Fall 2013

Nitrogen and Potassium Dynamics of Selected Indiana Soils

Chun Zhao
Purdue University

Follow this and additional works at: https://docs.lib.purdue.edu/open_access_dissertations

Part of the Soil Science Commons

Recommended Citation
https://docs.lib.purdue.edu/open_access_dissertations/12

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.
This is to certify that the thesis/dissertation prepared

By Chun Zhao

Entitled
Nitrogen and Potassium Dynamics of Selected Indiana Soils

For the degree of Doctor of Philosophy

Is approved by the final examining committee:

Brad Joern

Co-Chair
Jim Camberato

Darrell Schulze

Hao Zhang

To the best of my knowledge and as understood by the student in the Research Integrity and Copyright Disclaimer (Graduate School Form 20), this thesis/dissertation adheres to the provisions of Purdue University’s “Policy on Integrity in Research” and the use of copyrighted material.

Approved by Major Professor(s): Brad Joern

Approved by: Joseph Anderson 10/10/2013

Head of the Graduate Program Date
NITROGEN AND POTASSIUM DYNAMICS OF SELECTED INDIANA SOILS

A Dissertation
Submitted to the Faculty
of
Purdue University
by
Chun Zhao

In Partial Fulfillment of the
Requirements for the Degree
of
Doctor of Philosophy

December 2013
Purdue University
West Lafayette, Indiana
To Ben
ACKNOWLEDGEMENTS

I would like to thank my co-advisors, Dr. Brad Joern and Dr. Jim Camberato, for providing me this life-changing opportunity to study and do research here at Purdue. Their guidance and help through my six-year study are really appreciated. I also want to thank my committee, Dr. Darrell Schulze and Dr. Hao Zhang for their valuable input into my research program.

I want to thank all my instructors who taught me not only knowledge but also skills that benefit me for my future career. I want to thank Dr. George Van Scoyoc for providing me a teaching opportunity and many thanks to Sherry Fulk-Bringman who inspired my great interest in teaching.

I would like to thank all the people who helped me in my research program. Thanks to Dr. Eileen Kladivko for her help with the soil water pressure analyses. Thanks to Dr. Sylvie Brouder for providing the soil samples. Thanks to Judy Santini for assisting with statistical analysis. I also would like to thank my labmates Blucher, Branly, and Min for their suggestions and help to my study and research. I want to thank all the undergraduate lab workers who assisted me with laboratory analysis.

Last but not least, I want to thank my family and all my friends. Without all their love and support, I could not become who I am and could not go this far. I am so thankful.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xv</td>
</tr>
<tr>
<td>CHAPTER 1. NITROGEN MINERALIZATION IN SOILS: A LITERATURE REVIEW</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Soil Nitrogen Mineralization</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Factors Affecting Soil Nitrogen Mineralization</td>
<td>2</td>
</tr>
<tr>
<td>1.4 Prediction of Soil Nitrogen Mineralization</td>
<td>4</td>
</tr>
<tr>
<td>1.4.1 Laboratory Measurements</td>
<td>4</td>
</tr>
<tr>
<td>1.4.2 Field Estimates</td>
<td>6</td>
</tr>
<tr>
<td>1.4.3 Predicting Nitrogen Mineralization with Models</td>
<td>7</td>
</tr>
<tr>
<td>1.5 Nitrogen Cycling in the Soil</td>
<td>9</td>
</tr>
<tr>
<td>1.5.1 Immobilization</td>
<td>9</td>
</tr>
<tr>
<td>1.5.2 Nitrification</td>
<td>9</td>
</tr>
<tr>
<td>1.5.3 Denitrification</td>
<td>12</td>
</tr>
<tr>
<td>1.5.4 Ammonium Fixation</td>
<td>13</td>
</tr>
<tr>
<td>1.5.5 Ammonia Volatilization</td>
<td>14</td>
</tr>
<tr>
<td>1.5.6 Biological Nitrogen Fixation</td>
<td>17</td>
</tr>
<tr>
<td>1.5.7 Nitrate Leaching</td>
<td>18</td>
</tr>
<tr>
<td>1.5.8 Crop Uptake</td>
<td>19</td>
</tr>
<tr>
<td>1.6 Nitrogen Fertilizer Management</td>
<td>20</td>
</tr>
<tr>
<td>1.6.1 Application Rate</td>
<td>20</td>
</tr>
<tr>
<td>1.6.2 Application Methods</td>
<td>22</td>
</tr>
<tr>
<td>1.6.3 Application Timing</td>
<td>22</td>
</tr>
<tr>
<td>1.7 Concluding Remarks</td>
<td>23</td>
</tr>
<tr>
<td>1.8 Reference</td>
<td>25</td>
</tr>
<tr>
<td>CHAPTER 2. ESTIMATING POTENTIALLY MINERALIZABLE NITROGEN IN INDIANA SOILS</td>
<td>42</td>
</tr>
<tr>
<td>2.1 Abstract</td>
<td>42</td>
</tr>
</tbody>
</table>
APPENDICES

Appendix A Locations of Study Sites ............................................................ 177
Appendix B Summary of Analysis of Variance Tables .................................. 179
Appendix C Soil Water Retention Data .......................................................... 183
VITA ................................................................................................................. 185
LIST OF TABLES

Table | Page
--- | ---
Table 1.1 Nitrogen uptake in the harvested portions of selected agronomic crops†. | 40
Table 2.1 Selected properties of eight Indiana soils collected at 0-30 cm depth of the Ap horizon. | 74
Table 2.2 Predominant soil series and taxonomic class of soils for seven sites... | 75
Table 2.3 Properties of soils collected at four depths (0 to 15, 15 to 30, 30 to 45, and 45 to 60cm) from seven sites in Indiana. | 76
Table 2.4 The cumulative amount of nitrogen (NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+}) mineralized by eight soils during the 16 week incubation for the leaching incubation and static cup incubation methods. | 77
Table 2.5 Root mean square errors for zero-order and first-order models fitted to N mineralization data obtained for the leaching incubation and static cup incubation methods. | 77
Table 2.6 Plant uptake nitrogen, mineral nitrogen in soils before and after cropping, and observed net nitrogen mineralized under greenhouse conditions. | 78
Table 2.7 Predicted N0 and K values of four depth for seven soils†. The relative contribution from the top soil (0-15cm) was indicated. | 79
Table 2.8 Results from various indices for predicting potentially mineralizable nitrogen in seven soils of four depths. ................................................................. 80

Table 2.9 Estimated field soil nitrogen supply (in kg ha\(^{-1}\)) for seven soils in 2006, 2008, and 2010 ........................................................................................................................................ 81

