith and Ho Um (1990) recommend grinding samples to a particle size of at least 250 µm. Isotope Services, Inc. of Los Alamos, New Mexico, also stress the importance of fine grinding soil and plant samples. They contend that fibrous plant materials, stems and root fragments are most subject to heterogeneity problems and, if not ground finely enough, can cause turbulence during the analysis thus producing erroneous data. Furthermore, each sample must contain at least 100 µg of N to insure an accurate analysis. This can be a problem with soil and water samples that are low in N.

No matter which method one uses to prepare and analyze sample N for isotopic composition, it is vital that the method give near complete recovery of all N fractions. Even though, for instance, NO_3^--N levels of the sample may be low compared to the total N, the difference in ^{15}N concentrations between the

two fractions may be extremely high. This is not as crucial when only total N values are of interest, but when the N isotope-ratio of the sample is needed, it could be experimentally detrimental. For example, failure to recover NO_3^--N that has a ^{15}N enrichment higher than the ^{15}N enrichment of the total N in the plant will tend to underestimate the amount of labeled N taken up from the soil. Conversely, failure to recover NO_3^--N that has a ^{15}N enrichment lower than the ^{15}N enrichment of the total N in the plant will tend to overestimate the amount of labeled N taken up from the soil (Hauck, 1982).

To further illustrate this concept, assume a soil sample consists of 1000 mg N. Further suppose that this sample contains 100 mg NO_3^--N of which 5 mg is $^{15}NO_3^-$-N. When analyzed, the NO_3^--N fraction would have a ^{15}N concentration of 5.0 at. %, while total N (assuming NO_3^--N was the only fraction enriched in ^{15}N) would have a ^{15}N concentration of 0.5 at. % (Equation 2). If however, the same sample is prepared by a method that fails to recover 20% of the NO_3^--N, the NO_3^--N amount falls to 80 mg with a ^{15}N concentration of 4.0 at. % (assuming proportionate recovery of ^{14}N and ^{15}N molecules). The total N amount of this sample would be 980 mg with a ^{15}N concentration of 0.408 at. %. The difference in total N values is 0.092 at. %, which is well within the level of precision for most mass spectrometers and would result in an underestimation of ^{15}N recovery.

Applications of Nitrogen-15

<u>Biological transformations.</u> The internal N cycle embodies a vast array of biological and chemical transformations. Jansson (1958) discussed five basic biological transformations that have been discovered and studied throughout the latter half of the 19th century:

1. Mineralization. This is the process of converting organic N compounds to inorganic N compounds (NH_4^+ or NH_3) by microbial decomposition. This a general biological process that encompasses two specific reactions: 1) *aminization*, which is the decomposition of protein molecules to amino acids and carbonaceous amines; and 2) *ammonification*, which further decomposes the amino acids and amines to NH_3.

2. Immobilization. This process converts inorganic compounds (ammonium and nitrate) to organic N compounds. This process renders N unavailable to other organisms and plants.

3. Nitrification. The process in which NH_4^+ is oxidized to NO_3^- with NO_2^- as an intermediate product.

4. Nitrogen fixation. This is the formation of N compounds from atmospheric nitrogen. These compounds are usable in biological processes.

5. Denitrification. The process in which NO_3^- or NO_2^- is reduced to dinitrogen gas (N_2) with nitrogen oxides as intermediate products.

All of these transformations take place continuously and concurrently within the entire soil system. Consequently, researchers are forced to study and understand these transformations as they relate to improved N management practices. Since the first ^{15}N work by Norman and Werkman (1943), the heavy isotope of nitrogen has been used to study the extent to which these transformations take place and their effect on the fate of applied ^{15}N-enriched materials (Jansson, 1958; Owens, 1960; Broadbent and Tyler, 1962; Delwiche and Steyn, 1970; Vanden Heuvel et al., 1988; Mulvaney, 1988; Mulvaney and Vanden Heuvel, 1988).

Biological interchange and discrimination are two mechanisms associated with the N cycle transformations and are useful in explaining the fate of applied ^{15}N-enriched materials. Biological interchange deals more with

the actual N isotopic interchange between organic and inorganic fractions, whereas discrimination focuses more on the preferential utilization by microorganisms of N fractions containing a specific isotope. For example, Hauck (1973) explained that if the nitrification reaction does not go to completion, which is generally the case in nature, the substrate of the reaction, NH_4^+, will tend to have slightly higher ^{15}N enrichments while the products, NO_3^- and NO_2^-, will tend to have slightly lower enrichments.

Conversely, the residual nitrate of the denitrification and dissimilatory NO_3^- reduction reactions may be enriched in ^{15}N atoms while the products may have lower ^{15}N enrichments (Hauck, 1973; Kaplan, 1983; Heaton, 1986). The isotopic fractionation observed in these reactions is due to biological discrimination. That is, the autotrophic bacteria of the nitrification reaction prefer $^{14}NH_4^+$-N to $^{15}NH_4^+$-N, thus consuming more of the $^{14}NH_4^+$-N while simultaneously leaving a greater concentration of $^{15}NH_4^+$-N. Likewise, the facultative anaerobic organisms of the denitrification and dissimilatory nitrate reduction reactions prefer $^{14}NO_3^-$-N to $^{15}NO_3^-$-N, thus consuming more of the $^{14}NO_3^-$-N while simultaneously leaving a greater concentration of $^{15}NO_3^-$-N.

Delwiche and Steyn (1970) reported that isotope fractionation does take place in both the nitrification and denitrification reactions and can be significant in soils containing high levels of clay. They concluded that because of biological discrimination and isotope fractionation, it is doubtful that researchers will be able to quantify the extent of N cycling from the atmosphere to the soil and back. Isotope fractionation is more prevalent in studies involving natural ^{15}N abundance. Consequently, studies using ^{15}N-enriched fertilizers are generally not concerned with biological discrimination and isotope fractionation (Hauck and Bremner, 1976).

Tracer investigations of solute movement. Preferential or bypass flow as defined by Rice et al. (1991) is "the accelerated movement of water and solutes through preferential pathways." These pathways could be earthworm or gopher holes, channels formed by plant roots, or cracks associated with the shrinking and swelling processes of smectitic clays. Preferential flow has traditionally been thought to occur only in highly structured soils, but studies have indicated that this process can be influential in uniform soils having little structure (DeSmedt and Wierenga, 1984; DeSmedt et al., 1986).

Lawes et al. (1882) were the first researchers to observe the preferential flow phenomena. They found that water added to the soil moved immediately through open channels with little or no displacement of soil water (Thomas and Phillips, 1979). However, researchers since have ignored these findings and based their infiltration models on matrix or diffuse (Darcy) flow. Only in the 1970s, when ground water contamination became more evident, did soil scientists rediscover the finding of Lawes et al. (1882) and implement tracers to study preferential flow within the vadose zone.

In an article summarizing preferential flow results of three different soils in Arizona, Rice et al. (1991) discussed solute and herbicide velocities of 1.5 to 2.5 times faster than calculated by the traditional diffuse flow model. Moreover, they observed preferential flow in sandy loam soils and in soils with relatively no structure.

By using the conservative tracer Cl^- in their infiltration study, Richard and Steenhuis (1988) were able to conclude that preferential flow was responsible for Cl^- reaching the tile drain within hours as opposed to weeks as calculated by the traditional diffuse (Darcy) flow models. Also, tile drains show promise in integrating spatial variability into the sampling structure; however,

this method, according to these researchers, needs to be tested in different environments and with more precise tracer accountability.

According to Richard and Steenhuis (1988), preferential flow exhibits a high degree of spatial variability. This type of variability is generally analyzed through geostatistical approaches, but Richard and Steenhuis (1988) explored tile drainage as a means of integrating spatial variability within the sampling volume. This integration of spatial variability is based on the fact that tile drains collect and convey water generated from large volumes of soil. Consequently, the flux and solute concentration data collected at the drain's outlet is more representative of the whole soil system rather than just small-scale localized representations.

There have been few preferential flow studies done using ^{15}N as the tracer. This is largely due to the high cost of the enriched material and the high cost of the analysis. The use of ^{15}N should be confined to studies involving biological transformations and applied fertilizer recoveries or to studies whose objectives cannot be measured by any other means.

The use of nitrogen-15 as a nitrate source indicator. Nitrate is a mobile anion and, consequently, is subject to leaching and ground water contamination. Nitrate can be found in a variety of materials, for example, in soil organic matter, commercial fertilizers, crop residues, and wastes from septic systems. Nitrogen isotopes have been useful for discriminating among these various sources of nitrate contamination. For instance, Komor and Anderson (1993) studied five different land-use settings (livestock feedlots, cultivated-irrigated, residential septic systems, cultivated-nonirrigated, and natural settings) in the sand-plain aquifers of central Minnesota. By using the delta ^{15}N (Δ ^{15}N) values of nitrate, calculated as

$$\Delta\,^{15}N = \left[\frac{(\text{atom \% }^{15}\text{N of sample - atom \% }^{15}\text{N of standard})}{(\text{atom \% }^{15}\text{N of standard})}\right] \times 1000 \quad (5)$$

they were able to differentiate among the NO_3^--N sources, i.e., among the NO_3^--N derived from animal wastes, inorganic and organic fertilizers, and fertilizers found in the natural settings. Komor and Anderson (1993) concluded that NO_3^--N from commercial fertilizers did show up in natural, non-agricultural areas and that nitrate derived from animal waste entered the sand-plain aquifers from feedlots, septic systems, and fields containing organic manures.

Kohl et al. (1971) used natural variations of ^{15}N abundance to distinguish between soil and fertilizer-derived nitrate in tile drain effluent. They reported a drop in ^{15}N concentrations while simultaneously experiencing increases in NO_3^--N concentrations. They attributed this observation as being due to fertilizer-derived nitrate, with its lower ^{15}N content, diluting the higher ^{15}N-containing soil-derived nitrate. However, Edwards (1973) was skeptical of the study conducted by Kohl et al. and opted to run an incubation study aimed at evaluating their method. Edwards found that the ^{15}N content of soil-derived nitrate varies with time of incubation. There is a tendency for the ^{15}N content of nitrate to increase with incubation time, but not to the extent reported by Kohl et al., i.e., 0.0048 at. %. This notion was reinforced by Bremner and Tabatabai (1973) who reported no nitrate samples of enrichments greater than 0.0022 at. % ^{15}N after 22 weeks of incubation.

Prunty and Montgomery (1991) designed a lysimeter study using ^{15}N-enriched urea to determine residence times of NO_3^--N in a confined, coarse-textured soil system with a shallow water table. They began to detect ^{15}N elevations at approximately 315 days or 10.5 months. In a previous study, Montgomery et al. (1990) implemented a non-isotopic investigation and found

a lag time of approximately 12 months before fertilizer N appeared in the lysimeter drainage water.

Fertilizer N recovery. There are two common methods used to calculate fertilizer N recovery. One is the difference (indirect or net effect) method which is determined by subtracting the total plant N of the nonfertilized plot from the total plant N of the fertilized plot. The second method is the isotopic (direct) method which is based on actual recovery of the applied labeled nitrogen only. The difference method is satisfactory when only fertilizer response investigations are being conducted, but when there is an interest in fertilizer-soil N exchange, use of the isotopic method is imperative (Allison, 1966).

In studies comparing the two methods of fertilizer N recovery, many found that the difference method consistently gave higher results. For instance, Westerman and Kurtz (1974) found that the difference method greatly overestimated recovery of applied urea by 35% and 23% in 1966 and 1967, respectively. Moraghan et al. (1984a) found, in their 1981 vertisol study in the semi-arid tropics, that all treatments showed higher recoveries when calculated by the difference method. However, the indirect method yielded consistently lower results in their 1980 Alfisol study (Moraghan et al., 1984b). Torbert et al. (1992) also found that the difference method gave consistently higher recovery values when calculated for the Plainfield soil. Legg and Allison (1959) produced similar results since the recovery of applied fertilizer N based on the difference method was higher than the actual ^{15}N recovery values.

Many of the studies attribute these overestimations of the difference method to added nitrogen interaction (ANI) or the so-called "priming effect" (Torbert et al., 1992). The priming effect has been defined by some as an increase in microbial activity and subsequent mineralization due to the

addition of a N source (Westerman and Kurtz, 1973). This increase in mineralization makes N more available to the plant, thus enhancing the potential for plant N uptake. However, according to Jansson (1958), a priming effect of this sort can only occur and be reliable when net mineralization progresses to the point of net depletion of total soil organic nitrogen. Jansson found in his incubation studies that the isotope method gave lower recoveries because of molecular substitutions rather than a priming effect. In other words, Jansson subscribed to the internal nitrogen cycle theory.

According to the internal N cycle theory, the instant a tagged material is applied to the soil system, equilibrium is altered. To regain equilibrium, the soil system will undergo molecular substitutions between the tagged and non-tagged materials, i.e., tagged molecules will be substituted for non-tagged molecules (Jansson, 1958). As a result, recoveries by the difference method will be greater than those measured by the direct method.

Recoveries of soil-derived N based on non-isotopic methods is not always higher than isotopic recoveries (Westerman and Kurtz, 1974; Allison, 1966). For instance, when soil N levels are relatively high, e.g., in first-year check treatments, a smaller percentage of that nitrogen being mineralized will be used by the soil microflora in the decomposition of organic materials; therefore, more N will be available for plant uptake. As a result, both the aboveground plant parts and roots will have a high nitrogen content relative to the treated plants. When these plants of high N content are subtracted from N-treated plants of only slightly higher N content, recovery values are generally lower (Allison, 1966). Also, if the treated area receives a low N rate, most of the added material will become immobilized, and recovery will be lower (Allison, 1966). Moreover, if the ^{15}N content of the soil is included in the isotope recovery calculations, then differences between methods will be smaller.

Moraghan et al. (1984b) found that the difference method yielded lower fertilizer N recoveries than the direct method in their 1980 sorghum study. They contend that recoveries of this type, i.e., lower recoveries by the difference method, are atypical and can be attributed to high soil N availability. Fertilizer N use efficiency can decrease when N in the soil is available at levels greater than those needed for maximum yield. In addition, the difference method can yield lower recoveries if the applied labeled N is preferentially taken up by the crop early in the growing season. This may be due to positional or chronological factors, according to Moraghan et al. (1984b), and can result in lower plant uptake of mineralized N throughout the remaining growing season.

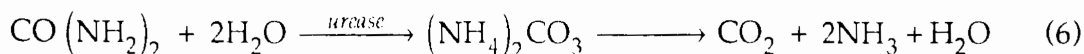
Westerman and Kurtz (1974) feel that fertilizer N recovery based on the traditional difference method must be cautiously interpreted. Researchers often assume that mineralization and immobilization are the same for both fertilized and non-fertilized soils which can lead to erroneous conclusions. According to Torbert et al. (1992), Fox and Piekielek (1987) found that fertilizer N efficiency calculated by the difference method depended upon differences in N uptake between treated and non-treated plots.

There are many uncertainties associated with fertilizer N recovery interpretation. The difference method falls suspect to added N interaction (ANI) or the "priming effect," whereas interpretations of the direct method are clouded by mineralization-immobilization turnover (MIT) processes (Torbert et al., 1992). Therefore, researchers stress the importance of realizing these limitations before interpreting recovery data.

Urea Transformations and Possible Losses

Urea $(NH_2)_2CO)$ is a simple organic compound containing approximately 46% N and has become the most widely used form of solid N fertilizer (Troeh and Thompson, 1993). To properly understand the fate of applied urea-N, it is important to understand the various transformations that take place once urea-N is appled to the soil system.

Urea hydrolysis. Urea-N reacts with water and hydrolyzes to form carbon dioxide and NH_3 with intermediate products of either $H_2NCOONH_4$ (carbamate) or $(NH_4)_2CO_3$ (ammonium carbonate) (Claypool, 1990; Christianson et al., 1979). The primary catalyst of urea hydrolysis is urease (urea amidohydrolase, EC 3.5.1.5), an enzyme first crystallized from the jack bean (*Canavalia ensiformis L.*) and found in most species of bacteria, yeast, fungi, and some higher plant forms (Gould et al., 1986). The urea hydrolysis reaction with $(NH_4)_2CO_3$ as the intermediate is



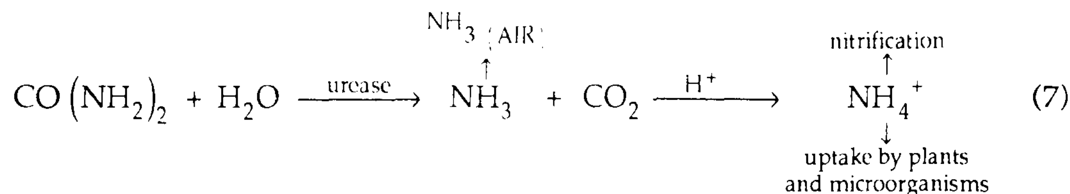
$$CO\left(NH_2\right)_2 + 2H_2O \xrightarrow{urease} \left(NH_4\right)_2CO_3 \longrightarrow CO_2 + 2NH_3 + H_2O \qquad (6)$$

The rate of urea hydrolysis depends on soil urease activity, soil temperature, and soil moisture (Claypool, 1990). According to Claypool (1990), urease activity is stimulated by urea applications and by rewetting air-dry soil. In addition, urease activity is highly correlated with organic carbon (C), total N, and cation exchange capacity (CEC). The average urease activity of several topsoils was found to be 16 µg urea-N g^{-1} h^{-1} at 37°C which according to Claypool (1990), can result in significant urea-N hydrolysis under field conditions. For instance, Mohammed et al. (1984) applied 100 kg urea-N ha^{-1} to the soil surface and found that 86% of the applied urea was hydrolyzed after 7

days. Rocous et al. (1988) found that after 8 days, only 2 kg N ha^{-1} remained as urea in the soil.

Soil temperature and moisture content have been shown to affect the rate of hydrolysis. Urea hydrolysis is directly proportional to soil temperatures up to 60 to 70 °C and inversely proportional at temperatures greater than 70°C (Gould et al., 1986). According to Gould et al. (1986), most studies showed soil moisture content had little effect on urease activity while others reported increases or decreases in hydrolysis rate with increasing moisture content. Malhi and Nyborg (1979) found by increasing soil water content at 20°C from -1500 to -33.3 kPa soil water tension, the rate of urea hydrolysis also increased.

Ammonia volatilization. Ammonia volatilization can be defined as the portion of NH_3 created from urea hydrolysis that is lost to the atmosphere because it does not gain a proton to form NH_4^+ and is thus 1) nitrified or 2) used by plants or microorganisms or fixed by soil colloids. The following equation is discussed by Claypool (1990) and illustrates possible urea transformations in the soil:

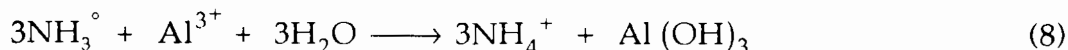


$$CO(NH_2)_2 + H_2O \xrightarrow{\text{urease}} NH_3\,(\uparrow NH_3 \text{ (AIR)}) + CO_2 \xrightarrow{H^+} NH_4^+ \quad (7)$$

According to Brady (1984) when ammonium-containing fertilizers or urea-N is applied to soil, hydrolysis proceeds rather quickly, forming ammonia. Losses of ammonia gas can be significant especially on dry soils, sandy soils, and alkaline or calcareous soils (Brady, 1984). Fenn and Kissel (1976) found that NH_3 volatilization is minimal from NH_4^+ fertilizers incorporated into soils possessing high CEC, high soil moisture content, and low pH. Fenn et al. (1981) reduced NH_3 volatilization by adding Ca and Mg salts to fertilizers. This

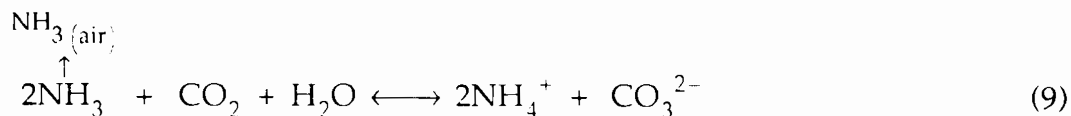
process is analogous to the soil cation exchange complex since the cation exchange complex is an excellent source for these cations.

An increase in soil water decreases NH_3 volatilization because there is more water available to hydrate NH_3 and form NH_4^+ (Claypool, 1990). Ammonia volatilization loss is less (greater) in acidic (alkaline) soils. In acid soils, the NH_3 could be protonated by soil acids like aluminum cations:



$$3NH_3^{\circ} + Al^{3+} + 3H_2O \longrightarrow 3NH_4^+ + Al(OH)_3 \qquad (8)$$

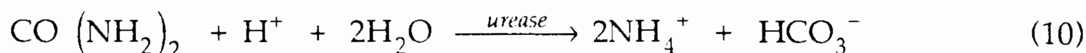
Conversely, alkaline or neutral soils are governed by the carbonic acid-bicarbonate-carbonate buffering system which controls NH_3 volatilization (Claypool, 1990):



$$\overset{NH_{3\,(air)}}{\overset{\uparrow}{2NH_3}} + CO_2 + H_2O \longleftrightarrow 2NH_4^+ + CO_3^{2-} \qquad (9)$$

If the soil system has an adequate water content, Eq. (9) will be driven to the right with the formation of NH_4^+; otherwise, NH_3 will be in greater supply and potentially lost to the atmosphere.

Increased H^+ buffering capacity lowers the potential for NH_3 volatilization. During hydrolysis, urea reacts with water, consumes H^+, and produces NH_4^+ and bicarbonate:



$$CO(NH_2)_2 + H^+ + 2H_2O \xrightarrow{urease} 2NH_4^+ + HCO_3^- \qquad (10)$$

Soils with a high H^+ buffering capacity can easily replenish the H^+ consumed by the reaction in Eq. (10), resulting in a smaller pH increase. This reaction will produce pH values between 7 and 9 in most soils (Claypool, 1990).

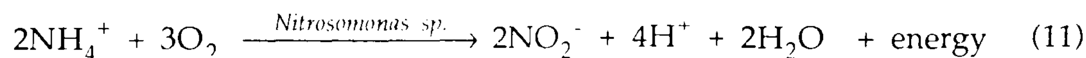
Patra et al. (1992) found a direct relationship between pH and NH_3 volatilization in urea-N treated soil. When urea-N was applied to the soil with an initital pH of 8.2, it hydrolyzed to form NH_4^+ and HCO_3^-. The increased log

activity of HCO_3^- in conjunction with H^+ consumption raised the pH and increased the rate of NH_3 volatilization. Consequently, lower fertilizer N recovery was experienced due to increased NH_3 volatilization.

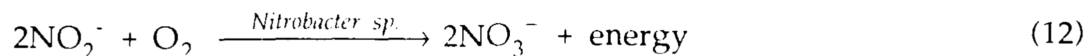
According to Troeh and Thompson (1993), ammonia volatilization from the soil is generally not a problem. Significant losses of NH_3 are more likely to occur from surface-applied urea-N because fewer opportunities exist for the ammonia to react with the soil colloids. In addition, surface temperature is usually greater than subsurface temperature, which increases the potential of ammonia volatilization (Brady, 1984).

Ammonia volatilization loss from aboveground biomass can be significant. According to Francis et al. (1993), a large amount of N (10 to 20% of the applied N) was volatilized from aboveground vegetation during the post-anthesis stage of corn development. Another study found 21% of the applied fertilizer N was lost as NH_3-N from the wheat foliage during senescence (Harper et al., 1987). Parton et al. (1988) found that significant amounts of NH_3 may be lost to the atmosphere from the plants themselves. That is, by observing the net NH_3 fluxes from plant to ambient air, they were able to conclude gaseous NH_3 losses of 2.8 and 4.4 kg ha^{-1} on a field-scale basis. They contend that these levels would typically be much higher, but because of the high ambient NH_3 levels and thus low NH_3 pressure gradients, gaseous NH_3 losses were lower than normal.

Nitrification and nitrite accumulation. Nitrification is a two-stage oxidation process in which ammonia is oxidixed to NO_2^-, and the NO_2^- is oxidized to NO_3^- (Troeh and Thompson, 1993):



$$2NH_4^+ + 3O_2 \xrightarrow{\textit{Nitrosomonas sp.}} 2NO_2^- + 4H^+ + 2H_2O + \text{energy} \quad (11)$$

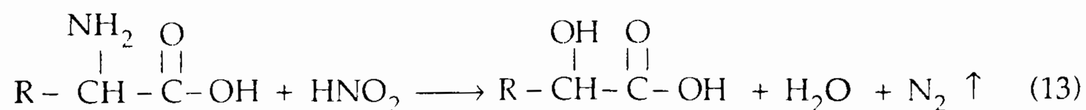


$$2NO_2^- + O_2 \xrightarrow{\textit{Nitrobacter sp.}} 2NO_3^- + \text{energy} \quad (12)$$

Nitrification occurs at a very rapid rate when soil temperature and moisture conditions are ideal and NH_4^+ is in adequate supply (Brady, 1984). Under most soil conditions, NO_2^- usually becomes oxidized to NO_3^- rather quickly and does not accumulate; however, research indicates that NO_2^- accumulations can be substantial and may lead to significant N loss when fertilizer N is band-applied (Magalhães et al., 1987).

When urea-N is band-applied, NH_4^+ concentrations and soil pH begin to rise in the area surrounding the fertilizer band. These alkaline conditions adversely affect the activity of *Nitrobacter sp.*, resulting in an accumulation of NO_2^- (Christianson et al., 1979). Magalhães et al. (1987) discussed how NO_2^- may diffuse from the alkaline environment surrounding the urea band into adjacent acid soil microzones. Here, nitrous acid (HNO_2) is formed (chemodenitrification) which may cause N losses to fixation or gaseous emission. Magalhães et al. (1987) found that NO_2^- accumulated in the majority of the soils treated with urea and reported a significant relationship between cumulative N_20 and N_2 emissions and maximum NO_2^- concentration. They concluded that NO_2^- accumulations are closely involved in gaseous N losses from soils during nitrification of alkaline-hydrolyzing fertilizers and that there is a direct relationship between NO_2^- accumulation and N deficits (Magalhães et al., 1987).

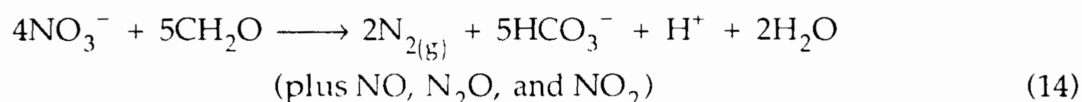
The Van Slyke reaction is a non-biological reaction where various amino compounds (amino acids, amines, and urea) react with HNO_2 to form N_2. It is thought by some to be the primary mechanism for N_2 evolution from NO_2^- (Gould et al., 1986):



$$R-CH(NH_2)-C(=O)-OH + HNO_2 \longrightarrow R-CH(OH)-C(=O)-OH + H_2O + N_2\uparrow \quad (13)$$

For example, Christianson et al. (1979) reported gaseous losses of N when NO_2^- accumulated during nitrification of the hydrolysis product of urea and attributed a large percentage (4.9%) of the N lost from the soil system to a Van Slyke-like reaction. Other studies, however, oppose the Van Slyke reaction contending it has very little effect on N_2 evolution from soil. For example, Bremner and Nelson (1968) concluded that phenolic substances rather than amino acids or urea were responsible for the fixation of NO_2^--N and subsequent volatilization as N_2 and N_2O.

Denitrification. Denitrification is the "biochemical reduction of NO_3^- or NO_2^- to gaseous N, either as molecular N or as an oxide of N" (Foth, 1984). Denitrification is carried out by facultative anaerobic organisms that use NO_3^- in place of O_2 in respiration, as follows:



$$4NO_3^- + 5CH_2O \longrightarrow 2N_{2(g)} + 5HCO_3^- + H^+ + 2H_2O \quad \text{(plus NO, } N_2O\text{, and } NO_2\text{)} \tag{14}$$

When the hydrolysis product of urea is oxidized to NO_3^-, it becomes available for plant uptake, denitrification, dissimilatory nitrate reduction (reduction of NO_3^- to NH_4^+), or leaching. Losses by denitrification are not thought to be very large in well-drained soils (Troeh and Thompson, 1993). For example, Mosier et al. (1986) reported denitrification losses of 5.6 kg ha^{-1} from a moderately well-drained soil in Colorado (Troeh and Thompson, 1993). Conversely, denitrification can account for N losses up to 110 kg ha^{-1} in a single growing season if the soil has been under saturated conditions for an extended period (Troeh and Thompson, 1993).

Equation (14) represents the traditional view of denitrification. Research indicates that denitrification processes can proceed in an aerobic medium possessing dissolved oxygen levels as high as 2 to 7 mg O_2 L^{-1} (Braun, 1991). In addition, Braun (1991) discusses several studies that reportedly found active

denitrification in cultures kept under aerobic conditions and having dissolved O_2 levels as high as 3 mg L^{-1}.

Leaching. Urea is a nonionic compound when applied. It is susceptible to leaching, but at a much slower rate than the uninhibited ions, Cl^- and NO_3^-. Urea can also form dicarboxyl bonds with soil organic matter (salt formation) and become retained within the soil. Under acidic conditions, urea can react with the soil acids, H^+ and Al^{3+}, and become protonated and behave as a cation (Gould et al., 1986). According to Gould et al. (1986), urea can be lost to leaching by two processes: 1) "urea is leached per se from the soil, and 2) urea migrates below the rooting zone, is hydrolyzed, nitrified, and then leached as NO_3^-."

Field Design and Treatment Layout

A study was initiated in June, 1993, and was conducted at the Best Management Practices (BMP) study site near Oakes, ND. The site was located on the NW1/4 of section 29 of T. 130 North and R. 59 West in Dickey County. Corn (*Zea mays* L.) has been grown on this site since the inception of the BMP project in 1989. The dominant soil series is a Hecla fine sandy loam and is classified as a sandy, mixed, Aquic Haploboroll. The site is owned by Herman Meyer and is operated by farmer-cooperator Stan Hokana (Stegman et al., 1990).

