1988

Preferential leaching of surface-applied nitrogen fertilizers in Iowa soils

David Lloyd Priebe
Iowa State University

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Preferential leaching of surface-applied nitrogen fertilizers in Iowa soils

Priebe, David Lloyd, Ph.D.

Iowa State University, 1988
Preferential leaching of surface-applied nitrogen fertilizers in Iowa soils

by

David Lloyd Priebe

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Agronomy
             Major: Soil Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work
Signature was redacted for privacy.
For the Major Department
Signature was redacted for privacy.
For the Graduate College

Iowa State University
Ames, Iowa

1988
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DEDICATION

To Carie
INTRODUCTION

It is generally accepted that significant amounts of N can be lost by ammonia volatilization when urea fertilizer is surface-applied to soils without incorporation. Ammonia volatilization is a greater problem with urea than with other N fertilizers because the hydrolysis of urea to ammonium can result in a localized increase in soil pH. This increase in pH favors the formation of ammonia, which easily can escape to the atmosphere.

Most knowledge concerning ammonia volatilization has been established in studies under controlled laboratory, greenhouse, or field conditions. Such studies are designed to evaluate the effects of one soil, climatic, or management factor, or one set of interacting factors, on the amounts of ammonia volatilized. Such studies, therefore, do not provide information necessary to identify the most important factors affecting ammonia volatilization losses under uncontrolled field conditions. And they do not provide information concerning the importance of ammonia volatilization relative to other mechanisms by which urea-N is lost following surface applications to agricultural soils. Such information is needed to select management practices that are most efficient for minimizing these losses.

Studies were initiated in 1982 to learn how frequently significant losses of N occur following surface applications of urea under field conditions typical for corn (Zea mays L.) production in Iowa. Although large losses of N were observed, they appeared to be unrelated to factors known to influence losses of N by ammonia volatilization. This finding
was contrary to initial expectations and prompted a series of follow-up studies, which were conducted during 1983 through 1987. These follow-up studies involved more than 5000 isotope ratio analyses. They provided overwhelming evidence that preferential leaching through soil macropores is an important fate of surface-applied urea in some soils. They also indicated that nitrate from surface-applied fertilizers was leached from soils more rapidly during rainfall than was soil-derived nitrate.

The initial studies and the follow-up studies are discussed in Parts I through V of this dissertation. Some of the information in Part I was presented in my master's thesis, which was completed at Iowa State University in 1985. However, the data have been further analyzed in view of findings gathered in the follow-up studies. Discussions that reflect the additional analyses are provided in Part I to enable more complete and accurate discussions in Parts II through V.
PART I. DISTRIBUTIONS OF UREA-DERIVED N-15 SIX WEEKS AFTER SURFACE APPLICATIONS TO IOWA SOILS
INTRODUCTION

It is generally accepted that significant amounts of N can be lost by ammonia volatilization when urea fertilizer is surface-applied to soils without incorporation. Ammonia volatilization is a greater problem with urea than with other fertilizers because the hydrolysis of urea to ammonium results in a localized increase in soil pH. This increase in pH favors the formation of ammonia, which easily can escape to the atmosphere.

The amount of volatilization that occurs is influenced by a number of factors, including rate and method of application, soil pH, calcium carbonate content, cation exchange capacity, soil organic matter content, soil moisture content, additions of water by rainfall or irrigation, losses of soil water by evaporation, wind speed or rate of aeration across the soil surface, soil and air temperatures, and amount and type of residues present on the soil surface (Terman, 1979; Nelson, 1982; Freney et al., 1983; Fenn and Hossner, 1985). Depending upon the combination of these factors under which ammonia volatilization is assessed, studies have shown that losses attributable to ammonia volatilization can range from less than 1% to greater than 50% of the N from surface-applied urea (Hauck, 1983; Fenn and Hossner, 1985).

Studies were initiated in 1982 to learn how frequently significant losses of N occur following surface applications of urea under field conditions, where all factors affecting ammonia volatilization interact. The field conditions studied were typical for corn (Zea mays L.) production in Iowa. Contrary to initial expectations, the results
suggested that ammonia volatilization was not the major mechanism of N loss, although large losses of N were observed. These findings prompted a series of follow-up studies (Parts II through V of this dissertation), which were conducted during 1983 through 1987. These follow-up studies, which involved more than 5000 isotope ratio analyses, provide overwhelming evidence that preferential leaching through soil macropores is an important fate of surface-applied urea in some soils and that such leaching, rather than ammonia volatilization, may have been the major mechanism of N losses that occurred in the 1982 study.

The objective of this report is to describe the 1982 study. In this report, I use the term macropores to denote soil pores large enough to provide preferential paths of flow so that mixing and transfer between these and other pores is limited. I use the term matrix pores to denote pores that transmit water and solutes at rates slow enough to allow transfer of molecules or ions between different pores (Skopp, 1981; Moore et al., 1986; Steenhuis and Muck, 1988). The water in macropores has been described as mobile water, and the water in matrix pores has been described as immobile water (van Genuchten and Wierenga, 1976; Addiscott, 1977). I use the term preferential movement to indicate that incoming water moves by bypassing the matrix pores and the term complete displacement to describe a situation in which no preferential movement occurs (i.e., when incoming water moves only by displacing water in all pores). Of course, preferential movement and complete displacement are extremes, and movement of water and solutes in a soil actually occurs by combinations of these processes.
MATERIALS AND METHODS

The study was conducted in the spring of 1982 at 10 sites selected to include major soil types used for corn production in Iowa and soils under conventional tillage (i.e., moldboard plow) and no-tillage management. Care was exercised to locate the study sites on areas of uniform soil flat enough to minimize the potential for surface runoff. Table 1 shows information concerning locations of the sites and characteristics of the soils at these sites.

Urea labeled with 5.2 atom percent $^{15}$N was applied to the surfaces of three microplots at each site. Each microplot was established by driving six stakes into the soil at equal intervals on the perimeter of a 2-m-diam. circle and then stretching strings between opposite stakes. The soil area to receive the urea application was identified by placing an 18-cm-diam. ring on the soil surface with its center directly below the point where the strings intersected. The labeled urea was applied within each ring as granules that were formed by compressing 1-g samples of urea powder in a die (2.5 cm in diameter) and slicing the resulting wafers into granules weighing between 10 and 30 mg. After drying these granules for 2 h at 105°C, 0.95-g samples were weighed into packets that were emptied onto the surfaces of individual microplots. Each packet contained 0.44 g urea-N, corresponding to an application rate of 175 kg N ha$^{-1}$. After application of the urea, the rings and strings were removed from the microplots, and wire mesh was placed over each no-till microplot to assure that plant residues remained on the microplot surface.

Forty to forty-five days after application of the urea, soil samples
Table 1. Locations of the study sites and characteristics of the soils at these sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Location (County)</th>
<th>Soil Series b</th>
<th>Drainage class c</th>
<th>pH</th>
<th>Carbonate d</th>
<th>Total N</th>
<th>Sand</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Boone</td>
<td>Salida</td>
<td>Excessive</td>
<td>8.1</td>
<td>4</td>
<td>0.096</td>
<td>65</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>Story</td>
<td>Dickinson</td>
<td>Somewhat excessive</td>
<td>6.5</td>
<td>0</td>
<td>0.135</td>
<td>62</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Monona</td>
<td>Monona</td>
<td>Well</td>
<td>6.1</td>
<td>0</td>
<td>0.174</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Monona</td>
<td>Ida</td>
<td>Well</td>
<td>8.1</td>
<td>11</td>
<td>0.136</td>
<td>6</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>O'Brien</td>
<td>Primghar</td>
<td>Moderately well</td>
<td>6.1</td>
<td>0</td>
<td>0.289</td>
<td>2</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>O'Brien</td>
<td>Primghar-NT</td>
<td>Moderately well</td>
<td>6.4</td>
<td>0</td>
<td>0.335</td>
<td>3</td>
<td>36</td>
</tr>
<tr>
<td>7</td>
<td>Boone</td>
<td>Nicollet-NT</td>
<td>Somewhat poor</td>
<td>6.6</td>
<td>0</td>
<td>0.225</td>
<td>31</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>Floyd</td>
<td>Readlyn</td>
<td>Somewhat poor</td>
<td>6.4</td>
<td>0</td>
<td>0.322</td>
<td>25</td>
<td>29</td>
</tr>
<tr>
<td>9</td>
<td>Floyd</td>
<td>Readlyn-NT</td>
<td>Somewhat poor</td>
<td>6.3</td>
<td>0</td>
<td>0.305</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>10</td>
<td>Boone</td>
<td>Harps</td>
<td>Poor</td>
<td>8.1</td>
<td>16</td>
<td>0.370</td>
<td>23</td>
<td>36</td>
</tr>
</tbody>
</table>

^a pH and carbonate, total N, sand, and clay contents were measured on soil from the surface 5 cm at the beginning of the study at each site.

^b NT designates soils under no-till management.

^c USDA-SCS drainage classification.

^d Calculated as CaCO₃.
were collected from each microplot as follows. (Plant residues were collected from the surface of each microplot under no-tillage management before the soil samples were collected.) Rings 22, 31, 38, and 60 cm in diameter were placed on the soil surface so that the center of each ring coincided with the center of the fertilized circle. Four soil samples were obtained from each of three 5-cm layers (i.e., 0-5 cm, 5-10 cm, and 10-15 cm) by using spatulas and other small digging tools to completely excavate the soil within the 22-cm ring, between the 22- and 31-cm rings, between the 31- and 38-cm rings, and between the 38- and 60-cm rings.

After these excavations, a 2.5-cm-diam. auger was used to obtain three soil samples from the 15-25 cm layer by collecting and compositing six soil cores within the 22-cm ring, eight cores between the 22- and 38-cm rings, and 12 to 15 cores between the 38- and 60-cm rings. By using a 1.5-cm-diam. auger in the holes created by the removal of these cores, three soil samples from the 25-50 cm layer and three soil samples from the 50-100 cm layer were obtained. Because of the large quantities of soil that were obtained between the 38- and 60-cm diameter rings in the 0-5 cm, 5-10 cm, and 10-15 cm layers of each microplot, these samples were thoroughly mixed in the field and 1-kg portions were used as samples for subsequent analyses. All samples were passed through a 2-mm sieve in their entirety, thoroughly mixed, and air-dried. Small portions of selected samples were taken before this air-drying for determinations of urea-N, ammonium-N, and moisture contents. Urea-N was determined by the method of Mulvaney and Bremner (1979). All other analyses were performed on portions of the
Residual plant materials collected from the no-tillage microplots were dried for several days at 65°C, ground with a Wiley Mill, and thoroughly mixed. Ten-gram subsamples of each were finely ground in a Cyclone Sample Mill and dried for 72 h at 65°C.

Concentrations of exchangeable ammonium-N and nitrate-N in the soils, total N contents of the soils and plant residues, and $^{15}$N contents of each of these fractions were determined by using the procedures and calculations described by Sanchez and Blackmer (1988). For some graphical presentations of the data, i.e., depth distributions of labeled nitrate, the concentrations of labeled nitrate found in the innermost circle of each microplot were corrected to include the small amounts of nitrate that diffused laterally from this circle. These corrections were made by dividing the total amount of labeled nitrate recovered in each layer by the mass of soil within the innermost circle of each layer.
RESULTS AND DISCUSSION

According to the initial experimental plan, microplots were to be sampled three weeks after urea applications, and sites that received heavy rainfall were to be abandoned. It was assumed that ammonia volatilization would be the major mechanism of N loss and that little of the labeled N would move below a depth of 15 cm. Under such conditions, accurate determinations of recovery could be obtained by extracting all the soil collected within the innermost rings to this depth and by making adjustments for small amounts of N that moved downward or laterally from this soil. However, an extended period of wet weather delayed sampling until six weeks after application. During this period, there was an unusually high frequency of light rainfall events, there were few sunny days (pan evaporation was about one-third of average at some sites), and the soils remained too wet for field work. Although the soils remained unusually wet, the rainfall amounts were near long-term averages (Table 2).

Because significant amounts of labeled N moved into volumes of soil that were too large to extract without subsampling, determinations of labeled N recovery required knowledge of soil bulk density, and the final accuracy of these determinations was most limited by the accuracy of determinations of soil bulk density. The variability among samples collected for bulk density was sufficiently high that errors in recovery of labeled N may have been as high as 10% of the amounts recovered. The possibility of errors of this magnitude obviates discussions concerning small losses of N, but it does not invalidate any of the discussion
Table 2. Amounts of rainfall that occurred during weekly intervals after urea application at each of the 10 study sites

<table>
<thead>
<tr>
<th>Site No.</th>
<th>First week</th>
<th>Second week</th>
<th>Third week</th>
<th>Fourth week</th>
<th>Fifth week</th>
<th>Sixth week</th>
<th>Total°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0 (0.0)</td>
<td>48</td>
<td>40</td>
<td>42</td>
<td>19</td>
<td>10</td>
<td>159 [154]</td>
</tr>
<tr>
<td>2</td>
<td>67 (7.6)</td>
<td>53</td>
<td>32</td>
<td>2.5</td>
<td>28</td>
<td>132</td>
<td>314 [165]</td>
</tr>
<tr>
<td>3</td>
<td>2.3 (0.0)</td>
<td>22</td>
<td>39</td>
<td>100</td>
<td>52</td>
<td>32</td>
<td>247 [138]</td>
</tr>
<tr>
<td>4</td>
<td>2.3 (0.0)</td>
<td>22</td>
<td>39</td>
<td>100</td>
<td>52</td>
<td>29</td>
<td>244 [129]</td>
</tr>
<tr>
<td>5</td>
<td>6.1 (4.8)</td>
<td>46</td>
<td>44</td>
<td>44</td>
<td>4.6</td>
<td>34</td>
<td>179 [175]</td>
</tr>
<tr>
<td>6</td>
<td>6.1 (4.8)</td>
<td>46</td>
<td>44</td>
<td>44</td>
<td>4.6</td>
<td>34</td>
<td>179 [175]</td>
</tr>
<tr>
<td>7</td>
<td>7.9 (0.5)</td>
<td>33</td>
<td>38</td>
<td>73</td>
<td>4.4</td>
<td>11</td>
<td>167 [157]</td>
</tr>
<tr>
<td>8</td>
<td>58 (46)</td>
<td>22</td>
<td>29</td>
<td>20</td>
<td>4.3</td>
<td>23</td>
<td>156 [159]</td>
</tr>
<tr>
<td>9</td>
<td>57 (3.8)</td>
<td>25</td>
<td>27</td>
<td>23</td>
<td>4.3</td>
<td>23</td>
<td>159 [171]</td>
</tr>
<tr>
<td>10</td>
<td>30 (0.0)</td>
<td>39</td>
<td>55</td>
<td>31</td>
<td>3.1</td>
<td>11</td>
<td>169 [167]</td>
</tr>
</tbody>
</table>

*Values in parentheses show amounts of rainfall that occurred during the first two days after application of urea.