Table 3.1 Summary of model parameter inputs ................................................................................................................................. 109

Table 3.2 Nitrogen model predictions at various fertilizer nitrogen rates from 2006 to 2011 at ACRE (Unit: kg ha\(^{-1}\)). ........................................................................................................................................ 110

Table 4.1 The amount of potassium removed in harvest portions of selected agronomic crops† .................................................................................................................. 135

Table 5.1 Soil characteristics in the upper 30 cm of the Ap horizon of the Chalmers, Pewamo, Pinhook, and Raub soil samples. ..................... 156

Table 5.2 Protected LSD(0.05) values for sources of variance in exchangeable (Ex\(_{\text{K}}\)) and nonexchangeable (NonEx\(_{\text{K}}\)) K levels (mg kg\(^{-1}\)) in Chalmers, Pewamo, Pinhook, and Raub soils. ................................................................................... 157

Table 6.1 Soil characterization of a bulk soil sample collected from five field sites. .................................................................................................................. 173

Appendix Table

Appendix Table A.1 Geographic coordinates of study sites for chapter 2, 3 and 5. ........................................................................................................................................ 178

Appendix Table B.1 Analysis of variance for mineralized N evaluated by different incubation methods ................................................................. 179

Appendix Table B.2 Analysis of variance for laboratory predicted mineralizable N (N\(_{0}\)), mineralization rate constant (k) and products of N\(_{0}\)Xk .................................. 180
Appendix Table B.3 Analysis of variance for pH, exchangeable (Ex_K) and nonexchangeable K (Nonex_K) levels in Chalmers, Pewamo, Pinhook, and Raub soils after injection of anhydrous ammonia. ....................... 181

Appendix Table B.4 Analysis of variance for soil test K levels as affected by drying................................................................. 182

Appendix Table C.1 Soil moisture contents at water retentions of 10 kPa, 33 kPa, 50 kPa, and 100 kPa for selected soils (unit: g g⁻¹). ......................... 183

Appendix Table C.2 Soil moisture contents at water retention of 10 kPa for selected soils at four depths. .......................................................... 184
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Nitrogen uptake rate of corn and wheat as a function of crop growth over time. Adapted from UCWRC, unknown publish year.</td>
<td>41</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Time course of N mineralization of eight Indiana soils through 16 weeks for the leaching incubation method. The cumulative N values obtained as a sum of NO$_3^-$-N and NH$_4^+$-N were mean of three replicates. Error bars indicate the standard deviation of the mean of three replicates.</td>
<td>82</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Time course of N mineralization of eight Indiana soils through 16 weeks for the static cup incubation method. The cumulative N values obtained as a sum of NO$_3^-$-N and NH$_4^+$-N were mean of three replicates. Error bars indicate the standard deviation of the mean of three replicates.</td>
<td>83</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>The linear relationship between mineralized nitrogen estimated from two laboratory incubation methods to greenhouse measurements of plant nitrogen uptake.</td>
<td>84</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Time course of N mineralization of four depths of soils from seven locations. The cumulative N values obtained as a sum of NO$_3^-$--N and NH$_4^+$--N were mean of three replicates. Error bars indicate the standard deviation of the mean of three replicates.</td>
<td>85</td>
</tr>
</tbody>
</table>
Figure 2.5 Correlation between nitrogen indices and mineralizable N estimated from long-term static cups incubation. ................................................ 86

Figure 2.6 Correlation between nitrogen indices and mineralization rate constant k estimated from long-term static cups incubation. ............................. 87

Figure 2.7 The relationship between laboratory soil N mineralization estimates and predicted soil N supply in the field. The horizontal error bars are the standard deviation of the mean of triplicate measurements of lab mineralization and the vertical error bars are the standard deviation of the mean of three years of observations in the field. ........................ 88

Figure 3.1 The N cycle considered in this model. ............................................. 111

Figure 3.2 An example of model output showing soil N accumulation and loss and crop N uptake resulting from an application of 224 kg ha\(^{-1}\) fertilizer N (as UAN) in 2008 at ACRE. .......................................................... 112

Figure 3.3 Relationship between model-simulated corn N uptake and measured corn grain yield for each individual site year. ................................. 113

Figure 3.4 Relationship between model-simulated corn N uptake and measured corn grain yield (A) and relative corn grain yield (B) across 2006 to 2011. ................................................................................................ 114

Figure 5.1 Soil pH over 28 days after injection of anhydrous ammonia as affected by distance from the anhydrous ammonia injection point in (A) Chalmers, (B) Pewamo, (C) Pinhook, and (D) Raub soil. Dash lines indicate initial soil pH. Soil pH values were obtained from a 1:2 slurry as mean of three replicates. Error bars indicate the standard deviation of the means................................................................. 158

Figure 5.2 Distribution of exchangeable K over time and distance from the anhydrous ammonia injection point in a Chalmers, Pewamo, Pinhook,
and Raub soil after injection of anhydrous ammonia. Dash lines indicate the exchangeable K concentration in untreated soils. The exchangeable K values are means of three replicates. Error bars indicate the standard deviation of the means.

Figure 5.3 Distribution of total nonexchangeable K over time and distance from the anhydrous ammonia injection point in a Chalmers, Pewamo, Pinhook, and Raub soil after injection of anhydrous ammonia. Dash lines indicate the total nonexchangeable K concentration in untreated soils. The nonexchangeable K values are means of three replicates. Error bars indicate the standard deviation of the means.

Figure 5.4 Distribution of total nonexchangeable K over distance from the anhydrous ammonia injection point in Pewamo soil seven days after injection of anhydrous ammonia. Total nonexchangeable K was extracted with boiling nitric acid (A) and by 7-d incubation in sodium tetraphenylboron (STPB) (B). The nonexchangeable K values are means of two replicates. Error bars indicate the standard deviation of the means.

Figure 6.1 The relationship between Mehlich-3 soil test K levels of oven-dried soils vs. Mehlich-3 soil test K levels of air-dried soils from five locations.