A randomized block design with four replicates was used for this study. 16 N plots were established parallel to the G and E-transect in 1993 and 1994, respectively (Fig. 1). Nitrogen plots for both growing seasons were established approximately 3 meters from the transect (Fig. 1). In 1993, all plots received preplant fertilizer with a grade analysis of 10-60-0 at the rate of 13.5 kg N ha^{-1}. On June 30, 1993, eight of the 16 plots received band applications of urea-N at 135 kg N ha^{-1}. Four of the eight treated plots received an enrichment of 4.25 at. % ^{15}N, while the other four treated plots received unlabled urea-N at 0.3664 at. % ^{15}N. The remaining eight plots were check plots and received only the 13.5 kg N ha^{-1} of the preplant material. Thus, there was a total of four replications with each replicate containing a labeled, a non-labeled, and two check treatments (Fig. 2). Urea-N was sidedressed 15 cm from the corn row and 5 cm deep. Nitrogen plots for 1993 were established over the tile line to accommodate objective number 2 of this study (Fig. 2).

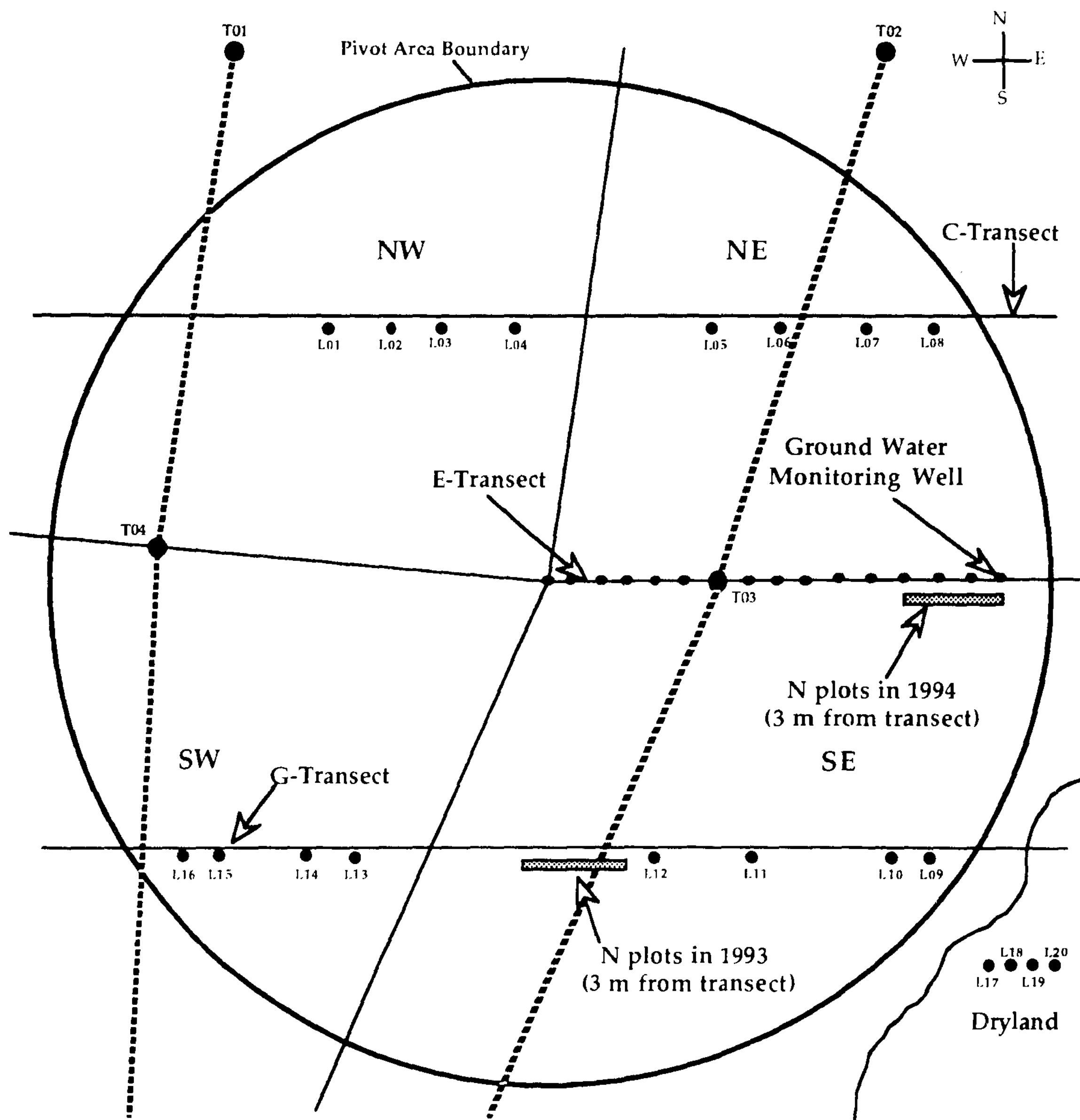


Figure 1. Best Management Practices field map illustrating irrigated quadrants, undisturbed lysimeters, N plots, tile drains, dryland lysimeters, C, E, and G-transects, and ground water monitoring wells (Steele et al., 1993). Map not drawn to scale.

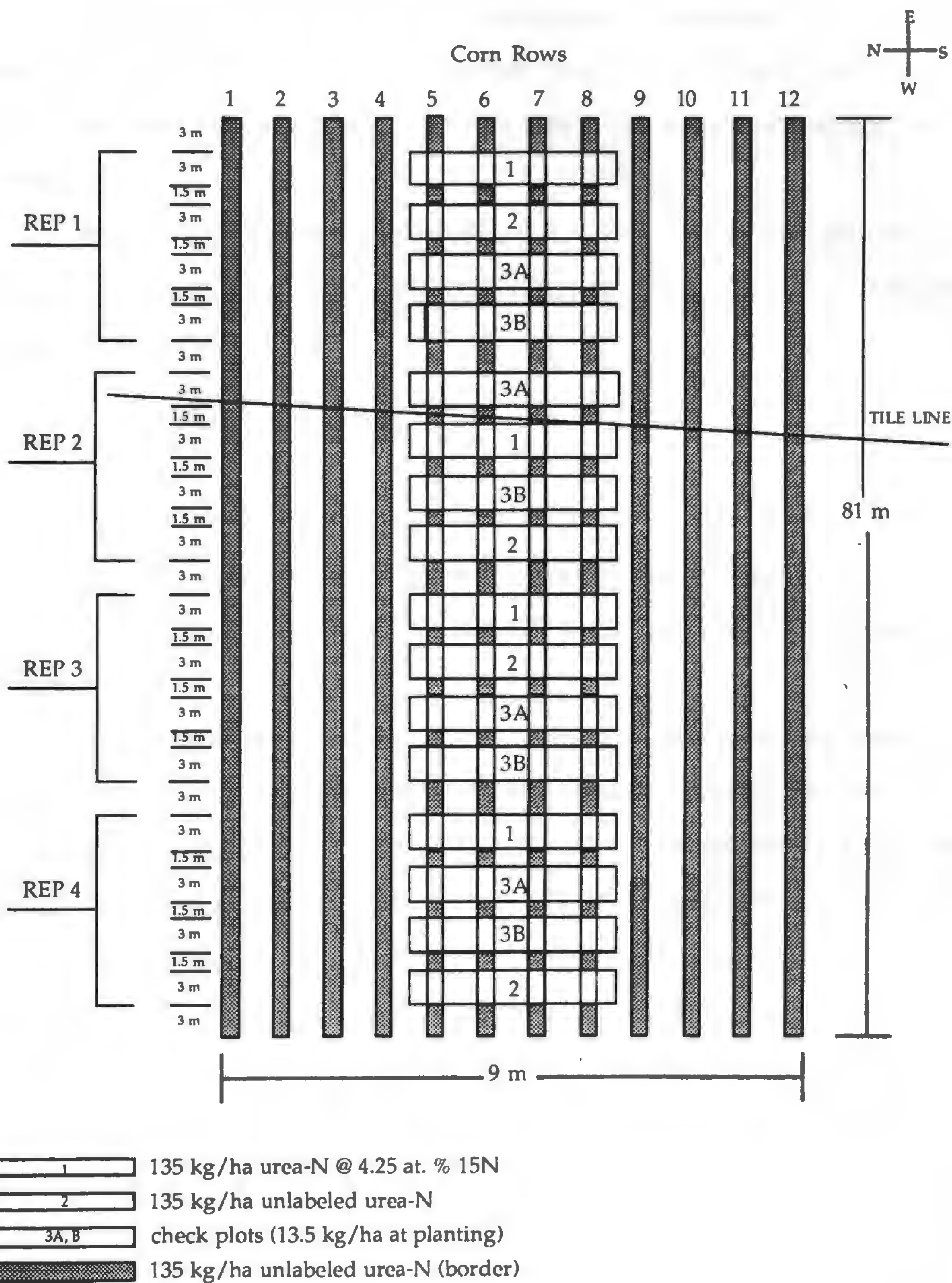


Figure 2. Nitrogen plot diagram for the 1993 ^{15}N investigation. Plots located along the G-transect. Diagram not drawn to scale.

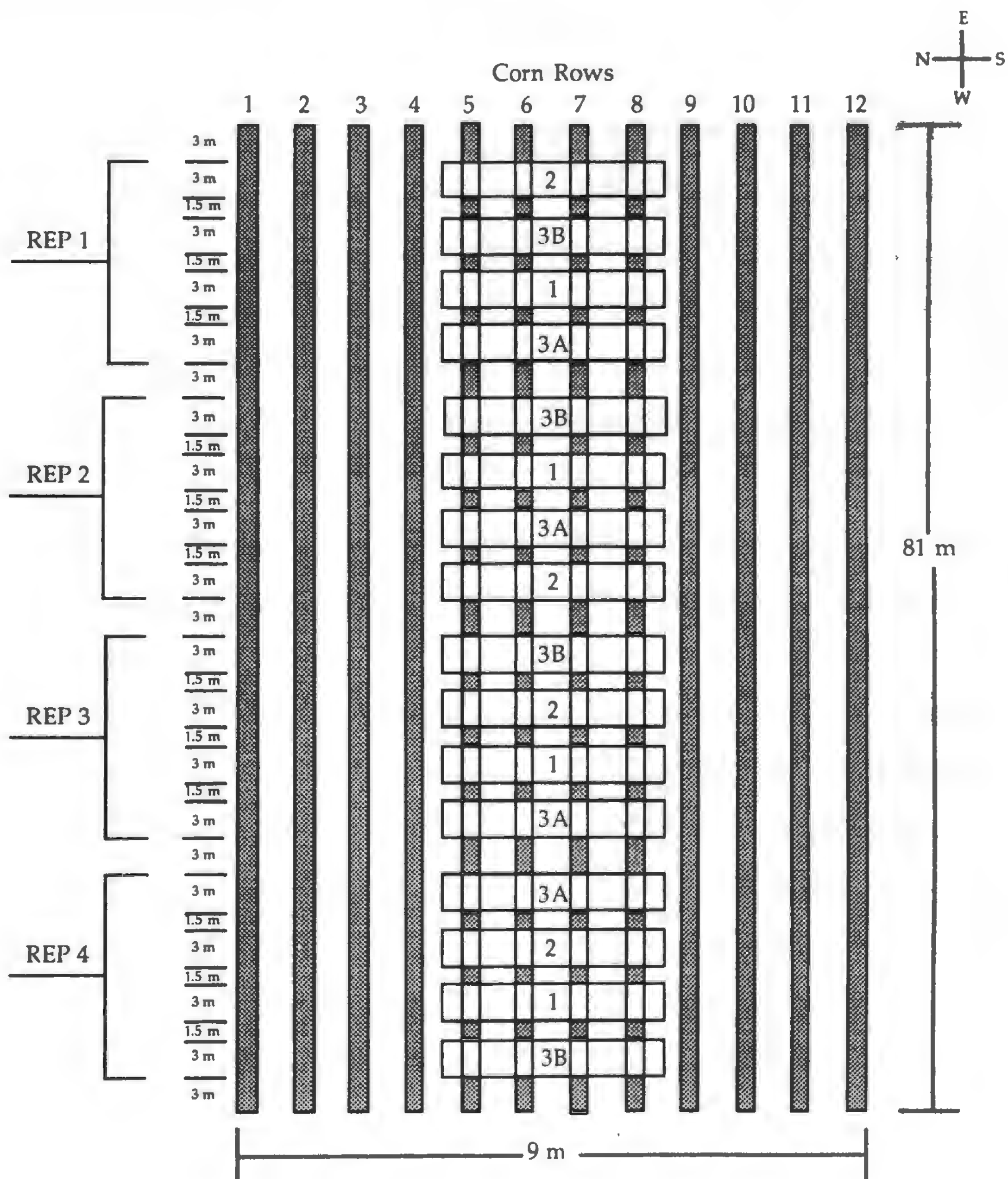
In addition to the N plots, all 20 undisturbed lysimeters (Fig. 1) received band applications of 2.0 at. % ^{15}N-enriched urea-N at 135 kg N ha^{-1}. Urea-N was sidedressed 15 cm from the corn row and 5 cm deep and was applied on June 29, 1993.

Urea-N with an initial enrichment of 5.122 at. % ^{15}N was diluted with non-labeled urea-N to create the 4.25 and 2.0 at. % ^{15}N enrichments. Dilutions needed were computed from

$$A_2 = \frac{[(T)(A_0) + (D)(A_1)]}{(T + D)} \tag{14}$$

where A_2 is the at. % ^{15}N desired, T and A_0 are the weight and at. % ^{15}N of nitrogen in the labeled urea, respectively, and D and A_1 are the weight and at. % ^{15}N of nitrogen in the non-labeled urea, respectively (Hauck and Bremner, 1976).

This experiment was duplicated in 1994 with the following exceptions and additions: 1) the N plots were established parallel to the E-transect (Fig. 1) with preplant application rates of 35.8 kg N ha^{-1} broadcast and 12.3 kg N ha^{-1} applied with the seed; 2) labeled and non-labeled urea-N was applied on June 13, 1994; 3) the urea-N applied to the ^{15}N treatments was enriched with ^{15}N atoms by 5.934% (Fig. 3); 4) urea-N, with the same ^{15}N enrichment, was applied at a rate of 83 kg N ha^{-1} to the first corn row of the E-transect only. The application extended westward to encompass all closely spaced ground water monitoring wells (Fig. 1), and 5) 10 of the 20 undisturbed lysimeters received urea-N applications at 67 kg N ha^{-1} with a ^{15}N enrichment of 5.934 at. % June 13, 1994. For this application, two lysimeters per quadrant were randomly selected. They were lysimeters 1 and 2 of the NW quadrant, 5 and 6 of the NE quadrant, 9 and 11 of the SE quadrant, 13 and 16 of the SW quadrant, and 17 and 19 of the dryland area (Fig. 1).



1 — 135 kg/ha urea-N @ 5.9347 at. % 15N

2 — 135 kg/ha unlabeled urea-N

3A, B — check plots (48 kg/ha at planting)

(shaded) — 135 kg/ha unlabeled urea-N (border)

Figure 3. Nitrogen plot diagram for the 1994 ^{15}N investigation. Plots are located along the E-transect. Diagram not drawn to scale.

Drainage samples. Leachate sample collection began July 8, 1993, and continued through October 27, 1994. All undisturbed lysimeters and the tile drain (T03) located in the southeast quadrant of the BMP quarter were sampled weekly. Samples from lysimeters were obtained via vacuum extraction and gravity drainage, whereas samples from the wells were extracted via a rotary vacuum pump. Samples were collected in plastic bottles and preserved until analysis by the deep-freeze method. This method, according to several investigators, (Macdonald and McLaughlin, 1982; Klingaman and Nelson, 1976; German Chemists Association, 1980) seems to be the most suitable method for NO_3^--N stabilization.

Samples were sent to Isotope Services, Inc. of Los Alamos, New Mexico, for elemental and isotopic N analysis by the Dumas Combustion Separation analyzer (Carlo Erba model 1500) and the VG Isomass mass spectrometer, respectively. The Dumas procedure allows for direct conversion of sample N to dinitrogen thus eliminating the need for traditional acid digestions. However, with the Dumas method of analysis, each sample must contain at least 100 micrograms of N. If this requirement is met, Isotope Services, Inc. found that duplicate isotopic analyses will have a 1% relative difference while N elemental composition can be measured to 0.01% N by weight. Since my drainage samples had very low nitrogen levels, a relatively large aliquot of the parent sample had to be concentrated by evaporation before analysis.

Before aliquot extraction, samples were thawed in a water bath with a temperature of approximately 40-50°C. Samples were shaken frequently to prevent localized overheating and to expedite the thawing process. Owing to possible "freezing out" effects, i.e., concentration differences between the solid

and liquid phases, samples were completely thawed and homogenized before aliquots were extracted from the parent sample (German Chemists Association, 1980). Thirty to 40 milliliters of the sample were added to a 25 x 95 mm glass vial and evaporated to complete dryness at less than 80°C. After the samples were completely dry, approximately 3 ml of deionized water was added to the vials and vortexed to place all the NO_3^- into solution. The vials were dried again, made air tight with parafilm and teflon® tape, and sent in the dry form to Los Alamos where they were reconstituted before analysis.

Shipping the samples in the dry form eliminated the worry of vial leakage as well as the need for alternative preservation methods. This was also beneficial to Isotope Services, Inc. as it preferred to analyze non-acidic samples.

Plant samples. Final harvest of corn plants took place at the R6 stage of development. Harvesting took place Sept. 25, 1993, and Sept. 24, 1994. Two 2.44 meter length rows were harvested and used for yield determinations. Ears were counted and weighed, stover was weighed and chopped, and all plant material was placed in cloth bags and dried at 60°C. The harvest rows consisted of 26 plants (Fig. 4) of which five were randomly selected and harvested to include their adventitious roots. The roots were washed thoroughly of any adhering soil and ground with the stover. The five randomly selected plants and adventitious roots were taken from outside the 75 x 90 cm soil sampling area. This eliminated disruption of the soil sampling area, thus optimizing soil ^{15}N recovery. Plant material was separated into grain, stover and adventitious roots, and cob fractions. All plant material was ground twice, first in a Wiley mill with a 1000 µm screen and second in a rotary grinder producing a particle size of approximately 500 µm. This method did not produce the "ideal" 250 µm

CORN ROWS

E
N S
W

1 2 3 4 5 6 7 8 9 10 11 12

3m
3m
1.5 m
3m
1.5 m
3m
1.5 m
3m

CORN ROWS

5 6 7 8

HARVEST
ROWS
R6 STAGE

Figure 4. Plant sampling diagram for the 1993 and 1994 growing seasons. Diagram not drawn to scale.

particle size recommended by Smith and Ho Um (1990), but it did insure duplicate isotopic and elemental N analyses to be within the limits of relative difference (1% and 0.01% by weight, respectively) recommended by Isotope Services, Inc. of Las Alamos, New Mexico.

To reduce the likelihood of cross-contamination, all samples were ground in the order from least ^{15}N concentration to greatest ^{15}N concentration. That is, the check samples were ground first followed by the unlabeled samples and finally the labeled samples. In addition, samples from ^{15}N treated plots were placed in separate ovens during the drying process.

All samples were sent to Los Alamos for total N and isotopic determinations. The total N in the aboveground plant parts derived from fertilizer N was calculated by both the indirect (difference) and direct (isotope) method. Plant N uptake by the indirect method was calculated as

$$\%\text{ Fertilizer N Recovery} = \frac{\left[(Y_{fert})(N_{fert}) - (Y_{non-fert})(N_{non-fert})\right]}{A} \qquad (15)$$

where Y_{fert} is dry matter yield in kg ha^{-1} of fertilized plots, N_{fert} is percent total N of fertilized plots, $Y_{non-fert}$ is dry matter yield in kg ha^{-1} of non-fertilized plots, $N_{non-fert}$ is percent total N of non-fertilized plots, and A is kg ha^{-1} of applied urea-N. Plant N uptake by the direct method was calculated as

$$\%\text{ Fertilizer N Recovery} = \frac{\left[(L_{fert})(N_L)(Q_P)\right]}{Q_S} \qquad (16)$$

where L_{fert} is dry matter yield in kg ha^{-1} of labeled treatments, N_L is percent total N of labeled treatments, Q_P is at. % excess ^{15}N in plant material, and Q_S is kg ha^{-1} excess ^{15}N applied to soil. The natural ^{15}N abundance of the plant material was determined by averaging the values of all check treatments.

Soil samples. Fall soil samples were taken Nov. 2, 1993, and on Oct. 28, 1994. All treatments were sampled to a depth of 1.8 m with increments of 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm, 90-120 cm, 120-150 cm, and 150-180 cm. Two 0.101 m^3 sections of soil were removed, mixed and composited for all ^{15}N treatments at the 0-15 cm and 15-30 cm depths, i.e., a 75 cm x 90 cm x 15 cm section was removed for the 0-15 cm subsample followed by another 75 cm x 90 cm x 15 cm section for the 15-30 cm subsample. For the remaining samples, two 3.75 cm cores were taken from the excavated section of soil. The cores were composited and a subsample obtained. The core holes were filled and the excavated soil returned and packed to its approximate original bulk density. The unlabeled and check plots were sampled similarly except the top 30 cm of soil was not removed. Instead, ten 1.88 cm cores plus the two 3.75 cm cores were composited for the 0-15 cm and 15-30 cm depths. This method was developed through personal communication with Dr. John T. Moraghan, professor of soil science at North Dakota State University, and from other similar recovery studies.

All soil samples were kept frozen until analysis. Subsamples were extracted moist with 2.0*M* KCl and distilled for their NH_4^+-N and NO_3^--N compositions (Keeney and Nelson, 1982). Because of the low concentrations and inaccuracy of the NH_4^+-N values, only NO_3^--N concentrations are reported (Table A1). After completing the distillations, soil samples were air dried, ground, ball-milled (all root fragments were retained) to a particle size of approximately 250 μm, and sent to Los Alamos for total N and isotopic determinations. All soil samples were ground similarly to plant samples in that the check samples were ground first followed by the unlabeled samples and finally the labeled samples. The percentage of labeled fertilizer N

remaining in the soil at the end of the 1993 and 1994 growing seasons was calculated by the following equation:

$$\% \, ^{15}\text{N Recovery} = \frac{\left[\left(\text{kg ha}^{-1}\text{ of N}\right)\left(\text{atom \% }^{15}\text{N excess in soil}\right)\right]}{\left[\left(\text{kg ha}^{-1}\text{ of N added to soil}\right)\left(\text{atom \% excess in urea}\right)\right]} \quad (17)$$

The natural ^{15}N abundance of the soil was determined by averaging the values of all check treatments.

To make use of equation (17), total N values must be converted from mg kg^{-1} to kg ha^{-1} by using the bulk density values of each sampling depth. The 1990 BMP annual report (Stegman et al., 1990) lists the bulk densities for all the undisturbed lysimeters according to horizon depth. From these bulk densities, weighted averages were calculated according to each soil sampling depth, i.e. 0-15, 15-30, 30-60, etc., and used to calculate percentage ^{15}N recoveries. The BMP field site possesses a very uniform, unstructured soil with bulk densities ranging from only 1.25 to 1.54 Mg m^{-3}. Accordingly, it sufficed to use weighted bulk densities in the mg kg^{-1} to kg ha^{-1} conversion. In soils that are highly structured and nonuniform, e.g., soils that contain high levels of silt and clay, it is imperative that bulk densities be taken at each sampling depth. If not, recovery values can be grossly over or underestimated. This project failed to take bulk density readings at each sampling depth; and consequently, ^{15}N recoveries may be suspect.

Residence Time of Applied ^{15}N-Enriched Urea-N

Residence times of applied ^{15}N-enriched urea-N among the 20 undisturbed lysimeters are depicted in Figures 5-24 (^{15}N concentrations reported in Table E1). The natural ^{15}N abundance is the average of 285 samples taken from July 8 through Oct. 27, 1993. Lysimeters showing gaps in data collection indicate sampling dates without drainage. For example, lysimeter 17 (Fig. 21) had only three dates in 1994 in which gravity drainage was present in the reservoir. Likewise, lysimeter 18 (Fig. 22) only had one gravity drainage collection for all of 1993 and 1994. Consequently, only the extraction data is reported for this lysimeter.

Except for lysimeters 13, 14, and 20, Figures 17, 18, and 24, respectively, all undisturbed lysimeters have shown ^{15}N elevations during the 1994 growing season. According to these results, the soil residence times of applied N agree with previous research at the study area. Prunty and Montgomery (1991) observed a lag of 10 to 13 months before detection of surface applied N at depths equivalent to drains in the undisturbed lysimeters (approximately 188 cm from the soil surface). Figure 12 illustrates the breakthrough of a pulse of ^{15}N at approximately 10 months after application. The average resident times for all undisturbed lysimeters receiving only the 1993 application were approximately 356 days or 11.7 months.

Although the residence times agree with previous research, there are definite indications of hydraulic property variations among lysimeters. For example, lysimeters 15 and 16 of the SW quadrant (Figs. 19 and 20, respectively), and lysimeter 1 of the NW quadrant (Fig. 5) began showing ^{15}N detections in

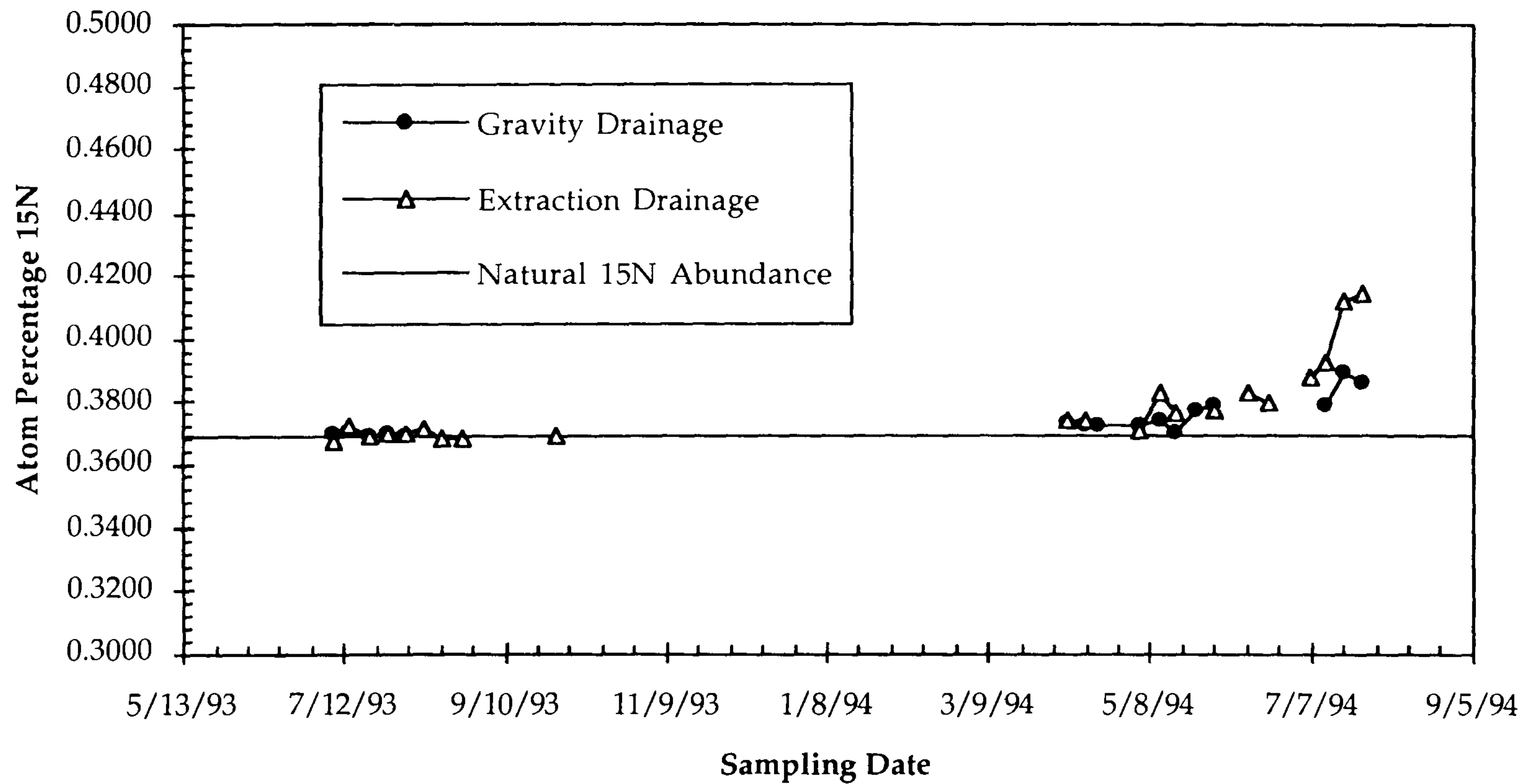


Figure 5. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #1 located in the NW quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