*Values in brackets show normal amounts of rainfall (based on averages during 1941-1970) between the date of application and the date of sample collection (National Oceanic and Atmospheric Administration, 1982.)
presented in this report.

The amounts, forms, and distributions of labeled N recovered in the surface 1-m layers of soil six weeks after application of urea at the 10 sites are shown in Table 3 and Figure 1. Recoveries ranged from 35% to 103%, with a mean recovery of 65% of the N applied. Most (mean of 70%, range of 39 to 88% among sites) of the labeled N recovered was in the form of nitrate (Figure 1) and only a small portion (mean of 3%) was present as exchangeable ammonium (Table 3). Analyses on selected samples in the field-moist condition revealed that no labeled N could be found as urea or nitrite. Less than 1% of the applied N was recovered in plant residues collected from microplots under no-tillage management.

Data in Table 3 show that significant portions (mean of 27%, range of 10 to 55% among sites) of the labeled N recovered in the surface 25 cm of soil were present as KMI-N (Kjeldahl minus inorganic-N). The term KMI-N, as defined by Sanchez and Blackmer (1988), is used because organic forms (soil organic matter, microbial biomass, or plant residues) as well as fixed or nonexchangeable ammonium are included in this fraction and because no attempt was made to distinguish between these forms. Most of the urea-derived N in this fraction was found in the 0-5 cm layer, an observation suggesting that it was formed soon after application of the urea. The presence of urea-derived ammonium in the soil at six weeks after application (see Table 3) suggests that some of this KMI-N was mineralized over time. Direct evidence for such mineralization has been provided by other tracer studies on similar soils (Sanchez, 1986; Part II of this dissertation).
Table 3. Urea-derived ammonium-, KMI-, and total N recovered in the surface 25 cm of soil at the 10 study sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth</th>
<th>As NH₄⁺</th>
<th>As KMI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- cm -</td>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1ᵇ</td>
<td>0-5</td>
<td>0.2</td>
<td>3.4</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.5</td>
<td>4.9</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0.3</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>nd</td>
<td>nd</td>
<td>4.7</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>0-5</td>
<td>0.7</td>
<td>17.6</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.1</td>
<td>2.4</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0.1</td>
<td>3.3</td>
<td>4.8</td>
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<tr>
<td></td>
<td>15-25</td>
<td>nd</td>
<td>nd</td>
<td>4.4</td>
</tr>
<tr>
<td>3</td>
<td>0-5</td>
<td>0.6</td>
<td>6.9</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.4</td>
<td>1.2</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0.2</td>
<td>0.1</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>0.2</td>
<td>nd</td>
<td>16.6</td>
</tr>
<tr>
<td>4</td>
<td>0-5</td>
<td>0.1</td>
<td>7.6</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.3</td>
<td>3.4</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>0.1</td>
<td>2.6</td>
<td>7.0</td>
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<tr>
<td>5</td>
<td>0-5</td>
<td>4.3</td>
<td>25.0</td>
<td>38.8</td>
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<td>5-10</td>
<td>0.7</td>
<td>7.6</td>
<td>19.7</td>
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<tr>
<td></td>
<td>10-15</td>
<td>0.3</td>
<td>1.7</td>
<td>7.9</td>
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<tr>
<td></td>
<td>15-25</td>
<td>0.4</td>
<td>nd</td>
<td>8.5</td>
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<td>6</td>
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<td>14.3</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.2</td>
<td>1.6</td>
<td>7.4</td>
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<td></td>
<td>10-15</td>
<td>0.2</td>
<td>1.0</td>
<td>4.8</td>
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<tr>
<td></td>
<td>15-25</td>
<td>0.1</td>
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<td></td>
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<td>0.3</td>
<td>0.9</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>0.1</td>
<td>nd</td>
<td>1.8</td>
</tr>
</tbody>
</table>

ᵃnd signifies that the value was not determined.

ᵇValues for these sites are means of two microplots. Values for all other sites are means of three microplots.
Table 3. Continued

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth</th>
<th>As NH₄⁺</th>
<th>As KMI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- cm -</td>
<td>---------</td>
<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>8</td>
<td>0-5</td>
<td>0.5</td>
<td>10.9</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.2</td>
<td>1.2</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0.2</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>0.3</td>
<td>nd</td>
<td>3.4</td>
</tr>
<tr>
<td>9</td>
<td>0-5</td>
<td>0.5</td>
<td>11.0</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.1</td>
<td>0.5</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0</td>
<td>0.1</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>0.3</td>
<td>nd</td>
<td>7.7</td>
</tr>
<tr>
<td>10</td>
<td>0-5</td>
<td>0.9</td>
<td>5.7</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.3</td>
<td>1.2</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td>0.1</td>
<td>0.2</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>15-25</td>
<td>0.1</td>
<td>nd</td>
<td>8.6</td>
</tr>
</tbody>
</table>
Figure 1. Mean concentrations of soil-derived and urea-derived nitrate at various depths six weeks after surface application of urea at ten sites.
Site 1
Recovery of $^{15}$N
As NO$_3^-$: 80%
Total: 93%

Site 2
Recovery of $^{15}$N
As NO$_3^-$: 28%
Total: 52%

Site 3
Recovery of $^{15}$N
As NO$_3^-$: 72%
Total: 82%

Site 4
Recovery of $^{15}$N
As NO$_3^-$: 64%
Total: 79%

Site 5
Recovery of $^{15}$N
As NO$_3^-$: 63%
Total: 103%

Site 6
Recovery of $^{15}$N
As NO$_3^-$: 54%
Total: 73%

Site 7
Recovery of $^{15}$N
As NO$_3^-$: 17%
Total: 44%

Site 8
Recovery of $^{15}$N
As NO$_3^-$: 27%
Total: 41%

Site 9
Recovery of $^{15}$N
As NO$_3^-$: 35%
Total: 48%

Site 10
Recovery of $^{15}$N
As NO$_3^-$: 26%
Total: 35%
Probable Mechanisms of N Loss

The results of this study provide little evidence that ammonia volatilization was a major mechanism of N loss because, across all sites, there was no significant relationship between recovery of labeled N and soil pH. Sites 3 and 4 provide an ideal comparison of calcareous and noncalcareous soils because they were less than 100 m apart, because urea was applied to both sites at the same time, and because several days elapsed before significant rainfall occurred. Total amounts of labeled N recovered in microplots at these two sites were not significantly different (Figure 1).

Detailed follow-up studies using $^{15}$N-labeled urea provide strong evidence that ammonia volatilization was not a major mechanism of N loss. Studies conducted in 1983 under conditions similar to those of the present study showed that losses of N occurred mostly after the urea-derived ammonium had been nitrified, i.e., after the potential for ammonia volatilization had largely diminished (Part II). Studies conducted in 1984 (Part III) showed that N losses attributable to ammonia volatilization are negligible if urea is applied to dry soil surfaces, as was done in the present study. Under such conditions, the urea remains on the soil surface until rainfall occurs, and this rainfall usually moves the urea to depths at which ammonia volatilization is not a problem.

The distributions of labeled nitrate in Figure 1 indicate that significant amounts of labeled N moved downward through the soil profiles. At some sites (notably, sites 1 and 4), the labeled nitrate
was present largely as a concentration "bulge" located well below the soil surface. Such concentration bulges would be expected if water and solutes moved by complete displacement (see Nye and Tinker, 1977; Frissel and van Veen, 1981; Wild and Cameron, 1981; Carsel et al., 1985; Jones and Kiniry, 1986). Because sites 1 and 2 were both coarse-textured soils that would be expected to have similar capacities for infiltration through matrix pores and because site 2 received about twice as much rainfall as did site 1, it is likely that the nitrate bulge was leached below the depth sampled at site 2.

At sites 7, 8, 9, and 10, there was no indication of a clearly defined nitrate bulge below the soil surface. Instead, the labeled nitrate was dispersed through the soil profiles in a manner that would be expected if water and urea or labeled nitrate moved preferentially through soil macropores. Preferential movement results in great dispersion of solutes initially present near the soil surface because some of the solute moves more rapidly and some more slowly than would be expected with complete displacement (Quisenberry and Phillips, 1976; Thomas and Phillips, 1979; Beven and Germann, 1982; Germann et al., 1984; White, 1985). Although it was not recognized when this study was conducted, the major difference among sites probably relates to drainage characteristics and to propensity for preferential movement of water through soil macropores. For this reason, the sites are ordered from best drained to most poorly drained in all tables and figures.

Compared to the soils at sites 1 through 4, the soils at sites 7 through 10 have greater propensities for preferential movement because
they have greater tendencies to develop shrink-swell cracks and because they have lower capacities for infiltration through matrix pores. During rainfalls, these soils also are more likely to have pools of free water (or water having low matric suction) at the soil surface or at a discontinuity in the profile. This free water can enter macropores and move rapidly through the profile. Such preferential movement has been demonstrated unequivocally by applying $^{18}$O-labeled water to a soil similar to site 7 (Part V). Other follow-up studies conducted on soils having drainage characteristics similar to sites 7 through 10 showed that urea-derived N was lost more rapidly than was soil-derived N during rainfall events (Part II). Similar observations were made with surface-applied nitrate (Part IV). Such preferential leaching can be explained if the labeled N tends to be in mobile water and soil-derived N tends to be in immobile water. As pointed out in Part IV, surface-applied fertilizers are readily dissolved in mobile water during rainfall soon after application.

It is unlikely that concentration bulges formed and then moved below the 1-m sampling depth at sites 5 through 10. Because the nitrate bulges did not reach the lowest depth sampled at sites 1, 3, and 4, such formation and movement would require that rainfall leach nitrate through matrix pores more efficiently in poorly drained soils than in excessively drained soils. That is, sites 1, 3, and 4 received amounts of rainfall that were similar to, or greater than, the amounts received at sites 5 through 10 (Table 2).

The design of this study does not permit resolution of losses by
leaching and denitrification, both of which are favored by excessive rainfall. However, evidence provided in follow-up studies on similar soils (Parts II, IV, and V of this dissertation) suggests that denitrification was not the major mechanism of N loss. As pointed out by Blackmer (1987) and as discussed in Part IV, losses by denitrification can be easily confused with losses by leaching when preferential movement occurs.

Figure 2 shows that little lateral movement of labeled N occurred in the better drained soils (i.e., sites 1 through 6) because, compared to the innermost ring, relatively small amounts of nitrate were detected in the outer rings of soil. When examining this figure, it is important to note that urea was applied only to the innermost circle of soil. The relative concentrations in the outer rings of soil were higher in the more poorly drained soils (i.e., sites 7 through 10). It is unlikely that labeled nitrate was moved from the volume of soil sampled by complete displacement in the more poorly drained soils because most nitrate did not escape from the excessively drained soils, because all sites had similar amounts of rainfall, and because rainfall moving by displacement should not be expected to move labeled N deeper in poorly drained soils than in excessively drained soils.

If macropores promote lateral movement, and they probably do (Part V), then an increase in lateral movement cannot be used as evidence that preferential movement through macropores is not important. If temporary water tables developed and labeled nitrate moved laterally with this water, then this labeled nitrate probably was lost from the rooting zones
Figure 2. Mean concentrations of urea-derived nitrate found in various volumes of soil six weeks after surface application of urea at 10 sites. Urea was applied only to the innermost ring.
as the water tables receded. Direct evidence to support this conclusion is provided by Sanchez et al. (1987), who worked on soils similar to those studied here and found that corn plants outside of plots treated with labeled N took up negligible amounts of this N. For these reasons and because preferential movement can result in rapid loss of nitrate from rooting zones, it makes little difference whether labeled nitrate moved straight downward or downward with a lateral component in the more poorly drained soils.

Overall, the amounts of labeled N lost from some microplots greatly exceeded initial expectations and probably did not occur by ammonia volatilization. These losses are especially important because they occur between the time N fertilizers are applied and the time this N is utilized by crops. Therefore, finding ways to minimize these losses offers clear economic benefits for crop producers as well as environmental benefits for society. The overall finding (from this study and from follow-up studies reported in Parts II, IV, and V) that leaching of urea-derived N may be responsible for N losses is important when selecting the most efficient management practices for minimizing these losses and when deciding where these management practices should be used.
SUMMARY

Studies were conducted to assess the fate of urea during the first six weeks after it is surface-applied to soils under field conditions typical for corn production in Iowa. Granular urea labeled with $^{15}$N was applied at a rate of 175 kg N ha$^{-1}$ to the surfaces of triplicate microplots at 10 sites in the spring of 1982. Soil samples were collected six weeks after application and analyzed to determine recoveries of the labeled N in the surface 1 m of the microplots. These recoveries ranged from 35% to essentially 100%, with a mean recovery of 65% of the N applied. Contrary to initial expectations, the losses appeared to be unrelated to factors known to influence losses of N by ammonia volatilization. The distributions of labeled N in the soil profiles from which the greatest losses occurred suggested that some labeled N may have been leached from these profiles by water moving preferentially through soil macropores. Leaching through macropores and denitrification are considered reasonable explanations for the significant N losses from the poorly drained soils studied because of the weather conditions during the study period. These findings indicate a need for studies that can distinguish between ammonia volatilization, leaching, and denitrification as mechanisms by which surface-applied urea N is lost from soils. This distinction is necessary for identifying situations where the potential for loss is greatest and for finding the most promising ways to prevent these losses.
REFERENCES


PART II. PREFERENTIAL LEACHING AS A FATE
OF N FROM SURFACE-APPLIED UREA IN IOWA SOILS
INTRODUCTION

Studies conducted in 1982 showed that significant amounts of urea-derived $^{15}$N were lost from the surface meter of some Iowa soils shortly after surface applications during a wet spring (Part I). Such losses might be attributed to ammonia volatilization, which is promoted by localized increases in soil pH that accompany hydrolysis of urea (Hauck, 1983; Gould et al., 1986). However, the extent of losses seemed unrelated to factors known to influence ammonia volatilization. The distributions of labeled N in the soil profiles from which the greatest losses occurred suggested that labeled N may have been leached from these profiles by water moving preferentially through soil macropores.

Numerous studies (Quisenberry and Phillips, 1976; Thomas and Phillips, 1979; Beven and Germann, 1982; Germann et al., 1984; White, 1985) have shown that preferential movement of water and solutes through macropores is important in some soils. Such preferential movement results in a marked dispersion of solutes initially present near the soil surface and rapid loss of some of this solute by leaching through the soil profile. Despite reports indicating that this process can occur, recent reviews (Stevenson, 1982; Hauck, 1984) give little indication that preferential movement through soil macropores is recognized as an important factor influencing the fate of N in agricultural soils. Accordingly, N management practices are not being selected to avoid problems associated with this preferential movement.