Figure 6.2 Relationship between the Mehlich-3 soil test K levels of moist soils from four locations (DPAC, NEPAC, SEPAC, and TPAC) and the percent change in soil test K upon drying as described by the logarithmic model \[ Y = a + b \times \log(x) \]. Soil test K levels upon drying were presented as the mean of air- and oven-dried samples. The vertical lines showed soil K critical levels predicted using model: Critical K = 75 + 2.5*CEC (Vitosh et al., 1995). The vertical dash lines showed soil K critical levels predicted using model: Critical K = 34.5 - 3.41*illite.
K+3.52×CEC (Cox et al., 1999) where illite K is measured by NaBPh₄⁺ extraction after soil was incubated in it for seven days. .......................... 175

Figure 6.3 Relationship between the Mehlich-3 soil test K levels of moist soils from PPAC and the percent change in soil test K upon drying. Soil test K levels upon drying were presented as the mean of air- and oven-dried samples. The vertical line showed soil K critical levels predicted using model: Critical K = 75 + 2.5×CEC (Vitoush et al., 1995). The vertical dash line showed PPAC soil K critical level predicted using model: Critical K = 34.5 - 3.41×illite K + 3.52×CEC (Cox et al., 1999) where illite K is measured by NaBPh₄⁺ extraction after soil was incubated in it for seven days. ................................................................. 176

Appendix Figure

Appendix Figure A.1 Locations of seven study sites where soil sample was collected ...................................................................................................................... 177
ABSTRACT


Nitrogen (N) is the most limiting essential nutrient for crop growth. Numerous studies have been performed to improve N fertilizer recommendations. Accurate prediction of soil N supply has been found to be one of the most important factors that determine optimum fertilizer N rates. Seven soils collected from various locations across Indiana at four different depths were tested for N mineralization potential. Results showed that laboratory mineralizable N in the top layer (0-15 cm) of the seven soils ranged from 50 to 68 mg N kg\(^{-1}\) soil. In addition, more than 50% of the total mineralizable N was contributed from the 15 to 60 cm depths. Different methodologies used for estimating soil N supply capacity were also compared in this study. We found that soil N mineralization estimated from long-term static laboratory incubation was correlated to crop N uptake under greenhouse conditions. Some chemical indices such as Illinois Soil Nitrogen Test, anaerobic-N, and Hot KCl-N also showed promises in predicting laboratory N mineralization potential. However, the mineralizable N estimated from laboratory incubations did not show any relationship with soil N supply in the field, which can be attributed to large weather variations under field conditions. Therefore, a process-based weather-driven N transformation and loss model was developed to improve the prediction of optimum in-season fertilizer N rates. So far through simple regression analyses from existing N response studies we found that
yearly plant N uptake simulated from this model was highly correlated to yield data under field conditions ($R^2 > 0.95$ for any site year, $R^2 > 0.80$ for combined site years).

Potassium (K) is also one of the most important essential nutrients for crop growth. The availability of K in the soil determines K fertilizer recommendations. Potassium ions can be fixed between the layers of 2:1 clay minerals in the soil, which decreases the availability of K for plant uptake. We conducted two studies to evaluate the impacts of different factors on soil K availability. One was to assess the effect of anhydrous ammonia (AA) injection on soil K fixation, and the other was to evaluate the effect of soil moisture on soil K test levels. Results of the first study showed that the injection of AA dramatically decreased the nonexchangeable K concentration in some soils up to 4.5 cm away from the injection point, but did not significantly affect the exchangeable K concentration in the soil. In the study about effects of moisture on soil test K (STK) levels, we found that soils with initially high exchangeable K concentrations fixed K upon drying, while soils with initially low exchangeable K concentration released K upon drying. The equilibrium soil K level at which no change in STK occurs upon drying varied with soils (106 to 241 mg kg⁻¹), and was positively related to the predicted soil K critical value. However, the mechanisms affecting K release/fixation still require more study.
CHAPTER 1. NITROGEN MINERALIZATION IN SOILS: A LITERATURE REVIEW

1.1 Introduction

Nitrogen (N) is considered the most limiting essential nutrient required for crop growth. Most plants take up greater amounts of N than any other nutrient, and N is a major component of proteins, nucleic acids and chlorophyll (Brady and Weil, 2008), which are all critical for plant growth.

A lack of N causes yellowish leaves, stunts growth and lowers yield, while an adequate supply of N leads to rapid crop growth with high yields and good quality. If N is oversupplied, excessive vegetative growth occurs and maturity can be delayed (Brady and Weil, 2008). In some cases, plant stems can become tall and weak and prone to lodging with heavy rain or wind. In addition, excessive N applications can lead to poor crop N uptake efficiency and may result in increased greenhouse gas emissions and nitrate loss to groundwater. Therefore, the development of optimum N fertilizer recommendations is important for agronomic, economic and environmental reasons.

The main sources of N input to cropland include N supplied via commercial fertilizers, manures and other N rich organic materials, biological N fixation from legumes and other N-fixing organisms, atmospheric deposition, and N mineralized from soil organic matter and crop residues (Cassman et al., 2002). Except commercial fertilizer and manure application, other N input sources are treated as an indigenous N supply. Typically the indigenous N supply ranges from 80 to 240 kg N ha\(^{-1}\), while corn takes up about 190 kg N ha\(^{-1}\) to produce a yield of 10,000 kg ha\(^{-1}\) (Cassman et al., 2002).
Research also has shown that mineralized soil N is able to provide 20 to 80% of the N required by crops (Broadbent, 1984). Improved estimates of soil N mineralization should allow us to develop more accurate N fertilizer recommendations to optimize crop yield and profitability while minimizing impacts on the environment.

1.2 Soil Nitrogen Mineralization

Plants mostly take up N as nitrate (NO$_3^-$) and ammonium (NH$_4^+$). However, in the soil 89 to 98% of the total N is in the organic form (Foth and Ellis, 1996). Organic N can be converted to mineral forms by a wide variety of heterotrophic bacteria and fungi in a process called mineralization.

In well-drained soils, about 2% of the organic N is mineralized annually (Foth and Ellis, 1996). Mineral soils with 2% organic matter contain nearly 2000 kg N ha$^{-1}$ in a 15-cm thick plow layer (based on a bulk density of 1.33 g cm$^{-3}$), so approximately 40 kg N ha$^{-1}$ would be mineralized annually from the surface soil layer. The amount of N from soil organic matter mineralization can be simply predicted by a mass balance approach: mineralized N = (plant-uptake N + N loss by leaching, volatilization, and denitrification + residual N) minus (inputs + initial N content) (Keeney, 1980). However, this approach is not reliable, because N loss is impossible measured precisely and plant N uptake depends on weather and management. So far a number of techniques have been used to estimate soil N mineralization rate, but no reference method is known to accurately measure soil N mineralization (Raison et al., 1987).