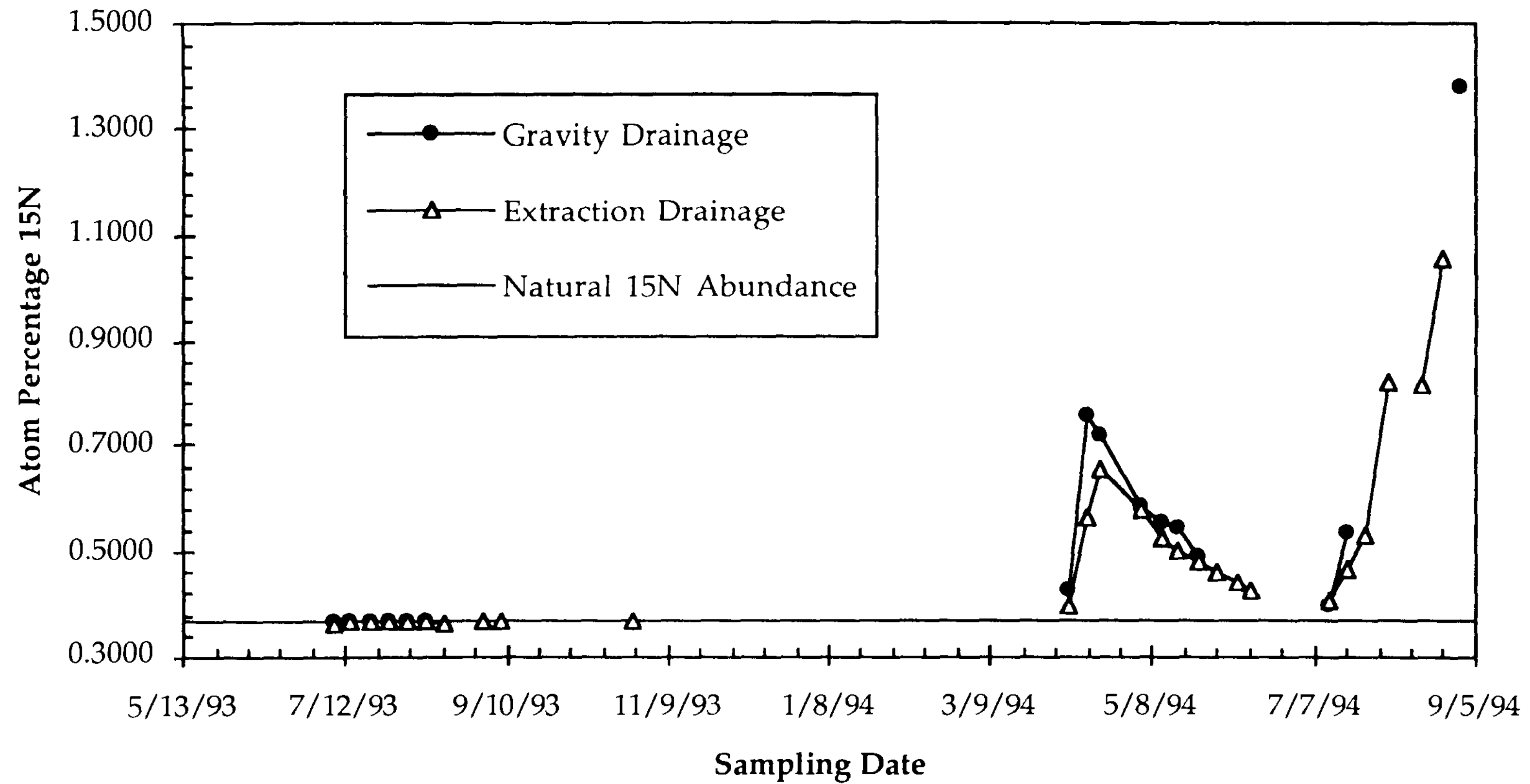


Figure 6. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #2 located in the NW quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

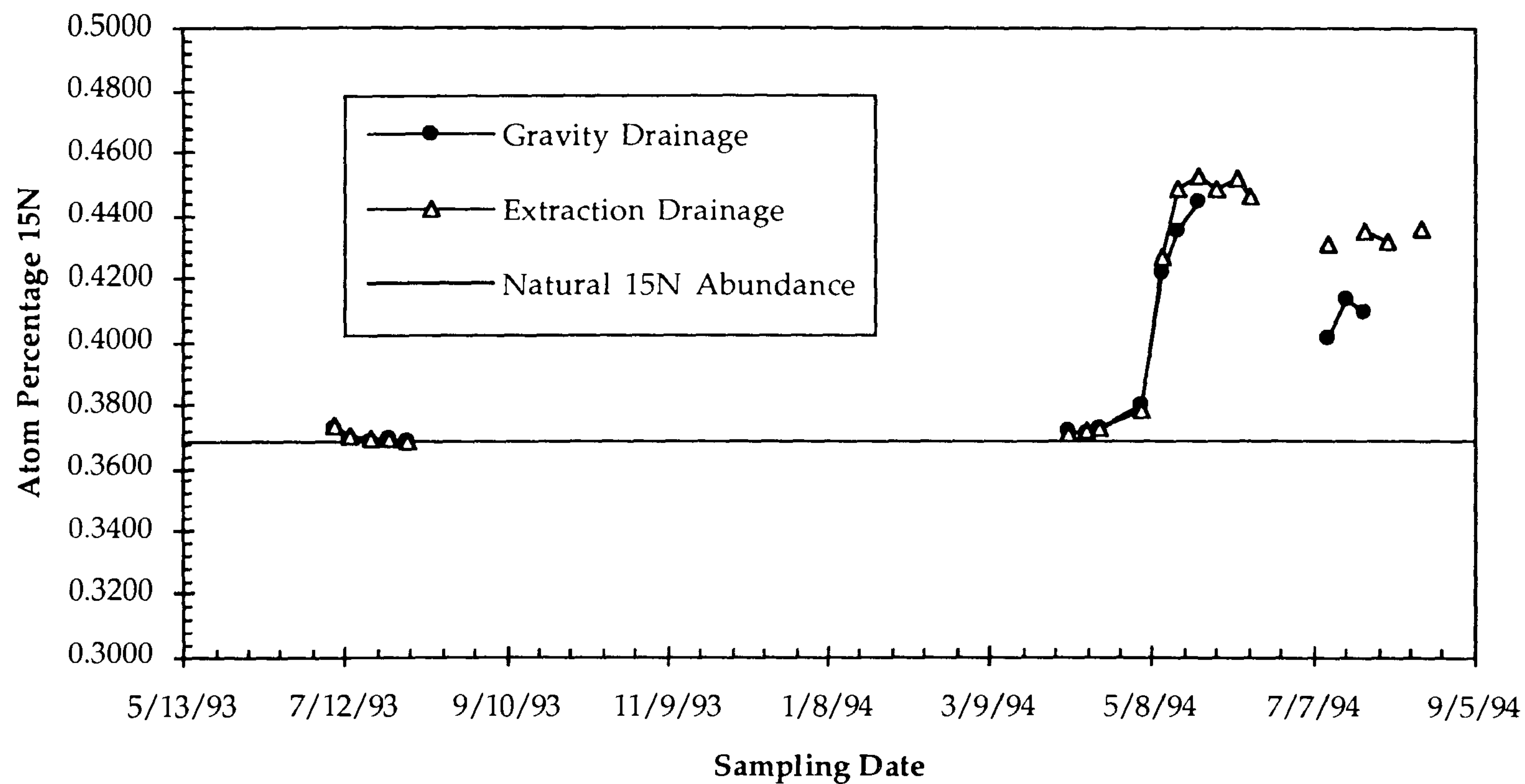


Figure 7. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #3 located in the NW quadrant. Urea-N applied June 29, 1993.

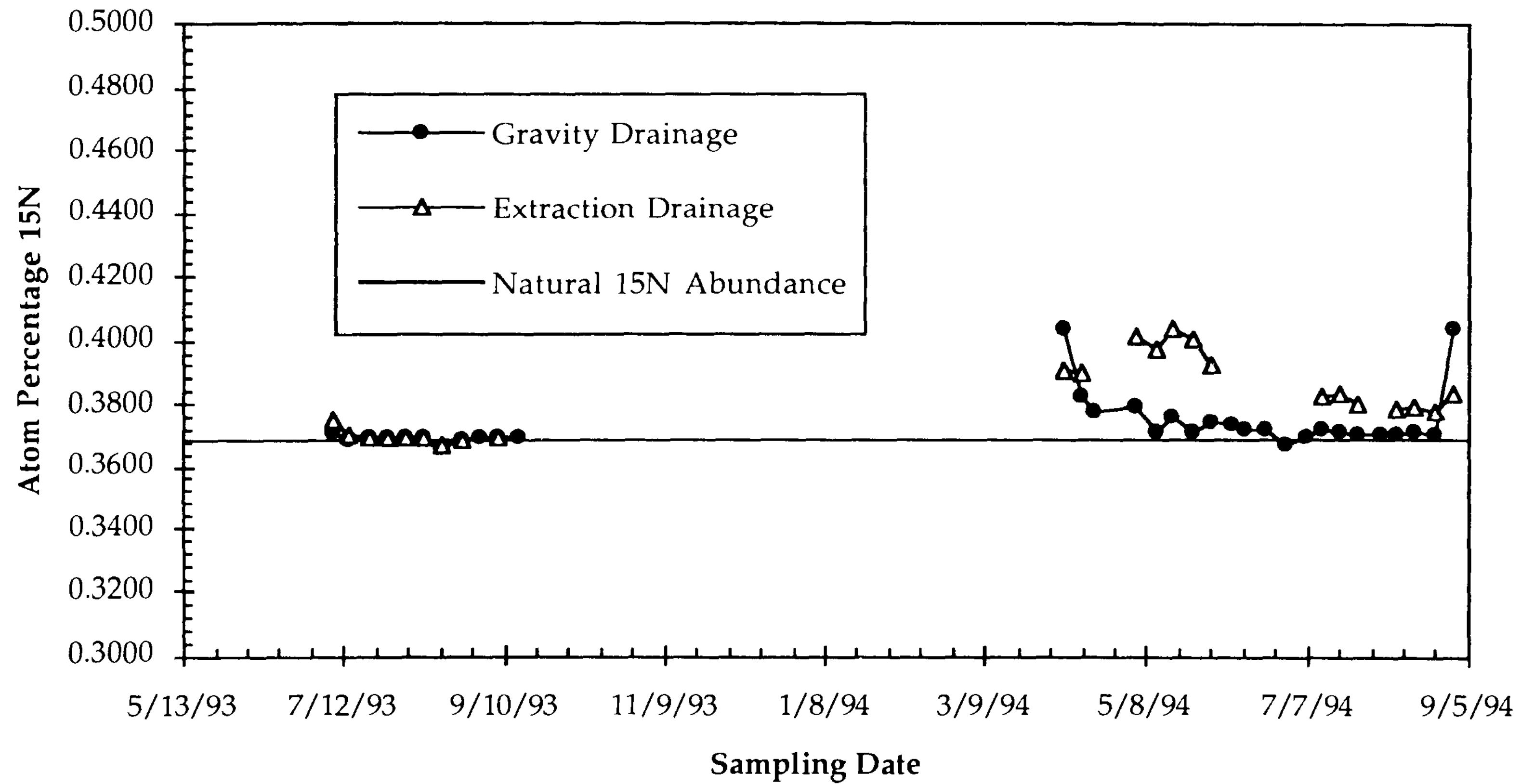


Figure 8. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #4 located in the NW quadrant. Urea-N applied June 29, 1993.

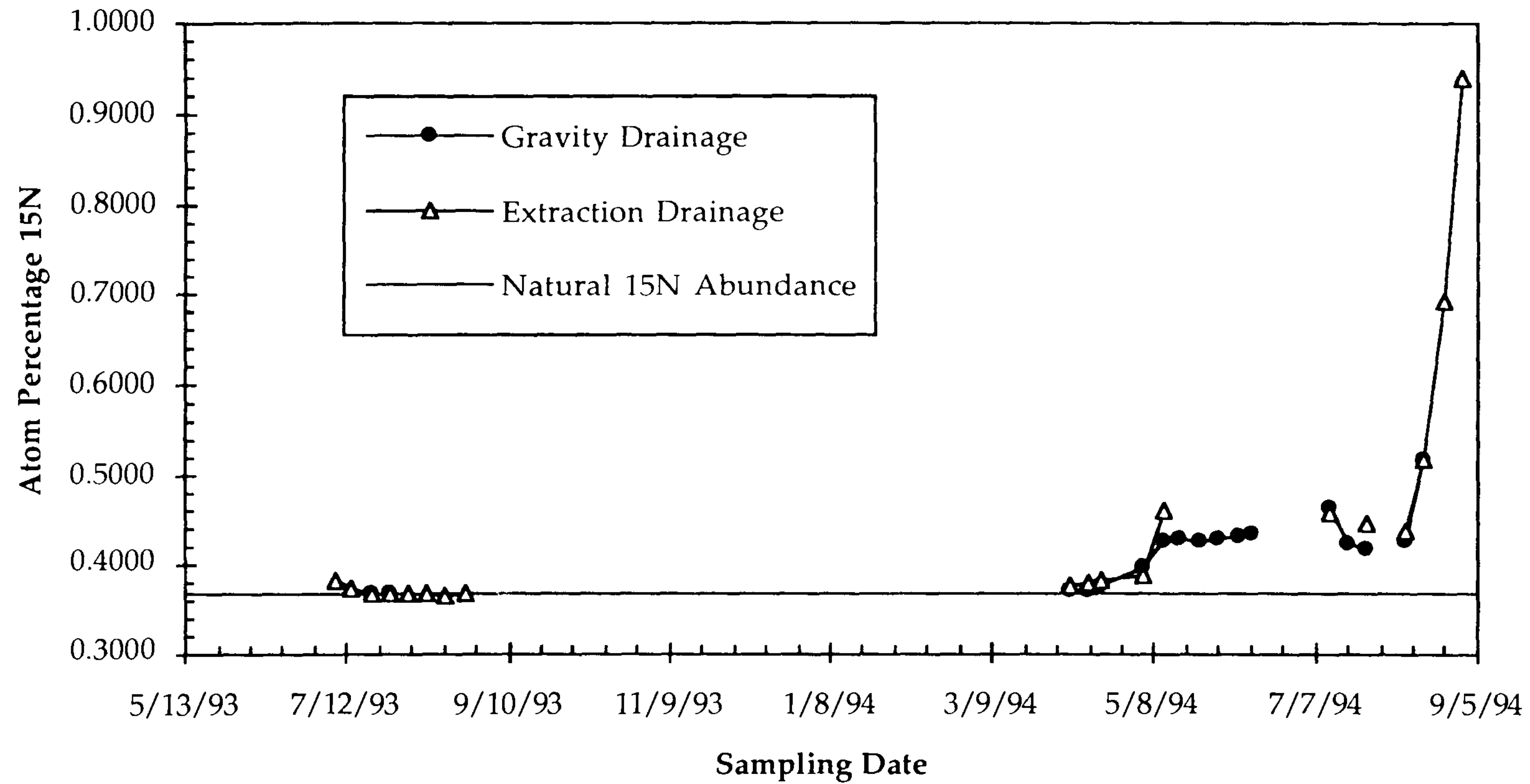


Figure 9. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #5 located in the NE quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

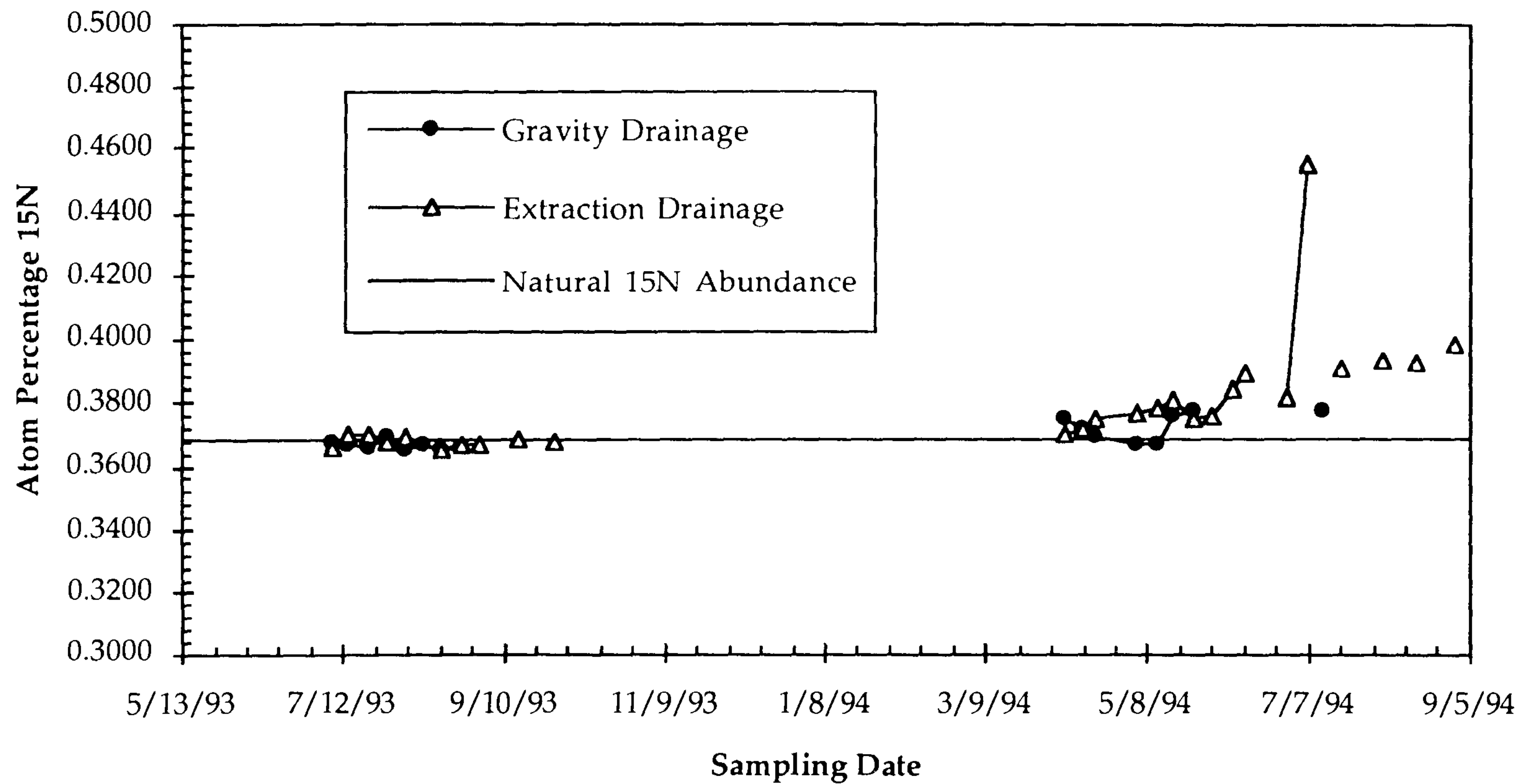


Figure 10. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #6 located in the NE quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

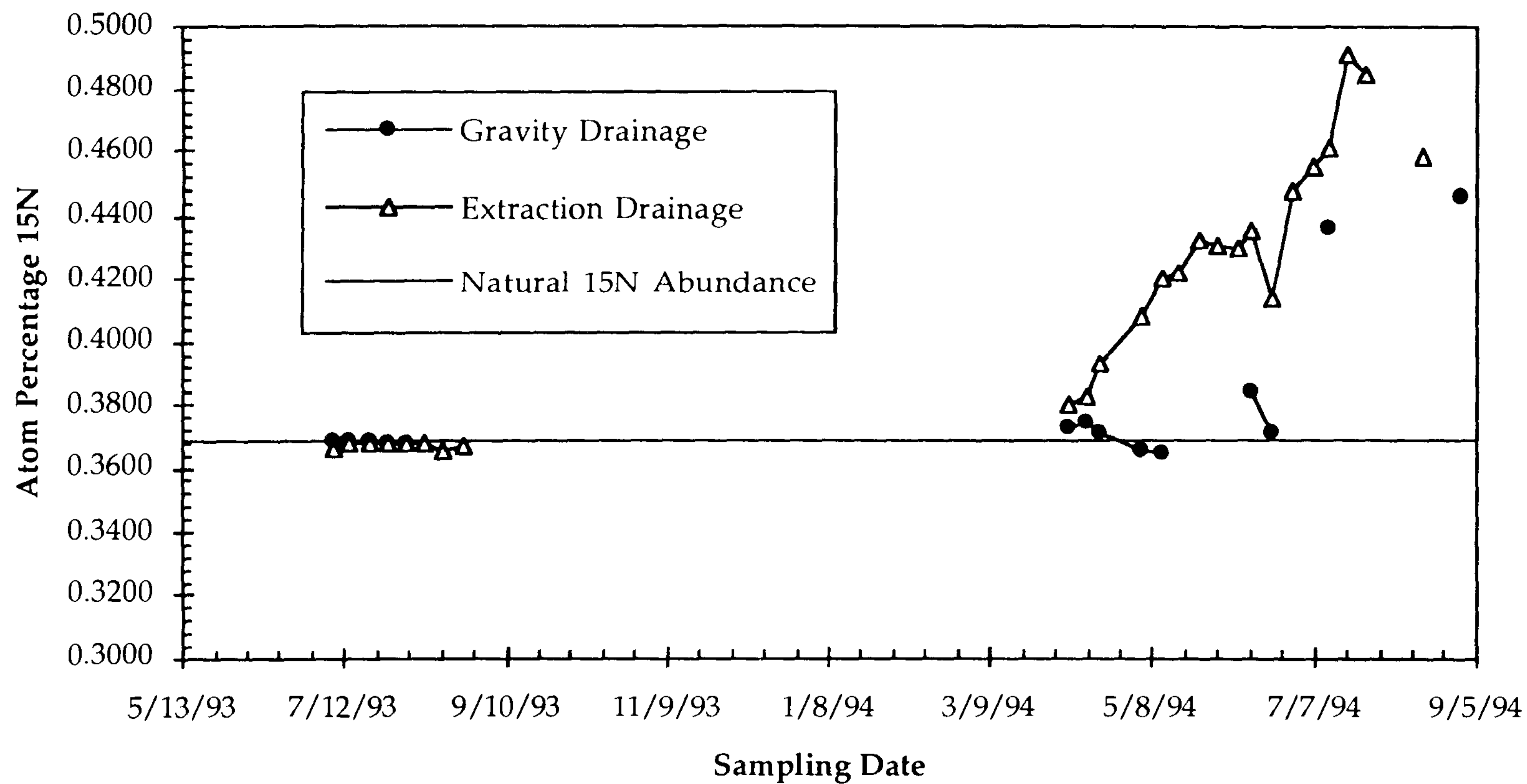


Figure 11. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #7 located in the NE quadrant. Urea-N applied June 29, 1993.

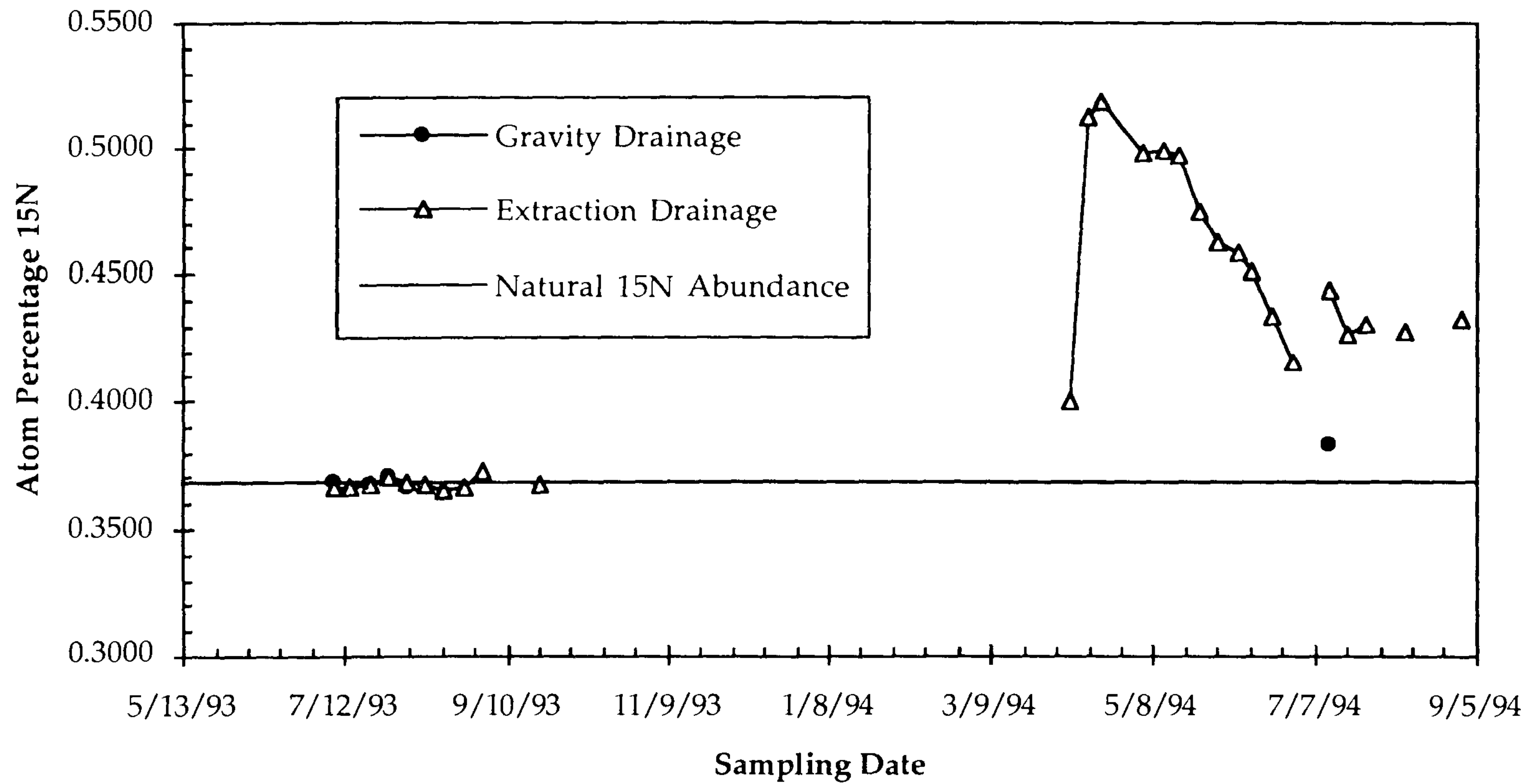


Figure 12. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #8 located in the NE quadrant. Urea-N applied June 29, 1993.

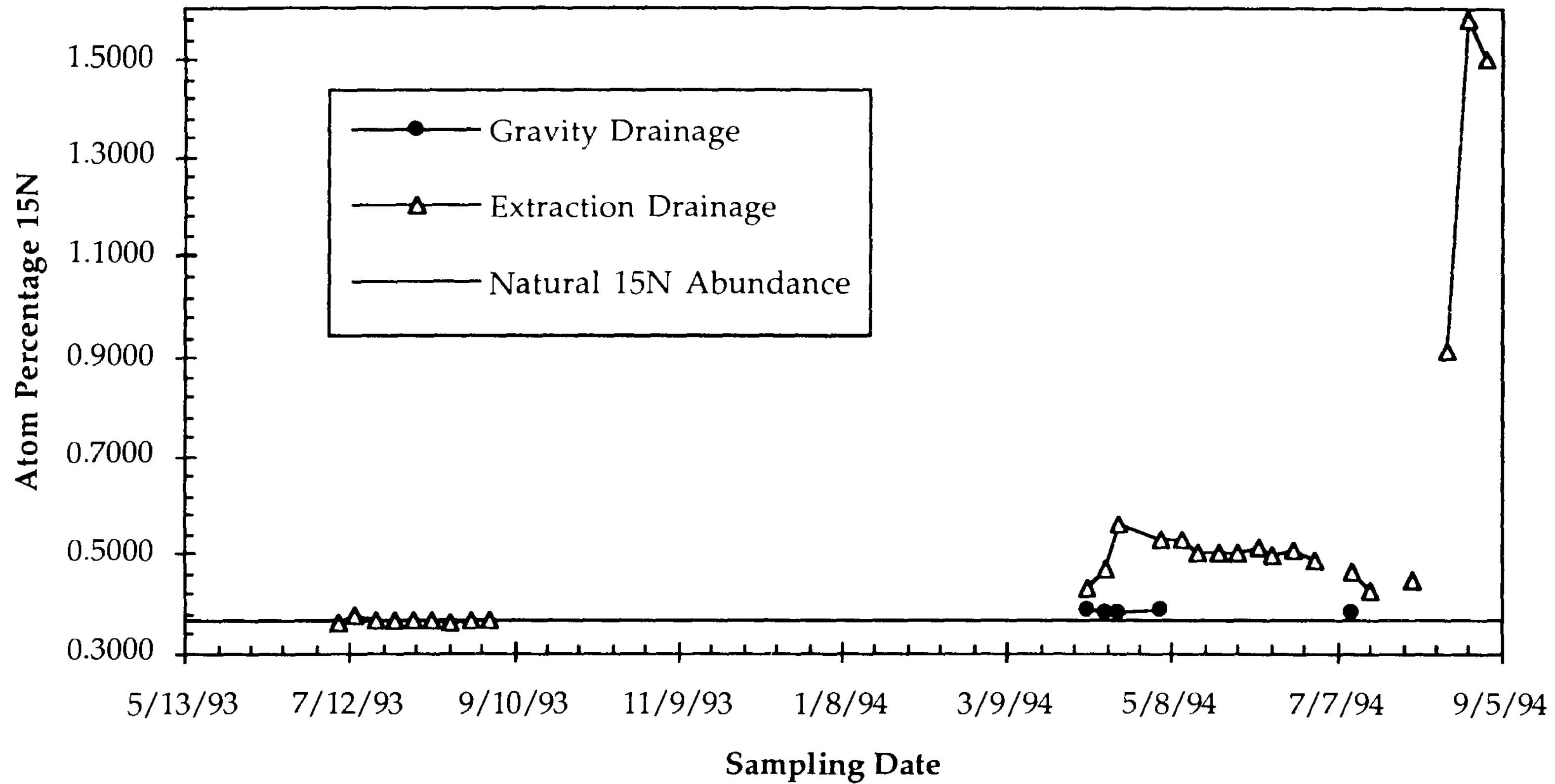


Figure 13. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #9 located in the SE quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

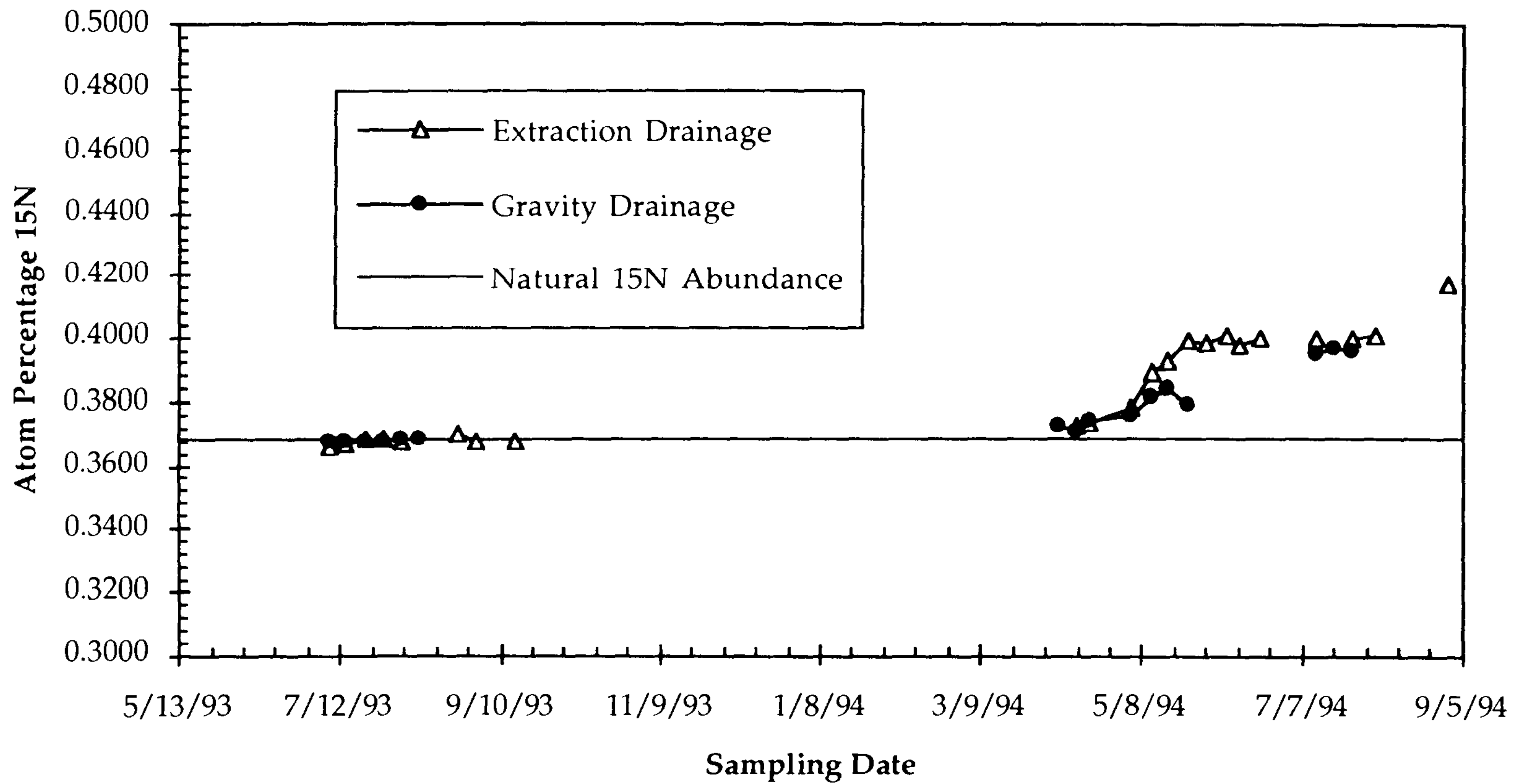


Figure 14. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #10 located in the SE quadrant. Urea-N applied June 29, 1993.