The objective of this report is to describe studies conducted in 1983 to distinguish between losses of N by ammonia volatilization and by
leaching or denitrification during the first two months after surface application of urea. The studies were conducted on soils similar to those showing large losses in 1982. Unlike the studies conducted in 1982, soils were sampled at four times after surface application of urea. The rationale for these studies was that sampling at different times after application would reveal when losses of N occurred and, therefore, the most probable mechanism(s) of this loss.

In this report, I use the terms complete displacement, preferential movement, macropores, and related terms as defined in Part I.
MATERIALS AND METHODS

The study was conducted at four sites during the spring and early summer of 1983. The sites were selected to include two calcareous soils (Canisteo and Calcareous Overwash) and two noncalcareous soils (Clarion and Webster) used for corn (Zea mays L.) production in central Iowa. All soils were managed by conventional tillage practices. Care was exercised to locate the study sites on areas of uniform soil flat enough to limit the potential for surface runoff. Table 1 shows information concerning the characteristics of the soils at these sites.

At each site, 12 microplots were established on a 10- by 15-m area by driving stakes into the soil on the perimeter of the area and stretching strings across opposite stakes. The points directly below the intersections of the strings were designated as the centers of the microplots. Rings 18 cm in diameter were placed on the soil at the microplot centers to mark the areas to be fertilized. Urea labeled with 5.2 atom percent $^{15}$N was applied within these rings as granules that were formed by compressing 1-g samples of urea powder in a die (2.5 cm in diameter) and slicing the resulting wafers into granules weighing 10 to 30 mg. These granules were dried for 2 h at 105°C and 0.95-g samples were weighed into packets that were emptied onto the surfaces of individual microplots. Each packet contained 0.44 g urea-N, corresponding to an application rate of 175 kg N ha$^{-1}$. Immediately after application of the urea, the rings and strings were removed from the microplots. Composite samples of soil from each site were collected (for
Table 1. Characteristics of the soils at the study sites

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Soil Series</th>
<th>Drainage class</th>
<th>pH</th>
<th>Carbonate</th>
<th>Total N</th>
<th>Sand</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Webster</td>
<td>Poor</td>
<td>6.6</td>
<td>0</td>
<td>0.332</td>
<td>28</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>Clarion</td>
<td>Well</td>
<td>6.2</td>
<td>0</td>
<td>0.205</td>
<td>36</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>Canisteo</td>
<td>Poor</td>
<td>7.9</td>
<td>9</td>
<td>0.292</td>
<td>34</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>Calcareous overwash</td>
<td>Poor</td>
<td>8.1</td>
<td>13</td>
<td>0.276</td>
<td>18</td>
<td>36</td>
</tr>
</tbody>
</table>

\(^a\) pH and carbonate, total N, sand, and clay contents were measured on soil from the surface 5 cm at the beginning of the study at each site.

\(^b\) USDA-SCS drainage classification.

\(^c\) Calculated as CaCO\(_3\).
determinations of soil-derived nitrate concentration) at depths of 0-5, 5-10, 10-15, 15-25, 25-50, and 50-100 cm by taking 10 soil cores from the microplot area.

Recoveries and distributions of the labeled N were determined at two, four, six, and eight weeks after application of urea by collecting and analyzing soil samples from triplicate microplots at each site as described in Part I. Where concentrations of labeled N are presented, these concentrations include an adjustment for lateral movement. That is, the values indicate concentrations of labeled N under the fertilized portion of the microplots after corrections for labeled N recovered in the outer rings of soil. The calculation used for making these corrections was described in Part I.
RESULTS AND DISCUSSION

Figure 1 shows when urea was applied, when microplots were sampled, and when rainfall occurred at each of the sites. About half of all rainfall during the study occurred within the last five days of June and the first four days of July. This period of heavy rainfall occurred between the third and fourth samplings at site 1 and between the second and third samplings at sites 2, 3, and 4. Total rainfall between the time of urea application and the fourth sampling at each site ranged from 80 to 140 mm greater than the 30-year mean rainfall for the area (National Oceanic and Atmospheric Administration, 1983). Therefore, it should be considered that above-average amounts of water moved through the soil profiles during this study.

The amounts and forms of urea-derived N recovered in the surface meter of the soils at various times after urea application are shown in Figure 2. Recoveries of the labeled N were high (mean of 100%, range of 90 to 109% among sites) at two weeks after application and generally decreased over time. By about eight weeks after urea application, less than half (mean of 37%, range of 25 to 51% among sites) of the labeled N was recovered in the surface meter of the microplots. Table 2 shows LSD values for evaluating differences in percentage recovery between sampling times. As discussed in Part I, uncertainties in soil bulk density may have introduced errors as great as 10% of the N recovered. Apparent increases (which were not statistically significant) in percentage recovery during some time periods probably reflect spatial variability in soil properties because different microplots were destructively sampled.
Figure 1. Rainfall events that occurred during the study in relation to date of urea application (A) and dates of sample collection (S) at each site.
Figure 2. Amounts and forms of urea-derived N recovered in the surface meter of soil at various times after urea application at each site (means of three microplots)
Recovery of urea-derived N (%)

- Webster Soil
- Clarion Soil
- Canisteo Soil
- Calcareous Overwash Soil

WEEKS AFTER APPLICATION:
- Two
- Four
- Six
- Eight

NH₄⁺-N  NO₃⁻-N  K⁺-N
Table 2. Least significant differences ($\alpha = 0.05$) between sampling times for the percentages recovery of labeled N in various forms shown in Figure 2

<table>
<thead>
<tr>
<th>Site</th>
<th>LSD values for percentage recovery</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As $\text{NH}_4^+$</td>
<td>As $\text{NO}_3^-$</td>
</tr>
<tr>
<td>1</td>
<td>3.1</td>
<td>18.1</td>
</tr>
<tr>
<td>2</td>
<td>8.1</td>
<td>35.0</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>8.9</td>
</tr>
<tr>
<td>4</td>
<td>1.1</td>
<td>16.4</td>
</tr>
<tr>
<td>Mean</td>
<td>1.9</td>
<td>8.8</td>
</tr>
</tbody>
</table>

at each date. These problems are unavoidable in field studies and obviate discussions concerning small differences in recovery of N, but they do not invalidate any of the discussion presented in this report.

It is noteworthy that seemingly large errors in percentage recovery of labeled N must be expected when large amounts of this N are lost and, therefore, that seemingly large errors do not necessarily indicate unacceptable variability. For example, 84% plus or minus 10% loss of N seems more acceptable than does 16% plus or minus 10% recovery of N, even though both describe the same situation (i.e., site 3 at six weeks after application).

Significant amounts (25 to 45%) of labeled N were found in the KMI-N (Kjeldahl minus inorganic-N) fraction at two weeks after application, but the amounts of labeled N in this fraction decreased over time (Figure 2).
The KMI-N fraction, as defined by Sanchez and Blackmer (1988), includes labeled N as organic matter and nonexchangeable ammonium, both of which are relatively immobile in soils. The immobility of these forms of N explains why most of the N in this fraction was found in the 0-5 cm layer at all sites and sampling times (Table 3). Incorporation of nitrate into microbial tissues may have caused slight increases in amounts of labeled N in the KMI-N fraction beneath the 0-5 cm layer at later sampling dates at some sites (Table 3). Mineralization undoubtedly accounts for the decreases in amounts of labeled N in this fraction over time. Such mineralization is evidenced by small amounts of exchangeable ammonium found at the later sampling dates (Table 4). These observations indicate that incorporation of urea-derived N into immobile fractions often is a major factor protecting this N from rapid losses by ammonia volatilization, leaching, or denitrification.

High concentrations of labeled ammonium in the surface layer at two weeks at some sites (especially sites 1 and 4, Table 4) indicate significant potential for ammonia volatilization during the first four weeks. However, even if all of the N lost during the first four weeks was lost by ammonia volatilization (which is unlikely), this could not have been the most important fate of the labeled N over the entire eight weeks because N losses were greater after the opportunity for ammonia volatilization essentially had passed. That is, mean recoveries decreased from 78 to 37% between four and eight weeks after application (Figure 2). These observations indicate that losses by leaching and (or) denitrification must have greatly exceeded losses by ammonia volatilization.
Table 3. Amounts of labeled N recovered as KMI-N in the surface 25 cm of microplots at various times after surface application of labeled urea (means of 3 microplots)

<table>
<thead>
<tr>
<th>Depth</th>
<th>At two weeks</th>
<th>At four weeks</th>
<th>At six weeks</th>
<th>At eight weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>- cm -</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>36.9 (63)</td>
<td>19.0 (33)</td>
<td>16.0 (28)</td>
<td>16.3 (28)</td>
</tr>
<tr>
<td>5-10</td>
<td>2.3 (4.0)</td>
<td>1.0 (1.8)</td>
<td>3.8 (6.6)</td>
<td>3.0 (5.2)</td>
</tr>
<tr>
<td>10-15</td>
<td>1.0 (1.6)</td>
<td>1.5 (2.6)</td>
<td>3.4 (5.9)</td>
<td>3.2 (5.6)</td>
</tr>
<tr>
<td>15-25</td>
<td>0.8 (0.6)</td>
<td>0.1 (0.3)</td>
<td>2.7 (2.2)</td>
<td>2.7 (1.7)</td>
</tr>
<tr>
<td>Site 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>18.0 (32)</td>
<td>15.1 (27)</td>
<td>8.5 (15)</td>
<td>7.6 (14)</td>
</tr>
<tr>
<td>5-10</td>
<td>4.8 (8.5)</td>
<td>2.2 (3.9)</td>
<td>1.8 (3.3)</td>
<td>1.3 (2.3)</td>
</tr>
<tr>
<td>10-15</td>
<td>1.7 (3.0)</td>
<td>1.6 (2.9)</td>
<td>1.5 (2.6)</td>
<td>1.1 (1.9)</td>
</tr>
<tr>
<td>15-25</td>
<td>0.6 (0.5)</td>
<td>1.4 (1.2)</td>
<td>3.1 (2.7)</td>
<td>1.8 (1.5)</td>
</tr>
<tr>
<td>Site 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>27.7 (48)</td>
<td>19.0 (33)</td>
<td>10.3 (18)</td>
<td>15.6 (27)</td>
</tr>
<tr>
<td>5-10</td>
<td>0.9 (1.5)</td>
<td>3.2 (5.6)</td>
<td>1.0 (1.8)</td>
<td>1.0 (1.8)</td>
</tr>
<tr>
<td>10-15</td>
<td>0.1 (0.1)</td>
<td>1.1 (1.9)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>15-25</td>
<td>0 (0)</td>
<td>1.1 (0.9)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Site 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>46.9 (87)</td>
<td>23.8 (44)</td>
<td>17.1 (32)</td>
<td>17.8 (33)</td>
</tr>
<tr>
<td>5-10</td>
<td>0.1 (0.2)</td>
<td>5.2 (9.6)</td>
<td>1.4 (2.7)</td>
<td>2.4 (4.4)</td>
</tr>
<tr>
<td>10-15</td>
<td>0 (0)</td>
<td>1.0 (1.9)</td>
<td>0.7 (1.2)</td>
<td>1.1 (2.1)</td>
</tr>
<tr>
<td>15-25</td>
<td>0 (0)</td>
<td>0.4 (0.4)</td>
<td>0.8 (0.7)</td>
<td>0.8 (0.7)</td>
</tr>
</tbody>
</table>

Values in parentheses indicate concentrations (mg N kg⁻¹ soil) of labeled KMI-N.
Table 4. Amounts of labeled N recovered as ammonium in the surface 25 cm of microplots at various times after surface application of labeled urea (means of 3 microplots)

<table>
<thead>
<tr>
<th>Depth</th>
<th>At two weeks</th>
<th>At four weeks</th>
<th>At six weeks</th>
<th>At eight weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>- cm -</td>
<td>--------------</td>
<td>---------------</td>
<td>--------------</td>
<td>---------------</td>
</tr>
<tr>
<td></td>
<td>Percentage recovery of labeled N as ammonium$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>22.7 (39)</td>
<td>8.0 (14)</td>
<td>1.9 (3.2)</td>
<td>1.9 (3.3)</td>
</tr>
<tr>
<td>5-10</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.2)</td>
<td>0.1 (0.2)</td>
<td>0.2 (0.3)</td>
</tr>
<tr>
<td>10-15</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0.1 (0.2)</td>
<td>0.2 (0.3)</td>
</tr>
<tr>
<td>15-25</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0.2 (0.1)</td>
<td>0.3 (0.2)</td>
</tr>
<tr>
<td>Site 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>10.1 (18)</td>
<td>3.9 (7.0)</td>
<td>1.4 (2.5)</td>
<td>0.9 (1.6)</td>
</tr>
<tr>
<td>5-10</td>
<td>0.6 (1.1)</td>
<td>0.1 (0.2)</td>
<td>0.1 (0.2)</td>
<td>0.1 (0.2)</td>
</tr>
<tr>
<td>10-15</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.2)</td>
<td>0.1 (0.2)</td>
</tr>
<tr>
<td>15-25</td>
<td>0 (0)</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.1)</td>
<td>0.1 (0.1)</td>
</tr>
<tr>
<td>Site 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>12.6 (22)</td>
<td>1.8 (3.1)</td>
<td>0.9 (1.5)</td>
<td>1.2 (2.1)</td>
</tr>
<tr>
<td>5-10</td>
<td>0 (0)</td>
<td>0.1 (0.1)</td>
<td>0 (0)</td>
<td>0.1 (0.2)</td>
</tr>
<tr>
<td>10-15</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>15-25</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Site 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-5</td>
<td>50.7 (94)</td>
<td>0.6 (1.2)</td>
<td>2.0 (3.6)</td>
<td>1.5 (2.8)</td>
</tr>
<tr>
<td>5-10</td>
<td>0 (0)</td>
<td>0.1 (0.2)</td>
<td>0.1 (0.1)</td>
<td>0.2 (0.3)</td>
</tr>
<tr>
<td>10-15</td>
<td>0 (0)</td>
<td>0 (0.1)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>15-25</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>0 (0)</td>
</tr>
</tbody>
</table>

$^a$Values in parentheses indicate concentrations (mg N kg$^{-1}$ soil) of labeled ammonium.
volatilization.

Figure 3 shows that labeled N moved downward through the soil profiles. Two observations indicate a degree of dispersion of labeled N that can be explained best by preferential movement of water and this N through soil macropores. The first is that rainfalls of as little as 50 or 60 mm (sites 3 and 4, Figure 1) moved labeled nitrate to the lowest depth sampled at four weeks. Because the surface layers were completely removed before the lower depths were sampled and because other precautions were taken, the presence of nitrate at the lower depths cannot be attributed to cross-contamination of samples. The second is that large amounts of rainfall did not leach all nitrate (especially all soil-derived nitrate) from the uppermost layers sampled. Most nitrate would have been leached from the uppermost layers if rainfall had moved through the soils largely by displacement.