1.3 Factors Affecting Soil Nitrogen Mineralization

Nitrogen mineralization in soils is affected by various factors, including carbon (C) input rate (Matus et al., 2008), cropping system (Deng and Tabatabai,
Carbon inputs from crop residues generally have significant and positive effects on soil N mineralization (Matus et al., 2008). However, this effect also depends on the capacity of soils to preserve soil organic C. In highly C saturated sandy forest soils, free organic matter accumulated in the sand-size fraction results in a considerable increase in N mineralization. However, cropped soils can sequester soil organic C in their clay and silt fractions, which causes substantial losses in labile C (Carter et al., 2003). Additionally, organic C inputs and the quality of plant residues returned to the soil can be affected by the cropping system (Moore et al., 2000). The effect of three crop rotation systems on N mineralization was studied by Senwo and Tabatabai (2005). They found that the amounts of N mineralized in soils from corn-oats-meadow-meadow rotation plots were greater than in soils from continuous corn and corn-soybean cropping systems, because crop rotations involving alfalfa or meadow increase organic C inputs and quality, resulting in greater microbial biomass and activity.

The effect of soil pH on N mineralization is not obvious in most situations because a wide range of organisms participate in this process. Studies showed liming soils to greater pH values (from 4.9 to 6.7) does not affect N mineralization rates (Dancer et al., 1973; Senwo and Tabatabai, 2005). However, liming effects can increase N mineralization at high temperatures (Senwo and Tabatabai, 2005). In some extremely acid situations, mineralization is minimal (Foth and Ellis, 1996).

Nitrogen mineralization generally increases with temperature and soil moisture until an optimum is reached (Stanford et al., 1973; Stanford and Epstein, 1974; Antonopouloos, 1999). Within the range of 5 to 35 °C, an Arrhenius function
describes the relationship between temperature and N mineralization as a 10-degree increase in temperature increases the mineralization rate two times (Stanford et al., 1973; Kladivko and Keeney, 1987). At optimum soil temperatures, mineralization increases with soil moisture up to near field capacity (Stanford and Epstein, 1974), but mineralization in water-saturated soil is limited due to oxygen deficiency (Campbell, 1978). However, the combined effect of moisture-temperature interactions is still not clear (Cassman and Munns, 1980; Kladivko and Keeney, 1987; Wennman and Kätterrer, 2006).

1.4 Prediction of Soil Nitrogen Mineralization

1.4.1 Laboratory Measurements

Numerous laboratory methods for estimating soil N availability have been proposed (Bremner, 1965; Keeney, 1980; Bundy and Meisinger, 1994; Griffin, 2008). The most satisfactory methods currently available are biological methods that measure mineral N produced when the soil is incubated under aerobic or anaerobic conditions. Although these measurements estimate the pools of potentially mineralizable N present at the time of sample collection, they may not be a reliable index of field N mineralization rates due to the disturbance of soil samples before laboratory incubation (Bremner, 1965; Keeney and Bremner, 1966; Raison et al., 1987) and the difference between incubation conditions in laboratory and weather variations at field scale (Jarvis et al., 1996).

A variety of chemical extraction methods for N mineralization have also been developed because these measurements are believed to be more rapid and precise than biological methods (Keeney and Bremner, 1966; Schomberg et al., 2009). However, none of these chemical techniques closely simulates the microbial processes involved in soil N mineralization (Keeney and Bremner, 1966). The accuracy of each chemical method is highly influenced by soil type,
molarities of the extracting solution, soil-solution ratio, extraction time and temperature (Ros et al., 2011a).

1.4.1.1 Biological Methods

The most widely used biological method for estimating soil N mineralization potential is the aerobic incubation method established by Stanford and Smith (1972). They predicted mineralizable soil N by a first-order exponential model obtained from a biologically based, long-term aerobic incubation method. The exponential equation is denoted by:

\[ N_m = N_0 (1 - \exp(-kt)) \]

where \(N_m\) is cumulative net N mineralization in time \(t\), \(N_0\) is the potentially mineralizable N, and \(k\) is the first order rate constant. Some researchers indicated that a two-pool model fits N mineralization data better than the one-pool model (Molina et al., 1980; Beauchamp et al., 1986; Cabrera and Kissel, 1988), because the pretreatment of soil samples (freezing and drying, or drying) can result in a flush of N released on rewetting of soil samples (Cabrera and Kissel, 1988; Wang et al., 2003). Such processes take place fast, most likely within the first four weeks of incubation. However, it is only a small pool of mineralizable N which can be ignored according to Cabrera and Kissel (1988).

Waring and Bremner (1964) developed the short-term anaerobic incubation method to estimate mineralizable N. This method quantifies the ammonium-N produced in the soil, which is incubated under waterlogged conditions for 14 days at 30 °C or 7 days at 40 °C. A strong relationship between the aerobic incubation method and anaerobic incubation method has been observed in several studies (Gianello and Bremner, 1986; Chan, 1997; Schomberg et al., 2009).

Exhaustive cropping under greenhouse conditions is also used to evaluate soil N availability (Keeney and Bremner, 1966). Soils are cropped with plants in the greenhouse and fertilized with a minus-N nutrient mixture. A cropping and
harvesting sequence is repeated for several months until the plants stop growing. Total plant biomass and root uptake is measured along with the mineral N concentration in the soils before and after cropping. It was found that the N content in the first cutting of crop was highly affected by the initial N concentration in the soil, while N uptake by the second and third cuttings was correlated with laboratory indexes of N availability (Keeney and Bremner, 1966).

1.4.1.2 Chemical Methods

Chemical methods used as indices of soil N availability include extraction with boiling water (Keeney and Bremner, 1966), hot or cold KCl (Gianello and Bremner, 1986), alkaline KMnO₄ (Subbiah and Asija, 1956), alkalai hydrolysis in NaOH (Cornfield, 1960), Illinois Soil Nitrogen Test (ISNT, Khan et al., 2001) and so on. Some of these methods were developed before 1980 and have been evaluated in several papers (Keeney and Bremner, 1966; Campbell et al., 1997; Schomberg et al., 2009). Some researchers found N extracted with boiling water was closely related to N mineralization rate (Keeney and Bremner, 1966; Ros et al., 2011a), while others found high correlations between hot KCl-extractable N and N mineralization (Gianello and Bremner, 1986; Schomberg et al., 2009). The ISNT was developed as a quick and simple alternative to determine amino sugar N as hydrolysable amino sugar N has been shown to predict mineralizable soil N (Bushong et al., 2008). However, there are also other reports that found low correlations between chemical indexes and biological methods (Groot and Houba, 1995; Jalil et al., 1996; Selles et al., 1999; Curtin et al., 2006). So far no single availability index of soil N mineralization/availability from chemical measurements has been widely accepted.