Figure 15. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #11 located in the SE quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

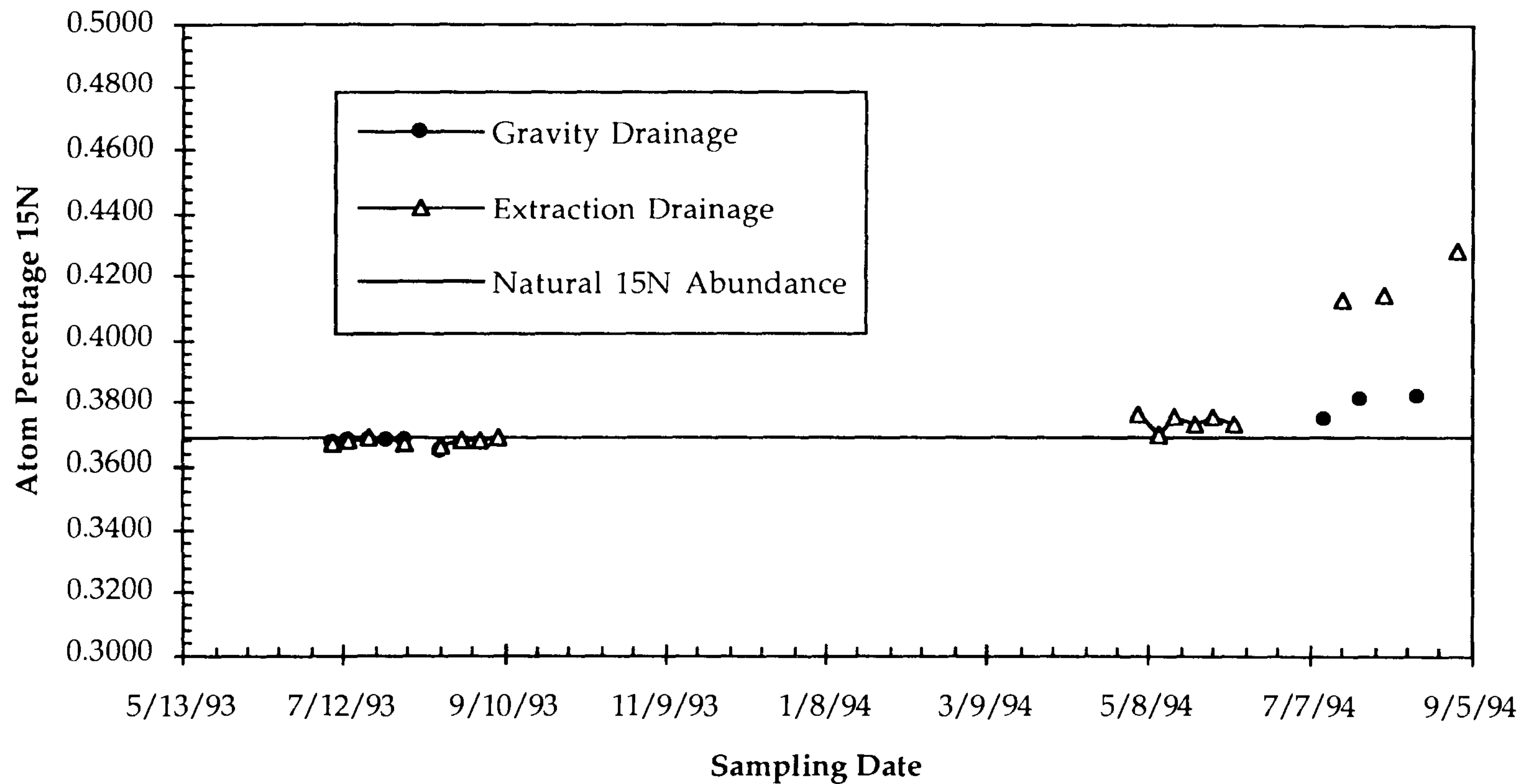


Figure 16. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #12 located in the SE quadrant. Urea-N applied June 29, 1993.

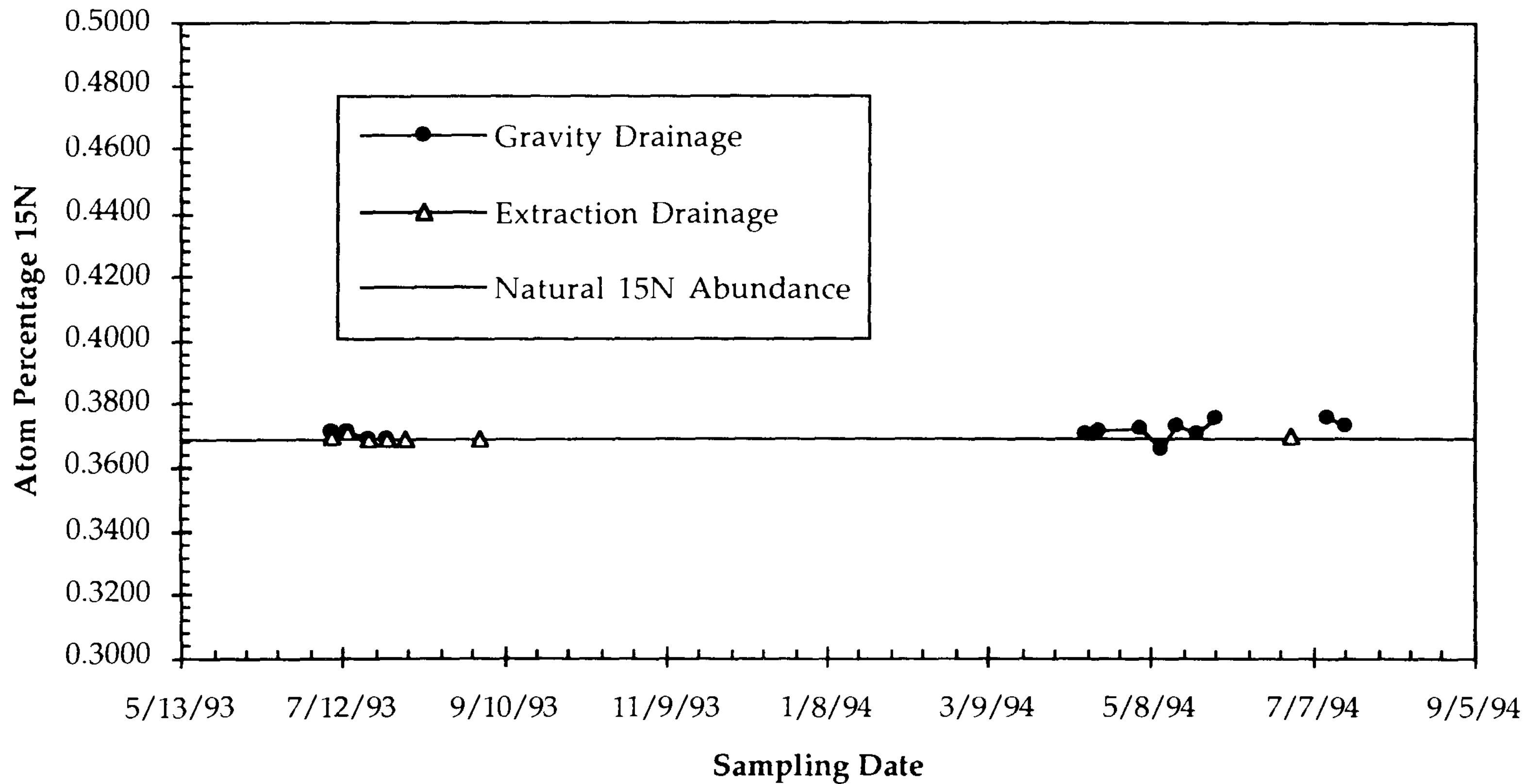


Figure 17. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #13 located in the SW quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

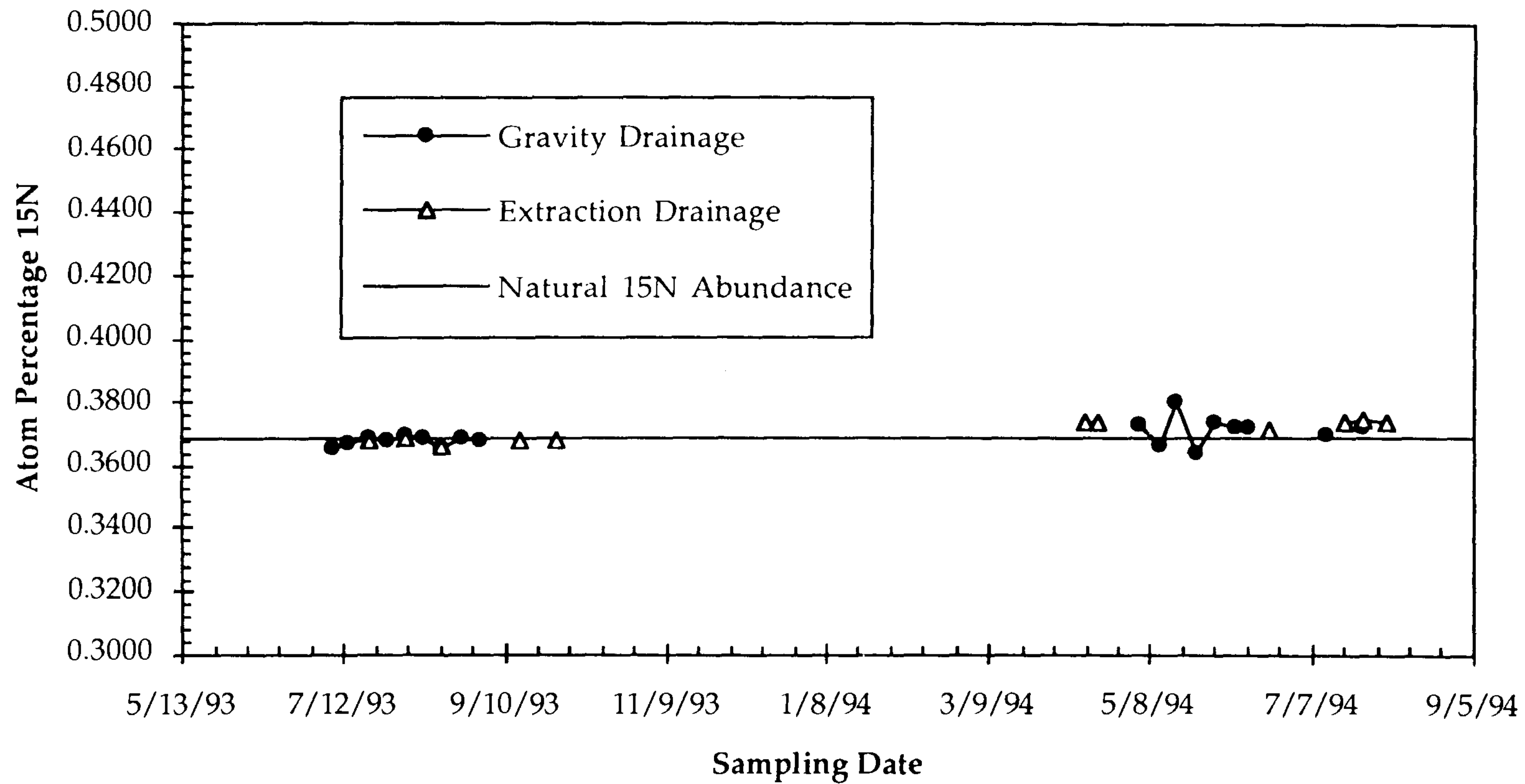


Figure 18. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #14 located in the SW quadrant. Urea-N applied June 29, 1993.

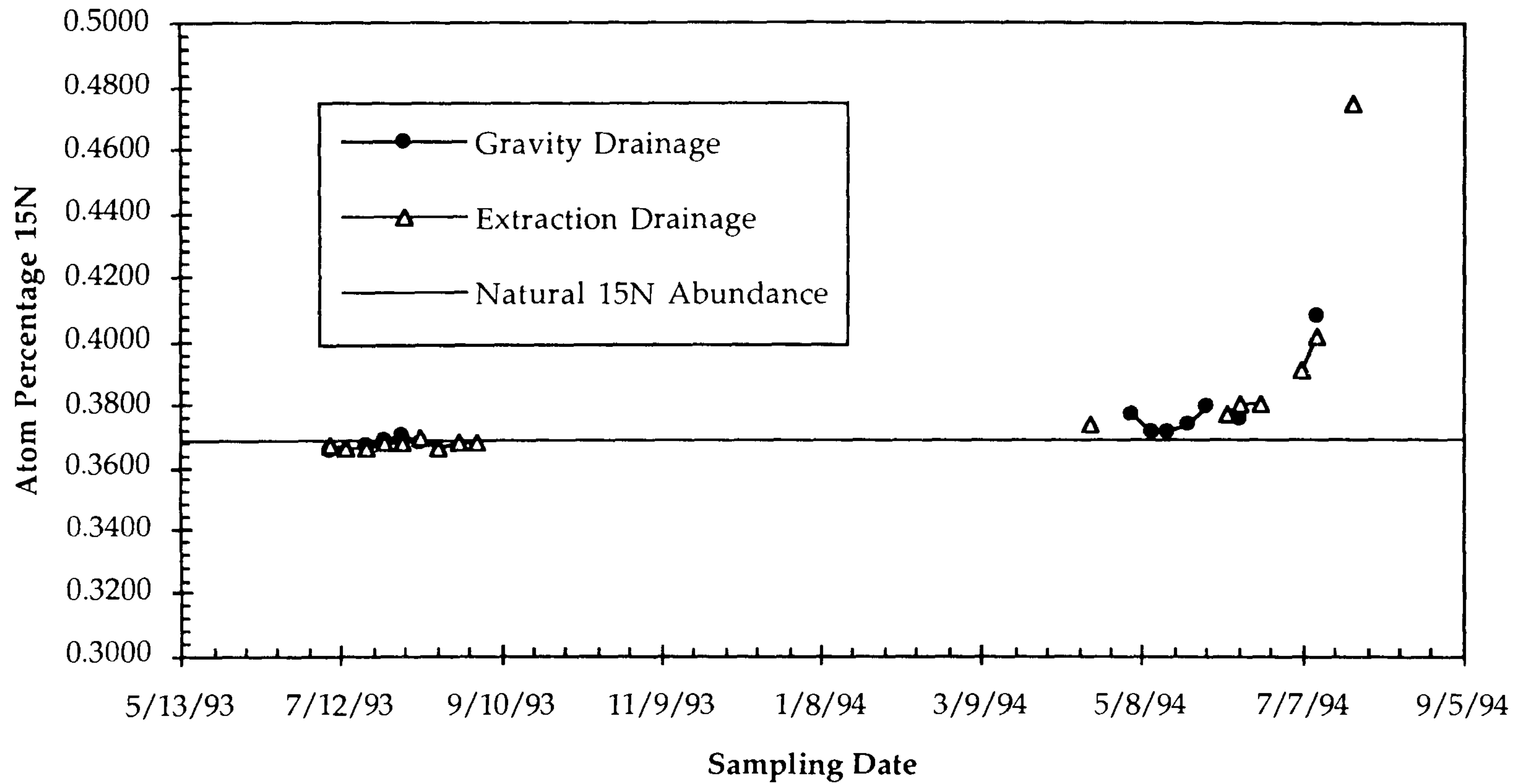


Figure 19. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #15 located in the SW quadrant. Urea-N applied June 29, 1993.

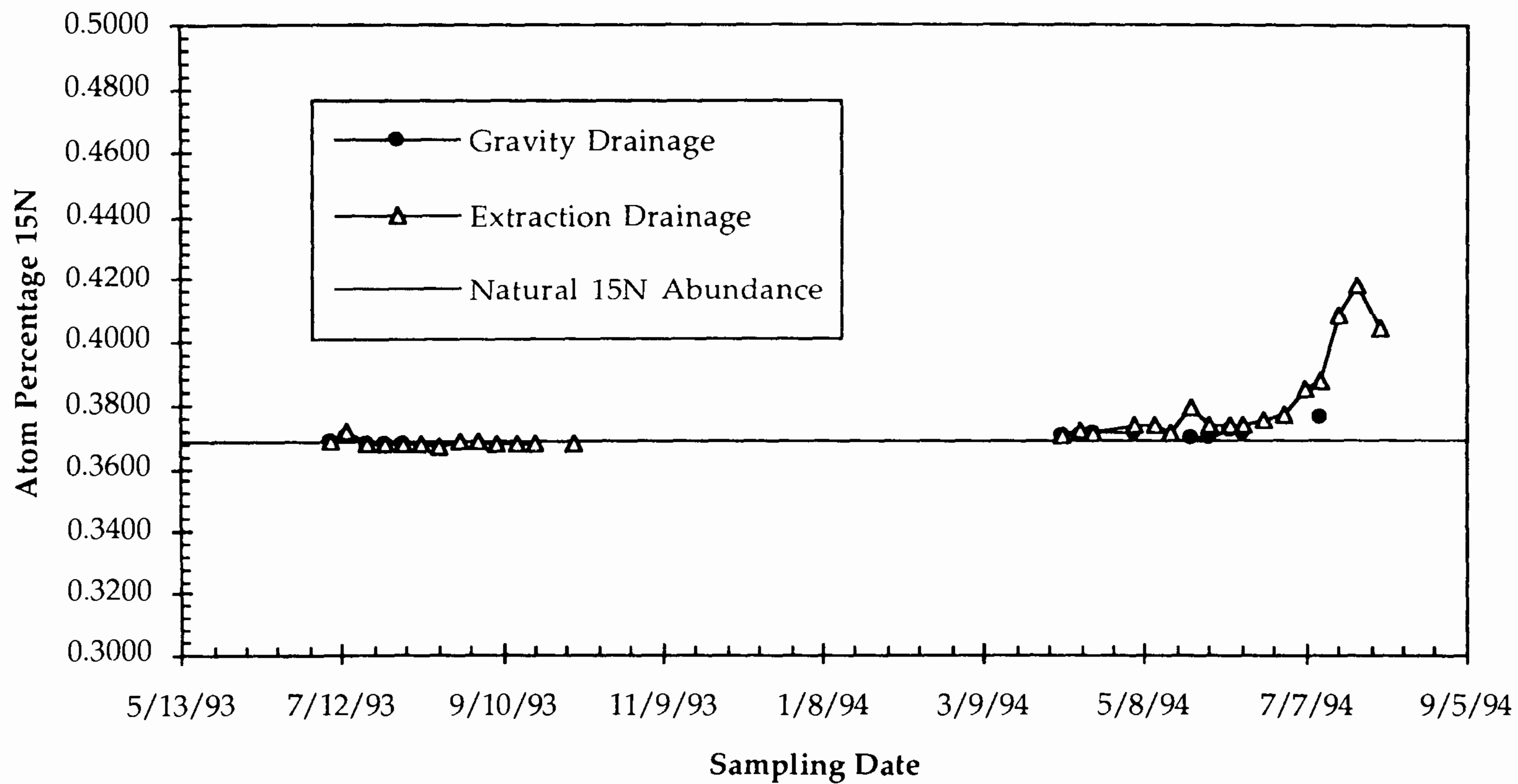


Figure 20. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #16 located in the SW quadrant. Urea-N applied June 29, 1993, and June 13, 1994.

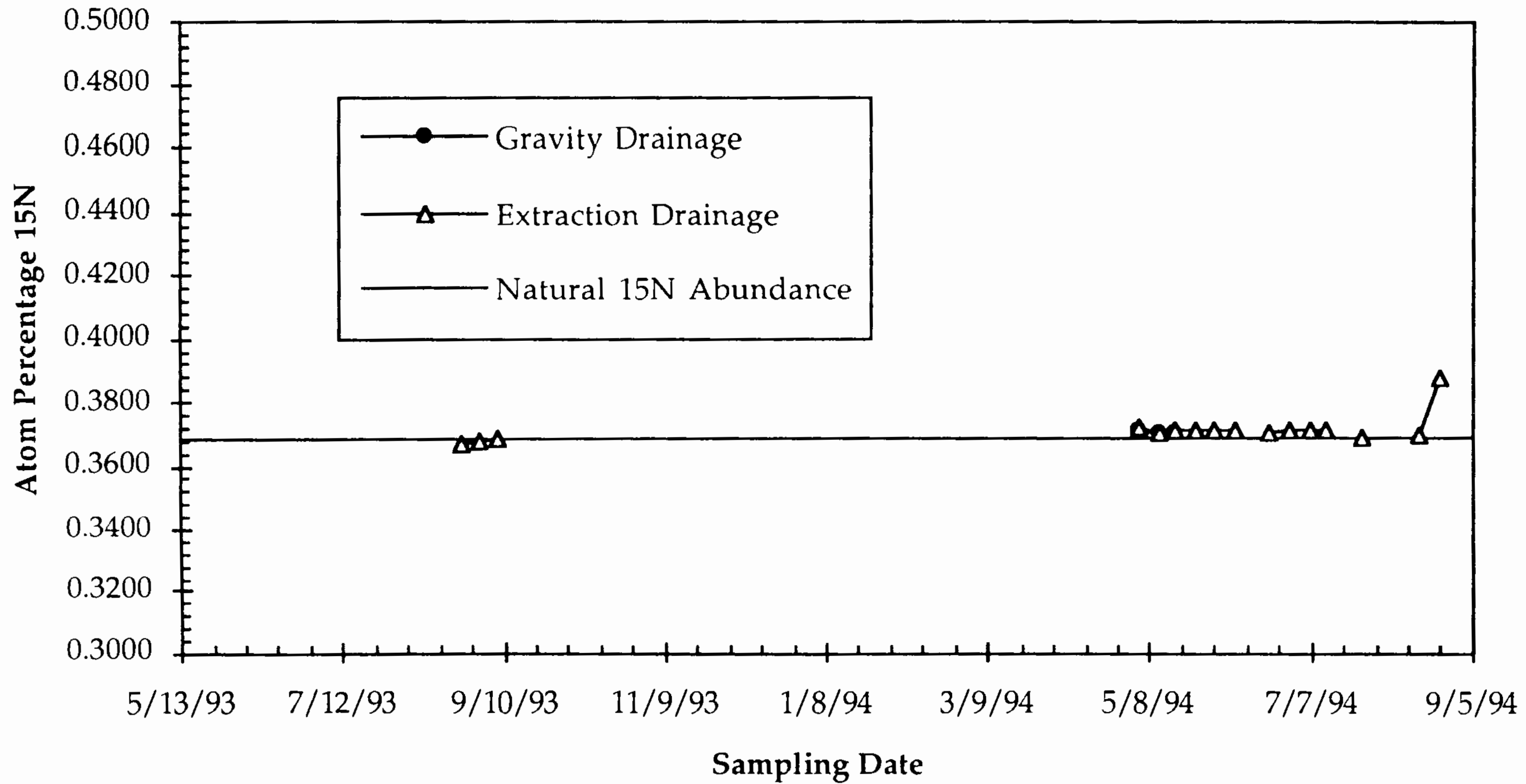


Figure 21. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #17 located in the dryland area. Urea-N applied June 29, 1993, and June 13, 1994.

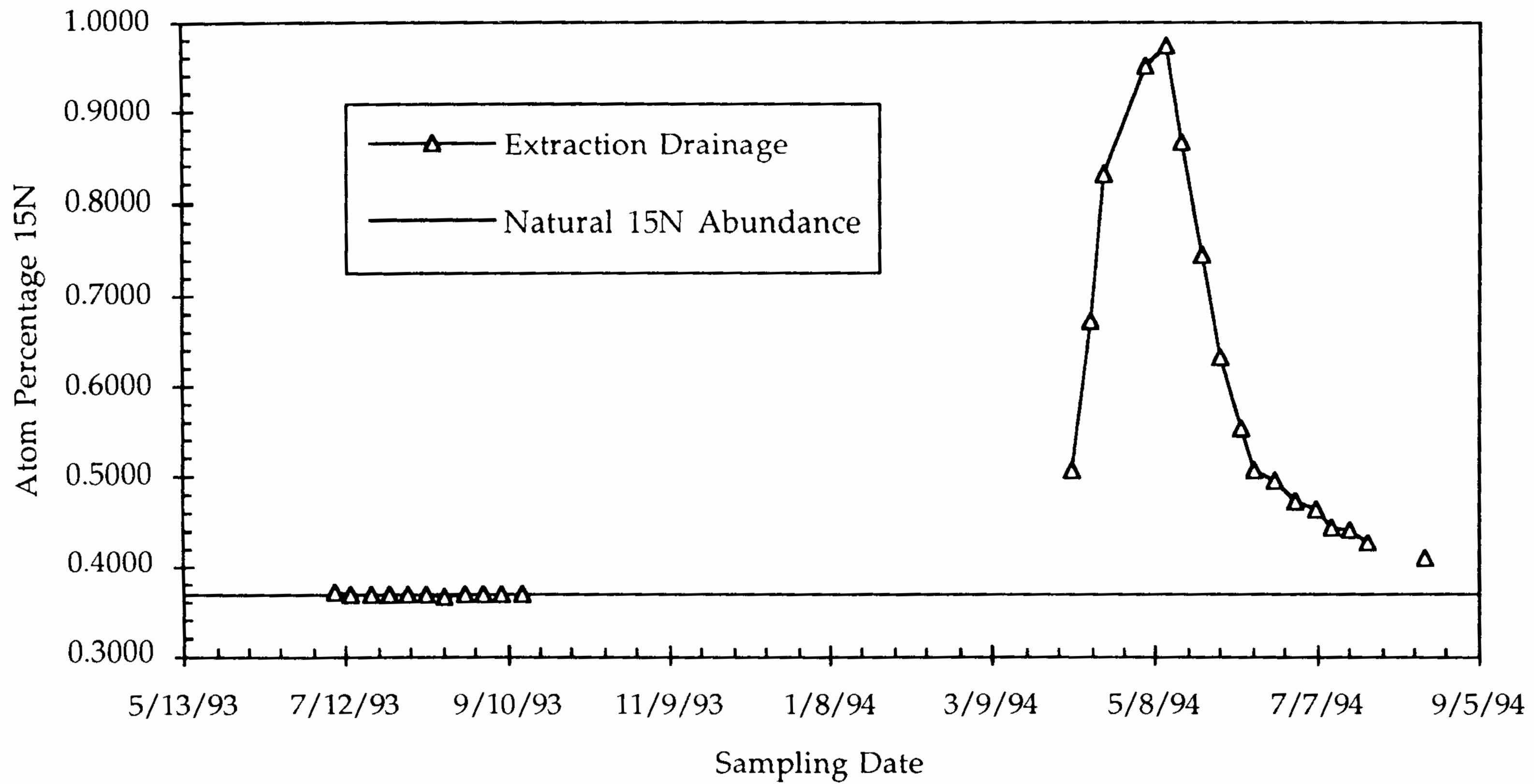


Figure 22. Atom percentage ^{15}N of extraction drainage versus time for lysimeter #18 located in the dryland area. Urea-N applied June 29, 1993.