The amounts and distributions of soil-derived nitrate were less influenced by rainfalls than were the amounts and distributions of labeled nitrate (Figure 3). This selective loss of labeled nitrate would be difficult to explain unless labeled nitrate tended to move with the mobile water in macropores and soil-derived nitrate tended to remain in the immobile water in matrix pores. Because the labeled urea was surface-applied, it is likely that it was readily dissolved in the mobile water during rainfall events soon after application. In contrast, soil-derived nitrate would tend to be in the matrix pores, either because it was formed there or because soil-derived nitrate near macropores had been leached by earlier rainfalls.
Figure 3a. Concentrations of soil-derived and urea-derived nitrate found in microplot profiles sampled at various times (means of three microplots). Concentrations less than 0.2 mg N kg$^{-1}$ are not shown.
Soil-derived NO$_3^-$

Urea-derived NO$_3^-$

Site 1
0 Weeks
2 Weeks
4 Weeks
6 Weeks
8 Weeks

Site 2
0 Weeks
2 Weeks
4 Weeks
6 Weeks
8 Weeks

DEPTH BELOW SOIL SURFACE (cm)

NITRATE CONCENTRATIONS (mg NO$_3^-$ N kg$^{-1}$ soil)
Figure 3b. Concentrations of soil-derived and urea-derived nitrate found in microplot profiles sampled at various times (means of three microplots). Concentrations less than 0.2 mg N kg$^{-1}$ are not shown.
Soil-derived NO<sub>3</sub>^−

Urea-derived NO<sub>3</sub>^−

NITRATE CONCENTRATIONS (mg NO<sub>3</sub>^− N kg<sup>−1</sup> soil)

DEPTH BELOW SOIL SURFACE (cm)

Site 3
0 Weeks
2 Weeks
4 Weeks
6 Weeks
8 Weeks

Site 4
0 Weeks
2 Weeks
4 Weeks
6 Weeks
8 Weeks

To 103
To 69
Studies (reported in Part V) in which $^{18}O$-labeled water and $^{15}N$-labeled urea were applied to undisturbed columns of soil similar to those studied here show that surface-applied urea tends to move with mobile water during rainfalls soon after application to soils having macropores. Although no attempt was made to quantitatively determine pore size distributions, the soils in the present study clearly had macropores. This was especially evident upon visual examination of soil beneath the plow layer, where the soils can be accurately described as densely packed, clayey materials having macropores formed by plant roots or soil fauna. The soil in the plow layer was highly aggregated and had numerous shrinkage cracks, worm channels, and decaying plant residues that can function as macropores. As noted in Part V, the importance of macropores under such conditions is easily appreciated by watching surface drainage from small puddles that form on the soil microrelief during rainfall events.

The results presented in Part V clearly indicate that urea as well as nitrate can be preferentially leached through soil macropores. Clearly, such movement of urea would inhibit losses of N by ammonia volatilization. Hydrolysis of urea by soil enzymes near macropores also could reduce the amount of urea leached through soil macropores because this N would become relatively immobile as exchangeable ammonium. When this ammonium is nitrified, however, the resulting nitrate would be near macropores and vulnerable to leaching with mobile water during the next rainfall.

Information in Figure 3 provides evidence that denitrification could
not account for the large losses of labeled nitrate. My reasoning is as follows. The soils were sufficiently aerobic that oxygen strongly inhibited denitrification. If this inhibition were reduced by high soil moisture contents, then the resulting denitrification would have occurred first in the centers of aggregates and last near soil macropores (Currie, 1961; Leffelaar, 1979, 1986; Smith, 1977, 1980). Because soil-derived nitrate tended to be where denitrification is most expected and labeled nitrate tended to be where denitrification is least expected, the finding that labeled nitrate disappeared more rapidly than soil-derived nitrate is strong evidence that denitrification was not a major mechanism of loss of labeled nitrate.

It should be noted that losses of nitrate by denitrification and by preferential leaching easily can be confused under field conditions if the consequences of preferential movement through soil macropores are not recognized. If, for example, it were assumed that nitrate leaching must be accompanied by the downward movement of a detectable concentration bulge, then any losses of nitrate before the concentration bulge reached the lower depths sampled would appear to be evidence that denitrification occurred. Such losses can also be evidence of the marked dispersion of nitrate that occurs during preferential movement.

Especially at the lower depths sampled, lateral movement may have been responsible for some of the observed losses of labeled N. It should be noted that the distributions of nitrate shown in Figure 3 have been corrected for lateral movement. That is, the concentrations of labeled nitrate shown in this figure indicate concentrations of labeled nitrate
under the fertilized portion of the microplots after corrections for N recovered in the outer rings of soil. Data presented in Part I showed that lateral movement of labeled nitrate was negligible in soils that showed no evidence for preferential movement through macropores. If macropores promote lateral movement, and they probably do (Part V), then it is possible that some labeled N was lost by lateral movement in the present study. Because preferential movement also promotes rapid loss of nitrate from rooting zones, however, it makes little difference whether this movement is straight downward or laterally downward. Direct evidence to support this conclusion was provided by Sanchez et al. (1987), who worked on soils similar to those studied here and found that corn plants outside of plots treated with labeled N took up negligible amounts of this N. It also must be concluded, therefore, that the undesirable consequences of underestimating the importance of lateral movement (in this study and in the study reported in Part I) are smaller than the undesirable consequences of continued failure to recognize the importance of preferential movement when selecting N management practices.

Preferential leaching could be detected in this study only because tracers were used. Amid the high and variable concentrations of soil-derived nitrate, it would have been impossible to determine that small amounts of rainfall moved urea-derived nitrate more than 75 cm deep (Figure 3) had tracers not been used. It also would have been much more difficult to determine that labeled nitrate was not conserved within concentration bulges that remained within the depths sampled. Because
only a limited number of studies have been conducted with labeled N under field conditions, it is not surprising that preferential leaching of fertilizer-derived N has received little attention.

Overall, the results of this study, which showed that large amounts of N from surface-applied urea are lost soon after application to soils having macropores during a wet spring, substantiate observations made in the 1982 study (Part I). This study provided direct evidence that the greatest losses of urea-derived N occurred after opportunity for ammonia volatilization had passed. The finding that amounts and distributions of soil-derived nitrate were little influenced by rainfalls that resulted in marked losses of urea-derived nitrate is strong evidence that preferential leaching of urea or urea-derived nitrate was a more important mechanism of labeled N loss than was denitrification.
SUMMARY

Concerns about using urea as a surface-applied fertilizer usually focus on the high potential for losses of N by ammonia volatilization. However, recent tracer studies indicate that N from surface-applied urea may also be vulnerable to loss by leaching through soil macropores. In the work reported here, field studies were conducted to acquire a better resolution of losses by ammonia volatilization and losses by leaching. Granular urea labeled with $^{15}$N was applied at a rate of 175 kg N ha$^{-1}$ to the surfaces of microplots at four sites. Losses of this N were assessed by determining recoveries of labeled N in the surface 1-m layers of soil at two, four, six, and eight weeks after application. Greater than average amounts of rainfall occurred during the study. Mean recoveries of the applied N decreased over time, ranging from 100% at two weeks to 37% at eight weeks. At all sites, the greatest N losses occurred after the opportunity for ammonia volatilization had passed. The distributions of labeled nitrate and soil-derived nitrate provided strong evidence that preferential movement of water and labeled nitrate through soil macropores occurred and, therefore, that preferential leaching was an important mechanism of N loss in this study. These results indicate that preferential leaching through soil macropores deserves greater attention as a fate of surface-applied urea.
REFERENCES


PART III. SOIL MOISTURE CONTENT AT TIME OF APPLICATION AS A FACTOR AFFECTING LOSSES OF N FROM SURFACE-APPLIED UREA
INTRODUCTION

It is generally accepted that N can be lost by ammonia volatilization after surface applications of urea to agricultural soils. The amount of volatilization that occurs is influenced by a number of factors, including rate and method of application, soil pH, calcium carbonate content, cation exchange capacity, soil organic matter content, soil moisture content, additions of water by rainfall or irrigation, losses of soil water by evaporation, wind speed or rate of aeration across the soil surface, soil and air temperatures, and amount and type of residues present on the soil surface (Terman, 1979; Nelson, 1982; Freney et al., 1983; Fenn and Hossner, 1985). The effects of each of these factors have been established largely in studies where all factors except the one being evaluated are carefully controlled. Although such studies provide clear information concerning how the various factors influence ammonia volatilization, they provide little information concerning how these factors interact under field conditions. A better knowledge of these interactions is necessary to identify the most important factors affecting N losses in practical field situations, to predict when ammonia volatilization is most likely to be a problem, and to select the most appropriate management practices for minimizing these losses.

Observations made in recent $^{15}$N tracer studies (Parts I and II) suggest that an interaction between initial soil moisture content and rainfall is an important factor affecting the fate of surface-applied urea under field conditions. In these studies, ammonia volatilization
was not significant in situations where it was expected to be significant. A likely explanation for this lack of volatilization is that, because the urea was applied only to dry soil surfaces, rainfall moved the urea into the soil before it was hydrolyzed. Several studies have shown that urea hydrolysis is inhibited at low soil moisture contents (Volk, 1966; Vlek and Carter, 1983; Ferguson and Kissel, 1986; McInnes et al., 1986; Reynolds and Wolf, 1987) and that ammonia volatilization losses can be largely avoided if urea remains unhydrolyzed on a dry soil surface until it is moved into the soil by rainfall (Marshall and DeBell, 1980; Fenn and Miyamoto, 1981; Fox and Hoffman, 1981; Craig and Wollum, 1982; Harper et al., 1983; Bouwmeester et al., 1985; Bundy and Oberle, 1988). These studies focus on conditions found in forests and grasslands (where soils are covered by a layer of plant residues), in irrigated agriculture (where inputs of water are controlled), and in dryland agriculture. The interaction of initial soil moisture content and rainfall, however, has received little attention when considering practical ways to minimize losses of N applied as urea to bare soils in the Corn Belt and other humid agricultural areas. Such applications are important because large amounts of fertilizer N are applied to bare soils during row crop production in these areas.

The objective of the work reported here was to evaluate the importance of the interaction between initial soil moisture content and rainfall as a factor affecting amounts of N lost by ammonia volatilization after surface applications of urea to bare soils under conditions often found when fertilizers are applied in the Corn Belt.
MATERIALS AND METHODS

The study was conducted in 1984 on a 30- by 40-m area of Harps clay loam soil (a fine-loamy, mesic Typic Calciaquoll) at the Agronomy and Agricultural Engineering Research Center near Ames. The soil at this site had 15% free calcium carbonate and was without plants in 1983 and 1984. A rectangular grid system designed to accommodate 60 microplots was established by driving stakes into the soil at 3-m intervals on the perimeter of this area and stretching strings across opposite stakes. The points directly below the intersections of the strings were designated as the centers of the microplots.

Dry-surface and wet-surface microplots were established on each of 10 dates during the spring and early summer. The experiment had a randomized block design, with dates of application (referred to as "sets" in the Results and Discussion section) as whole plots and treatments (i.e., wet soil surface and dry soil surface) as split plots and with each treatment replicated three times within each application date. Each application date was selected so that no measurable precipitation had occurred during the previous 36 h. The dry-surface microplots had ambient moisture contents. The wet-surface microplots were established by slowly (over a period of 2 h) adding the equivalent of 25 mm of water through a coiled tube (1 cm i.d. by 8 m) that had small holes at 12-cm intervals. When placed on the surface of the microplot, this tube uniformly wetted a soil area 1 m in diameter.

Wire rings 40 cm in diameter were centered on the microplots 3 to 4 h after the additions of water. Urea labeled with 5.2 atom percent $^{15}\text{N}$
was surface-applied within these rings as granules that were formed by compressing 1-g samples of urea powder in a die (2.5 cm in diameter) and slicing the resulting wafers into granules weighing 10 to 30 mg. These granules were dried for 2 h at 105°C, and 4.7-g samples were weighed into packets that were emptied onto the surfaces of individual microplots. Each packet contained 2.2 g urea-N, corresponding to an application rate of 175 kg N ha⁻¹. Immediately after the urea applications, composite samples of soil were collected (for moisture determinations) at depths of 0-4, 4-8, 8-12, 12-16, 16-20, 20-25, 25-50, and 50-75 cm by taking three soil cores near each microplot. The rings and strings that identified the locations of the microplots were then removed.

About three weeks after application of the urea, soil samples were collected from each microplot. A ring 20 cm in diameter was placed on each microplot so that the center of the ring coincided with the center of the fertilized circle. By using spatulas and similar small digging tools, the soil within this ring was removed in two 4-cm layers (0-4 cm and 4-8 cm). By using a 10-cm-diameter bucket auger in the hole created by this excavation, samples of soil were taken from four layers to a depth of 25 cm below the surface (8-12, 12-16, 16-20, and 20-25 cm). A 7.5-cm-diameter bucket auger was used in this same hole to obtain samples of soil in several layers to a depth of 1.5 m (25-35, 35-45, 45-55, 55-75, 75-100, 100-125, and 125-150 cm). All samples were passed through a 2-mm sieve in their entirety, thoroughly mixed, and air-dried. Recoveries of the applied N were determined from analyses of representative subsamples by using the procedures and calculations
outlined by Sanchez and Blackmer (1988). Soil bulk density values used in these calculations were 1.1 Mg m$^{-3}$ for the 0- to 12-cm layers, 1.25 for the 12- to 16-cm layer, 1.35 for the 16- to 25-cm layers, 1.4 for the 25- to 35-cm layer, 1.45 for the 35- to 75-cm layers, and 1.5 Mg m$^{-3}$ for the 75- to 150-cm layers.
RESULTS AND DISCUSSION

The design of the study was based on the idea that the most practical way to study cumulative amounts of N lost by ammonia volatilization during the first few weeks after surface applications of urea under field conditions was to determine recovery of urea-derived $^{15}$N in the soil under conditions where leaching and denitrification are unlikely. This method of assessing ammonia volatilization has previously been used by Nommik (1966, 1973), Marshall and DeBell (1980), Hargrove et al. (1987), Katyal et al. (1987), and Reynolds and Wolf (1988). To minimize the possibility of confusing losses by ammonia volatilization with losses by leaching or denitrification, plots that received more than 70 mm of rainfall during the first three weeks after application are not considered here. The amounts of rainfall that occurred on the microplots considered here are shown in Table 1.