1.4.2 Field Estimates

Numerous techniques have been developed to measure or estimate N mineralization under field conditions, because these methods cause less soil disturbance that can markedly affect soil mineralization rates (Bremner, 1965;
Keeney and Bremner, 1966; Raison et al., 1987) and take full consideration of environmental changes (Raison et al., 1987). However, measuring soil N mineralization in situ is not an easy task. Various methods exist, including placing disturbed soil in plastic bags buried in the field (Eno, 1960), or undisturbed soil columns using open-ended polyvinyl chloride (PVC) tubes (Adams and Attiwill, 1986; Kolberg et al., 1997; Gurlevik et al., 2004). These methods demand more replications due to high spatial variability in N mineralization (Macduff and White, 1985). In addition, predictions of mineralizable N were significantly worse when mineralization was measured in the field compared with measurements under controlled conditions (Ros et al., 2011a). One of the greatest challenges with in-field measurements is the inherent variability imposed by weather from site to site and year to year. Although these climate variability issues are not an issue with traditional biological and chemical laboratory methods, temporal changes in mineralizable soil N are a reality at field scale.

1.4.3 Predicting Nitrogen Mineralization with Models

Nitrogen mineralization under field conditions has also been simulated through modeling approaches by considering field fluctuations in temperature and moisture (Cameron and Kowalenko, 1976; Myers et al., 1982; Antonopoulos, 1999). First-order kinetic models are used to quantify the mineralization process (Stanford and Smith, 1972; Cameron and Kowalenko, 1976), where the mineralization rate is proportional to the amount of potentially mineralizable soil N, and is defined by the equation:

\[ \frac{dN}{dt} = -kN_0 \]

where \( N_0 \) is the amount of soil mineralizable N and \( k \) is the mineralization rate constant. This equation can also be expressed as:

\[ N_m = N_0 (1 - \exp(-kt)) \]
where $N_m$ is cumulative net N mineralization in time $t$, $N_0$ is the potentially mineralizable N, and $k$ is the first order rate constant. The potentially mineralizable N is the fraction of organic N in the soil which is readily mineralized. Ros et al. (2011b) indicated that the size of soil organic matter pools and fractions is the primary factor that controls soil N mineralization potential.

To incorporate weather factors into the equation, the mineralization rate constant $k$ is adjusted by soil temperature and moisture factors, and based on a model presented by Antonopouloos (1999), the equation is expressed as:

\[ k_1 = k e_t e_w \]

where $e_t$ is a temperature factor, and $e_w$ represents the effect of water content. Johnsson et al. (1987) suggested the $Q_{10}$ relationship to define the effect of temperature on soil mineralization as follows:

\[ e_t = Q_{10}^{(T_1-T_2)/10} \]

where $T_1$ is the soil temperature, $T_2$ is the incubation temperature at which $e_t$ is equal to 1, and $Q_{10}$ represents the change in N mineralization rate when temperature is changed 10 degrees. $Q_{10}$ of N mineralization is approximately 2 (Stanford et al., 1973; Kladiávko, and Keeney, 1987) in the temperature range of 5 to 35°C. The soil moisture factor $e_w$ is a function of the soil water filled pore space (WFPS) (Lafoilie et al., 1997).

\[ e_w = \begin{cases} \frac{(\theta - \theta_w)}{(\theta_l - \theta_w)}^2 & \text{when } \theta < \theta_l; \\ 1 & \text{when } \theta_l \leq \theta \leq \theta_h; \\ 0.6 + (1 - 0.6)\left[\frac{(\theta_s - \theta)}{(\theta_h - \theta_h)}\right]^2 & \text{when } \theta > \theta_h; \end{cases} \]

where $\theta_s$, $\theta_h$, $\theta_l$, and $\theta_w$ are WFPS at saturation (WFPS=1), 60% and 50% of WFPS, and WFPS at wilting point, respectively.

In the model presented by Cameron and Kowalenko (1976), the interaction effect of temperature and moisture was also considered in the equation, and the
relationship between the mineralization rate constant $k$ and the environmental factors is expressed as:

$$k = 10^{-6}(-2.655 + 0.01943T\theta - 0.2064T + 0.1606)$$

where $T$ is the soil temperature in Celsius, and $\theta$ is soil gravimetric water content (g/g) in percentage.

1.5 **Nitrogen Cycling in the Soil**

1.5.1 **Immobilization**

The C:N ratio of a substrate is considered the most critical factor controlling mineralization/immobilization (Foth and Ellis, 1996). The C:N ratio of soil organic matter is relatively constant. When substrates with a wide C:N ratio (> 25:1) are applied, soil C/N balance is destroyed, and the heterotrophic microorganisms have to accumulate mineral N due to the N deficiency in these substrates. The process of conversion of the mineral N into organic N is called immobilization.

After application of N fertilizers like urea and ammonium salts, immobilization dominated over mineralization for a few days (Overrein, 1967; Overrein, 1972). Addition of 250 kg N ha$^{-1}$ increased the humus total N content from 1.4 to 2%, and the net N mineralization for plots treated with urea or ammonium salts was about twice that of the plots without fertilizer application, because the immobilized fertilizer N was more active than native organic N (Williams, 1972).

1.5.2 **Nitrification**

In aerobic soils, $\text{NH}_4^+$ is oxidized by chemoautotrophic bacteria or Archaea, and converted to nitrite ($\text{NO}_2^-$), and eventually to $\text{NO}_3^-$. This process is called nitrification (Foth and Ellis, 1996). Two steps are involved in this process. The first step is to oxidize the $\text{NH}_4^+$ to $\text{NO}_2^-$ as follows:
\[ 2 \text{NH}_4^+ + 3\text{O}_2 = 2 \text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+ \]

Bacteria of the genus *Nitrosomonas* and several other bacteria are responsible for this conversion. This step produces protons and is considered a natural soil acidification process. The second step is conversion from \( \text{NO}_2^- \) to \( \text{NO}_3^- \) by *Nitrobacter* as follows:

\[ 2\text{NO}_2^- + \text{O}_2 = 2\text{NO}_3^- \]

Ammonium is immobile in the soil because it is commonly adsorbed on the surface of clay minerals or fixed in between the layers of clay minerals, and \( \text{NH}_4^+ \) is readily available for plant uptake. However, \( \text{NO}_3^- \) is subject to loss from soils by leaching or denitrification. Thus, a low rate of nitrification is desirable from the standpoint of increasing fertilizer use efficiency and improving groundwater quality.