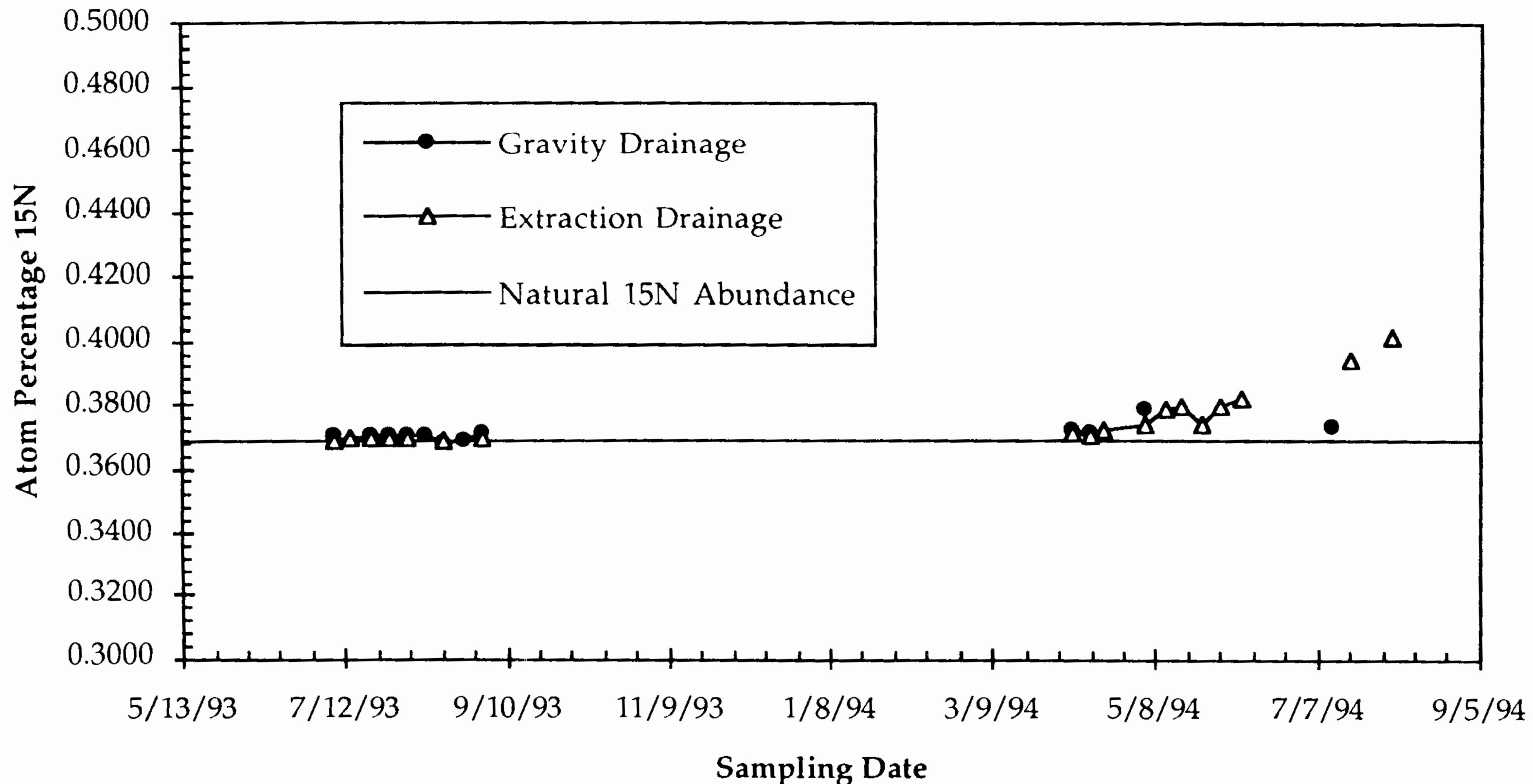


Figure 23. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #19 located in the dryland area. Urea-N applied June 29, 1993, and June 13, 1994.

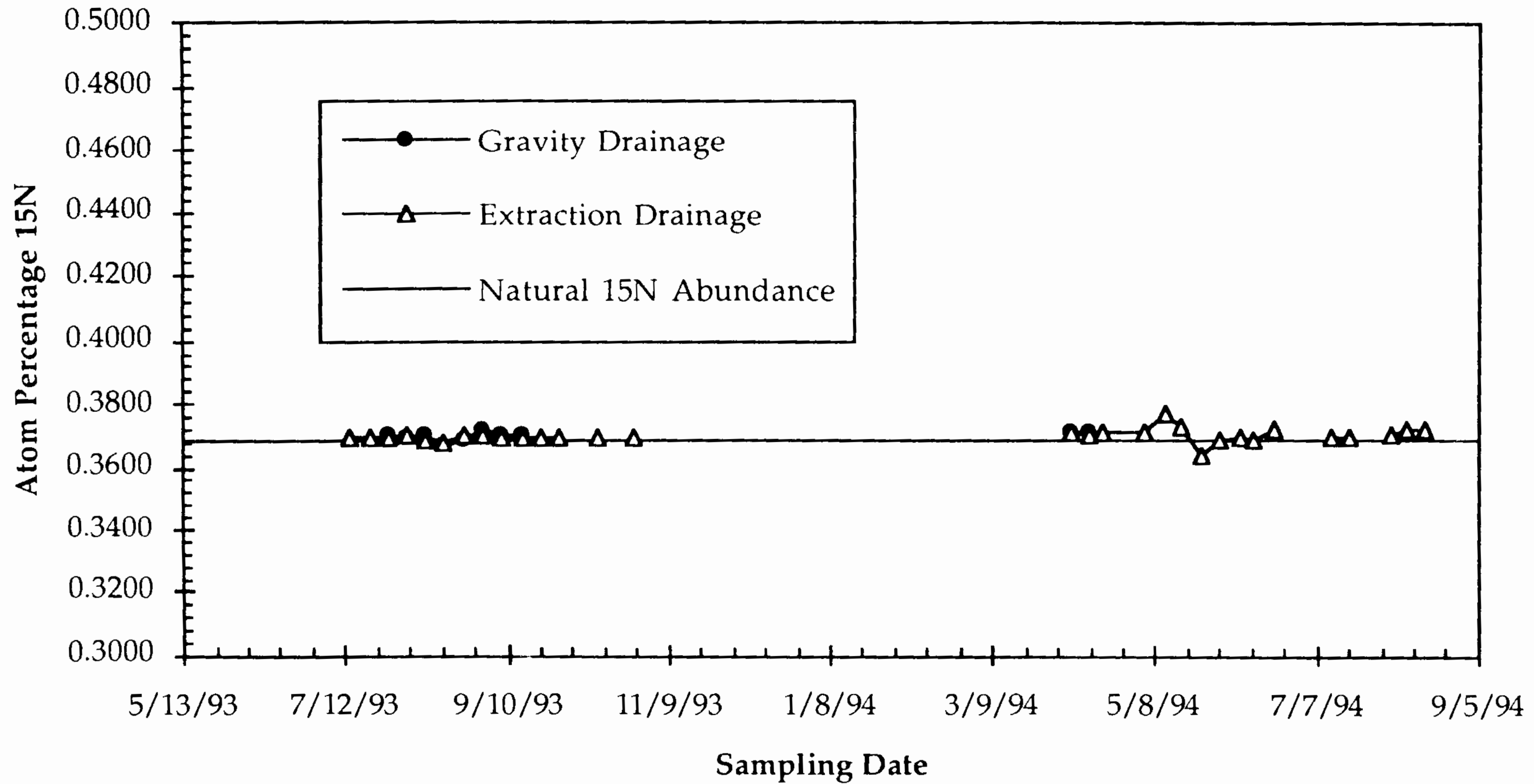


Figure 24. Atom percentage ^{15}N of extraction and gravity drainage versus time for lysimeter #20 located in the dryland area. Urea-N applied June 29, 1993.

both the gravity and extraction drainage within the last week of June and first week of July, 1994. A similar occurrence can be seen with the gravity drainage of lysimeter 7 (Fig. 11) in which ^{15}N concentrations began increasing around mid June of 1994. Lysimeters 2, 5, 10, and 11, Figures 6, 9, 14, and 15, respectively, began showing ^{15}N concentrations in both the gravity and extraction drainage during the end of April and first part of May, 1994. Similarly, lysimeters 6, 9, and 19, Figures 10, 13, and 23, respectively, began showing elevated ^{15}N concentrations in just the extraction drainage.

The peak concentrations of ^{15}N are also variable among the undisturbed lysimeters. For instance, lysimeter 18 (Fig. 22) had a peak concentration of nearly 1.0 at. % ^{15}N, while lysimeters 19 and 20, lysimeters directly adjacent to lysimeter 18, exhibited ^{15}N peak concentrations of only 0.402 and 0.377 at. %, respectively. Likewise, lysimeter 8 depicts a peak ^{15}N concentration of 0.5185 at. % while lysimeter 12 (Fig. 16) depicts a peak ^{15}N concentration of 0.4282 at. %.

The peak concentration differences and differences in residence times can be most easily explained by the preferential or bypass flow phenomena in which the enriched material bypasses part of the soil mass and travels much more quickly to the drainage resevoir (Rice et al., 1991; Steenhuis et al., 1990; Richard and Steenhuis, 1988). This type of flow pattern is best demonstrated by lysimeter numbers 2, 5, 6, and 9 in which a bi-modal distribution of ^{15}N mass appears indicating two distinct flow regimes. Bypass flow has traditionally been thought to occur only in soil matrices possessing a greater distribution of macropores, i.e., soils possessing a greater percentage of silt and clay size particles. However, research indicates that preferential flow pathways can and do exist in uniform, sandy soil (Rice et al., 1991; DeSmedt et al., 1986; DeSmedt and Wierenga, 1984). The remaining lysimeters, especially lysimeter 3,

demonstrate a more homogeneous flow pattern indicative of the traditional diffuse (Darcy) flow models, i.e., models based on convection and dispersion processes.

The 1993 2.0 at. % ^{15}N application had not been detected by March 1994. For fear that the 1993 urea-N application was too low an enrichment, another was applied in 1994. This application was to alleviate the potential of isotopic dillution and insure detection of ^{15}N in the drainage effluent. Urea-N was applied in 1994 to ten randomly selected lysimeters and the first corn row of the E-transect. The enrichment of this application was 5.934 at. % ^{15}N.

Lysimeters 2, 5, and 9 were three of the ten lysimeters to receive this application. On July 7, 1994, the BMP quarter received 9.53 cm of precipitation over a two-day period. These lysimeters, having faster breakthrough and possibly preferential pathways, experienced a second, large elevation of ^{15}N at the end of August (Figs. 6, 9, and 13, respectively). When the BMP quarter received this intense precipitation event, $^{15}NO_3$-N was possibly transported via preferential pathways directly to the drainage reservoir within a residence time of approximately two months. This same phenomenon is seen with lysimeter 17; however, it is the first detection in this lysimeter (Fig. 21).

Lysimeters 4 and 8 did not receive the 1994 urea-N application, but yet exhibited primary and secondary ^{15}N elevated concentrations (Figs. 8 and 12, respectively). The first increase in concentrations is from the spring thaw and recharge events of 1994. The increased concentrations associated with lysimeters 2, 5, and 9 are most probably the direct result of the early July 1994 precipitation event and the additional ^{15}N fertilization. It is presumed that, since the increased secondary ^{15}N concentrations of lysimeters 2, 5, and 9 are of such magnitude, e.g., 1.5 at. %, they could not have possibly come from the 2.0 at. % ^{15}N application of 1993.

Lysimeters 4, 7, 9, and 12 exhibited large differences in ^{15}N concentrations between the gravity and extraction drainage. Lysimeter 4 had a cumulative gravity and extraction drainage for Mar. 7 through Aug. 30, 1994, of 765.7 and 125.0 mm, respectively. Conversely, lysimeters 7, 9, and 12 had a cumulative gravity and extraction drainage of 67.4, 256.9, 41.2, 459.6, 34.9, and 92.3 mm, respectively. Lysimeters 7, 9, and 12 had substantially greater extraction drainage and, consequently, greater ^{15}N concentrations. However, lysimeter 4 had approximately 6x as much gravity as extraction drainage and still exhibited higher ^{15}N concentrations in the extraction drainage. Therefore, data generated from lysimeter 4 may be suspect.

Differences in microbial activity among the undisturbed lysimeters may effect these concentration differences. For instance, research indicates that through anaerobic microbial discrimination of the lighter ^{14}N isotope, reactants of the denitrification or dissimilatory nitrate reduction reaction (NO_3^-) tend to become enriched while the products (N_2 and N_2O) become depleted in ^{15}N (Kaplan, 1983; Heaton, 1986; Hauck, 1973). This reaction is generally thought to occur beneath the water table under oxygen-deficient conditions, but research indicates that denitrification can progress in aerobic environments possessing O_2 concentrations ranging from 2 to 7 mg O_2 L^{-1} (Braun, 1991).

Biological interchange is the process in which labeled ions or molecules are fortuitously replaced with unlabeled ions or molecules (or vice versa) by means of microbial synthesis or decomposition. This process may help to explain the reason for the variations in ^{15}N concentrations. For instance, lysimeter 18 may possess higher concentrations of $^{15}NO_3^-$-N than lysimeter 19 because fewer of the ^{15}N atoms were transpositioned into the organic fraction through immobilization. Likewise, lysimeter 19 may have lower concentrations of $^{15}NO_3^-$-N than lysimeter 18 because more of the ^{15}N atoms

were transpositioned into the organic fraction through immobilization. Since no attempt was made to separate the drainage samples into their respective N fractions, i.e., organic and inorganic N, it is difficult to make inferences regarding the extent of ^{15}N transpositioning between the microbial assimilation and mineralization processes.

The influence of biological discrimination and interchange is more predominant in studies involving natural ^{15}N abundance, i.e., studies that investigate delta ^{15}N. Since this study involved an ^{15}N-enriched fertilizer application, contributions of the biological discrimination and interchange processes, although very likely contributing to the observed concentration differences, are masked and therefore are impossible to quantify (Hauck and Bremner, 1976).

Figure 25 shows NO_3^--N concentrations and atom percentage ^{15}N over time for tile drain number 3 (T03). On Aug. 24, 1994, tile drain effluent showed a maximum ^{15}N elevation of 0.4871 at. % (Table E2). This breakthrough occurred approximately 2 to 3 months later than the average breakthrough of 11.7 months reported for the undisturbed lysimeters. The increase in concentration occurred at precisely the same time as the increased secondary ^{15}N concentrations of lysimeters 2, 4, 5, and 9. Presumably, this is the result of the July 7-8, 1994, rainfall event since tile line T03 runs directly below the first corn row of the E-transect (^{15}N applied June 13, 1994). However, since lysimeters 4 and 8 experienced increased secondary ^{15}N concentrations, residence time of $^{15}NO_3$-N to the tile line could be 14 months.

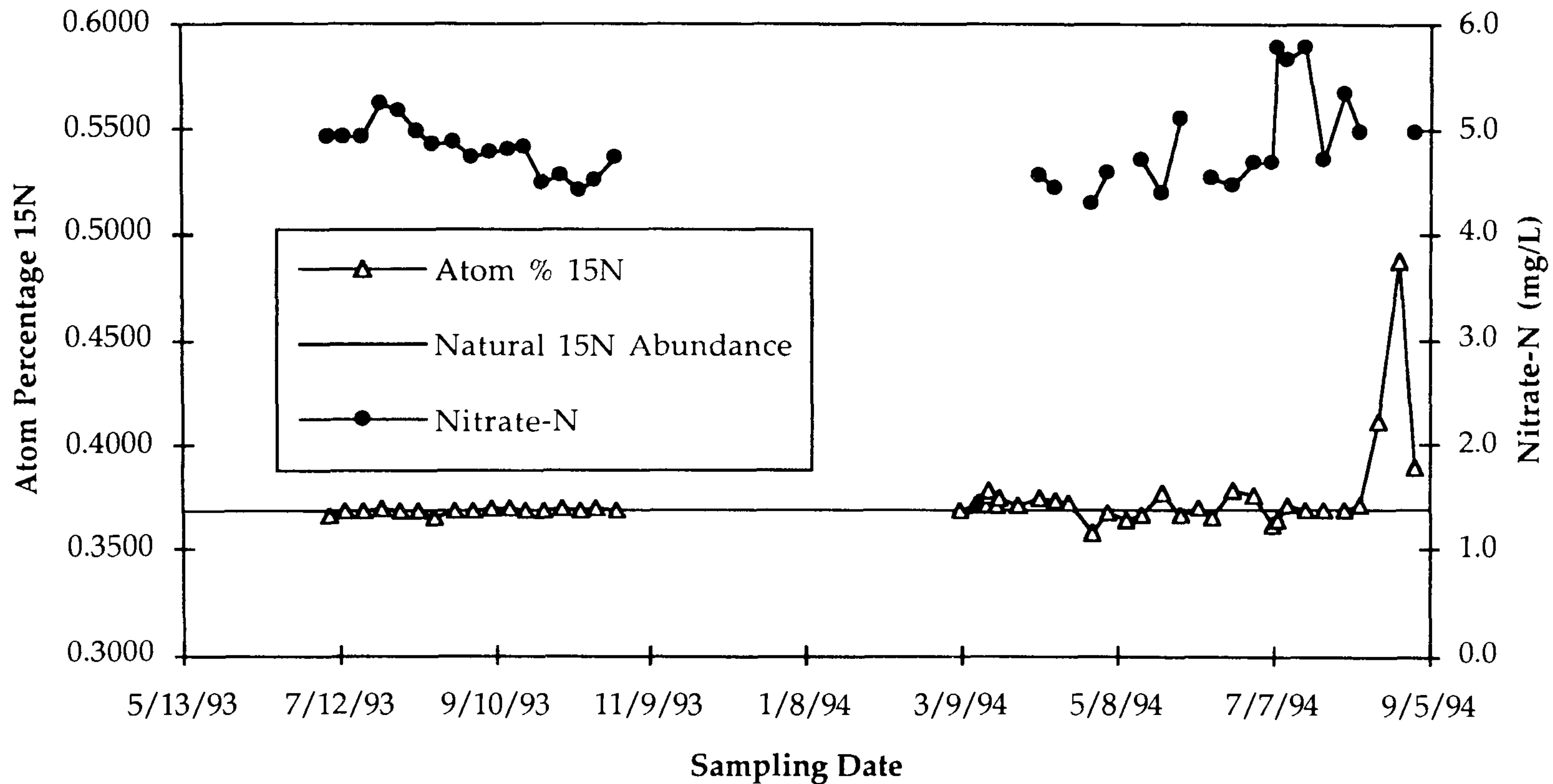


Figure 25. Nitrate-N concentration and atom percentage ^{15}N versus time for tile drain T03 located in the SE quadrant.

Under "normal" growing conditions at the BMP site, i.e., growing seasons that experience infrequent, low-intensity precipitation events, residence times of applied N are approximately 10-13 months (Prunty and Montgomery, 1991). However, with the presence of preferential pathways, high intensity rainfalls can expedite solute transport times. In this study, residence times for the 1993 urea-N application agreed with Prunty and Montgomery (1990) in that a lag of 10-13 months must elapse before detection of surface-applied N at depths equivalent to drains in the undisturbed lysimeters (approximately 188 cm). Data indicate that preferential pathways coupled with the high intensity rainfall event of June 7-8, 1994, caused secondary ^{15}N elevations among several undisturbed lysimeters and possibly tile drain T03.

Nitrate-N concentrations of tile drain T03 ranged from 4.3 to 5.79 mg L^{-1} (Table E2). Nitrate-N showed a decreasing trend from July 1 through October of 1993 and an increasing trend from April through August of 1994 (Fig. 25). The decreasing trend in NO_3^--N is probably due to decreased flows, allowing longer residence time in tile drain for denitrification or immobilization. There appears to be variability in the NO_3^--N and atom percentage ^{15}N levels starting at spring recharge. The time of these variations coincide with the initial breakthrough times dipicted in many of the undisturbed lysimeters and may be the result of spatial variability. Grab samples taken from the T03 manhole represent the ^{15}N concentrations of the entire SE quadrant rather than the area directly below the established 1993 N plots (Richard and Steenhuis, 1988). The increase in NO_3^--N concentrations and atom percentage ^{15}N is presumably a result of the July 7-8, 1994, precipitation event.

Figure 25 seems to indicate a negative correlation between ^{15}N and NO_3-N concentrations from approximately May 1 through July 7, 1994. That is, as the NO_3-N increased, the ^{15}N concentrations decreased. This phenomenon is

presumably real and not coincidental since the NO_3-N was determined by the U.S. Bureau of Reclamation laboratory at Bismarck, North Dakota, and the ^{15}N values were determined by Isotope Services, Inc. This could be interpreted as leached NO_3-N with slightly lower natural ^{15}N concentrations diluting the residual NO_3-N of slightly higher ^{15}N enrichment. However, it is very difficult to draw conclusions. There was no control established nor was there any attempt to determine the potential of denitrification (Edwards, 1973).

Plant Uptake of Sidedressed ^{15}N-Enriched Urea-N

The 1993 and 1994 growing seasons differed considerably. The growing degree unit (GDU) accumulations in the Oakes area were 11% below the long-term average (1960-1990) for 1993 and were 5.3% above the long-term average for 1994 (Steele et al., 1993). In addition, the 1993 growing season had an average irrigation plus total rainfall of 50 cm, whereas in 1994, the average irrigation plus total rainfall was 48.9 cm (Steele et al., 1993). Corn plants were harvested on Sept. 25, 1993. The temperature Sept. 18, 1993, dropped to -1.1°C (30°F) which forced physiological maturity of the corn plants. Conversely, freezing temperatures did not occur before plant harvest in 1994, thus allowing the plants to dry "normally" in the field and thereby assimilate more soil N. The cooler, wetter season of 1993 hindered corn growth and production and resulted in lower plant N uptake and dry matter yields (Tables 1 and 2, respectively).

Table 3 depicts the fraction of total N in the grain, cob, and stover (+ adventitious roots) portions of the aboveground plant materials derived from labeled and non-labeled N for the 1993 and 1994 growing seasons. The values

Table 1. Average plant nitrogen content (kg ha^{-1}) of aboveground plant parts at the end of the 1993 and 1994 growing seasons

	Plant N*					
	Grain		Stover		Cob	
N Plots	1993	1994	1993	1994	1993	1994
	--------kg ha^{-1}--------					
Labeled and Unlabeled†	88a	162b	35c	41d	4.4e	3.8
Checks A and B†	52a	143b	19c	30d	2.6e	3.7

† Average value of eight replicates.

* Mean values between years are significant at $\alpha = 0.05$. P-values < 0.023.
Mean values followed by a common letter are significant at $\alpha = 0.01$. p-values < 0.0037.

Table 2. Average dry matter yield (kg ha^{-1}) of aboveground plant parts at the end of the 1993 and 1994 growing seasons

	Dry matter*					
	Grain		Stover		Cob	
Treatment	1993	1994	1993	1994	1993	1994
	--------kg ha^{-1}--------					
Labeled and Unlabeled†	5,791a	11,765b	4,933c	6,621d	1,236e	1,589f
Checks A and B†	4,327a	11,428b	4,217c	6,018d	814e	1,496f

† Average value of eight replicates.

* Mean values between years are significant at $\alpha = 0.05$. P-values < 3.6×10^{-6}.
Mean values followed by a common letter are significant at $\alpha = 0.05$. p-values ≤ 0.01.

Table 3. Fertilizer N recovery in grain, cob, and stover (+ adventitious roots) portions derived from isotopic N (direct method, Eqn. 8) and the difference in fertilized and non-fertilized treatments (indirect method, Eqn. 7) at the end of the 1993 and 1994 growing seasons

	Fertilizer N Recovery‡															
	Grain				Cob				Stover				Total			
N	Direct		Indirect		Direct		Indirect		Direct		Indirect		Direct		Indirect	
Plots†	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)
	%															
Rep 1	30.53	39.50	28.74	15.93	1.45	0.63	1.86	0.05	12.35	9.44	8.07	12.31	44.33	49.57	38.67	28.29
Rep 2	33.82	24.77	23.84	11.27	1.53	0.62	1.04	0.12	12.22	4.35	15.11	4.02	47.57	29.74	39.99	15.41
Rep 3	31.25	31.14	24.53	14.06	1.88	0.68	1.26	0.03	12.66	5.92	12.88	7.39	45.79	37.74	38.67	21.48
Rep 4	29.93	33.53	27.80	13.66	1.35	0.69	0.98	0.14	10.07	7.55	9.70	8.22	41.35	41.77	38.48	22.02
*Mean	31.38	32.23a	26.23b	13.73ab	1.55c	0.65cd	1.29e	0.09de	11.83f	6.82f	11.44	7.99	44.76g	39.70h	38.95gi	21.80hi

† N plots established along the G and E-transects in 1993 and 1994, respectively.
‡ Statistical comparisons with each method between years and between method and within years.
* Mean values followed by a common letter are significant at the 0.05 probability level.

presented here in which N recovery is calculated by the direct method agree with other investigations (Moraghan et al., 1984a, b; Walters and Malzer, 1990; Torbert et al., 1992). However, the recovery values based on the difference method are not as agreeable. That is, in studies comparing the percentage N recovery estimated by both the isotopic and difference methods, almost all cases report higher recovery values using the difference method, which is contrary to the findings of this investigation.

According to the internal N cycle theory, the instant a tagged material is applied to the soil system, equilibrium is altered. To regain equilibrium, the soil system will undergo molecular substitutions between the tagged and non-tagged materials, i.e., tagged molecules will be substituted for non-tagged molecules (Jansson, 1958). As a result, recoveries by the difference method will be greater than those measured by the direct method. Also, when a labeled material is added to the soil system, a considerable amount will be immobilized in the soil and, thus, become unavailable to the plant. Therefore, fertilizer N recovery by the direct method will be lower. Studies disregarding the internal N cycle theory attribute the higher recovery values of the difference method to the so-called "priming effect."

The "priming effect" has been defined by some as an increase in microbial activity and subsequent mineralization due to the addition of a N source. This increase in mineralization places nitrogen in fractions that are more available to the plant, thus enhancing the potential for plant N uptake. If this is truly the case, then plots receiving a fertilizer application would have a higher mineralization rate than the control plots. Consequently, fertilizer N recovery by the difference method would be higher.

The direct method, according to Table 3, shows higher average fertilizer N recovery in all aboveground plant fractions for 1993 and 1994 and lower, but

not significantly different, average fertilizer N recovery in the stover fraction for the 1994 growing season. Average fertilizer N recoveries by the direct and indirect methods were not significantly different among the grain, cob, and stover fractions for the 1993 growing season. This suggests minimal pool substitution of applied N with soil N or MIT (Rocous et al., 1988; Moraghan et al., 1984a). Average fertilizer N recoveries by the direct and indirect methods were, however, significantly different between the grain and cob fractions for 1994. Although there are numerical differences between the direct and indirect methods and between 1993 and 1994, by no means has the difference method overestimated fertilizer N recovery. In fact, in this investigation, the difference method consistently produced lower recovery values than the direct method.

Recoveries by the direct and indirect methods will be similar if only one harvest is considered (Westerman and Kurtz, 1974), if soil N availability is high, or if N application to the treated plots is low (Allison, 1966; Moraghan et al., 1984b). Data indicate that soil N availability was high for the 1993 and 1994 growing seasons. The total N uptake of the control plots was greater than the difference between ^{15}N uptake and total N uptake. More precisely, the average total N uptakes of the aboveground plant parts within the check plots for 1993 and 1994 were 74 and 176.8 kg ha^{-1}, respectively. The difference between ^{15}N uptake and total N uptake for 1993 and 1994 were $^{-}78.8$ and $^{-}74.9$ kg ha^{-1}, respectively. This indicates that the "priming effect" was not a major factor in this investigation and that plants did not take up more soil N where fertilizer N was added (Westerman and Kurtz, 1974). According to Torbert et al. (1992), the "priming effect" often manifests itself when soil N availability is low.

The difference method in this project did not overestimate fertilizer N recovery because the check plots were newly established in 1993 and 1994. The soil N availability within the check plots was high because soil N was not

cropped down. According to the average BMP figures used for yield-goal based N applications, approximately 24.6 and 44.8 kg of NO_3^--N ha^{-1} were present in the top 60 cm of the soil profile and available for plant uptake at the start of the 1993 and 1994 growing seasons, respectively. In addition, approximately 17.1 and 18.4 kg of NO_3^--N was present in the top 30 cm of the soil profile before the 1993 fertilizer N application for the treated and check plots, respectively (Table F1). The check plots contained high levels of residual NO_3^--N relative to the treated plots, and these high levels are evident in crop N uptake (Table 1). Consequently, when a check plot of high N concentration is subtracted from a treated plot with only a slightly higher N concentration, the percentage recovery by the difference method will generally be lower. Even though the N content of the check plots is significantly lower than the treated plots, this difference is apparently not large enough to result in the overestimation of fertilizer N uptake that is often experienced by the difference method.

Similar results were reported and discussed by Moraghan et al. (1984b) where the difference method yielded lower fertilizer N recoveries than the direct method in their 1980 sorghum study. They believe the lower recoveries of the difference method were abnormal and attribute this phenomenon to high soil N availability.

Rocous et al. (1988) did a study regarding the fate of ^{15}N-enriched urea and ammonium nitrate applied to winter wheat. They found that plant N uptake from the soil inorganic pool was similar for both the fertilized and unfertilized plots. They reported that the Real Utilization Coefficient (RUC) or the direct method and the Apparent Utilization Coefficient (AUC) or the difference method were similar at harvest with a plant N uptake of 49 and 51%, respectively. They attributed these similarities in fertilizer recovery to no "apparent N interaction" (ANI), or "priming effect." Rocous et al. (1988)

continued that this lack of "priming effect" has been seen in other studies as well (Machet et al., 1987; Nielsen et al., 1988).

Torbert et al. (1992) studied the effects soil type and moisture regimes have on fertilizer N efficiency calculation methods and attributed high recoveries by the difference method to the "priming effect" or ANI. They discussed that because of low soil N availability and, hence, extremely limited uptake of N by the control plants, the difference method yielded much higher fertilizer N recovery. That is, the difference in N uptake between the treated plants and the control plants was of a greater magnitude. It is under such conditions, according to Torbert et al. (1992), that ANI will become evident because of the increased root growth and microbial activity that often follow a fertilizer N application.

In addition, Torbert et al. (1992) discussed the effects varying moisture treatments have on fertilizer N efficiency calculations and found no difference between the direct and indirect methods with the Plainfield soil. They contend that because of the low organic carbon content and coarse texture of this soil, microorganism activity was low; and, thus, the difference between the two methods was small. Consequently, there tends to be minimal interaction between soil and fertilizer N through mineralization-immobilization turnover (MIT). In most studies investigating plant N uptake, MIT is often accused for low residual soil ^{15}N recovery by the direct, isotopic method. For this reason, fertilizer N efficiency calculations based on ^{15}N-enriched fertilizers should be defined in terms of the soil-plant system, i.e., soil samples should be collected, analyzed for their ^{15}N content, and included in the recovery summary.