Results presented in Table 2 show that recoveries of urea-derived N were greater in the dry-surface microplots than in the wet-surface microplots. Analyses of variance showed that the effects of soil moisture content on recovery of urea-derived N in the KMI-N, exchangeable ammonium, and nitrate fractions were significant at the 95% confidence level. Analyses showed that urea was not present three weeks after application. More than half (mean of 67%) of the N recovered was present as nitrate, and little (mean of 5% of the N recovered) was present as exchangeable ammonium. A mean of 28% of the N recovered was present in the fraction referred to as KMI-N (Kjeldahl minus inorganic-N). The term "KMI-N", which was defined by Sanchez and Blackmer (1988), is used here
Table 1. Amounts of rainfall that occurred during various periods after applications of urea

<table>
<thead>
<tr>
<th>Set</th>
<th>0-3 days</th>
<th>4-6 days</th>
<th>7-9 days</th>
<th>10-12 days</th>
<th>13-15 days</th>
<th>16-18 days</th>
<th>19-21 days</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11 (1.8)</td>
<td>T</td>
<td>2.1</td>
<td>0</td>
<td>5.8</td>
<td>6.6</td>
<td>T</td>
<td>26 [70]</td>
</tr>
<tr>
<td>B</td>
<td>1.3 (T)</td>
<td>0.8</td>
<td>5.8</td>
<td>6.6</td>
<td>18</td>
<td>1.5</td>
<td>5.1</td>
<td>39 [68]</td>
</tr>
<tr>
<td>C</td>
<td>5.8 (5.8)</td>
<td>6.6</td>
<td>20</td>
<td>0</td>
<td>14</td>
<td>5.6</td>
<td>0</td>
<td>52 [59]</td>
</tr>
<tr>
<td>D</td>
<td>18 (0)</td>
<td>1.5</td>
<td>5.1</td>
<td>9.1</td>
<td>5.6</td>
<td>T</td>
<td>27</td>
<td>66 [65]</td>
</tr>
<tr>
<td>E</td>
<td>14 (5.1)</td>
<td>5.6</td>
<td>0</td>
<td>26</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>47 [58]</td>
</tr>
</tbody>
</table>

\( \text{^a} \) \( T \) = trace of precipitation.

\( \text{^b} \) Dates of urea application were 6 June, 20 June, 25 June, 7 July, and 14 July for sets A through E, respectively.

\( \text{^c} \) Values in parentheses are amounts of rainfall that occurred during the 36-h period immediately after urea application.

\( \text{^d} \) Values in brackets show normal amounts of rainfall (based on averages during 1951-1980) between the date of application and the date of sample collection (National Oceanic and Atmospheric Administration, 1984).
Table 2. Amounts of labeled N recovered in wet-surface and dry-surface microplots three weeks after surface applications of urea

<table>
<thead>
<tr>
<th>Set</th>
<th>As KMI-N Wet</th>
<th>As NH₄⁺ Wet</th>
<th>As NO₃⁻ Wet</th>
<th>Total Wet</th>
<th>As KMI-N Dry</th>
<th>As NH₄⁺ Dry</th>
<th>As NO₃⁻ Dry</th>
<th>Total Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18</td>
<td>3.8</td>
<td>10</td>
<td>36</td>
<td>55</td>
<td>58</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>1.9</td>
<td>11</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>14</td>
<td>1.4</td>
<td>3.8</td>
<td>54</td>
<td>70</td>
<td>69</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>8.4</td>
<td>0.6</td>
<td>1.2</td>
<td>32</td>
<td>64</td>
<td>41</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>31</td>
<td>1.3</td>
<td>4.7</td>
<td>49</td>
<td>63</td>
<td>81</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>LSD</td>
<td>5.7</td>
<td>3.6</td>
<td>14</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEAN</td>
<td>18</td>
<td>1.8</td>
<td>6.2</td>
<td>44</td>
<td>62</td>
<td>64</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>LSD</td>
<td>2.6</td>
<td>1.6</td>
<td>6.6</td>
<td>8.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \)Means of three microplots.

\( ^b \)Least significant difference (\( \alpha = 0.05 \)) for testing the hypothesis that D - W > 0, for individual set means.

\( ^c \)Least significant difference (\( \alpha = 0.05 \)) for testing the hypothesis that D - W > 0, for overall means.

because N from both organic matter and nonexchangeable ammonium is included in this fraction and because no attempt was made to distinguish between these forms. Although the percentage of recovered N found as exchangeable ammonium was slightly lower on the wet-surface microplots, initial soil moisture content had no important effect on the distribution
of labeled N among the fractions.

The high recoveries of labeled N (Table 2) indicate that significant amounts of this N were not lost by denitrification on the dry-surface microplots. It is unlikely that the water added to establish the wet-surface microplots caused significant losses of labeled N by denitrification because substantial drying of the soil would have occurred before this N was converted to nitrate and made available for denitrification. Also, this water rapidly dispersed through the soil profile before the urea was applied (Table 3).

Most of the labeled N recovered was in the surface 40 cm of soil (Figure 1), and negligible amounts were found below 50 cm. Because only small amounts of rainfall occurred, it is unlikely that leaching below the depths sampled was a major fate of the unrecovered N. There is, however, a possibility that some of the labeled N lost from the microplots was lost by preferential leaching through soil macropores (Parts I and II). High moisture contents at the soil surface could be expected to promote such preferential leaching, which occurs when all the smaller pores are filled with water and additional water from rainfall bypasses most of the soil matrix by moving through macropores (Part IV). Urea (or nitrate formed from urea) at the soil surface can be leached through a soil profile without leaving more than traces of the urea at lower depths within the profile (Part V). The observation that the additions of 25 mm of water resulted in rapid increases in soil moisture content as deep as 25 cm (Table 3) provides evidence that conditions were favorable for preferential leaching through soil macropores. However,
Table 3. Gravimetric moisture contents found in various soil layers of wet- and dry-surface microplots immediately before urea application

<table>
<thead>
<tr>
<th>Set</th>
<th>Dry- or wet-surface microplot</th>
<th>Moisture contents found in various soil layers (kg H₂O kg⁻¹ soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0-4 cm</td>
</tr>
<tr>
<td>A</td>
<td>Dry</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>0.09</td>
</tr>
<tr>
<td>B</td>
<td>Dry</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>0.08</td>
</tr>
<tr>
<td>C</td>
<td>Dry</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>0.07</td>
</tr>
<tr>
<td>D</td>
<td>Dry</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>0.12</td>
</tr>
<tr>
<td>E</td>
<td>Dry</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Wet</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>Difference</td>
<td>0.11</td>
</tr>
<tr>
<td>Mean</td>
<td>Difference</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Figure 1. Distributions of urea-derived N found in wet-surface and dry-surface microplots three weeks after application. Concentrations less than 0.2 ppm are not shown.
Table 1: Comparison of N concentrations between DRY and WET-SURFACE PLOTS.

**Urea-derived KMI-N**
- DRY-SURFACE PLOTS: 0.5
- WET-SURFACE PLOTS: 1.0

**Urea-derived NH₄⁺-N**
- DRY-SURFACE PLOTS: 0.4
- WET-SURFACE PLOTS: 1.0

**Urea-derived NO₃⁻-N**
- DRY-SURFACE PLOTS: 0.4
- WET-SURFACE PLOTS: 1.0

**N Concentration (ppm)**
- DRY-SURFACE PLOTS: 0 to 60
- WET-SURFACE PLOTS: 0 to 60
all conclusions concerning ammonia volatilization are valid even if preferential leaching (or denitrification) was responsible for some of the N losses observed.

Because significant losses of urea-derived nitrate by leaching and denitrification were unlikely and because all other forms of urea-derived N were accounted for, ammonia volatilization probably was the major mechanism of N loss during the study. It did not seem worthwhile to qualitatively show that ammonia volatilization occurred by directly measuring ammonia evolution because numerous studies have shown that substantial ammonia volatilization losses can occur after surface applications of urea to wet soil surfaces (Ernst and Massey, 1960; Kresge and Satchell, 1960; Meyer et al., 1961; Volk, 1966; Baligar and Patil, 1968; Harper et al., 1983; Bouwmeester et al., 1985). It did not seem worthwhile to attempt measurements of ammonia volatilization that were both quantitative and direct because the study lasted three weeks and because amounts of ammonia volatilized are influenced by methods that provide direct measurements (Terman, 1979; Nelson, 1982).

The most likely explanation for the differences in recovery of the labeled N between the wet-surface and dry-surface microplots is essentially as summarized by Bouwmeester et al. (1985) and Fenn and Hossner (1985). On the dry-surface microplots, the surface layer of soil had insufficient moisture for dissolution and hydrolysis of urea. Therefore, hydrolysis was delayed until rainfall occurred and moved the urea into the soil to depths where ammonia volatilization was not a problem. The distributions of urea-derived N observed (Figure 1)
indicate that rainfall could have moved urea to such depths. On the wet-surface microplots, the surface layers of soil had sufficient moisture for rapid dissolution and hydrolysis of urea. This resulted in ammonium being present at the soil surface, where ammonia volatilization can occur. This ammonium is relatively immobile in soils and would remain near the soil surface even if rainfall occurred.

Overall, the results of this study indicate that soil moisture content should be recognized as an important factor affecting the fate of surface-applied urea in the Corn Belt. These results suggest that the problem of N losses by ammonia volatilization after surface applications of urea can be greatly reduced merely by assuring that urea is applied to soils only when the surface few millimeters are dry. The effect of initial soil moisture content is important in humid areas like the Corn Belt because farmers often apply urea to wet soil surfaces. That is, decisions concerning when soils are too wet for fertilization usually are based on the ability of the soil to bear the weight of the fertilizer applicator rather than on the wetness of the soil surface. A soil that is dry enough to support the weight of an applicator can still be wet enough in the surface few millimeters for hydrolysis of urea and ammonia volatilization loss to occur. In such cases, merely delaying urea application for a few hours may be a practical alternative to urease inhibitors or other relatively expensive practices intended to reduce ammonia volatilization. Because many studies of ammonia volatilization have been conducted on soils having wet surfaces and because urea often is applied to soils having dry surfaces in production agriculture, the
importance of ammonia volatilization as a mechanism of N loss may have been overestimated for some conditions of practical importance.
SUMMARY

Results of recent $^{15}$N tracer studies in Iowa do not support the commonly accepted idea that ammonia volatilization is a significant problem after surface applications of urea to bare soils. The work reported here was conducted to examine the possibility that ammonia volatilization was not a problem because the urea was applied to dry soil and remained unhydrolyzed on the surface until it was moved into the soil by rainfall. This possibility was assessed by comparing amounts of labeled N recovered three weeks after surface applications of $^{15}$N-labeled urea to dry (ambient soil moisture contents when significant rainfall had not occurred for more than 36 h) and wet (irrigated with 25 mm of water 4 h before application) microplots on a calcareous soil. Recoveries averaged 94% and 64%, respectively, for the dry- and wet-surface microplots that received insufficient rainfall for significant losses by leaching or denitrification. These recoveries indicate that ammonia volatilization is less important when urea is applied to dry soil surfaces than when it is applied to wet soil surfaces. This suggests that merely delaying urea application for a few hours to avoid wet soil surfaces may be a practical alternative to urease inhibitors or other relatively expensive practices intended to reduce ammonia volatilization in humid areas such as the Corn Belt. Because many studies of ammonia volatilization have been conducted on soils having wet surfaces and because urea often is applied to soils having dry surfaces in production agriculture, the importance of ammonia volatilization as a mechanism of N
loss may have been overestimated for some conditions of practical importance.
REFERENCES


PART IV. PREFERENTIAL LEACHING OF SURFACE-APPLIED NITRATE IN IOWA SOILS DURING A WET SPRING
INTRODUCTION

Nitrate leaching from agricultural soils is a matter for concern because amounts of fertilizer N applied for crop production have increased markedly over the past few decades and because increases in concentrations of nitrate in groundwater have been observed (National Research Council, 1978; Hallberg, 1986; Blackmer, 1987). Losses of fertilizer N during corn (*Zea mays* L.) production deserve special attention because large amounts of N are applied for this crop and because N fertilizers represent a major cost of corn production. Unlike crops having higher value per hectare, there are clear economic incentives for crop producers to adopt management practices that minimize losses of fertilizers during corn production.

Although it is generally accepted that nitrate leaching can result in losses of N from Corn Belt soils, the rate and nature of this leaching have not been described with sufficient accuracy to answer questions important to corn producers. Such questions often relate to amounts of N lost from the rooting zone between application and plant uptake. The inability to answer these questions can be attributed to the difficulties associated with studying and describing nitrate leaching under field conditions. Some of these difficulties result from the multiplicity of N transformations that consume and produce nitrate within soils. Other difficulties relate to spatial and temporal variability in factors that influence the amounts of leaching that occur. Although numerous models (van Genuchten and Wierenga, 1976; Nye and Tinker, 1977; Scotter, 1978; Thomas et al., 1978; Edwards et al., 1979; Hoogmoed and Bouma, 1980;
Beven and Germann, 1981; Frissel and van Veen, 1981; Wild and Cameron, 1981; Bouma et al., 1982; Carsel et al., 1985; Jones and Kiniry, 1986; Richter, 1987) have been proposed to describe the leaching process, these models are based on a variety of assumptions and often yield very different conclusions concerning the amounts of nitrate leached from rooting zones. Many of these models use complex parameters to describe relevant soil conditions, and appropriate values for these parameters can be obtained only by observing nitrate movement under field conditions.

One major difference among models concerns the assumed importance of preferential movement of water through soil macropores. In this report, I use the term macropores to denote soil pores large enough to provide preferential paths of flow so that mixing and transfer between these and other pores is limited. I use the term matrix pores to denote pores that transmit water and solutes at rates slow enough to allow transfer of molecules between different pores (Skopp, 1981; Moore et al., 1986; Steenhuys and Muck, 1988). The water in macropores has been described as mobile water, and the water in matrix pores has been described as immobile water (van Genuchten and Wierenga, 1976; Addiscott, 1977). I use the term preferential movement to indicate that incoming water moves by bypassing the matrix pores and the term complete displacement to describe a situation in which no preferential movement occurs (i.e., when incoming water moves only by displacing water in all pores). Of course, preferential movement and complete displacement are extremes, and movement of water and solutes in a soil actually occurs by combinations of these processes. Although many studies have shown that preferential
movement through soil macropores is important under some conditions, this process generally has not been recognized as being important in the Corn Belt and, therefore, has received little attention when selecting N management practices in this region.