The primary factors that control nitrification in soil are temperature, moisture, pH, \( \text{NH}_4^+ \) concentration and the use of nitrification inhibitors. Generally, nitrification rates increase with temperature from 0 to 30 °C. The activities of nitrifying bacteria cease below 0 °C (Sabey et al., 1959; Malhi and McGill, 1981) and perform very slowly when the soil temperature is below 5 °C (Brady and Weil, 2008). The optimum temperature for nitrification is generally between 20 to 30 °C (Brady and Weil, 2008). Malhi and McGill (1981) found that nitrification rate was maximized at 20 °C and ceased at 30 °C in soils from central Alberta. However, Russell et al. (1925) reported a maximum nitrification rate at 37 °C and that activity ceased at 55 °C. Sabey et al. (1959) found that the specific impact of temperature on soil nitrification was largely dependent on the climatic zone of the study.

The optimum soil moisture content for nitrifying bacteria is about the same as the optimum moisture for plant growth, which is about 60% WFPS (Brady and Weil, 2008). However, the optimum moisture for nitrification differs slightly among
soils (Parton et al., 1996). Below the optimum soil moisture, nitrification rate declines as soil moisture decreases (Malhi and McGill, 1982; Gilmour, 1984; Parton et al., 1996). When soil is too wet, nitrification is not appreciable due to the shortage of O₂ in the soil system (Miller and Johnson, 1964; Malhi and McGill, 1982).

The effect of soil pH on nitrification rate is significant. Nitrification generally increased with soil pH over the range of 4.9 to 7.2 (Gilmour, 1984). Dancer et al. (1973) reported that nitrification rates were similar for pH from 5.3 to 6.6, but significantly decreased at pH 4.7.

Besides temperature, moisture and soil pH, the abundance of NH₄⁺ present in the soil also plays an important role in the activities of nitrifying microorganisms. Malhi and McGill (1982) indicated that an increase in nitrification rate was observed when NH₄⁺-N concentration increased from 50 to 200 µg·g⁻¹ soil, but nitrification rate decreased when the NH₄⁺-N concentration increased to 300 µg·g⁻¹ soil due to the combined effect of low pH and high salt content.

As indicated previously, a low rate of nitrification is desirable because NO₃⁻ is more mobile and prone to loss through leaching or denitrification. Frozen temperatures, a long dry season, extremely low pH, or absence of NH₄⁺ all can lead to low nitrification rates. However, none of these conditions are favorable for plant growth. Conversely, most factors that favor optimum plant growth also favor nitrification. Therefore, to slow nitrification rates under these conditions, chemicals that can inhibit the nitrification process are sometimes used. These chemicals are called nitrification inhibitors (NIs), and they can kill or interfere with the metabolism of nitrifying bacteria and prevent the conversion from NH₄⁺ to NO₂⁻, thereby reducing nitrate leaching potential and increasing N fertilizer use efficiency. Many studies have reported an increase in corn yield with the application of NIs (Malzer et al., 1979; Hoeft, 1984; Nelson and Huber, 1992; Wolt, 2004). However, the effectiveness of NIs can be influenced by different soil properties, environmental factors and application techniques. For example,
nitrapyrin [2-chloro-6-(trichloromethyl) pyridine], the most commonly used NI in US, is generally less effective on soils with a high soil organic matter content (Hendrickson and Keeney, 1979; Chancy and Kamprath, 1987; Wolt, 2000), or at high temperatures (Bundy and Bremner, 1973; Touchton et al., 1979).

1.5.3 Denitrification

Denitrification is the process of reducing NO$_3^-$ to gaseous N forms such as nitric oxide (NO), nitrous oxide (N$_2$O), and nitrogen gas (N$_2$). This process occurs under an anaerobic environment where bacteria use NO$_3^-$ as a terminal electron acceptor during respiration in the absence of O$_2$. Denitrification is favored in anaerobic, warm, near-neutral soils containing adequate carbon and substrate sources (Keeney, 1980). Denitrification is an important N loss process in poorly drained surface soils of forests with high nitrification rates (Davidson and Swank, 1987).

In general, denitrification is favored by high soil moisture content, high soil temperature, a low rate of oxygen diffusion as well as the presence of soluble organic matter and NO$_3^-$ (Luo et al., 1999).

Soil moisture content can markedly affect gaseous N loss (Myrold, 1988; Jarvis et al., 1991; de Klein and van Logtestijn, 1994). These studies showed that above a critical soil water threshold, denitrification rates increased sharply with increased soil water content. Below that, soil moisture content does not appear to be the predominant control factor (Pilot and Patrick, 1972; Klemedtsson et al., 1991). According to a model by Davidson (1991), N$_2$O is primarily derived from denitrification at 60 to 80% WFPS due to decreased O$_2$ supply. Liu et al. (2007) reported that N loss rates were increased by a factor of 1.63 at 75% WFPS compared to 60% WFPS in a clay loam soil. Temperature is also an important factor controlling denitrification rates. Increase in temperature has both a direct and an indirect effect on denitrification rates (Smith and Arah, 1990). Temperature directly affects denitrification rates following the Arrhenius equation,
whereas the indirect effect is caused by an increase in the volume of anaerobic zones.

The effect of moisture and temperature on denitrification varies with soil type. The soil water threshold point for denitrification to occur differs with varying soil texture (Barton et al., 1999). Generally, greater threshold soil moisture content is observed in coarse-textured soils than in fine-textured soils with reported values of 74% to 83% WFPS for sandy and sandy loam soils, 62% to 83% WFPS for loam soils, and 50% to 74% for clay loam soils. Groffman and Tiedje (1991) attributed such observations to the effect of soil texture on oxygen availability. In fine-textured soils with smaller pores, it is easier to create anaerobic microsites at lower water content. Maag and Vinther (1996) found that the denitrification activity in a sandy loam soil responded significantly to both increased soil moisture and increased temperature, whereas the coarse sandy soil only reacted to increased temperature.

1.5.4 Ammonium Fixation

Ammonium ions have a similar ionic radius and energy of hydration as potassium (K⁺) ions, so they can also be fixed in the interlayer region of 2:1 clay minerals (Foth and Ellis, 1996). It has been reported that no equilibrium exists between exchangeable and fixed NH₄⁺ due to the competitive relationship between the K⁺ ions and NH₄⁺ ions for exchange sites (Nieder et al., 2011). Solution and exchangeable NH₄⁺ are considered readily available for plant uptake. While fixed NH₄⁺ is not immediately available to plants, it is released when solution NH₄⁺ is depleted by plant uptake or nitrification. Ammonium fixation is faster than NH₄⁺ release (Foth and Ellis, 1996; Steffens and Sparks, 1997). Drury et al. (1991) found that 18 to 23% of added NH₄⁺ was fixed within 15 days of incubation, and Allison et al. (1953) found that only about 5 to 24% of fixed NH₄⁺ became available to nitrifying bacteria during a period of 2 months.
Clay type is considered the dominant factor affecting NH$_4^+$ fixation capacity in the soil. Considerable fixation (about 1.6 to 3.8 cmol kg$^{-1}$ soil) occurs in soil if the predominant clay mineral is illite or vermiculite, while smectitic and kaolinitic soils fix little NH$_4^+$ (about 0 to 0.9 cmol kg$^{-1}$ soil) (Allison et al., 1953; Said, 1973). Ammonium fixation is an important factor in fertilizer use efficiency when NH$_4^+$ fertilizers are added to micaceous soils, especially where band-injection of anhydrous ammonium (AA) is widely applied, because 5 to 10 times greater fixation of NH$_4^+$ has been reported with AA than NH$_4^+$ salt fertilizers (Young and Cattani, 1962).