The results of this study indicate the importance of year-specific data for estimating crop N needs. According to Vanotti and Bundy (1994), too much emphasis has been placed on yield goal-based N recommendations often

resulting in high fertilizer N applications. Vanotti and Bundy (1994) discussed how average grain yield goals selected by corn growers in a 4-year Nebraska study exceeded actual grain yields by 35.8 kg ha^{-1}. This resulted in an over-application of approximately 35 kg N ha^{-1}. In years of less-than-optimal growing conditions such as 1993, plant N uptake efficiency is lessened, thus increasing the level of available soil N for subsequent cropping. The 1994 plant N uptake and dry matter yield data (Tables 1 and 2, respectively) indicate little numerical difference between the treated and non-treated plots among all aboveground plant portions. This indicates small agronomic response to the applied fertilizer N and, hence, possible overapplication.

Labeled Fertilizer and Soil-N Remaining in the Soil

Table 4 depicts the percentage of applied labeled N remaining in the soil profile at the end of the 1993 and 1994 growing seasons. Approximately 41.5 and 35.7% of the applied labeled N was accounted for in the soil at the end of 1993 and 1994, respectively. In spite of careful, even distribution of fertilizer N, there was considerable variability in ^{15}N recovery among the replicates and between 1993 and 1994. For instance, at all depths, except for at 30-60, 60-90, and 120-150 cm, the means between 1993 and 1994 significantly differed at the 0.01 probability level. However, the means between 1993 and 1994 at depths 30-60 and 60-90 cm are not significantly different at the 0.05 level, but numerically look significantly different. According to the coefficients of variation (standard deviation expressed as a percentage of the mean), no significant variation exists among replicates for 1993 and 1994 at either the 30-60 or 60-90 cm depth (Table 4).

Table 4. Recovery of labeled fertilizer N (Eqn. 9) remaining in the soil at the end of the 1993 and 1994 growing seasons

^{15}N Plots	Nitogen-15 recovery according to depth increment in cm† 0-15 ('93)	0-15 ('94)	15-30 ('93)	15-30 ('94)	30-60 ('93)	30-60 ('94)	60-90 ('93)	60-90 ('94)	90-120 ('93)	90-120 ('94)	120-150 ('93)	120-150 ('94)	150-180 ('93)	150-180 ('94)	Total ('93)	Total ('94)
	%															
Rep 1	18.24	12.28	5.85	3.53	4.78	4.27	1.49	13.79	0.44	8.20	2.07	0.04	0.89	0.00	33.76	42.11
Rep 2	20.62	11.32	4.33	2.20	3.90	4.26	0.85	25.28	0.29	10.95	0.32	0.99	0.57	0.10	30.88	55.10
Rep 3	17.63	11.01	4.96	2.38	12.22	1.25	9.27	2.32	2.43	4.22	0.57	0.44	0.42	0.06	47.51	21.70
Rep 4	25.23	7.26	5.01	2.18	17.32	0.91	4.48	3.54	0.75	9.24	0.38	0.57	0.61	0.09	53.77	23.79
Mean*	20.43a	10.47a	5.04b	2.57b	9.55	2.67	4.02	11.23	0.98c	8.15c	0.84	0.51	0.62d	0.06d	41.48	35.68
CV‡	16.8	21.0	12.4	25.0	66.8	68.9	95.4	95.1	101.3	35.0	99.2	76.6	31.8	68.9	26.4	44.4

† Statistical comparison between years for each depth increment.
* Mean values followed by a common letter are significant at the 0.01.
‡ CV = coefficient of variation.

Difference in water table levels between the G and E-transects can easily explain much of this variability in ^{15}N recovery between 1993 and 1994 and among replicates. Figure 1 shows that the N plots for the 1993 and 1994 investigations were established parallel to the G and E-transect, respectively. The average depth to water table in those areas ranged from 205 to 288 cm and from $^{-}21$ to 234 cm for the G and E-transect, respectively. On July 8, 1994, the water table was 21 cm above the soil surface on the E-transect, i.e., the water was ponded. In the following three weeks, July 12, 20, and 26, the water table subsided to depths of 36.6, 48.7, and 70 cm below the soil surface, respectively. Consequently, much of the applied fertilizer N not yet assimilated by the plant was transported deeper in the profile.

This is a low-lying area along the E-transect and corresponds directly to N plot replicate number 2. According to Table 4, replicate number 2 shows the greatest recovery of ^{15}N to be within the 60-90 cm depth for 1994. This confirmation can also be seen indirectly in Tables 3 and G3. Table 3 shows that replicate number 2 had the lowest ^{15}N recovery in the grain, cob, and stover portions of the plant for 1994. Moreover, Table G3 indicates that plants in replicate number 2 of the ^{15}N treated plots did not vary much in total percentage N and dry matter yields when compared to the other replicates, but did however show consistently lower ^{15}N assimilation among all plant fractions. There was simply less ^{15}N available for plant uptake in replicate 2. Conversely, the G-transect experienced very little water table fluctuation in 1993; and hence the majority of the applied labeled fertilizer N appeared within the 0-15 cm depth (Table 4). These data coincide with numerous studies in which a high percentage of the labeled N remained in the top 15 cm of the soil profile (Moraghan et al., 1984a, b; Walters and Malzer, 1990; Torbert et al., 1992). In addition, the shallow water table of 1994 could have contributed to the small

differences in plant yield between the checks and treated plots. That is, because of the shallow water table, N from the ground water was more readily available for plant uptake.

Figure 26 depicts the average NO_3^--N and total ^{15}N concentration at the end of 1993 and demonstrates the utility of ^{15}N in N management studies. The average NO_3^--N concentration from the check and treated plots began increasing below the 75 cm depth or near the bottom of the root zone. In reference to the means plus or minus one standard deviation, the NO_3^--N concentrations of both the check and treated plots were not significantly different at these depths (indicative of native soil NO_3^--N), but were, however, significantly different at the shallower depths. Moreover, average ^{15}N concentrations showed a continued decline with depth, and essentially no ^{15}N was transported beyond the rooting zone. In other words, no 1993 fertilizer N made it past the root zone except for that which may have passed via preferential pathways (Table 4).

Figure 27 shows the average NO_3^--N and total ^{15}N concentration at the end of 1994. The water table subsidence in the weeks of July 12 through the 26 was primarily responsible for the increased ^{15}N concentrations within the 60-90 cm depth. These ^{15}N concentrations correspond directly to N plot replicate number 2 which occupied a low-lying area along the E-transect. Nitrate-N concentrations between the check and treated plots indicate no significant difference at the 0-60 and 120-180 cm depths, but do indicate significance at the 60-120 cm depths. In addition, NO_3^--N concentrations in both the check and treated plots began low and continued to increase with depth. This indicates that plants in both the check and treated plots consumed more soil NO_3^--N in 1994 because of the warmer and longer growing season.

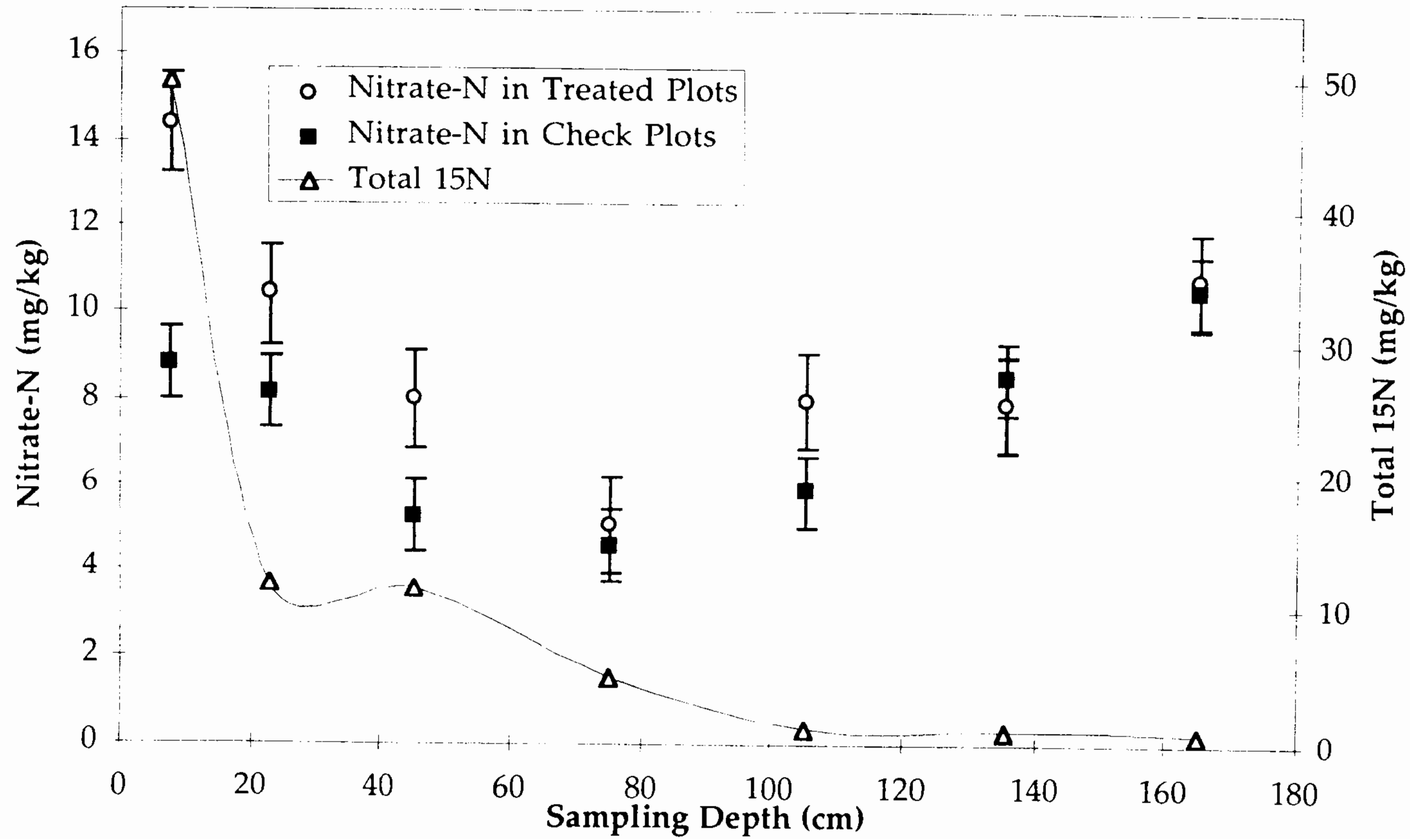


Figure 26. Average soil nitrate-N and total ^{15}N concentration with depth at the end of the 1993 growing season.

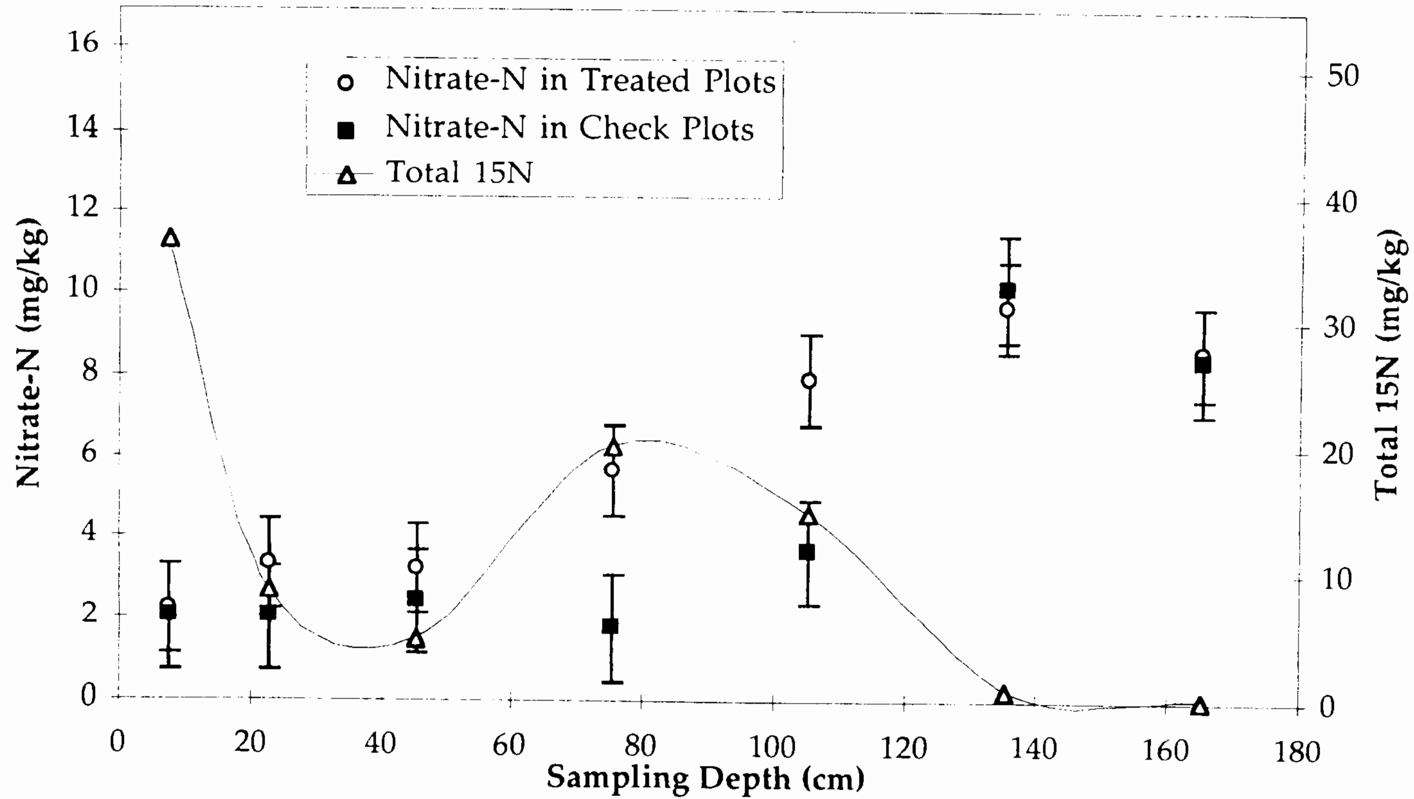


Figure 27. Average soil nitrate-N and total ^{15}N concentration with depth at the end of the 1994 growing season.

The Fate of Applied Labeled Fertilizer N

A balance sheet showing the fate of applied labeled urea-N for 1993 and 1994 is presented in Table 5. The quantity of labeled fertilizer N accounted for within the plant-soil system at the end of 1993 and 1994 was 86.2% and 75.4%, respectively. Consequently, 13.8% and 24.6% of the labeled fertilizer N was not accounted for at the end of 1993 and 1994, respectively. Nearly 41.5% and 35.7% of the labeled fertilizer N remained in the soil at the end of 1993 and 1994, respectively. Approximately 39% and 27% of the applied fertilizer N was found to be within the rooting zone at the end of 1993 and 1994, respectively, and potentially available for subsequent cropping. For 1993, we hoped that 15 to 20% of the applied fertilizer N would have shown up in the tile drain effluent. Because of the high flow rate and isotopic dilution, however, no levels of such magnitude were ever detected.

Since no attempt was made to collect and analyze the evolved nitrogen oxides, I am reluctant to conclude the gaseous losses of 13.8% and 24.6% in 1993 and 1994, respectively, as a result of denitrification. Denitrification processes were traditionally thought not to occur in soil similar to that of the BMP field site because of its sandy texture and aerobic potential (Troeh and Thompson, 1993; Mosier et al., 1986). However, research indicates that denitrification can proceed in an aerobic medium possessing dissolved oxygen levels as high as 2 to 7 mg O_2 L^{-1} (Braun, 1991). The lower fertilizer N recovery of 1994 can, at least partly, be attributed to the shallow, fluctuating water table of the E-transect. Not only did much of the applied N move deeper in the profile (Table 4 and Fig. 27), but much of the soil profile was placed in a saturated, denitrifying condition as well.

Table 5. Fate of labeled urea-N applied at 135 kg ha^{-1} under Best Management Practices for the 1993 and 1994 growing seasons

Rep	Nitrogen-15 recovery									
	Soil		Grain		Stover		Cob		Total	
#	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)	('93)	('94)
	%									
1	33.76	42.11	30.53	39.50	12.35	9.44	1.45	0.63	78.09	91.68
2	30.88	55.10	33.82	24.77	12.22	4.35	1.53	0.62	78.45	84.84
3	47.51	21.70	31.25	31.14	12.66	5.92	1.88	0.68	93.30	59.44
4	53.77	23.79	29.93	33.53	10.07	7.55	1.35	0.69	95.12	65.56
Mean	41.48	35.68	31.38	32.23	11.83	6.82	1.55	0.65	†86.2	‡75.4

Total mean values between 1993 and 1994 are not significant at $\alpha = 0.05$. All p-values > 0.43

† Coefficient of variation = 10.7%.

‡ Coefficient of variation = 20.3%.

Volatilization is another mechanism of N loss that can help to explain the lack of N accountability in this study. According to Claypool (1990), NH_3 volatilization in an alkaline soil is controlled by the carbonic acid-bicarbonate-carbonate buffering system. When urea-N becomes hydrolyzed, the NH_3 reacts with H_2O and CO_2 to form CO_3^{-2} and NH_4^+. This reaction results in a pH increase (with subsequent pH decrease due to nitrification and H^+ evolution) and, with an optimal soil moisture content, will reduce the effects of NH_3 volatilization by increasing the formation of NH_4^+.

A laboratory incubation and greenhouse study were conducted by Patra et al. (1992) using labeled urea-N and ammonium sulfate fertilizers to

determine gaseous N loss in opium poppy (*Papaver somniferum L.*). The soil used in this study had an initial pH of 8.2 which is very similar to that of the BMP field site. Three days following the urea-N and ammonium sulfate applications, pH increased to 9.0 and 9.4 and decreased to 8.0 and 7.8 for the 600 and 1200 mg N pot^{-1} applications, respectively. Thirty days following the urea-N and ammonium sulfate applications, soil pH leveled off to approximately 9.25 and 7.4, respectively. Total ^{15}N recovered in the soil-plant system from the urea-N application ranged from 77.4 to 82.0%, while total ^{15}N recovered in the soil-plant system from the ammonium sulfate application ranged from 88.6 to 91.3%. In addition, the unaccounted for N ranged from 18 to 23% and 9 to 11% in the urea-N and ammonium sulfate treated soils, respectively.

Patra et al. (1992) found a direct relationship between pH and NH_3 volatilization in urea-N treated soil. When urea-N was applied to the soil, it hydrolysed, forming ammonium and bicarbonate (HCO_3^-). The increased log activity of HCO_3^- raised the pH and increased the rate of NH_3 volatilization. Consequently, Patra et al. (1992) attributed the lower fertilizer N recovery of the urea-N application to increased NH_3 volatilization.

Ammonia gas diffusion from soil to atmosphere can be significant when urea-N is applied to alkaline or calcareous soils, dry soils, or sandy soils (Brady, 1984). However, it probably was not of major importance in this investigation since urea-N was band-applied approximately 5.0 cm below the soil surface. Significant losses of NH_3 are more likely to occur from surface-applied urea-N (Troeh and Thompson, 1993) or when NH_4^+ fertilizers are not incorporated into the soil (Fenn and Kissel, 1976).

Moraghan et al. (1984b) discussed how gaseous N loss from plants can be significant, especially between anthesis and maturity and under conditions

fertilizer N recovery for 1993 and 1994. Some of the applied N may have been transported via preferential pathways from the sampling depth zone or in positions undetectable by the soil sampling probe. For instance, since the lysimeter walls do not extend to the soil surface, i.e., the walls of the lysimeter are approximately 35 cm below the soil surface, preferential flowpaths could have directed the fertilizer away from the lysimeter, resulting in poor ^{15}N recovery (Figs. 17, 18, and 24).

The data presented in this thesis regarding the leaching to ground water as a potential fate of N are not quantitatively conclusive. However, many data have been generated from the BMP project showing a continual increase of N in the drainage and in the ground water (Stegman et al., 1990; Steele et al., 1993). This suggests that leaching of the ^{15}N is highly likely.

CONCLUSIONS

Temporal and spatial variations in NO_3^--N movement do exist among many of the undisturbed lysimeters. These variations are explained by the presence of preferential pathways or bypass flow within the soil matrix. That is, during spring thaw and recharge events or at times of intense precipitation, solutes of high solubility, e.g., NO_3^- or Cl^-, will bypass much of the soil mass and proceed directly to the drainage reservoir with little to no soil solution mixing or displacement. The 1993 urea-N application produced residence times of approximately 10 to 12 months with an average resident time of 11.7 months. Secondary ^{15}N elevations were detected in several undisturbed lysimeters approximately 2 months after an early July precipitation event in 1994. Presumably, these elevations were a result of the 1994 urea-N application of 5.934 at. % ^{15}N.

Similar secondary ^{15}N elevations were seen in several undisturbed lysimeters that did not receive the 1994 urea-N application. These elevations coincide with the secondary elevations depicted among lysimeters that did receive the 1994 urea-N application and are a result of the July 1994 precipitation event.

Nitrate-N concentrations of tile drain T03 ranged from 4.3 to 5.79 mg L^{-1} (July 8, 1993, to Aug. 30, 1994). On Aug. 24, 1994, tile drain effluent showed a maximum ^{15}N elevation of 0.4871 at. % (Table A2). Presumably, this is the result of the July 1994 rainfall event since T03 runs directly below the first corn row of the E-transect. However, since several lysimeters experienced secondary ^{15}N elevations and had not received the 1994 urea-N application, residence time of $^{15}NO_3$-N to the tile line could be 14 months.

Nitrogen fertilizer efficiency as calculated by the isotope (direct) and difference (indirect) methods indicate an average plant fertilizer N uptake for 1993 and 1994 of approximately 44.7% and 39.7% and 38.9% and 21.8%, respectively. Added N interaction (ANI) or the "priming effect" was not a major factor in this study, since soil N availability was high and total N uptake of the control plots was greater than the difference between ^{15}N uptake and total N uptake. Consequently, the difference method did not overestimate fertilizer N recovery.

The average quantity of applied labeled N remaining in the soil (180 cm profile depth) at the end of the 1993 and 1994 growing seasons was 41.5% and 35.7%, respectively. Approximately 39% and 27% of the applied fertilizer N was found to be within the rooting zone (90 cm) at the end of 1993 and 1994, respectively, and potentially available for subsequent cropping. The average quantity of labeled fertilizer N accounted for within the plant-soil system at the end of 1993 and 1994 was 86.2% and 75.4%, respectively. Consequently, 13.8% and 24.6% of the labeled fertilizer N was not accounted for at the end of 1993 and 1994, respectively.

The presence of preferential pathways at the BMP quarter (verified from the lysimeter data in this study) may partly explain the lack of fertilizer N recovery for 1993 and 1994. Some of the applied N may have been transported via preferential pathways from sampling depth or in positions undetectable by the soil sampling probe.

Denitrification is often accused when fertilizer N is not completely accounted for. Since no attempt was made to collect and analyze the evolved nitrogen oxides, I am reluctant to conclude that unaccounted N is a result of denitrification. However, since research indicates that denitrification can

proceed in an aerobic medium, it can, at least partly, explain the lack of fertilizer N accountability with this investigation.

In addition, current research indicates that volatile N losses from soil and aboveground plant biomass can be significant and can often explain N deficits. Ammonia-N volatilization from the soil surface is reportedly significant when urea-N is the fertilizer choice. This is especially true when urea-N is applied to alkaline soils, as was the case with this investigation. Volatile N losses from aboveground vegetation can account for as much as 21% of the applied fertilizer N. Again, since no attempt was made to directly (gaseous loss) or indirectly (plant ^{15}N uptake at varying growth stages) measure the evolved gases in this study, it is difficult to conclude with any degree of certainty the reason(s) for the 13.8% and 24.6% labeled fertilizer N deficits at the end of 1993 and 1994 growing seasons, respectively. Consequently, further research needs to be done under similar experimental conditions, paying particular attention to the mechanism(s) responsible for these fertilizer N deficits. By doing so, one will be better able to develop a cropping system that optimizes fertilizer N use efficiency and maximizes plant yields while concurrently reducing the potential of groundwater contamination.

The Dumas Combustion Separation Procedure has become increasingly popular in nitrogen management studies and in studies involving ^{15}N applications. This procedure eliminates much of the time spent in the laboratory performing traditional acid digestions and ammonium distillations. This study found that the Dumas procedure performed accurate, precise total N and isotope-ratio analyses on soil and plant tissue. Almost all duplicate isotopic and elemental N analyses were within the limits of relative difference recommended by Isotope Services, Inc. of Las Alamos, New Mexico.

Drainage samples that consist mainly of inorganic-N species and that are to be analyzed for their isotope-ratios by the Dumas combustion method can be adequately prepared through evaporative concentration. This process can be accomplished without the need for acidic or alkaline pretreatments and without the worry of isotopic fractionation, provided dry-down temperatures remain less than 80°C and sample pH is closely monitored. Further research, however, needs to be conducted regarding total N analyses of drainage samples by the Dumas procedure. The Dumas procedure performed accurate and precise isotope-ratio analyses on the drainage samples; however, it failed to produce accurate, quantitative total N values when samples were prepared in the fashion discussed in this thesis. This method produced variable total drainage N values with recoveries as low as 75% and as high as 97%. Consequently, the Dumas procedure was a successful analytical tool for the tracer portion of this investigation, but was seemingly unacceptable for mass ^{15}N leachate recovery.

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APPENDIX A

ISOTOPIC FRACTIONATION AND INORGANIC N RECOVERY

Being cognizant of sample pH is very important when concentrating a large volume of an aqueous solution. Ammonium nitrogen can be lost if the solution is alkaline, and NO_3^--N and NO_2^--N can be lost under acidic conditions (Hauck, 1982). A series of laboratory tests were performed to confirm this fact and to develop a scheme that adequately prepares drainage samples for the Dumas analysis. Table A1 illustrates three trials in which known NH_4^+-N and NO_3^--N standards were evaporated in accordance with the previously mentioned preparatory procedures (pages 32-33). In trials 1 and 2, 20 mL of standard was added to a vial and acidified with 5 ml of a 0.02*N* sulfuric acid solution. In trial 3, 20 mL of standard was added to each vial. Three of the eight samples in trial three were made alkaline by adding 2 mL of 0.10*N* NaOH solution while the remaining five samples were left untreated. All of the standards contained approximately 50 mg L^{-1} of NH_4^+-N and 50 mg L^{-1} of NO_3^--N. Ammonium and NO_3^-- N of the standard samples were separated by the steam distillation methods discussed by Keeney and Nelson (1982).

To further test the efficacy of this dry-down procedure, a fourth laboratory test using 5 mL aliquots as opposed to 20 mL was performed. Table A2 shows the recovery data of the known (NH_4^+ + NO_3^--N) standard solution after evaporative concentration at approximately 75 °C. Again, NH_4^+-N and NO_3^--N were determined by the steam distillation methods discussed by Keeney and Nelson (1982).

Table A1. Ammonium and NO_3^--N recovery of acidified, alkaline, and non-treated oven-dried standards

Sample†	NH_4^+-N recovered	NO_3^--N recovered
	----------------mg L^{-1}----------------	
AS1.1	49.03	32.43
AS1.2	47.03	36.78
AS1.3	50.61	39.24
AS1.4	50.17	39.56
AS2.1	48.04	8.76
AS2.2	47.22	8.91
AS2.3	47.98	9.22
AS2.4	47.09	10.52
NT3.1	44.94	46.82
NT3.2	43.01	45.84
NT3.3	47.00	47.69
NT3.4	44.50	47.50
NT3.5	45.50	47.91
AK3.6	1.19	46.04
AK3.7	0.89	46.40
AK3.8	1.47	46.23
Mean AS	48.40	23.18
Mean NT	44.99	47.15
Mean AK	1.18	46.22

† Samples contained approximately 50 mg L^{-1} of NH_4^+-N and 50 mg L^{-1} NO_3^--N in 20 mL. AS, NT, AK = acidified, non-treated, and alkaline samples, respectively. First number in sample identification represents trial number while the second number is the individual standard sample, e.g., AS1.1 is the first sample of trial number 1.

Table A2. Recovery of standard NH_4^+ and NO_3^--N solutions dried at approximately 75°C

†Sample	NH_4^+-N recovered	NO_3^--N recovered
	----------------mg L^{-1}----------------	
RS	46.25	47.46
RS	45.08	47.04
DS1	47.52	47.69
DS2	45.40	46.26
DS3	47.05	46.82
DS4	45.59	46.45
DS5	46.74	47.18
DS6	45.12	46.85
DS7	46.49	47.80
DS8	45.23	46.87
DS9	46.40	47.77
DS10	45.54	46.87
RS Mean	45.66	47.25
DS Mean	46.11	47.06

† Samples contained approximately 50 mg L^{-1} of NH_4^+-N and 50 mg L^{-1} NO_3^--N.
DS = Dried Standards.
RS = Regular Standard solution from refrigerator.

Based on the data presented in Table A1 (trials 1 and 2), there was considerable loss of the NO_3^--N with nearly 100% recovery of the NH_4^+-N when samples were acidified. It was hypothesized when the standard samples were acidified, nitric acid was formed and was volatilized. Conversely, trial 3 (AK samples) show that there was considerable loss of the NH_4^+-N when the standards were treated with the alkali and nearly 100% recovery of the NO_3^--N. However, there was virtually 100% recovery of both the NO_3^--N and NH_4^+-N fractions when the standards were left untreated (Tables A1 and A2).

Therefore, based on these laboratory tests, I was able to conclude that drainage samples possessing primarily inorganic N fractions can be adequately and accurately prepared for the Dumas Combustion Separation Procedure through evaporative concentration. This process can be accomplished without the need for acidic or alkaline pretreatments and without the worry of isotopic fractionation, provided dry-down temperatures remain less than 80°C. In addition, this procedure assumes that the majority of the N species present in the drainage samples are from inorganic sources, i.e., samples not containing high levels of organic N, as would be the case in wetlands.