The objective of the research described here was to acquire a better understanding of nitrate leaching in Iowa by observing movement of fertilizer nitrate through surface soils under conditions found shortly after fertilizers are applied for corn production.
MATERIALS AND METHODS

The study was conducted at three sites in the spring and early summer of 1984. Two of the sites were located near Ames, one on a Clarion loam (well drained; fine-loamy, mixed, mesic Typic Hapludolls) and the other on a Harps loam (poorly drained; fine-loamy, mesic Typic Calciaquolls). The third site was located near Kanawha on a Webster clay loam (poorly drained; fine-loamy, mixed, mesic Typic Haplaquolls). These soils are important for corn production in northcentral Iowa and southern Minnesota. At each site, a rectangular grid system designed to accommodate 18 microplots was established by driving stakes into the soil at 3-m intervals on the perimeter of a 12- by 20-m area and stretching strings across opposite stakes. The points directly below the intersections of the strings were designated as the centers of the microplots.

Potassium nitrate labeled with 4.7 atom percent $^{15}$N was surface-applied on three different dates at each site. Six microplots were fertilized on each date by placing 40-cm-diam. rings on the soil surface at the centers of the microplots and then applying 50 mL of a solution containing 42.43 g NO$_3^-$-N L$^{-1}$ to the soil within these rings. A volumetric pipette was used to ensure accurate delivery and even distribution of the solution aliquots, which contained the equivalent of 170 kg NO$_3^-$-N ha$^{-1}$. Immediately after the nitrate applications, composite samples of soil were collected (for determinations of initial soil nitrate concentrations) at depths of 0-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90, 90-120, 120-150, and 150-180 cm by taking
two soil cores near each microplot. The rings and strings that identified the locations of the microplots were then removed.

At about two, four, and six weeks after each application, soil samples were collected from duplicate microplots. Strings were again stretched across opposite stakes, and a 20-cm-diam. ring was placed on each microplot so that the center of the ring coincided with the center of the fertilized circle. By using a 10-cm-diam. bucket auger to bore into the soil at the center of this ring, samples were obtained from the 0-10, 10-20, 20-30, 30-40, 40-50, and 50-60 cm layers of soil. A 7.5-cm-diam. bucket auger was then used in this same hole to obtain samples of soil between 60 and 180 cm below the soil surface (i.e., from the 60-70, 70-80, 80-90, 90-100, 100-110, 110-120, 120-130, 130-140, 140-150, 150-160, 160-170, and 170-180 cm layers of soil). Cross-contamination among samples was avoided by thoroughly cleaning the bucket augers between each sample. All samples were air-dried, crushed, and ground to pass through a 2-mm sieve.

Representative subsamples of the soils collected were analyzed to determine concentrations of labeled and unlabeled (soil-derived) NO$_3^-$-N. Kjeldahl analyses were performed on selected samples to determine concentrations of labeled N in forms other than nitrate. The methods and calculations used for these determinations are described by Sanchez and Blackmer (1988).
RESULTS

This study included 66 days, and measurable rainfall occurred on 28 of these days. More than half occurred between 8 June and 17 June, when 140 mm of rainfall occurred at the Clarion and Harps sites and 220 mm of rainfall occurred at the Webster site. Long-term average amounts of rainfall during 2-wk periods in May, June, and July at these sites range from 40 to 60 mm (National Oceanic and Atmospheric Administration, 1984). It is obvious, therefore, that the study was conducted during an unusually wet spring and that above-average amounts of water moved through the soil profiles during this study.

Figures 1, 2, and 3 show depth distributions of labeled nitrate found at various times after this nitrate was applied. These distributions indicate that a downward movement of labeled nitrate occurred and that this movement was characterized by a high degree of dispersion. This dispersion was great enough that significant amounts (often more than half) of the labeled nitrate were lost from the surface 1.8 m of soil before the center of mass of the recovered nitrate moved below one-third of this distance. In no microplot did the center of recovered mass move below 70 cm. Analyses (data not presented) showed that only small amounts of the $^{15}$N that were not recovered as nitrate remained within the soil as ammonium or organic matter. It is clear, therefore, that most of the unrecovered $^{15}$N was lost from the soils sampled.

The concentration distributions and amounts of soil-derived nitrate in the profiles were relatively unaffected by rainfall events during the
Figure 1. Distributions of labeled nitrate found in the Clarion soil (CR: cumulative rainfall since application; FN: fraction of the applied N recovered as nitrate in the surface 1.8 m of soil; CM: center of mass of the recovered nitrate)
APPLIED 21 MAY
5 June
CR = 105 mm
FN = 0.7
CM = 37 cm

APPLIED 1 JUNE
19 June
CR = 154 mm
FN = 0.9
CM = 19 cm

APPLIED 11 JUNE
20 June
CR = 125 mm
FN = 0.9
CM = 17 cm

a. 0.9
5 June
CR = 105 mm
FN = 0.7
CM = 37 cm
d. 0.3
19 June
CR = 154 mm
FN = 0.9
CM = 19 cm
g. 0.5
20 June
CR = 125 mm
FN = 0.9
CM = 17 cm

b. 0.7
19 June
CR = 154 mm
FN = 0.9
CM = 19 cm
e. 0.4
20 June
CR = 125 mm
FN = 0.9
CM = 17 cm
h. 0.8
6 July
CR = 151 mm
FN = 0.8
CM = 14 cm

6 July
CR = 276 mm
FN = 0.3
CM = 64 cm

2 July
CR = 167 mm
FN = 0.9
CM = 25 cm

16 July
CR = 212 mm
FN = 0.5
CM = 26 cm

20 July
CR = 198 mm
FN = 0.3
CM = 17 cm

Labeled NO₃⁻ Concentration (mg NO₃⁻ - N kg⁻¹ soil)
Figure 2. Distributions of labeled nitrate found in the Harps soil (CR: cumulative rainfall since application; FN: fraction of the applied N recovered as nitrate in the surface 1.8 m of soil; CM: center of mass of the recovered nitrate)
APPLIED 16 MAY

- 0.7
- 0.3

30 May
CR = 117 mm
FN = 0.7
CM = 18 cm

APPLIED 30 MAY

- 0.5
- 0.9

11 June
CR = 28 mm
FN = 1.0
CM = 9 cm

APPLIED 5 JUNE

- 0.4
- 0.7

19 June
CR = 146 mm
FN = 0.9
CM = 19 cm

- 0.5
- 0.3

20 June
CR = 154 mm
FN = 0.9
CM = 21 cm

- 0.4
- 0.3

6 July
CR = 171 mm
FN = 0.9
CM = 18 cm

- 0.4
- 0.5

9 July
CR = 180 mm
FN = 0.9
CM = 21 cm

- 0.4
- 0.3

20 July
CR = 218 mm
FN = 0.7
CM = 26 cm

Labeled NO₃⁻ Concentration (mg NO₃⁻ - N kg⁻¹ soil)

Depth Below the Soil Surface (cm)
Figure 3. Distributions of labeled nitrate found in the Webster soil (CR: cumulative rainfall since application; FN: fraction of the applied N recovered as nitrate in the surface 1.8 m of soil; CM: center of mass of the recovered nitrate)
APPLIED 24 MAY
APPLIED 7 JUNE

a. 7 June
CR = 56 mm
FN = 0.7
CM = 31 cm

b. 21 June
CR = 271 mm
FN = 0.3
CM = 46 cm

c. 5 July
CR = 329 mm
FN = 0.1
CM = 30 cm

d. 0.7 21 June
CR = 241 mm
FN = 0.2
CM = 38 cm

e. 0.6 21 June
CR = 273 mm
FN = 0.2
CM = 46 cm

f. 0.2 19 July
CR = 335 mm
FN < 0.1
CM = 60 cm

DEPTI BELOW THE SOIL SURFACE (cm)

LABELED NO₃ CONCENTRATION
(mg NO₃⁻ - N kg⁻¹ soil)
study (Figure 4). Either negligible amounts of soil-derived nitrate were lost from the profiles or losses that occurred were masked by formation of nitrate. Because mineralization from soil organic matter and losses of nitrate are favored by different conditions, it is highly unlikely that mineralization of soil N would so nearly equal losses across all sites and rainfalls and depths.
Figure 4. Distributions of soil-derived nitrate found (CR: cumulative rainfall since initiation of the study; $N_{30}, N_{180}$: kg N ha$^{-1}$ soil-derived nitrate found in the surface 30-cm and 180-cm layers of soil, respectively)
DISCUSSION

The observations that small amounts of rainfall moved traces of nitrate to several decimeters below the soil surface (e.g., Figures 2d and 3a) and that large amounts of rainfall did not remove all of the labeled nitrate from the surface layers (e.g., Figures 1f and 2i) indicate a high degree of dispersion of labeled nitrate, which can be explained only by preferential movement of water through soil macropores. Preferential movement results in marked dispersion of solutes initially present near the surface because some of this solute moves more rapidly and some more slowly than would be expected with complete displacement (Quisenberry and Phillips, 1976; Thomas and Phillips, 1979; Beven and Germann, 1982; Germann et al., 1984; White, 1985). Such dispersion does not occur with complete displacement, a process in which solutes initially present near the soil surface are moved downward as a band, or a concentration bulge, that is moved progressively deeper with each additional amount of water passing through the soil (Nye and Tinker, 1977; Frissel and van Veen, 1981; Wild and Cameron, 1981; Carsel et al., 1985; Jones and Kiniry, 1986).

Conditions in this study were conducive to preferential movement of water and labeled nitrate through soil macropores for four major reasons. The first is that the soils had macropores. This was especially evident upon visual examination of soil beneath the plow layer, where the soil can be accurately described as densely packed, clayey material having macropores formed by plant roots or soil fauna. The soil in the plow layer was highly aggregated and had numerous shrinkage cracks, worm
channels, and decaying plant residues that can function as macropores. The importance of these macropores is easily appreciated by watching surface drainage from small puddles that form on the soil microrelief during rainfall events (Part V).

The second reason is that the soil profiles had sufficient moisture that the matrix pores were largely water-filled. Therefore, water from rainfalls must preferentially enter and drain through macropores. Because this drainage usually occurs within minutes, there is only limited exchange between the draining (mobile) water in macropores and the (immobile) water in the matrix pores. Such preferential movement has been demonstrated unequivocally by applying \(^{18}\)O-labeled water to a soil similar to those studied here (Part V). This moisture status is relevant to leaching of fertilizers in the Corn Belt because soils of this region often are saturated with water during the winter and are fertilized about as soon as free water drains from the soil in the spring.

The third reason is that relatively intense rainfall events occurred. Such events favor the formation of small puddles of free water (on the soil surface or at a discontinuity in the soil profile) that can drain into soil macropores. The observation that small puddles frequently formed on the soil surface during the rainfalls indicates that rainfalls during this study were intense enough to promote preferential movement. Obviously, the intensity of rainfall needed to promote such preferential movement depends on the rate at which water can move through the soil matrix and, therefore, varies with soil properties. This conclusion is supported by observations (Part I) that sands and some
loess soils, which had relatively high conductivities through matrix pores, showed less tendency for preferential movement than did more poorly drained soils receiving similar rainfall. In the better drained soils, unlike those studied here, well-defined concentration bulges moved below the soil surface and labeled N was largely conserved within these bulges.

The fourth reason is that the labeled nitrate was surface-applied and, therefore, readily dissolved in the mobile water during rainfall events soon after application. In contrast, soil-derived nitrate would tend to be in the matrix pores, either because it was formed there or because soil-derived nitrate near macropores had been leached by earlier rainfalls. It should be noted that light rainfall events shortly after application can promote movement of labeled nitrate into the matrix pores by displacement and, therefore, decrease the tendency for preferential leaching of this nitrate with later rainfalls. For this reason, no simple relationship between rainfall and recovery of labeled nitrate should be expected under the conditions studied.

Preferential leaching could be detected in this study only because tracers were used. Amid the high and variable concentrations of soil-derived nitrate, it would have been impossible to determine that small amounts of rainfall moved labeled nitrate more than 75 cm deep (see Figures 2d and 3a). It also would have been much more difficult to determine that labeled nitrate was not conserved within concentration bulges that remained within the depths sampled. Because only a limited number of studies have been conducted with labeled nitrate under field
conditions, it is not surprising that preferential leaching of fertilizer-derived nitrate has received little attention.

The tracer data also provide evidence that denitrification could not account for the large losses of labeled nitrate. The soils were generally aerobic, and oxygen would have strongly inhibited denitrification. If high soil moisture contents had promoted denitrification, it would have occurred first in the centers of aggregates and last near soil macropores (Currie, 1961; Leffelaar, 1979, 1986; Smith, 1977, 1980). Because soil-derived nitrate tended to be where denitrification is most expected and labeled nitrate tended to be where denitrification is least expected, the finding that labeled nitrate disappeared more rapidly than soil-derived nitrate is strong evidence that denitrification was not a major mechanism of loss of labeled nitrate.

It should be noted that losses of nitrate by denitrification and by preferential leaching easily can be confused under field conditions if the consequences of preferential movement through soil macropores are not recognized. If it were assumed that nitrate leaching must be accompanied by the downward movement of a detectable concentration bulge and tracers had not been used, then any losses of nitrate before the concentration bulge reached the lower depths sampled would appear to be evidence that denitrification occurred.

A high degree of spatial variability in soil properties was indicated by differences between replicate microplots in recovery of labeled nitrate. Overall, the standard deviation for recoveries was 45%
of the means of duplicate microplots. Such variability should be expected where preferential movement is important because some microplots would have more macropores than others. Because different microplots were sampled at each date, spatial variability undoubtedly explains why recovery of labeled nitrate seemed to increase during some time periods shown in Figures 1, 2, and 3.

Especially at the lower depths sampled, lateral movement may have been responsible for some of the losses of labeled nitrate observed. I attempted to minimize this problem by applying labeled nitrate to an area much larger than was sampled. Even if significant lateral movement occurred, however, the observations that small amounts of rainfall moved traces of nitrate several decimeters below the soil surface and that large rainfall events did not leach all labeled nitrate from the uppermost layers sampled constitute definitive evidence for preferential movement. By analysis of soil in concentric rings outside and below microplots, it was found that lateral movement of labeled nitrate was negligible in soils that showed no evidence for preferential movement (Part I). If macropores promote lateral movement, and they probably do (Part V), then an increase in lateral movement cannot be used to belittle the importance of preferential movement through macropores. Because preferential movement results in rapid loss of nitrate from rooting zones, it makes little difference whether this movement is straight downward or downward with a lateral component. Direct evidence to support this conclusion was provided by Sanchez et al. (1987), who worked on soils similar to those studied here and found that corn plants outside
of plots treated with labeled N took up negligible amounts of this N. It also must be concluded, therefore, that the undesirable consequences of underestimating the importance of lateral movement in this study are small compared to the undesirable consequences of continued failure to recognize the importance of preferential movement when selecting N management practices.