1.5.5 Ammonia Volatilization

The process of ammonia (NH$_3$) emission from the soil into the atmosphere is called volatilization. Volatilization commonly occurs after the application of manures or chemical fertilizers like anhydrous ammonia and urea (Brady and Weil, 2008). This process is expressed as the following reversible reaction:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

Therefore, soils with greater amounts of OH$^-$ ions (high pH) drive the reaction to the right and enhance the volatilization process. Since volatilization is a source of N loss, understanding the factors that influence volatilization is important if we are to minimize NH$_3$ loss from soils through improved N management. In general, soil and weather conditions, fertilizer sources and application techniques all impact NH$_3$ volatilization (Brady and Weil, 2008).

Ammonia volatilization increases with soil pH (Brady and Weil, 2008). He et al. (1999) found volatilization from surface applied (NH$_4$)$_2$SO$_4$ was minimal in soils with an initial pH of 3.5, but the volatilization rate rapidly increased from pH 4.5 up to pH 8.5. Nitrogen fertilizers like urea and anhydrous ammonia increase soil pH and also increase NH$_3$ volatilization (Fan and Mackenzie, 1993; Jones and Jacobsen, 2001). However, changes in soil pH following fertilizer
applications are resisted in well-buffered soils. Therefore, soil properties such as texture, organic matter content and cation exchange capacity (CEC) can also have a significant effect on NH$_3$ volatilization (Jones and Jacobsen, 2001). Whitehead and Raistrick (1990) reported that following urea application, 23.5% of the total applied N volatilized in a soil with a clay content of 230 g kg$^{-1}$, an organic matter content of 48 g kg$^{-1}$ and a CEC value of 12.8 cmol$_c$ kg$^{-1}$, whereas 38% of the total applied N volatilized in a soil with a clay content of 100 g kg$^{-1}$, an organic matter content of 26 g kg$^{-1}$ and a CEC value of 7.4 cmol$_c$ kg$^{-1}$. As indicated by O’Toole et al. (1985), when soil CEC (determined by BaCl$_2$ buffered at pH 8.2 with triethanolamine) is lower than 26.8 cmol$_c$·kg$^{-1}$, NH$_3$ losses increase rapidly with CEC decreases, while above this critical value, minimal NH$_3$ losses were observed. However, Sommer and Ersball (1996) found no reduction in NH$_3$ volatilization from urea with increasing CEC (7.7 to 12 cmol$_c$·kg$^{-1}$; determined by saturating the soil with Na$^+$ and extracting the Na$^+$ with ammonium acetate), though the CEC of the soils in this study were below 26.8 cmol$_c$·kg$^{-1}$. They explained the reduced effect of CEC resulted from the increased pH and exchangeable Ca$^{2+}$ concentration.

Temperature has a significant positive effect on NH$_3$ volatilization. Huijsmans et al. (2003) found that the percentage of NH$_3$ volatilized increased from 35% to 56% of total ammoniacal N applied as temperature increased from 10 to 20 °C 96 hours after a surface-application of liquid swine manure. Fenn and Kissel (1974) indicated that both the volatilization rate and total NH$_3$ loss increased when temperature increased from 12 to 32 °C. He et al. (1999) found the amount of NH$_3$ volatilized from (NH$_4$)$_2$SO$_4$ in 60 days increased 3-fold as the incubation temperature increased 25 °C to 45 °C, because the increasing temperature not only increased the chemical reaction rate from NH$_4^+$ to NH$_3$ and the diffusion rate of NH$_3$, but also decreased the activities of nitrifying bacteria which resulted in a greater level of NH$_4^+$ available for conversion to NH$_3$ with time.
The effect of soil moisture on NH$_3$ volatilization is indirect. When soil is dry, less NH$_3$ volatilizes from urea due to decreased hydrolysis rates (Ferguson and Kissel, 1986; Al-Kanani et al., 1991). Urea hydrolysis can be expressed by following reaction equations:

\[(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3\]

\[(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O\]

\[NH_3 + H_2O \rightarrow NH_4^+ + OH^-\]

Ferguson and Kissel (1986) found that when the soil is dry, urea is not readily hydrolyzed and NH$_3$ loss is significantly reduced. Ammonia volatilization has also been shown to be relatively low when manure is applied to a dry soil, possibly due to increased infiltration (Sogaard et al., 2002). However, greater losses of NH$_3$ were observed after anhydrous ammonia was injected into a dry soil, which could be explained by the rapid emission of NH$_3$ through cracks and voids between the dry soil particles (Sommer and Christensen, 1992).

Ammonia volatilization is greatly influenced by fertilizer sources, fertilizer application techniques and fertilizer rates. For surface application of different fertilizer sources, He et al. (1999) found in a sandy soil (pH=7.9) the NH$_3$ volatilization potential (% of applied NH$_4$-N) predicted under laboratory conditions increased in the following order: NH$_4$NO$_3$ (17.6%) < (NH$_2$)$_2$CO (21.4%) < (NH$_4$)$_2$SO$_4$ (21.7%) < NH$_4$HCO$_3$ (23.2%). Al-Kanani et al. (1991) indicated that the NH$_3$ loss resulting from surface applied urea ammonium nitrate (UAN) solution was greatly reduced compared to the NH$_3$ loss from surface applied urea. Whitehead and Raistrick (1990) determined that NH$_3$ volatilization varied greatly when five N sources (mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP), ammonium sulfate (AS), ammonium nitrate (AN), and urea) were applied to the surface of four soils. For example, on a soil with a CEC of 7.4
cmol·kg\(^{-1}\), the maximum loss of NH\(_3\) was much greater from urea (40% of total N) compared to AS (5% of total N). However, on another soil with CEC of 15.6 cmol·kg\(^{-1}\), AS had the greatest NH\(_3\) loss (up to 30% of the total N). Therefore, the impact of different N sources on volatilization is a combined effect of both the fertilizer N source and soil properties. Ammonia volatilization can be greatly reduced by incorporating fertilizers below the soil surface, applying them during cooler periods or by splitting the application (Jones and Jacobsen, 2001). With manure application, Huijsmans et al. (2003) found that 68% of the total ammoniacal N applied was lost via volatilization for surface spreading, compared to 17% for surface incorporation and 2% for deep placement. With urea, NH\(_3\) loss was negligible by banding at a depth of 2.5 cm (Bouwmeester et al., 1985).