APPENDIX B

TOTAL DUMAS NITROGEN RECOVERY

The Dumas procedure supposedly produces total plant N values comparable to those generated by the traditional Kjeldahl digestion procedure. However, in this project, the Dumas procedure failed to recover quantitatively all N present in the drainage water samples. That is, upon summarizing the total N values of the drainage samples, I learned that the Dumas method was consistently producing lower total N values than the NO_3^--N values we had been receiving from the U.S. Bureau of Reclamation laboratory at Bismarck, North Dakota. Fortunately, this project was only concerned with residence times of applied fertilizer N, hence, needing only isotope-ratio information for the drainage samples and not total N values. My major adviser and I felt it imperative to determine why the Dumas method failed to generate accurate total N values for the drainage water samples, so a study was conducted in cooperation with Isotope Services, Inc. of Los Alamos.

In this test, seven samples of known nitrogen concentration were prepared in duplicate and in a slightly different manner. These seven samples were labeled as TDN #1 through TDN #14 and were prepared differently to isolate and identify possible reasons for the low N recoveries. Because NO_3^--N is the predominate N fraction present in the drainage effluent at the BMP site, a standard NO_3^--N solution and a representative sample of tile drain effluent were used to conduct this test.

The standard NO_3^--N solution was prepared from KNO_3. To ascertain the exact NO_3^--N concentration of the standard solution, NO_3^--N was reduced with Devarda's alloy by the steam separation procedure outlined by Keeney and Nelson (1982). To obtain total N values of samples TDN #7 through TDN #12,

Kjeldahl digestions were performed using the salicylic acid-sodium thiosulfate modification (Bremner and Mulvaney, 1982). Two aliquots from each digest were distilled for their NH_4^+-N content for a total of 12 NH_4^+-N values. These values were averaged and used for percentage recovery comparison with the Dumas procedure. Each set of duplicate samples were prepared as follows:

TDN #1 and #2:

Ten mL of a standard NO_3^--N solution of known composition was added to a 25 x 90 mm glass vial and evaporated to complete dryness at < 80°C. The vials were reconstituted with 3 ml of deionized water, vortexed, and evaporated to dryness. *This is the procedure used for this project.*

TDN #3 and #4:

Same as TDN #1 and #2, except the vials were again reconstituted with 0.5 mL of deionized water, vortexed, and evaporated to dryness. *Theoretically, this procedure should have concentrated the NO_3^--N in a lower portion of the vial.*

TDN #5 and #6:

Same as TDN #1 and #2, except the vials were not evaporated to dryness after reconstitution with the 3 mL of deionized water. *Theoretically, with this procedure, all NO_3^--N should have been in solution.*

The following samples were spiked with a standard solution because 1) it insures high enough N levels for an accurate Dumas analysis and 2) I thought I might be able to compare any chemical differences in the dry-down process. Total Kjeldahl N was performed on these samples.

TDN #7 and #8:

Twenty mL of tile drain effluent + 5 mL of a known standard NO_3^--N solution were added to a 25 x 90 mm glass vial and evaporated to complete dryness at < 80°C. The vials were reconstituted with 3 mL of deionized water, vortexed, and evaporated to dryness. *This procedure is similar to TDN #1 and #2, except that it involved a sample of tile drain effluent with the addition of a known NO_3^--N standard.*

TDN #9 and #10:

Same as TDN #7 and #8, except the vials were reconstituted with 0.5 mL of deionized water, vortexed, and evaporated to dryness. *Theoretically, this procedure should have concentrated the N in a lower portion of the vial. This procedure is similar to TDN #3 and #4, except that it involved a sample of tile drain effluent with the addition of a known NO_3^--N standard.*

TDN #11 and #12:

Same as TDN #7 and #8, except the vials were not evaporated to dryness after reconstitution with the 3 mL of deionized water. *Theoretically, with this procedure, all NO_3^--N should have been in solution. This procedure is also similar to TDN #5 and #6, except that it involved a sample of tile drain effluent with the addition of a known NO_3^--N standard.*

TDN #13 and #14:

Three mL of a known standard NO_3^--N solution.

Table B1 shows the percentage recovery of the standard NO_3^--N solution and standard NO_3^--N solution plus tile drain effluent as determined by the Dumas Combustion Separation Procedure. The percentage recovery is based on the total microgram amount of N in the sample. The results indicate that the Dumas procedure still failed to recover about 25% of the standard NO_3^--N solution. If the Dumas procedure were recovering all the NO_3^--N, samples TDN #13 and #14 would have shown 100% recovery, since these aliquots were extracted directly from the parent standard solution and were not exposed to the dry-down process. However, the average percentage recoveries of these duplicates agree almost identically with the other three sets of duplicate samples. This reaffirms that NO_3^--N is not being lost during the dry-down process, but rather the Dumas procedure is failing to recover all NO_3^--N.

Table B1 also indicates about a 2% increase in NO_3^--N recovery when the sample is reconstituted for the second time with 0.5 mL of deionized water (TDN #3 & #4). The purpose of this reconstitution was to concentrate the NO_3^--N in a lower portion of the glass vial. I thought by decreasing the surface area, the likelihood of a higher percentage recovery by the Dumas method would result. I believe, however, that this 2% increase is an analytical error and has nothing to do with increased NO_3^--N solubility. Intuitively, if the Dumas method only recovers 75.9% of the NO_3^--N in the parent standard solution (samples not exposed to the dry-down process), samples TDN #1 through TDN #6 could only, at best, be equal to 75.9% and not greater than 75.9%.

As seen in Table B1, the percentage recovery by the Dumas procedure increased substantially when the standard NO_3^--N solution was added to the drainage sample. This increase can also be seen among treatments. Recall that samples TDN #7 and #8 were prepared by my original dry-down procedure

Table B1. Percentage recovery of standard NO_3^--N solution and standard NO_3^--N solution plus tile drain effluent as determined by the Dumas Combustion Separation Procedure

Sample ID	Sample NO_3^--N	NO_3^--N by Dumas Method	*Total Kjeldahl N	Total Dumas N	Recovery by Dumas Method
	------------------------μg------------------------				%
TDN #1 & #2	900	682	---	---	75.8
TDN #3 & #4	900	701	---	---	77.8
TDN #5	900	683	---	---	75.8
TDN #7 & #8	---	---	1041.3	876	84.1
TDN #9 & #10	---	---	1041.3	962	92.4
TDN #11 & #12	---	---	1041.3	1014	97.4
TDN #13 & #14	558	424	---	---	75.9

* Average total N value of 12 distillates.

and that samples TDN #9 and #10 were concentrated in a lower portion of the vial which shows an increased recovery of 8%. However, the greatest recovery, 97.4%, came from samples TDN #11 and #12 which were reconstituted with 3 ml of deionized water, vortexed, and left in solution.

This test indicates differences in water chemistry during the dry-down and analytical processes. The Dumas procedure failed to recover 25% of the standard NO_3^--N solution, but exhibited relatively high recovery when the standard NO_3^--N solution was added to the tile drainage sample. I do not know

why this was the case, but I suspect that the NO_3^- from the KNO_3 source (standard NO_3^--N solution) as opposed to the presumed $Ca(NO_3)_2$ of the drainage effluent was taking a different combustion path during the dry oxidation procedure, resulting in lower N recoveries.

Based on these results, the following conclusions were made: 1) The Dumas procedure failed to recover 25% of the standard NO_3^--N solution when potassium nitrate (KNO_3) was the N source. 2) The percentage recovery by the Dumas procedure substantially increased when the standard NO_3^--N solution was added to the tile drain effluent. This increase in recovery was also seen among treatments and in the following order from highest to lowest recovery:

> Dried aliquot reconstituted with 3 ml of water, vortexed, and left in solution > Dried aliquot reconstituted a second time with 0.5 ml of water, vortexed, and dried > Dried aliquot reconstituted with 3 ml of water, vortexed, and dried.

3) When drainage samples low in organic N are prepared for total N analyses by the Dumas procedure, aliquots should be evaporated to complete dryness, reconstituted with 3 ml of deionized water, vortexed, and sealed for shipment. However, with this method, sample preservation and "holding time" becomes an issue and must be considered.

Isotope Services, Inc. later informed me that water samples are subject to another error. Since they use a micro-pipett with disposable tips to extract 0.1 ml of solution, it is extremely difficult to accurately measure this small amount. According to their recent measurements, the micro-pipett extracts aliquot amounts could result in a N recovery as low as 75% or as high as >99%. This may substantiate conclusions number 1 and 2.

APPENDIX C

REDUCING AGENTS USED WITH THE DUMAS PROCEDURE

All drainage samples sent to Isotope Services, Inc. generated very large mass-30 peaks when measured with the mass spectrometer. These large peaks were consistently between 22 and 47% of the mass-28 peaks and were unique only to the drainage samples, not to the soil and plant samples. According to Isotope Services, Inc., such a magnitude of the mass-30 peak is atypical and should be well below 1% of the mass-28 peak. Consequently, Isotope Services decided to run its own experiment concurrent with the experiment discussed in Appendix B.

Isotope Services, Inc. ran 14 samples in two separate batches. In the first run, the nitrogen oxide species were reduced with the usual chopped copper wire producing very large mass-30 peaks. It attributed these large mass-30 peaks to nitric oxide ions (NO^+) surviving the hot copper reduction tube following the forced combustion. It contended that the NO_3^--N of the drainage samples was following a different combustion path than the nitrogen forms of the soil and plant samples. In the second run, Isotope Services, Inc. removed the chopped copper wire and refilled the reduction tube with small copper shot. It was able to reduce the mass-30 peak to 0.1-0.3% of the mass-28 peak while reporting higher total N and smaller atom percentage ^{15}N values (Table C1). Isotope Services cannot explain why this phenomenon occurred, especially since the calculated surface area of both reducing agents, i.e., the chopped copper wire and copper shot, were similar.

Table C1. Comparison of total N and atom percentage ^{15}N values as determined by the Dumas Combustion Separation Procedure utilizing chopped copper wire and copper shot as the reducing agents

Sample ID	Total N*		Nitrogen-15*	
	Chopped copper wire	Copper shot	Chopped copper wire	Copper shot
	----------µg----------		----------atom %----------	
TDN #1 & #2	614	682	0.37175	0.36802
TDN #3 & #4	604	701	0.37157	0.36779
TDN #5 & #6	641	683	0.37352	0.36771
TDN #7 & #8	818	876	0.37087	0.36769
TDN #9 & #10	837	962	0.37100	0.36761
TDN #11 & #12	967	1,014	0.37454	0.36805
TDN #13 & #14	450	424	0.39312	0.36741
Mean	704a	763a	0.37519b	0.36775b

* Average of the two duplicate samples. Mean values followed by letter, a, are significant at $\alpha = 0.05$. p-value = 0.016. Mean values followed by letter, b, are not significant at $\alpha = 0.05$. p-value = 0.0523

This experiment was not duplicated and tested for reproducibility; therefore, the results are not totally conclusive and may be suspect. Other variables such as electrical conductivity and pH at high concentrations were not investigated. B. B. McInteer (personal communication), president of Isotope Services, Inc., assured me that these variables do not affect the Dumas analysis. These findings, however, are very useful and important for future ^{15}N

research. More research needs to be done regarding the utility of the Dumas procedure in analyzing water samples for their total N content.

APPENDIX D

TOTAL PLANT N COMPARISON BETWEEN THE DUMAS AND KJELDAHL METHODS

To monitor the accuracy of the Dumas Combustion Separation Procedure, 23 plant samples were selected at random and their total percent N determined using the traditional Kjeldahl digestion and distillation procedure (Bremner and Mulvaney, 1982). Table D1 is a comparative summary of total N values generated by both the Dumas and Kjeldahl procedures. A paired t-test was performed to determine any difference between methods with the hypothesized mean difference set equal to zero and $\alpha = 0.01$. The null hypothesis was not rejected (p-value = 0.32), indicating not enough evidence to conclude a difference between the two methods.

Table D1. Total nitrogen comparisons of plant material between the Kjeldahl digestion procedure and the Dumas Combustion Separation Procedure

Plant material	Total N	
	Kjeldahl	Dumas
	%	
Stover	0.602	0.581
Cob	0.357	0.348
Grain	1.197	1.178
Cob	0.321	0.328
Stover	0.735	0.764
Grain	1.185	1.253
Grain	1.295	1.309
Cob	0.357	0.363
Stover	0.444	0.444

Table D1. (continued)

Plant material	Total N	
	Kjeldahl	Dumas
	----------%----------	
Stover	0.588	0.581
Stover	0.700	0.627
Grain	1.220	1.244
Grain	1.520	1.500
Stover	0.780	0.875
Grain	1.580	1.517
Grain	1.200	1.216
Grain	1.210	1.190
Stover	0.68	0.653
Cob	0.260	0.281
Cob	0.290	0.408
Cob	0.340	0.348
Cob	0.360	0.410
Cob	0.310	0.328
Average % Total N*	0.762	0.772

* Average % Total N not significant at p-value = 0.32

APPENDIX E

^{15}N CONCENTRATIONS FOR UNDISTURBED LYSIMETERS AND TILE DRAIN T03

Table E1. Atom percentage ^{15}N of gravity and extraction drainage for the 20 undisturbed lysimeters

Lysimeter	Sampling date	Nitrogen-15 extraction*	Nitrogen-15 gravity*
		------------atom %------------	
L01	7/8/93	0.3668	0.3695
L01	7/14/93	0.3720	0.3703
L01	7/21/93	0.3683	0.3691
L01	7/28/93	0.3695	0.3693
L01	8/4/93	0.3691	0.3687
L01	8/11/93	0.3713	NS
L01	8/17/93	0.3678	NS
L01	8/25/93	0.3682	NS
L01	9/29/93	0.3690	NS
L01	4/7/94	0.3737	0.3724
L01	4/13/94	0.3734	0.3723
L01	4/18/94	NS	0.3719
L01	5/4/94	0.3704	0.3719
L01	5/11/94	0.3823	0.3734
L01	5/17/94	0.3762	0.3699
L01	5/25/94	NS	0.3772
L01	6/1/94	0.3770	0.3782
L01	6/13/94	0.3823	NS
L01	6/21/94	0.3789	NS
L01	7/6/94	0.3876	NS
L01	7/12/94	0.3922	0.3788
L01	7/19/94	0.4124	0.3893
L01	7/26/94	0.4142	0.3855
L01	8/9/94	0.4141	NS
L01	8/24/94	0.4356	NS
L01	8/30/94	NS	0.4360
L02	7/8/93	0.3625	0.3686
L02	7/14/93	0.3669	0.3679
L02	7/21/93	0.3689	0.3685

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		-------------atom %-------------	
L02	7/28/93	0.3685	0.3680
L02	8/4/93	0.3679	0.3675
L02	8/11/93	0.3681	0.3681
L02	8/17/93	0.3652	NS
L02	9/1/93	0.3682	NS
L02	9/8/93	0.3688	NS
L02	10/27/93	0.3685	NS
L02	4/7/94	0.3999	0.4282
L02	4/13/94	0.5671	0.7549
L02	4/18/94	0.6532	0.7186
L02	5/4/94	0.5779	0.5843
L02	5/11/94	0.5277	0.5552
L02	5/17/94	0.4996	0.5443
L02	5/25/94	0.4787	0.4916
L02	6/1/94	0.4593	NS
L02	6/8/94	0.4429	NS
L02	6/13/94	0.4296	NS
L02	7/12/94	0.4082	0.3957
L02	7/19/94	0.4662	0.5373
L02	7/26/94	0.5327	NS
L02	8/3/94	0.8189	NS
L02	8/16/94	0.8174	NS
L02	8/24/94	1.0576	NS
L02	8/30/94	NS	1.3777
L03	7/8/93	0.3735	0.3731
L03	7/14/93	0.3701	0.3693
L03	7/21/93	0.3691	0.3685
L03	7/28/93	0.3694	0.3691
L03	8/4/93	0.3689	0.3687
L03	4/7/94	0.3713	0.3719
L03	4/13/94	0.3719	0.3714
L03	4/18/94	0.3728	0.3724
L03	5/4/94	0.3784	0.3801
L03	5/11/94	0.4270	0.4215
L03	5/17/94	0.4485	0.4351
L03	5/25/94	0.4533	0.4448
L03	6/1/94	0.4487	NS

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %	------------
L03	6/8/94	0.4520	NS
L03	6/13/94	0.4468	NS
L03	7/12/94	0.4305	0.4012
L03	7/19/94	NS	0.4135
L03	7/26/94	0.4349	0.4098
L03	8/3/94	0.4318	NS
L03	8/16/94	0.4358	NS
L04	7/8/93	0.3753	0.3713
L04	7/14/93	0.3705	0.3685
L04	7/21/93	0.3699	0.3695
L04	7/28/93	0.3697	0.3695
L04	8/4/93	0.3696	0.3693
L04	8/11/93	0.3695	0.3694
L04	8/17/93	0.3670	0.3664
L04	8/25/93	0.3686	0.3683
L04	9/1/93	NS	0.3693
L04	9/8/93	0.3697	0.3695
L04	9/15/93	0	0.3696
L04	4/7/94	0.3908	0.4041
L04	4/13/94	0.3901	0.3822
L04	4/18/94	NS	0.3779
L04	5/4/94	0.4016	0.3796
L04	5/11/94	0.3977	0.3710
L04	5/17/94	0.4041	0.3762
L04	5/25/94	0.4008	0.3713
L04	6/1/94	0.3923	0.3741
L04	6/8/94	NS	0.3735
L04	6/13/94	NS	0.3722
L04	6/21/94	NS	0.3716
L04	6/29/94	NS	0.3674
L04	7/6/94	NS	0.3697
L04	7/12/94	0.3823	0.3719
L04	7/19/94	0.3832	0.3712
L04	7/26/94	0.3804	0.3703
L04	8/3/94	NS	0.3703
L04	8/9/94	0.3788	0.3703
L04	8/16/94	0.3796	0.3708

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %------------	
L04	8/24/94	0.3778	0.3704
L04	8/30/94	0.3834	0.4041
L05	7/8/93	0.3820	NS
L05	7/14/93	0.3734	NS
L05	7/21/93	0.3685	0.3692
L05	7/28/93	0.3692	0.3695
L05	8/4/93	0.3693	NS
L05	8/11/93	0.3679	NS
L05	8/17/93	0.3660	NS
L05	8/25/93	0.3678	NS
L05	4/7/94	0.3776	0.3719
L05	4/13/94	0.3813	0.3722
L05	4/18/94	0.3814	0.3773
L05	5/4/94	0.3879	0.3963
L05	5/11/94	0.4614	0.4249
L05	5/17/94	NS	0.4282
L05	5/25/94	NS	0.4246
L05	6/1/94	NS	0.4294
L05	6/8/94	NS	0.4301
L05	6/13/94	NS	0.4339
L05	7/12/94	0.4560	0.4630
L05	7/19/94	NS	0.4228
L05	7/26/94	0.4450	0.4168
L05	8/9/94	0.4378	0.4260
L05	8/16/94	0.5170	0.5170
L05	8/24/94	0.6913	NS
L05	8/30/94	0.9422	NS
L06	7/8/93	0.3665	0.3675
L06	7/14/93	0.3701	0.3668
L06	7/21/93	0.3705	0.3663
L06	7/28/93	0.3676	0.3692
L06	8/4/93	0.3696	0.3652
L06	8/11/93	NS	0.3674
L06	8/17/93	0.3652	0.3650
L06	8/25/93	0.3667	0.3662
L06	9/1/93	0.3669	NS

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %------------	
L06	9/15/93	0.3690	NS
L06	9/29/93	0.3681	NS
L06	4/7/94	0.3705	0.3750
L06	4/13/94	0.3722	0.3719
L06	4/18/94	0.3754	0.3696
L06	5/4/94	0.3768	0.3670
L06	5/11/94	0.3784	0.3672
L06	5/17/94	0.3811	0.3760
L06	5/25/94	0.3753	0.3780
L06	6/1/94	0.3761	NS
L06	6/8/94	0.3844	NS
L06	6/13/94	0.3888	NS
L06	6/29/94	0.3814	NS
L06	7/6/94	0.4557	NS
L06	7/12/94	NS	0.3775
L06	7/19/94	0.3906	NS
L06	8/3/94	0.3934	NS
L06	8/16/94	0.3924	NS
L06	8/30/94	0.3980	NS
L07	7/8/93	0.3665	0.3685
L07	7/14/93	0.3676	0.3687
L07	7/21/93	0.3680	0.3687
L07	7/28/93	0.3679	0.3682
L07	8/4/93	0.3681	0.3678
L07	8/11/93	0.3682	NS
L07	8/17/93	0.3653	NS
L07	8/25/93	0.3667	NS
L07	4/7/94	0.3804	0.3728
L07	4/13/94	0.3824	0.3740
L07	4/18/94	0.3929	0.3710
L07	5/4/94	0.4079	0.3656
L07	5/11/94	0.4200	0.3647
L07	5/17/94	0.4217	NS
L07	5/25/94	0.4322	NS
L07	6/1/94	0.4309	NS
L07	6/8/94	0.4300	NS
L07	6/13/94	0.4355	0.3839

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %------------	
L07	6/21/94	0.4137	0.3711
L07	6/29/94	0.4484	NS
L07	7/6/94	0.4557	NS
L07	7/12/94	0.4608	0.4368
L07	7/19/94	0.4918	NS
L07	7/26/94	0.4848	NS
L07	8/16/94	0.4584	NS
L07	8/24/94	NS	NS
L07	8/30/94	NS	0.4464
L08	7/8/93	0.3665	0.3681
L08	7/14/93	0.3664	NS
L08	7/21/93	0.3674	0.3677
L08	7/28/93	0.3702	0.3704
L08	8/4/93	0.3681	0.3669
L08	8/11/93	0.3671	NS
L08	8/17/93	0.3650	NS
L08	8/25/93	0.3661	NS
L08	9/1/93	0.3725	NS
L08	9/22/93	0.3678	NS
L08	4/7/94	0.4006	0.3804
L08	4/13/94	0.5127	0.3832
L08	4/18/94	0.5185	NS
L08	5/4/94	0.4981	NS
L08	5/11/94	0.4996	NS
L08	5/17/94	0.4976	NS
L08	5/25/94	0.4753	NS
L08	6/1/94	0.4622	NS
L08	6/8/94	0.4586	NS
L08	6/13/94	0.4514	NS
L08	6/21/94	0.4334	NS
L08	6/29/94	0.4153	NS
L08	7/12/94	0.4439	0.3826
L08	7/19/94	0.4272	NS
L08	7/26/94	0.4305	NS
L08	8/9/94	0.4276	NS
L08	8/30/94	0.4324	NS
L09	7/8/93	0.3608	NS

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %------------	
L09	7/14/93	0.3777	NS
L09	7/21/93	0.3672	NS
L09	7/28/93	0.3676	NS
L09	8/4/93	0.3667	NS
L09	8/11/93	0.3685	NS
L09	8/17/93	0.3659	NS
L09	8/25/93	0.3708	NS
L09	9/1/93	0.3685	NS
L09	4/7/94	0.4311	0.3890
L09	4/13/94	0.4709	0.3831
L09	4/18/94	0.5595	0.3846
L09	5/4/94	0.5288	0.3908
L09	5/11/94	0.5272	NS
L09	5/17/94	0.5002	NS
L09	5/25/94	0.5017	NS
L09	6/1/94	0.5038	NS
L09	6/8/94	0.5103	NS
L09	6/13/94	0.4985	NS
L09	6/21/94	0.5063	NS
L09	6/29/94	0.4873	NS
L09	7/12/94	0.4670	0.3861
L09	7/19/94	0.4270	NS
L09	8/3/94	0.4483	NS
L09	8/16/94	0.9135	NS
L09	8/24/94	1.5813	NS
L09	8/30/94	1.5039	NS
L10	7/8/93	0.3666	0.3675
L10	7/14/93	0.3672	0.3677
L10	7/21/93	0.3683	0.3679
L10	7/28/93	0.3684	0.3681
L10	8/4/93	0.3680	0.3684
L10	8/11/93	NS	0.3684
L10	8/25/93	0.3705	NS
L10	9/1/93	0.3681	NS
L10	9/15/93	0.3682	NS
L10	4/7/94	NS	0.3728

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		-------------atom %-------------	
L10	4/13/94	0.3724	0.3714
L10	4/18/94	0.3735	0.3743
L10	5/4/94	0.3788	0.3757
L10	5/11/94	0.3895	0.3820
L10	5/17/94	0.3923	0.3839
L10	5/25/94	0.3986	0.3796
L10	6/1/94	0.3984	NS
L10	6/8/94	0.4003	NS
L10	6/13/94	0.3972	NS
L10	6/21/94	0.3998	NS
L10	7/12/94	0.3999	0.3947
L10	7/19/94	NS	0.3965
L10	7/26/94	0.3996	0.3955
L10	8/3/94	0.4004	NS
L10	8/30/94	0.4168	NS
L11	7/8/93	0.3661	NS
L11	7/14/93	0.3730	NS
L11	7/21/93	0.3688	0.3692
L11	7/28/93	0.3684	0.3696
L11	8/4/93	0.3690	NS
L11	8/17/93	0.3674	NS
L11	8/25/93	0.3677	NS
L11	4/7/94	NS	0.3728
L11	4/13/94	0.3827	0.3776
L11	4/18/94	0.3865	0.3826
L11	5/4/94	0.3852	0.3918
L11	5/11/94	0.3976	0.3960
L11	5/17/94	0.3879	0.3974
L11	5/25/94	NS	0.4028
L11	6/8/94	0.3947	NS
L11	6/13/94	NS	0.3968
L11	7/6/94	0.4100	NS
L11	7/12/94	0.4121	0.4065
L11	7/19/94	NS	0.4211
L11	7/26/94	NS	0.4184
L12	7/8/93	0.3672	0.3674
L12	7/14/93	0.3679	0.3678

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %	------------
L12	7/21/93	0.3684	0.3675
L12	7/28/93	NS	0.3676
L12	8/4/93	0.3673	0.3676
L12	8/17/93	0.3660	0.3644
L12	8/25/93	0.3682	NS
L12	9/1/93	0.3682	NS
L12	9/8/93	0.3684	NS
L12	5/4/94	0.3761	NS
L12	5/11/94	0.3695	NS
L12	5/17/94	0.3752	NS
L12	5/25/94	0.3731	NS
L12	6/1/94	0.3752	NS
L12	6/8/94	0.3729	NS
L12	7/12/94	NS	0.3746
L12	7/19/94	0.4130	NS
L12	7/26/94	NS	0.3813
L12	8/3/94	0.4145	NS
L12	8/16/94	0	0.3817
L12	8/30/94	0.4280	NS
L13	7/8/93	0.3691	0.3714
L13	7/14/93	0.3709	0.3714
L13	7/21/93	0.3684	0.3686
L13	7/28/93	0.3685	0.3689
L13	8/4/93	0.3686	NS
L13	9/1/93	0.3683	NS
L13	4/13/94	NS	0.3707
L13	4/18/94	NS	0.3715
L13	5/4/94	NS	0.3719
L13	5/11/94	NS	0.3657
L13	5/17/94	NS	0.3731
L13	5/25/94	NS	0.3702
L13	6/1/94	NS	0.3754
L13	6/29/94	0.3692	NS
L13	7/12/94	NS	0.3755
L13	7/19/94	NS	0.3724
L14	7/8/93	NS	0.3655
L14	7/14/93	NS	0.3673

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %------------	
L14	7/21/93	0.3679	0.3683
L14	7/28/93	NS	0.3682
L14	8/4/93	0.3689	0.3694
L14	8/11/93	NS	0.3685
L14	8/17/93	0.3664	0.3656
L14	8/25/93	NS	0.3688
L14	9/1/93	NS	0.3675
L14	9/15/93	0.3681	NS
L14	9/29/93	0.3682	NS
L14	4/13/94	0.3733	NS
L14	4/18/94	0.3732	NS
L14	5/4/94	NS	0.3726
L14	5/11/94	NS	0.3661
L14	5/17/94	NS	0.3803
L14	5/25/94	NS	0.3636
L14	6/1/94	NS	0.3738
L14	6/8/94	NS	0.3723
L14	6/13/94	NS	0.3717
L14	6/21/94	0.3707	NS
L14	7/12/94	NS	0.3698
L14	7/19/94	0.3736	NS
L14	7/26/94	0.3742	0.3718
L14	8/3/94	0.3735	NS
L15	7/8/93	0.3668	0.3651
L15	7/14/93	0.3662	NS
L15	7/21/93	0.3663	0.3673
L15	7/28/93	0.3677	0.3683
L15	8/4/93	0.3678	0.3703
L15	8/11/93	0.3691	0.3678
L15	8/17/93	0.3661	NS
L15	8/25/93	0.3682	NS
L15	9/1/93	0.3678	NS
L15	4/18/94	0.3732	NS
L15	5/4/94	NS	0.3771
L15	5/11/94	NS	0.3712
L15	5/17/94	NS	0.3708
L15	5/25/94	NS	0.3737

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		-------------atom %	-------------
L15	6/1/94	NS	0.3791
L15	6/8/94	0.3771	NS
L15	6/13/94	0.3801	0.3755
L15	6/21/94	0.3799	NS
L15	7/6/94	0.3909	NS
L15	7/12/94	0.4012	0.4080
L15	7/26/94	0.4754	NS
L16	7/8/93	0.3688	0.3684
L16	7/14/93	0.3719	0.3700
L16	7/21/93	0.3675	0.3677
L16	7/28/93	0.3680	0.3681
L16	8/4/93	0.3679	0.3681
L16	8/11/93	0.3681	NS
L16	8/17/93	0.3671	NS
L16	8/25/93	0.3686	NS
L16	9/1/93	0.3690	NS
L16	9/8/93	0.3681	NS
L16	9/15/93	0.3681	NS
L16	9/22/93	0.3681	NS
L16	10/6/93	0.3682	NS
L16	4/7/94	0.3706	0.3700
L16	4/13/94	0.3717	0.3699
L16	4/18/94	0.3714	0.3709
L16	5/4/94	0.3735	0.3712
L16	5/11/94	0.3734	NS
L16	5/17/94	0.3707	NS
L16	5/25/94	0.3793	0.3693
L16	6/1/94	0.3735	0.3691
L16	6/8/94	0.3735	0.3716
L16	6/13/94	0.3734	0.3712
L16	6/21/94	0.3748	NS
L16	6/29/94	0.3769	NS
L16	7/6/94	0.3849	NS
L16	7/12/94	0.3877	0.3763
L16	7/19/94	0.4077	NS
L16	7/26/94	0.4181	NS
L16	8/3/94	0.4040	NS