Overall, the results of this study provide strong evidence that preferential movement of water through soil macropores deserves greater recognition as a major factor affecting the fate of fertilizer N in agricultural soils. Recognition that preferential movement through soil macropores is important, when it is important, should enable identification of improved N management practices. One such example is the late-spring soil test for N, which has been shown to have great promise in Iowa (Blackmer et al., 1987). It was considered worthwhile to evaluate this test in the deep soils of the Corn Belt only after it was recognized that (1) most of the nitrate in the rooting zone of corn usually remains in the surface 30-cm layer of soils even after large amounts of rainfall (Pottker et al., 1987) and (2) such concentration distributions can be explained by preferential movement of water through soil macropores.

Another example relates to estimation of the amounts of N supplied by legumes to succeeding crops. These amounts usually are assessed by adding fertilizer, measuring plant responses to this fertilizer, and using the fertilizer N as a standard to evaluate amounts of legume-derived N available to plants. When fertilizer N is preferentially
leached in such studies, the amounts of N supplied by legumes are overestimated. Accurate determinations of the amounts of N left in the soil by legumes is important when comparing the availability of N from fertilizers and from legumes for crops and for leaching.

A third example relates to the finding that preferential movement of water through soil macropores often results in significant losses of surface-applied urea soon after application (Parts I, II, and V). Previously, ammonia volatilization was recognized as the only reason to avoid surface applications of urea, and there seemed to be no reason to avoid surface applications of nitrate. In soils where preferential movement of water is important, losses by leaching could be minimized by deliberate placement of fertilizer N to avoid mobile water. In this way, the effects of preferential movement of water could be used to the advantage of the crop producer.
SUMMARY

Leaching of nitrate from agricultural soils results in economic losses for crop producers and degradation of groundwater supplies. Studies were conducted to acquire a better understanding of nitrate leaching by observing the movement of \(^{15}\)N-labeled nitrate during the first six weeks after fertilizers are applied for corn production. Such observations are needed to assess the importance of preferential movement of water and nitrate through soil macropores and to select appropriate models for describing nitrate leaching. The results showed that rainfalls resulted in a marked dispersion of the labeled nitrate through the soil profiles. Significant fractions, often more than half, of this nitrate were lost from the surface 1.8-m layers of the soils during 6 weeks of unusually wet weather. However, the distributions and amounts of soil-derived nitrate in the profiles were relatively unaffected by these rainfall events. The preferential losses of labeled nitrate can be explained by preferential movement of water and this nitrate through soil macropores. Overall, the results suggest that such preferential movement is important in these soils and that better recognition of this importance probably will enable identification of new ways to improve N management in the Corn Belt.
REFERENCES


PART V. PREFERENTIAL MOVEMENT OF O-18-LABELED WATER AND
N-15-LABELED UREA THROUGH MACROPORES IN A NICOLLET SOIL
INTRODUCTION

It is generally accepted that solutes such as nitrate (an anion) and urea (a small, uncharged molecule) move with water in soils and that these solutes can be leached from surface layers of soils during excessive rainfall. The leaching process is most frequently described by assuming that water entering any layer of soil displaces water already in that layer and that solutes initially present near the soil surface are moved downward as a "band", or a "concentration bulge", that is moved progressively deeper with each additional amount of water passing through the soil (see Nye and Tinker, 1977; Frissel and van Veen, 1981; Wild and Cameron, 1981; Carsel et al., 1985; Jones and Kiniry, 1986). Under such conditions, the downward movement of nitrate is easily detected by monitoring the depth of the concentration bulge. Although it is generally recognized that this bulge becomes more dispersed as it is moved deeper, most discussions related to N management (see National Research Council, 1978; Aldrich, 1980; Nielsen et al., 1982) give the impression that this dispersion usually is sufficiently small that relatively small amounts of nitrate would be lost from the rooting zone of a crop such as corn (i.e., below a depth of 1 to 2 m) until after the concentration bulge had moved well into this rooting zone.

Recent field studies (Parts I, II, and IV) employing $^{15}$N tracers to determine recoveries of surface-applied urea and nitrate in Iowa soils have shown that substantial amounts of the labeled N often are lost from the surface meter of some soils within two to eight weeks after spring applications. Losses of labeled N tend to be greatest during periods
having significant rainfall. These losses also tend to be greatest in highly structured soils, where the greatest concentrations of solutes usually remain in the surface few centimeters. If it is assumed that water moves through soils by displacement with relatively little dispersion, then the most reasonable explanation for these losses is that denitrification or ammonia volatilization was primarily responsible for the N losses. However, field observations (Quisenberry and Phillips, 1976; Thomas and Phillips, 1979; Tyler and Thomas, 1981; Beven and Germann, 1982) and models (van Genuchten and Wierenga, 1976) suggest that leaching also could be responsible for these losses of N if significant amounts of water moved preferentially through soil macropores (i.e., cracks, channels formed by plant roots or worms, and other relatively large voids in soil). Such preferential movement can result in sufficient dispersion of solutes that a portion of the solutes initially present at the soil surface moves downward distances of a meter or more before the concentration bulge moves out of the top few centimeters. This dispersion occurs when water and solutes bypass many of the smaller pores without displacing the contents of these pores. The possibility that leaching through macropores contributed to N losses in the recent tracer studies deserves attention because macropores usually were visible in the soils from which the greatest losses occurred.

The objective of the studies reported here was to evaluate the importance of preferential flow of water through macropores on urea movement in columns of soil taken from an area where large losses of fertilizer N have been observed in field studies. The use of
isotopically labeled water and urea under controlled laboratory conditions was considered essential to obtain precise information concerning depths of movement of the added materials and to distinguish between leaching and other mechanisms of N loss.
Six undisturbed soil columns (20-cm diameter, 50-cm height) were obtained from a soil area mapped as the Nicollet series (fine-loamy, mixed, mesic Aquic Hapludolls) near Ames in May 1987. The area had been cropped with continuous corn for several years under a reduced tillage management program. Soil samples taken within this area had bulk densities ranging from 1.06 to 1.34 (SD, 0.13), from 1.19 to 1.31 (SD, 0.06), and from 1.19 to 1.36 (SD, 0.08) Mg m\(^{-3}\) in the 0- to 15-cm, 15- to 30-cm, and 30- to 45-cm soil layers, respectively.

The procedure used to obtain each soil column was as follows. A ring 20 cm in diameter was placed on the soil surface to mark the perimeter of the top of the column. Soil outside this perimeter was carefully removed to a depth of 50 cm by using small digging tools. A sheet metal form (a 30-gauge heating duct 30 cm in diameter and 55 cm high) was placed around the cylinder of soil and masonry cement was poured into the 5-cm space between the soil and this form. The cement had a thin consistency and was poured with tamping to ensure intimate contact with the soil. The cement was allowed to harden for seven days before the column plus cement casing was transported to the laboratory. When encased in the cement, movement of the column resulted in a fracture of the soil, giving a relatively flat surface for the bottom of the column.

Each column was brought to water-holding capacity by slowly (over a period of 6 h) lowering it into a container of water, leaving it in this container for 24 h, and then removing it and permitting it to drain for
24 h. Granular urea labeled with 5.3 atom % $^{15}$N was applied to the surface of each soil column at a rate (550 mg urea-N per column) equivalent to 175 kg N ha$^{-1}$. Immediately after this application, water labeled with 0.76 atom % $^{18}$O was applied to the soil in an amount (800 mL water per column) equivalent to 25.4 mm of rainfall. This water was sprayed from a bottle fitted with a small hand pump to simulate a rainfall having the greatest intensity possible without flooding more than about one-third of the soil surface. The effluent from each soil column was collected in increments (100 or 200 mL) for 24 h after initiation of the simulated rainfall. Flow from each column was monitored by catching these increments in pans on a balance. The soil was then excavated from each column in 5-cm layers, and soil moisture contents were determined by oven-drying subsamples of each layer at 105°C for 24 h. The leachates and soil layers were analyzed to determine recoveries of the labeled N and labeled water.

To obtain samples of soil water for $^{18}$O analysis, the moist soil samples were placed in plastic bags and kneaded to crush soil aggregates and, therefore, mix water contained in pores of various sizes. Samples of the kneaded soil were placed in 1-L glass jars fitted with two-hole stoppers. Each jar was heated under an infrared lamp, and a flow of dry $N_2$ gas was directed into the jar through one hole of the stopper. The gas emitted from the other hole was directed into a cold trap that condensed and collected the soil water.

The $^{18}$O content of each water sample was determined by equilibrating a 10-mL aliquot of the water with 20 mg of $CO_2$ in a sealed 50-mL flask at
room temperature for 12 h, chromatographically separating the CO\textsubscript{2} from other headspace gases, and analyzing this CO\textsubscript{2} in an isotope ratio mass spectrometer as described by Priebe and Blackmer (1986). The CO\textsubscript{2}-H\textsubscript{2}O fractionation factor suggested by Dugan et al. (1985) was used to calculate the \textsuperscript{18}O content of the water.

Concentrations of urea-N in soils and leachates were determined by the colorimetric method described by Mulvaney and Bremner (1979) and concentrations of ammonium- and (nitrite + nitrate)-N were determined by the steam distillation method described by Keeney and Nelson (1982). The \textsuperscript{15}N contents of the inorganic N fractions were determined by reacting each fraction with alkaline sodium hypobromite in evacuated Rittenberg flasks as described by Hauck (1982) and analyzing the resulting N\textsubscript{2} in an isotope ratio mass spectrometer.

To determine the amounts of labeled water associated with the cement at the soil-cement contact, several small pieces of cement were allowed to equilibrate with deionized water at room temperature for 24 h. The cement pieces were gently blotted to remove excess water from their surfaces and then placed in beakers containing \textsuperscript{18}O-labeled water for 24 h. After this equilibration with labeled water, the \textsuperscript{16}O and \textsuperscript{18}O contents of this water were determined.

To determine amounts of water that were held in the soil when it was oven-dry, 200-g samples of the soil were passed through a 2-mm sieve, placed in 1-L glass jars, dried in an oven for 24 h at 105°C, cooled to room temperature, and then equilibrated for 48 h with 50 mL of \textsuperscript{18}O-
labeled water. After this equilibration, the $^{16}_O$ and $^{18}_O$ contents of the soil water were determined.
RESULTS AND DISCUSSION

The soil moisture status used in this study was selected to represent conditions often found when N fertilizers are applied to Iowa soils in the spring. At this time of year, rainfalls occur frequently and temporary water tables often develop in the surface meter of soils similar to the one studied. Specifically, the study simulated soil having a water table at 50 cm below the surface and the intense rainfall events that often accompany thunderstorms. Although some time is required after rainfalls for water to redistribute within the columns, additions of water to the surface of columns having this moisture status should result in loss of equivalent amounts of water from the bottoms of the columns. The amount of water collected from the bottoms of the columns within 24 h after rainfall was equivalent to 94% (mean over the six columns) of the water applied.

The time required for infiltration (i.e., disappearance from the surface) of the simulated rainfall into the soil columns ranged from 20 to 65 min (Table 1). The time between onset of this rainfall and first loss of water from the bottom of the columns ranged from 5 to 28 min. In four of the six columns, the equivalent of half of the rainwater was collected as leachate within 1 h after the onset of rainfall. In columns II and V, this quantity was collected within 0.5 h. The water lost from columns II and V during this half hour contained 14 and 3% of the labeled N and 23 and 13% of the labeled water applied, respectively (Table 2). Although some large pores were visible in all columns, only columns II and V had earthworms and burrows that clearly extended from top to
Table 1. Synopsis of timed events during water application and leachate collection in the six undisturbed columns of Nicollet soil

<table>
<thead>
<tr>
<th>Event(^{a})</th>
<th>Column I</th>
<th>Column II</th>
<th>Column III</th>
<th>Column IV</th>
<th>Column V</th>
<th>Column VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>All H(_2)O applied</td>
<td>46</td>
<td>20</td>
<td>65</td>
<td>26</td>
<td>21</td>
<td>52</td>
</tr>
<tr>
<td>Breakthrough</td>
<td>5</td>
<td>5</td>
<td>21</td>
<td>16</td>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td>Increment 1</td>
<td>19</td>
<td>10</td>
<td>45</td>
<td>22</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>Increment 2</td>
<td>27</td>
<td>15</td>
<td>57</td>
<td>26</td>
<td>14</td>
<td>45</td>
</tr>
<tr>
<td>Increment 3</td>
<td>36</td>
<td>17</td>
<td>70</td>
<td>33</td>
<td>17</td>
<td>56</td>
</tr>
<tr>
<td>Increment 4</td>
<td>45</td>
<td>20</td>
<td>83</td>
<td>46</td>
<td>21</td>
<td>67</td>
</tr>
<tr>
<td>Increment 5</td>
<td>54</td>
<td>28</td>
<td>106</td>
<td>70</td>
<td>27</td>
<td>89</td>
</tr>
<tr>
<td>Increment 6</td>
<td>71</td>
<td>78</td>
<td>165</td>
<td>130</td>
<td>47</td>
<td>105</td>
</tr>
</tbody>
</table>

\(^{a}\)Times given for leachate increments indicate times when collection of the 100-mL increments were completed. A seventh increment was collected between the sixth increment and 24 h after initiation of the rainfall.

The shapes of the \(^{15}\)N and \(^{18}\)O-labeled water concentration profiles revealed upon excavation of the columns were similar in that concentrations were greatest in the surface layers and gradually decreased with increasing depth below the surface (Figures 1 and 2). The amounts of labeled ammonium found indicate that a significant portion of...
Table 2. Amounts of labeled N and labeled water recovered in leachates from the six undisturbed columns of Nicollet soil 24 h after application

<table>
<thead>
<tr>
<th>Leachate increment</th>
<th>Column I (mg N)</th>
<th>Column II (mg N)</th>
<th>Column III (mg N)</th>
<th>Column IV (mg N)</th>
<th>Column V (mg N)</th>
<th>Column VI (mg N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>15.8</td>
<td>0.4</td>
<td>0.1</td>
<td>7.9</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>17.8</td>
<td>0.1</td>
<td>0.1</td>
<td>3.6</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>12.9</td>
<td>0.1</td>
<td>0.1</td>
<td>2.9</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>17.5</td>
<td>0.0</td>
<td>0.0</td>
<td>1.4</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>10.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>2.5</td>
<td>0.1</td>
<td>0.0</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>1.6</td>
<td>2.5</td>
<td>0.2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td>2.4</td>
<td>79.0</td>
<td>0.9</td>
<td>0.6</td>
<td>17.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leachate increment</th>
<th>Column I (g H₂O)</th>
<th>Column II (g H₂O)</th>
<th>Column III (g H₂O)</th>
<th>Column IV (g H₂O)</th>
<th>Column V (g H₂O)</th>
<th>Column VI (g H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>23.7</td>
<td>0.6</td>
<td>0.0</td>
<td>35.2</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>41.4</td>
<td>0.3</td>
<td>0.0</td>
<td>23.7</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>47.6</td>
<td>0.2</td>
<td>0.0</td>
<td>28.9</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>45.0</td>
<td>0.2</td>
<td>0.0</td>
<td>13.5</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>25.1</td>
<td>0.2</td>
<td>0.0</td>
<td>5.6</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>5.3</td>
<td>0.2</td>
<td>0.2</td>
<td>2.6</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>3.0</td>
<td>0.2</td>
<td>0.1</td>
<td>1.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>3.0</td>
<td>191.1</td>
<td>1.9</td>
<td>0.3</td>
<td>111.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 1. Amounts, forms, and distributions of labeled N recovered from the soil columns
Figure 2. Amounts and distributions of labeled water recovered from the soil columns
The figures depict the concentration of labeled water (g H₂O kg⁻¹ soil) below the soil surface. Each column shows the recovery of labeled H₂O in soil and leachates, with specific measurements for different columns:

**COLUMN I**
- Recovery of labeled H₂O:
  - In soil: 740g
  - In leachates: 3g

**COLUMN II**
- Recovery of labeled H₂O:
  - In soil: 535g
  - In leachates: 191g

**COLUMN III**
- Recovery of labeled H₂O:
  - In soil: 787g
  - In leachates: 2g

**COLUMN IV**
- Recovery of labeled H₂O:
  - In soil: 761g
  - In leachates: 11g

**COLUMN V**
- Recovery of labeled H₂O:
  - In soil: 649g
  - In leachates: 111g

**COLUMN VI**
- Recovery of labeled H₂O:
  - In soil: 814g
  - In leachates: 0g

The graphs show the concentration of labeled water across different depths below the soil surface.
the urea was hydrolyzed during the 24-h period between rainfall and excavation. The amounts of labeled nitrate found indicate that only small amounts of urea-derived N were nitrified during this period. Because ammonium is relatively immobile in soils and because most of the labeled nitrate probably was formed after water had ceased to move, most movement of labeled N probably occurred as urea. The observed small differences between the distributions of labeled N and labeled water should be expected because the urea was dissolved and carried into the soil by the first third of the water applied.

Data reported in Figures 1 and 2 show that recoveries ranged from 91 to 102% (mean of 96% among the six columns) of the labeled water applied and from 94 to 101% (mean of 97% among the six columns) of the labeled N applied. The high recoveries of labeled N indicate that losses of N by denitrification or ammonia volatilization were not significant in this study. Much of the variability among columns probably can be explained by variability in soil bulk density, which introduces errors when calculating percentage recoveries. Because of experimental difficulties associated with determining bulk density on each column, bulk density was determined by collecting samples within the small area in the field where the undisturbed columns were obtained.

The recoveries of labeled water reported in Figure 2 include small adjustments for amounts of water in oven-dry soil and for amounts of water associated with cement at the soil-cement interface in the columns. Adjustments were made because the labeled water equilibrated with these waters, but these waters were not included in the determinations of soil
water content. The adjustments made are shown in Table 3. Although these adjustments are significant when considering percentage recovery of labeled water, they have negligible importance when considering depth of water movement.

Calculations based on soil water contents measured when the columns were excavated show that labeled water would have moved no deeper than about 7 cm (mean of 7.2 cm, range of 7.1 to 7.6 cm among columns) below the surface if this water had moved by complete displacement (i.e., without bypassing any water-filled pores). Data presented in Table 2 and Figures 1 and 2 show that significant quantities of the tracer materials moved below this depth. In columns II and V, where earthworms were found, 62 and 92% of labeled water and 46 and 48% of the labeled N recovered, respectively, moved deeper than expected if water moved by complete displacement. In the remaining columns, percentages of the tracer materials that moved farther than expected with displacement ranged from 28 to 45% of the labeled water and from 39 to 59% of the labeled N recovered. Even in the column where least movement occurred, the mean distance traveled by N was twice the distance expected if movement occurred by complete displacement.

It is unlikely that preferential flow along the cement-soil interface contributed significantly to the movement of water and N observed in these columns because cement occupied small pores in the soil at the interface. This was evident upon examination of the surface of the cement after the soil was removed. It also was evident that pores at the cement-soil interface were very small compared with natural soil
Table 3. Amounts of labeled water recovered in the soil layers of the six undisturbed soil columns and adjustments to these quantities to account for water retained in the soil in its oven dry state and for water adsorbed onto the cement casings of these columns

<table>
<thead>
<tr>
<th>Soil column</th>
<th>Unadjusted recovery of water in soil</th>
<th>Adjustment^a because of water in oven-dry soil</th>
<th>Adjustment^b because of water adsorbed onto cement casing</th>
<th>Adjusted recovery of water in soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>683</td>
<td>25</td>
<td>32</td>
<td>740</td>
</tr>
<tr>
<td>II</td>
<td>495</td>
<td>17</td>
<td>22</td>
<td>534</td>
</tr>
<tr>
<td>III</td>
<td>729</td>
<td>25</td>
<td>33</td>
<td>787</td>
</tr>
<tr>
<td>IV</td>
<td>704</td>
<td>25</td>
<td>32</td>
<td>761</td>
</tr>
<tr>
<td>V</td>
<td>604</td>
<td>20</td>
<td>25</td>
<td>649</td>
</tr>
<tr>
<td>VI</td>
<td>752</td>
<td>27</td>
<td>35</td>
<td>814</td>
</tr>
</tbody>
</table>

^a Calculated from a concentration of 10 g H2O per kg oven-dry soil (determined by equilibrating soil with 18O-labeled water). Differences among columns reflect differences in amounts of labeled water in the columns after 24 h.

^b Calculated from a concentration of 0.082 g H2O adsorbed per cm^2 cement surface area (determined by equilibrating small pieces of the cement casing with 18O-labeled water).

Macropores. Therefore, the results of this study support earlier conclusions (Quisenberry and Phillips, 1976; Thomas and Phillips, 1979; Beven and Germann, 1982; Germann, et al., 1984; White, 1985) that preferential flow of water through macropores is important in soils and
that water in macropores can move into or below the rooting zone in a matter of minutes after the addition of water to a soil surface.

There are two major reasons that it is likely that this study underestimates the importance of preferential movement of water through soil macropores during intense rainfalls on the soil studied. The first is that the relatively small surface areas of the columns studied reduced the possibility of lateral flow of water through surface puddles to macropores. The importance of such lateral movement to macropores is easily observed during intense rainfall events. Such observations convincingly indicate that cracks, worm channels, and decaying corn roots and residues provide surface drainage for small puddles that form on the microrelief of soils used for corn production. This phenomenon makes surface-applied materials more vulnerable than incorporated materials to movement with water that flows through soil macropores.

The second major reason is that some macropores having horizontal as well as vertical components were undoubtedly truncated by the cement casing. The relatively large amount of labeled water found at about 20 cm below the surface in column V (Figure 2) probably resulted from such a truncation. The importance of the horizontal components of soil macropores became evident during attempts (in a study not reported in this dissertation) to demonstrate preferential movement of water under field conditions by digging pits in the soil, tunneling under blocks (1 m by 1 m) of soil beside the pits, applying water to the soil surfaces above the tunnels, and collecting water that fell from the ceilings of the tunnels. The pits were similar in design to those used by Shaffer et
al. (1979). The ceilings of the tunnels became wet soon after additions of water to the soil surfaces and drops of water formed on these ceilings. However, even with continued applications of water to the soil surfaces, water would not drop from the ceilings. These observations suggest the existence of a macropore system that enables significant lateral movement of water when this water is held at very small matric suctions. Attempts to avoid this lateral movement by increasing the areas to which water was applied resulted in sudden collapses of soil into the pits and tunnels.

Figures 1 and 2 illustrate that, as suspected during the recent field studies (Parts I, II, and IV), significant amounts of surface-applied N can be leached from a soil profile even when the greatest concentrations of N remain at the soil surface and when only trace amounts remain below the surface layers. Clearly, the distributions of labeled water and N found in the columns do not provide a reliable indicator of the quantities of labeled materials that were lost from the columns. If labeled N in the effluent from the columns had not been determined, it would have been impossible to distinguish between losses of N by leaching, denitrification, or ammonia volatilization. The experimental methods were selected with the idea that existing knowledge would cause most informed readers to select denitrification and (or) ammonia volatilization over leaching as the most likely mechanisms of N loss in this study, which involved only 25 mm of rainfall on 50-cm columns of wet soil. The data obtained not only indicate that leaching through macropores must be considered a mechanism by which surface-
applied urea can be lost from soils, they also illustrate that losses of N by this mechanism are easily confused with losses of this N by ammonia volatilization or denitrification.

Extensive $^{15}N$-tracer studies during the past few years to determine the fate of surface-applied urea and nitrate have revealed some situations in which the observed distributions of labeled N could best be explained if water moved only by displacement (i.e., where there was a clearly defined concentration bulge significantly below the soil surface). These situations usually occurred in sands and some silty soils (see Part I). However, the distributions of labeled N found at most sites suggest that preferential movement of water through macropores may be more the rule than the exception in Iowa soils. This possibility also is supported by recent studies (Pottker et al., 1987) of the distributions of nitrate found in late spring in two long-term rotation-fertility studies in Iowa.

Overall, the results of this study, together with the related studies reported in this dissertation, suggest that preferential movement of water through soil macropores is more important as a factor affecting N movement in Iowa soils than has been generally realized. A better understanding of where and when this preferential movement is important and how it influences movement of N and other solutes in soils is greatly needed to advance efforts to identify management practices that reduce losses of N and other chemicals from agricultural soils to the environment.
SUMMARY

Studies were conducted to evaluate the possibility that preferential movement of water through soil macropores was an important factor in previously observed losses of surface-applied urea and nitrate from Iowa soils. Granules of $^{15}$N-labeled urea were applied to the surfaces of undisturbed soil columns at their water-holding capacities, and then $^{18}$O-labeled water was applied to simulate a 25-mm rainfall event. Effluent from the bottoms of the columns was incrementally collected and analyzed. Soil from the columns was removed in layers 24 h after initiation of the rainfall, and each layer was analyzed to determine depths of movement of labeled water and N. Significant amounts of labeled water and urea were present in the first increment of effluent from some columns. Labeled water and urea moved much deeper and were more dispersed in all soil columns than would be expected in absence of preferential movement of water through macropores. The results suggest that preferential movement of water through macropores is more important as a factor affecting the movement and fate of nitrogen in Iowa soils than generally has been recognized. A better understanding of where and when this preferential movement occurs and how it influences leaching of nitrogen and other solutes in soils is needed to advance efforts to identify management practices that reduce losses of nitrogen and other chemicals from agricultural soils to the environment.
REFERENCES


GENERAL SUMMARY

Field and laboratory studies were conducted to acquire a better understanding of the fate of nitrogen fertilizers during the first few weeks after surface applications to Iowa soils. The conditions studied were typical of conditions under which fertilizers often are applied in the spring for corn production.

The initial study (Part I) employed $^{15}$N-labeled urea to determine how frequently significant losses of this N occur after surface applications under field conditions. Losses of the labeled N from the surface 1-m layers of soil at 10 sites ranged from 0 to 65% during the first six weeks after application. Contrary to initial expectations, these losses appeared to be unrelated to factors known to influence losses of N by ammonia volatilization. The distributions of labeled N in some of the soil profiles suggested that significant losses may have occurred by denitrification or by leaching through soil macropores. These findings indicate a need for studies that can distinguish between ammonia volatilization, leaching, and denitrification as mechanisms by which surface-applied urea N is lost from soils.

The study reported in Part II was designed to monitor transformations, movement, and losses of urea-$^{15}$N during the first eight weeks after surface applications to four soils under field conditions. Results showed that, at all sites, the greatest N losses occurred after the opportunity for ammonia volatilization had passed. The distributions of labeled nitrate and soil-derived nitrate provided strong evidence that preferential movement of water and labeled nitrate through soil
macropores occurred. These results suggest that preferential leaching deserves greater attention as a possible fate of surface-applied urea.

The study reported in Part III examined the effect of soil moisture content on N losses following surface applications of urea to a calcareous soil under field conditions. Losses attributable to ammonia volatilization averaged 6% and 36% of the urea $^{15}$N applied to plots having dry and wet surfaces, respectively. The results suggested that ammonia volatilization was limited in the studies reported in Parts I and II because the urea was applied only to dry soil surfaces, where it remained unhydrolyzed until it was moved into the soil by rainfall. These findings suggest that merely delaying urea application for a few hours to avoid wet soil surfaces may be a practical alternative to urease inhibitors or other relatively expensive practices intended to reduce ammonia volatilization in humid areas such as the Corn Belt.

The study reported in Part IV was conducted to acquire a better understanding of the movement of surface-applied nitrate in soils under conditions typically found when fertilizers are applied for corn production. By using $^{15}$N-labeled nitrate, it was shown that significant downward movement and loss of surface-applied nitrate occurred without concomitant downward movement and loss of soil-derived nitrate. These results suggest that the surface-applied nitrate was leached with water moving preferentially through soil macropores.

The study reported in Part V involved surface applications of $^{15}$N-labeled urea and simulated rainfalls of $^{18}$O-labeled water to soil columns under controlled laboratory conditions to evaluate the importance of
preferential movement of water through soil macropores. This study provided unequivocal evidence that this movement is an important factor affecting the fate of nitrogen in many Iowa soils. Together with findings presented in Parts I, II, and IV, this evidence suggests that preferential leaching is a more important fate of surface-applied N fertilizers than generally has been recognized. Because leaching of fertilizer N from agricultural soils results in economic losses for crop producers and often causes degradation of groundwater supplies, selecting N management practices to minimize preferential leaching could have substantial economic and environmental benefits.
I wish to express my sincere appreciation to Dr. Alfred M. Blackmer for his encouragement, guidance, and friendship throughout my years at Iowa State University and for generously sharing his creative energy during the research and writing of this dissertation.

I also would like to thank Drs. James L. Baker, Robert Horton, Thomas E. Loynachan, and Michael L. Thompson for time and advice freely given while serving on my graduate committee.

I am grateful to Farmland Industries, Inc., and the Iowa State Water Resources Research Institute for financial support of my research, and to the United States Department of Agriculture for three years of support through its Food and Agricultural Sciences National Needs Fellowship program.

I also wish to acknowledge the following special persons: Manuel Cerrato, Gary Huber, and Gary Green, for invaluable research assistance; R. Owen Pope, Nick Basta, and Susan Bennett, for friendship and for hospitality during the past year; Susan White, for gracious assistance with statistical analyses; and Dr. Nael M. El-Hout, for advice, friendship, hospitality, and other kindnesses too numerous to mention.