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		-------------atom %-------------	
L17	8/25/93	0.3674	NS
L17	9/1/93	0.3682	NS
L17	9/8/93	0.3689	NS
L17	5/4/94	0.3717	0.3714
L17	5/11/94	0.3701	0.3701
L17	5/17/94	0.3715	0.3702
L17	5/25/94	0.3714	NS
L17	6/1/94	0.3713	NS
L17	6/8/94	0.3708	NS
L17	6/21/94	0.3701	NS
L17	6/29/94	0.3710	NS
L17	7/6/94	0.3710	NS
L17	7/12/94	0.3709	NS
L17	7/26/94	0.3688	NS
L17	8/16/94	0.3698	NS
L17	8/24/94	0.3874	NS
L18	7/8/93	0.3703	NS
L18	7/14/93	0.3697	NS
L18	7/21/93	0.3677	NS
L18	7/28/93	0.3672	NS
L18	8/4/93	0.3670	NS
L18	8/11/93	0.3675	NS
L18	8/17/93	0.3660	NS
L18	8/25/93	0.3685	NS
L18	9/1/93	0.3674	NS
L18	9/8/93	0.3678	NS
L18	9/15/93	0.3674	NS
L18	4/7/94	0.5061	0.3844
L18	4/13/94	0.6735	NS
L18	4/18/94	0.8325	NS
L18	5/4/94	0.9523	NS
L18	5/11/94	0.9770	NS
L18	5/17/94	0.8676	NS
L18	5/25/94	0.7456	NS
L18	6/1/94	0.6323	NS
L18	6/8/94	0.5521	NS
L18	6/13/94	0.5051	NS

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		-------------atom %-------------	
L18	6/21/94	0.4941	NS
L18	6/29/94	0.4705	NS
L18	7/6/94	0.4619	NS
L18	7/12/94	0.4440	NS
L18	7/19/94	0.4393	NS
L18	7/26/94	0.4266	NS
L18	8/16/94	0.4098	NS
L19	7/8/93	0.3688	0.3699
L19	7/14/93	0.3693	NS
L19	7/21/93	0.3695	0.3703
L19	7/28/93	0.3696	0.3704
L19	8/4/93	0.3695	0.3705
L19	8/11/93	NS	0.3703
L19	8/17/93	0.3683	0.3676
L19	8/25/93	NS	0.3689
L19	9/1/93	0.3699	0.3712
L19	4/7/94	0.3713	0.3719
L19	4/13/94	0.3705	0.3714
L19	4/18/94	0.3722	NS
L19	5/4/94	0.3734	0.3782
L19	5/11/94	0.3783	NS
L19	5/17/94	0.3790	NS
L19	5/25/94	0.3739	NS
L19	6/1/94	0.3793	NS
L19	6/8/94	0.3819	NS
L19	7/12/94	NS	0.3729
L19	7/19/94	0.3943	NS
L19	8/3/94	0.4015	NS
L20	7/14/93	0.3694	NS
L20	7/21/93	0.3691	NS
L20	7/28/93	0.3693	0.3701
L20	8/4/93	0.3699	0.3698
L20	8/11/93	0.3689	0.3700
L20	8/17/93	0.3680	0.3673
L20	8/25/93	0.3703	0.3688
L20	9/1/93	0.3699	0.3716

Table E1. (continued)

Lysimeter	Sampling date	Nitrogen-15 extraction	Nitrogen-15 gravity
		------------atom %	------------
L20	9/8/93	0.3696	0.3703
L20	9/15/93	0.3692	0.3705
L20	9/22/93	0.3692	NS
L20	9/29/93	0.3693	NS
L20	10/13/93	0.3695	NS
L20	10/27/93	0.3698	NS
L20	4/7/94	0.3712	0.3711
L20	4/13/94	0.3705	0.3710
L20	4/18/94	0.3715	NS
L20	5/4/94	0.3709	NS
L20	5/11/94	0.3767	NS
L20	5/17/94	0.3728	NS
L20	5/25/94	0.3638	NS
L20	6/1/94	0.3684	NS
L20	6/8/94	0.3696	NS
L20	6/13/94	0.3683	NS
L20	6/21/94	0.3720	NS
L20	7/12/94	0.3696	NS
L20	7/19/94	0.3697	NS
L20	8/3/94	0.3701	NS
L20	8/9/94	0.3717	NS
L20	8/16/94	0.3715	NS

* NS = no sample

Table E2. Nitrate-N concentration and atom percentage ^{15}N for tile drain T03

Sampling date	NO_3^--N*	Nitrogen-15
	(mg L^{-1})	atom %
7/8/93	4.92	0.3664
7/14/93	4.94	0.3690
7/21/93	4.93	0.3687
7/28/93	5.25	0.3697
8/4/93	5.18	0.3686
8/11/93	4.97	0.3683
8/17/93	4.85	0.3645
8/25/93	4.88	0.3687
9/1/93	4.73	0.3682
9/8/93	4.79	0.3695
9/15/93	4.81	0.3700
9/22/93	4.83	0.3692
9/29/93	4.48	0.3685
10/6/93	4.57	0.3699
10/13/93	4.41	0.3686
10/19/93	4.52	0.3695
10/27/93	4.73	0.3683
3/8/94	ND	0.3683
3/14/94	ND	0.3715
3/15/94	ND	0.3728
3/17/94	ND	0.3731
3/18/94	ND	0.3708
3/19/94	ND	0.3759
3/19/94	ND	0.3785
3/22/94	ND	0.3714
3/23/94	ND	0.3753
3/30/94	ND	0.3705
4/7/94	4.56	0.3743
4/13/94	4.45	0.3740
4/18/94	ND	0.3727
4/27/94	4.30	0.3576
5/4/94	4.60	0.3679
5/11/94	ND	0.3641
5/17/94	4.72	0.3667
5/25/94	4.40	0.3777
6/1/94	5.11	0.3659
6/8/94	ND	0.3703
6/13/94	4.55	0.3654

Table E2. (continued)

Sampling date	NO_3^--N*	Nitrogen-15
	(mg L^{-1})	atom %
6/21/94	4.47	0.3786
6/29/94	4.69	0.3762
7/6/94	4.69	0.3610
7/8/94	5.79	0.3631
7/12/94	5.68	0.3711
7/19/94	5.78	0.3684
7/26/94	4.70	0.3680
8/3/94	5.35	0.3682
8/9/94	4.97	0.3707
8/16/94	ND	0.4119
8/24/94	ND	0.4871
8/30/94	4.98	0.3896

* ND = not determined.

APPENDIX F

RESIDUAL NITRATE-N FOR SPRING 1993

Table F1. Residual NO_3^--N present in the top 30 cm of the soil profile before the 1993 fertilizer N application

Trt. ID	Rep. #	Depth	NO_3^--N
		cm	kg ha^{-1}
14N	1	0-6	15.6
14N	1	6-12	22.6
14N	2	0-6	13.8
14N	2	6-12	16.6
14N	3	0-6	14.2
14N	3	6-12	16.1
14N	4	0-6	13.5
14N	4	6-12	19.8
15N	1	0-6	17.0
15N	1	6-12	24.1
15N	2	0-6	17.2
15N	2	6-12	15.7
15N	3	0-6	15.3
15N	3	6-12	13.3
15N	4	0-6	17.6
15N	4	6-12	21.1
CHECK	1A	0-6	17.3
CHECK	1A	6-12	22.8
CHECK	1B	0-6	20.3
CHECK	1B	6-12	20.1
CHECK	2A	0-6	20.2
CHECK	2A	6-12	19.2
CHECK	2B	0-6	16.1
CHECK	2B	6-12	17.9
CHECK	3A	0-6	16.2
CHECK	3A	6-12	18.1
CHECK	3B	0-6	17.0
CHECK	3B	6-12	19.7
CHECK	4A	0-6	14.0
CHECK	4A	6-12	18.8

Table F1. (continued)

Trt. ID	Rep. #	Depth	NO_3^--N
		cm	kg ha^{-1}
CHECK	4B	0-6	14.4
CHECK	4B	6-12	22.0

Table F1. (continued)

Trt. ID	Rep. #	Depth	NO_3^--N
		cm	kg ha^{-1}
CHECK	4B	0-6	14.4
CHECK	4B	6-12	22.0

APPENDIX G

1993 AND 1994 CORN PLANT DATA

Table G1. Plant nitrogen content (kg ha^{-1}) of aboveground plant parts at the end of the 1993 and 1994 growing seasons

	Plant N*					
	Grain		Stover		Cob	
N Plots	1993	1994	1993	1994	1993	1994
	kg ha^{-1}					
Labeled & Unlabeled						
Rep 1	85.6	158.2	38.0	44.1	4.7	3.3
Rep 2	83.6	164.7	34.4	37.4	4.1	3.9
Rep 3	91.2	162.3	34.5	38.2	4.7	3.9
Rep 4	91.5	160.8	31.0	43.7	3.8	4.1
Mean**	87.9a	161.5b	34.5c	40.9d	4.4e	3.8
Checks A&B						
Rep 1	46.9	136.8	27.3	27.5	2.2	3.2
Rep 2	51.3	149.5	14.3	32.0	2.7	3.8
Rep 3	56.2	143.3	16.8	28.4	3.0	3.8
Rep 4	54.1	142.5	18.2	32.6	2.5	3.9
Mean**	52.2a	143.0b	19.2c	30.1d	2.6e	3.7

* Mean values between years are significant at $\alpha = 0.05$. All p-values < 0.023.

** Mean values followed by a common letter are significant at $\alpha = 0.01$. All p-values < 0.0037.

Table G2. Dry matter yield (kg ha^{-1}) of aboveground plant parts at the end of the 1993 and 1994 growing seasons

	Dry matter*					
	Grain		Stover		Cob	
Treatment	1993	1994	1993	1994	1993	1994
	kg ha^{-1}					
Labeled & Unlabeled						
Rep 1	5,435	11,910	5,130	6,593	1,222	1,540
Rep 2	5,892	11,771	4,950	6,608	1,251	1,625
Rep 3	6,027	11,703	4,688	6,702	1,246	1,599
Rep 4	5,808	11,675	4,963	6,580	1,223	1,594
Mean	5,791a	11,765b	4,933c	6,621d	1,236e	1,589f
Checks A&B						
Rep 1	3,954	11,459	4,142	5,977	635	1,383
Rep 2	4,215	11,423	3,862	5,942	787	1,558
Rep 3	4,733	11,478	4,653	6,028	1,028	1,515
Rep 4	4,406	11,351	4,210	6,125	806	1,530
Mean**	4,327a	11,428b	4,217c	6,018d	814e	1,496f

* Mean values between years are significant at $\alpha = 0.05$. P-values $< 3.6 \times 10^{-6}$.

** Mean values followed by a common letter are significant at $\alpha = 0.05$. P-values ≤ 0.01.

Table G3. Percent total N, ^{15}N concentrations, and dry matter yield of corn plant materials at the end of the 1993 and 1994 growing seasons

Trt. ID	Rep. #	Plant Material	Total N ('93)	Total N ('94)	Nitrogen-15 ('93)	Nitrogen-15 ('94)	Dry Matter Yield ('93)	Dry Matter Yield ('94)
			--------%------		-----atom %-----		------kg ha^{-1} -----	
14N	1	GRAIN	1.50	1.33	0.3803	0.3667	5368.3	12007.2
14N	2	GRAIN	1.36	1.39	0.3687	0.3695	5797.0	11819.0
14N	3	GRAIN	1.52	1.43	0.3700	0.3713	5790.0	11488.3
14N	4	GRAIN	1.53	1.42	0.3688	0.3681	6139.1	11544.7
14N	1	COB	0.41	0.22	0.4068	0.3665	1188.5	1544.8
14N	2	COB	0.32	0.24	0.5499	0.3693	1274.5	1652.3
14N	3	COB	0.35	0.22	0.5181	0.3697	1240.9	1622.7
14N	4	COB	0.31	0.28	0.5296	0.3682	1259.7	1606.6
14N	1	STOVER	0.65	0.70	0.4326	0.3668	5044.7	6648.5
14N	2	STOVER	0.63	0.55	0.4460	0.3682	4963.9	6699.4
14N	3	STOVER	0.58	0.54	0.4327	0.3710	4463.1	6719.0
14N	4	STOVER	0.55	0.67	0.5139	0.3683	5224.1	6705.8
15N	1	GRAIN	1.65	1.33	2.1243	2.2576	5502.0	11813.6
15N	2	GRAIN	1.48	1.40	2.3665	1.4953	5987.6	11723.6
15N	3	GRAIN	1.51	1.35	2.0939	1.8220	6263.3	11917.2
15N	4	GRAIN	1.62	1.34	2.1262	1.9601	5477.1	11804.2
15N	1	COB	0.36	0.21	2.0252	1.8480	1255.1	1535.4
15N	2	COB	0.33	0.25	2.3199	1.5405	1227.5	1597.2
15N	3	COB	0.41	0.26	2.2775	1.5963	1251.7	1575.7
15N	4	COB	0.32	0.24	2.2024	1.7555	1187.1	1581.1
15N	1	STOVER	0.83	0.64	1.8644	2.0525	5215.5	6536.4
15N	2	STOVER	0.76	0.58	2.0596	1.2298	4935.3	6516.4
15N	3	STOVER	0.88	0.60	1.9047	1.4705	4913.0	6685.8
15N	4	STOVER	0.71	0.66	1.9429	1.6995	4701.9	6454.1
CHECK	1A	GRAIN	1.18	1.20	0.3708	0.3692	4018.1	11559.5
CHECK	1B	GRAIN	1.20	1.19	0.3702	0.3693	3890.2	11357.9
CHECK	2A	GRAIN	1.19	1.33	0.3722	0.3705	4719.6	11380.7
CHECK	2B	GRAIN	1.25	1.29	0.3722	0.3687	3709.6	11465.4
CHECK	3A	GRAIN	1.22	1.41	0.3716	0.3689	4603.5	11355.2
CHECK	3B	GRAIN	1.24	1.09	0.3709	0.3701	4861.9	11601.2
CHECK	4A	GRAIN	1.31	1.24	0.3709	0.3684	4176.8	11337.7

Table G3. (continued)

Trt. ID	Rep. #	Plant Material	Total N ('93)	Total N ('94)	Nitrogen-15 ('93)	Nitrogen-15 ('94)	Dry Matter Yield ('93)	Dry Matter Yield ('94)
			--------%------		-----atom %-----		------kg ha^{-1} -----	
CHECK	4B	GRAIN	1.15	1.27	0.3696	0.3693	4635.3	11364.6
CHECK	1A	COB	0.31	0.22	0.3717	0.3690	680.3	1274.5
CHECK	1B	COB	0.38	0.25	0.3717	0.3683	590.2	1492.3
CHECK	2A	COB	0.38	0.23	0.3728	0.3703	785.2	1539.4
CHECK	2B	COB	0.30	0.25	0.3727	0.3687	790.5	1575.7
CHECK	3A	COB	0.26	0.25	0.3709	0.3690	1007.0	1482.9
CHECK	3B	COB	0.33	0.25	0.3737	0.3702	1048.7	1546.1
CHECK	4A	COB	0.35	0.25	0.3710	0.3681	808.0	1556.9
CHECK	4B	COB	0.28	0.26	0.3727	0.3707	804.0	1503.1
CHECK	1A	STOVER	0.72	0.44	0.3751	0.3664	4437.5	6017.3
CHECK	1B	STOVER	0.59	0.48	0.5397	0.3693	3846.1	5937.0
CHECK	2A	STOVER	0.44	0.57	0.6427	0.3695	4102.2	5932.4
CHECK	2B	STOVER	0.29	0.51	0.6479	0.3691	3621.4	5952.5
CHECK	3A	STOVER	0.35	0.58	0.5168	0.3677	4680.4	6098.7
CHECK	3B	STOVER	0.37	0.36	0.5887	0.3704	4626.3	5956.4
CHECK	4A	STOVER	0.39	0.55	0.6846	0.3685	4036.2	6134.7
CHECK	4B	STOVER	0.47	0.52	0.4966	0.3686	4384.5	6115.3

APPENDIX H

1993 AND 1994 SOIL DATA

Table H1. Percentage total N, NO_3^--N, ^{15}N concentrations and total N (kg ha^{-1}) of soil at the end of the 1993 and 1994 growing seasons

Trt. ID	Rep. #	Depth	Total N ('93)	Total N ('94)	NO3-N ('93)	NO3-N ('94)	Nitrogen-15 ('93)	Nitrogen-15 ('94)	Total N ('93)	Total N ('94)
		cm	--------%------		---mg kg $^{-1}$---		----atom %----		-----kg ha^{-1} ----	
14N	1	0-15	0.106	0.098	8.37	1.65	0.3658	0.3683	2270.8	2099.4
14N	1	15-30	0.089	0.078	8.50	10.05	0.3696	0.3689	1947.2	1706.5
14N	1	30-60	0.046	0.046	3.10	1.58	0.3702	0.3697	1975.1	1975.1
14N	1	60-90	0.019	0.042	5.45	2.92	0.3709	0.3691	785.1	1735.6
14N	1	90-120	0.024	0.023	9.92	1.49	0.3702	0.3680	986.6	945.5
14N	1	120-150	0.015	0.017	5.76	2.32	0.3734	0.3693	630.3	714.4
14N	1	150-180	0.014	0.016	10.38	10.08	0.3697	0.3680	588.7	672.9
14N	2	0-15	0.108	0.135	14.80	3.31	0.3690	0.3690	2313.6	2892.0
14N	2	15-30	0.091	0.115	9.33	4.00	0.3691	0.3692	1991.0	2516.1
14N	2	30-60	0.047	0.104	5.02	4.97	0.3699	0.3691	2018.0	4465.3
14N	2	60-90	0.021	0.040	2.95	8.89	0.3710	0.3691	867.8	1652.9
14N	2	90-120	0.017	0.021	8.62	4.91	0.3686	0.3695	698.9	863.3
14N	2	120-150	0.016	0.018	5.94	6.73	0.3717	0.3671	672.4	756.4
14N	2	150-180	0.015	0.014	11.53	6.72	0.3710	0.3703	630.8	588.7
14N	3	0-15	0.099	0.138	15.47	3.44	0.3694	0.3691	2120.8	2956.3
14N	3	15-30	0.092	0.127	7.86	2.93	0.3697	0.3692	2012.9	2778.6
14N	3	30-60	0.053	0.121	5.23	2.65	0.3712	0.3690	2275.6	5195.3
14N	3	60-90	0.021	0.041	3.46	2.08	0.3709	0.3691	867.8	1694.3
14N	3	90-120	0.018	0.019	8.92	2.45	0.3693	0.3679	740.0	781.1
14N	3	120-150	0.012	0.015	8.65	4.12	0.3692	0.3700	504.3	630.3
14N	3	150-180	0.015	0.019	12.89	10.16	0.3735	0.3694	630.8	799.0
14N	4	0-15	0.105	0.122	17.24	2.01	0.3693	0.3690	2249.3	2613.5
14N	4	15-30	0.112	0.096	13.84	2.75	0.3693	0.3694	2450.4	2100.4
14N	4	30-60	0.066	0.126	9.65	3.34	0.3714	0.3692	2833.8	5409.9
14N	4	60-90	0.030	0.082	8.01	5.57	0.3697	0.3696	1239.7	3388.5

Table H1. (continued)

Trt. ID	Rep. #	Depth	Total N ('93)	Total N ('94)	NO3-N ('93)	NO3-N ('94)	Nitrogen-15 ('93)	Nitrogen-15 ('94)	Total N ('93)	Total N ('94)
		cm	--------%------		---mg kg $^{-1}$---		----atom %----		-----kg ha^{-1} ----	
CHECK	3A	90-120	0.020	0.030	6.04	1.55	0.3704	0.3695	822.2	1233.3
CHECK	3A	120-150	0.018	0.019	9.82	6.16	0.3724	0.3695	756.4	798.4
CHECK	3A	150-180	0.017	0.019	6.55	7.31	0.3703	0.3710	714.9	799.0
CHECK	3B	0-15	0.103	0.143	11.57	2.79	0.3691	0.3690	2206.5	3063.4
CHECK	3B	15-30	0.090	0.126	9.97	2.24	0.3697	0.3696	1969.1	2756.7
CHECK	3B	30-60	0.052	0.105	7.44	1.91	0.3704	0.3684	2232.7	4508.3
CHECK	3B	60-90	0.037	0.044	3.93	1.14	0.3703	0.3693	1529.0	1818.2
CHECK	3B	90-120	0.023	0.019	4.77	3.17	0.3700	0.3695	945.5	781.1
CHECK	3B	120-150	0.016	0.019	7.43	4.25	0.3716	0.3684	672.4	798.4
CHECK	3B	150-180	0.018	0.016	12.93	7.34	0.3721	0.3686	757.0	672.9
CHECK	4A	0-15	0.049	0.136	12.37	2.57	0.3691	0.3687	1049.7	2913.4
CHECK	4A	15-30	0.097	0.107	8.11	2.45	0.3691	0.3692	2122.2	2341.0
CHECK	4A	30-60	0.060	0.141	4.98	4.05	0.3702	0.3690	2576.2	6054.0
CHECK	4A	60-90	0.035	0.070	4.53	2.64	0.3691	0.3693	1446.3	2892.6
CHECK	4A	90-120	0.022	0.021	7.95	4.31	0.3723	0.3693	904.4	863.3
CHECK	4A	120-150	0.010	0.015	10.38	14.53	0.3701	0.3670	420.2	630.3
CHECK	4A	150-180	0.015	0.015	14.70	7.11	0.3719	0.3688	630.8	630.8
CHECK	4B	0-15	0.110	0.112	13.64	1.49	0.3689	0.3690	2356.5	2399.3
CHECK	4B	15-30	0.094	0.116	13.56	2.19	0.3697	0.3694	2056.6	2537.9
CHECK	4B	30-60	0.059	0.135	5.08	3.00	0.3695	0.3699	2533.2	5796.4
CHECK	4B	60-90	0.028	0.057	4.63	2.42	0.3710	0.3695	1157.1	2355.4
CHECK	4B	90-120	0.017	0.024	8.54	3.65	0.3715	0.3704	698.9	986.6
CHECK	4B	120-150	0.014	0.020	10.72	14.49	0.3728	0.3687	588.3	840.5
CHECK	4B	150-180	0.013	0.012	12.78	8.96	0.3701	0.3681	546.7	504.6

Table H1. (continued)

Trt. ID	Rep. #	Depth	Total N ('93)	Total N ('94)	NO3-N ('93)	NO3-N ('94)	Nitrogen-15 ('93)	Nitrogen-15 ('94)	Total N ('93)	Total N ('94)
		cm	--------%	------	---mg kg $^{-1}$	---	----atom	%----	-----kg ha^{-1}	----
14N	4	90-120	0.024	0.032	10.69	21.21	0.3731	0.3693	986.6	1315.5
14N	4	120-150	0.016	0.018	10.22	25.37	0.3746	0.3694	672.4	756.4
14N	4	150-180	0.013	0.174	16.02	12.11	0.3723	0.3689	546.7	7317.3
15N	1	0-15	0.110	0.106	14.08	1.76	0.4107	0.4096	2356.5	2270.8
15N	1	15-30	0.102	0.079	11.25	1.27	0.3840	0.3844	2231.6	1728.4
15N	1	30-60	0.056	0.046	6.32	2.71	0.3807	0.3853	2404.4	1975.1
15N	1	60-90	0.026	0.029	4.64	6.08	0.3775	0.4553	1074.4	1198.4
15N	1	90-120	0.022	0.020	6.73	11.56	0.3729	0.4437	904.4	822.2
15N	1	120-150	0.022	0.020	7.88	14.53	0.3820	0.3695	924.5	840.5
15N	1	150-180	0.016	0.010	8.09	5.79	0.3772	0.3692	672.9	420.5
15N	2	0-15	0.109	0.139	16.88	1.76	0.4164	0.3976	2335.0	2977.7
15N	2	15-30	0.083	0.116	11.40	1.72	0.3828	0.3756	1815.9	2537.9
15N	2	30-60	0.070	0.130	7.75	3.20	0.3771	0.3748	3005.5	5581.7
15N	2	60-90	0.040	0.048	3.97	11.96	0.3730	0.4645	1652.9	1983.5
15N	2	90-120	0.025	0.027	5.59	6.12	0.3718	0.4430	1027.8	1110.0
15N	2	120-150	0.024	0.019	7.78	6.38	0.3720	0.3785	1008.6	798.4
15N	2	150-180	0.025	0.015	8.03	6.69	0.3731	0.3703	1051.3	630.8
15N	3	0-15	0.110	0.141	8.30	1.98	0.4094	0.3964	2356.5	3020.6
15N	3	15-30	0.104	0.099	10.28	2.48	0.3817	0.3774	2275.4	2166.0
15N	3	30-60	0.081	0.131	11.59	3.80	0.3887	0.3708	3477.8	5624.6
15N	3	60-90	0.061	0.082	6.44	3.97	0.3895	0.3743	2520.7	3388.5
15N	3	90-120	0.055	0.035	4.22	11.75	0.3759	0.3911	2261.1	1438.9
15N	3	120-150	0.024	0.016	7.90	6.90	0.3733	0.3740	1008.6	672.4
15N	3	150-180	0.017	0.017	9.52	9.62	0.3734	0.3698	714.9	714.9
15N	4	0-15	0.116	0.118	20.29	1.82	0.4233	0.3906	2485.0	2527.8
15N	4	15-30	0.108	0.094	10.89	1.54	0.3814	0.3771	2362.9	2056.6
15N	4	30-60	0.087	0.154	15.41	3.76	0.3945	0.3702	3735.4	6612.1
15N	4	60-90	0.046	0.105	5.74	4.00	0.3826	0.3752	1900.9	4338.9
15N	4	90-120	0.032	0.036	9.23	4.02	0.3733	0.4158	1315.5	1480.0
15N	4	120-150	0.021	0.018	9.36	10.89	0.3726	0.3748	882.5	756.4
15N	4	150-180	0.018	0.013	9.51	7.57	0.3745	0.3703	757.0	546.7
CHECK	1A	0-15	0.102	0.122	9.94	1.46	0.3694	0.3689	2185.1	2613.5

Table H1. (continued)

Trt. ID	Rep. #	Depth	Total N ('93)	Total N ('94)	NO3-N ('93)	NO3-N ('94)	Nitrogen-15 ('93)	Nitrogen-15 ('94)	Total N ('93)	Total N ('94)
		cm	--------%------		---mg kg $^{-1}$---		----atom %----		-----kg ha^{-1} ----	
CHECK	1A	15-30	0.088	0.044	8.17	1.62	0.3695	0.3693	1925.3	962.7
CHECK	1A	30-60	0.060	0.057	6.82	1.35	0.3696	0.3697	2576.2	2447.4
CHECK	1A	60-90	0.031	0.046	3.07	0.75	0.3705	0.3696	1281.0	1900.9
CHECK	1A	90-120	0.020	0.023	6.44	2.32	0.3718	0.3687	822.2	945.5
CHECK	1A	120-150	0.017	0.017	10.19	8.80	0.3702	0.3684	714.4	714.4
CHECK	1A	150-180	0.023	0.010	10.33	5.49	0.3705	0.3677	967.2	420.5
CHECK	1B	0-15	0.107	0.092	5.25	1.63	0.3690	0.3681	2292.2	1970.9
CHECK	1B	15-30	0.079	0.067	5.13	1.13	0.3709	0.3696	1728.4	1465.9
CHECK	1B	30-60	0.037	0.057	2.90	1.35	0.3715	0.3697	1588.6	2447.4
CHECK	1B	60-90	0.027	0.037	4.95	1.65	0.3701	0.3690	1115.7	1529.0
CHECK	1B	90-120	0.016	0.024	3.29	1.57	0.3712	0.3685	657.8	986.6
CHECK	1B	120-150	0.016	0.019	7.02	14.75	0.3732	0.3698	672.4	798.4
CHECK	1B	150-180	0.018	0.018	7.81	14.36	0.3687	0.3678	757.0	757.0
CHECK	2A	0-15	0.117	0.135	6.92	2.43	0.3689	0.3691	2506.4	2892.0
CHECK	2A	15-30	0.094	0.128	7.54	2.31	0.3697	0.3692	2056.6	2800.5
CHECK	2A	30-60	0.064	0.105	5.54	2.12	0.3697	0.3692	2747.9	4508.3
CHECK	2A	60-90	0.033	0.035	4.61	1.95	0.3704	0.3692	1363.7	1446.3
CHECK	2A	90-120	0.032	0.020	4.64	6.22	0.3694	0.3692	1315.5	822.2
CHECK	2A	120-150	0.013	0.016	5.83	6.97	0.3675	0.3697	546.3	672.4
CHECK	2A	150-180	0.019	0.015	10.43	7.14	0.3709	0.3686	799.0	630.8
CHECK	2B	0-15	0.106	0.132	5.65	1.38	0.3692	0.3697	2270.8	2827.8
CHECK	2B	15-30	0.089	0.116	6.82	2.46	0.3698	0.3695	1947.2	2537.9
CHECK	2B	30-60	0.055	0.118	5.23	2.83	0.3705	0.3700	2361.5	5066.4
CHECK	2B	60-90	0.024	0.047	6.25	2.35	0.3699	0.3698	991.8	1942.2
CHECK	2B	90-120	0.019	0.027	5.17	6.57	0.3697	0.3695	781.1	1110.0
CHECK	2B	120-150	0.014	0.019	6.68	11.26	0.3679	0.3681	588.3	798.4
CHECK	2B	150-180	0.032	0.016	8.59	9.20	0.3699	0.3699	1345.7	672.9
CHECK	3A	0-15	0.099	0.124	5.54	2.54	0.3691	0.3689	2120.8	2656.4
CHECK	3A	15-30	0.087	0.097	6.19	1.74	0.3703	0.3693	1903.5	2122.2
CHECK	3A	30-60	0.049	0.125	4.18	2.68	0.3710	0.3692	2103.9	5367.0
CHECK	3A	60-90	0.024	0.072	4.86	1.35	0.3690	0.3699	991.8	2975.3