1.5.6 Biological Nitrogen Fixation

Seventy-eight percent of air is N\(_2\). Nitrogen gas can be converted to forms of N that are available to plants and other forms of life. This process is called “N fixation”. There are three major N fixation processes: ammonia fertilizer production, lightning, and biological fixation (Jones and Jacobsen, 2001). Among these three, the fixation process which is carried out by organisms in the natural environment is known as biological N fixation. Approximately 145 to 200 million tons of N can be fixed through biological fixation worldwide on an annual basis (Jones and Jacobsen, 2001). Therefore, besides plant photosynthesis, biological N fixation is considered the most important biochemical reaction for life on earth (Brady and Weil, 2008).

Only a limited number of bacteria are capable of carrying out biological N fixation. The major species involved include *Rhizobium*, *actinomycetes*, and *cyanobacteria* (Brady and Weil, 2008). Biological N fixation can be classified into three categories: symbiotic fixation with legumes, symbiotic fixation with non-legumes, and non-symbiotic fixation. Since symbiotic fixation with legumes is the most important source for fixed N in corn-soybean cropping systems, it will be discussed in the following paragraph.
For symbiotic fixation with legumes, legumes such as clovers and beans are the host plants. Bacteria species including *Rhizobium* and *Bradyrhizobium* infect the root hairs and the cortical cells of the host plants, and ultimately induce the formation of root nodules that serve as the site of N fixation (Brady and Weil, 2008). The amount of N biologically fixed from the root nodules can be quite high and is able to adequately meet the N needs of several plant species. The rate of biological N fixation depends on soil and climatic conditions, such as soil pH, soil salinity, nutrient content, temperature and moisture. Commonly, the legume-*Rhizobium* associations have higher requirement than other plants for Mo, Ca and neutral pH (Cooper et al., 1983; Hungria and Vargas, 2000). However, high levels of available N in the soil tend to depress biological N fixation (Brady and Weil, 2008).

1.5.7 Nitrate Leaching

In the soil system, available N is gained through mineralization, biological fixation, and human inputs as manures and fertilizers and other amendments, while soil N can also be lost due to plant uptake, denitrification, volatilization and NO$_3^-$ leaching. Nitrate is a highly soluble, negatively charged ion which is not absorbed to dominantly negatively charged soil particles, so NO$_3^-$ is prone to move through the soil with excess water.

Nitrate leaching is a major source of N loss, especially in areas with excessive applications of N fertilizer and frequent precipitation or irrigation. For example, in Indiana the average annual NO$_3^-$-N losses from drainage can be more than 67 kg N ha$^{-1}$ (Kladivko, 2001) which is approximately one quarter of the total amount of N required for a high yielding corn crop. Nitrate leaching to groundwater can cause human and animal health concerns. Because high NO$_3^-$ levels decrease the oxygen carrying capacity of hemoglobin and lead to respiratory distress and even death of newborn babies, the USEPA issued a drinking water standard of 10 mg L$^{-1}$ NO$_3^-$-N. When the NO$_3^-$-contaminated groundwater moves downstream, it also can cause more widespread damage to
aquatic ecosystems (Brady and Weil, 2008). The Gulf of Mexico “Dead Zone”, which covers up to 14,000 to 22,000 km\(^2\) is an area of hypoxic water caused by nutrient enrichment from the Mississippi River. Most of the N that enters the Mississippi River comes from Midwest farming states through surface runoff, erosion, and nitrate leaching. The enriched nutrients in the water system lead to excessive growth of algae, which depletes the dissolved oxygen in the water and can cause fish kills and significantly alter biodiversity.

The two principle factors that affect NO\(_3^-\) leaching are the amount of water moving through the soil profile and the amount of NO\(_3^-\) present in the soil solution. Strategies used to reduce N loss through leaching include optimum N fertilizer application rates and timing, the use of nitrification inhibitors, proper irrigation management and growing cover crops.

1.5.8 Crop Uptake

In general only about 50% of applied fertilizer N is used by the intended crop, while the rest is lost through various N transformation processes including leaching, denitrification, and volatilization (Craswell and Godwin, 1984; Jones and Jacobsen, 2001). Therefore, to increase fertilizer N use efficiency, it is important to time fertilizer applications with crop N demand (Doerge et al., 1991).

The amount of N taken up by crops varies from approximately 56 to 224 kg ha\(^{-1}\) per year, depending on crop type and yields (Jones and Jacobsen, 2001). Table 1.1 lists N removal in the harvested portion of selected agricultural crops. Plant N uptake rates vary greatly at different plant growth stages. In winter wheat, pre-anthesis N uptake accounts for 75% to 90% of total N uptake at harvest (Heitholt et al., 1990; Delogu et al., 1998). For corn, the total amount of N uptake is not greatly different from that for wheat. However, the N demand by corn is high for a relatively short time (Figure 1.1) (UCWRC, unknown publish year).
1.6 Nitrogen Fertilizer Management

Nitrogen fertilizer application is critical for optimum crop growth. However, excessive applications of N fertilizer result in significant N losses and severe environmental problems. Therefore, fertilizer N management strategies have always been hot topics in agricultural production.

A fertilizer management strategy has to answer three essential questions: “When”, “How”, and “How much”. When to apply the fertilizer? What application method should be used? And what is the fertilizer application rate? The most effective management strategy will be one that matches the release of fertilizer N with crop N demand. Thus, each fertilizer management strategy will be case-specific, and highly dependent on soil conditions, nutrient sources, and crop types.

1.6.1 Application Rate

Until recently, Indiana used yield-based fertilizer recommendations and recommended N fertilizer rates were based on the following relationship:

$$N \text{ application rate (lb/A)} = -27 + (1.36*\text{yield potential}) - N \text{ credit}$$

where the N credit is given based upon the previous crop. For example, a 30 lb/A N credit is used if the previous crop was soybean (Vitosh et al., 1995). A 27 lb/A credit is given for soil N supply. However, the 27 lb N/acre credit underestimates N supply abilities of most Indiana soils, which results in an over application of N fertilizer (Emmert, 2009). On the other hand, soil N supply capacity varies from soil to soil. Soil N supply capacity is related to various soil properties including soil organic matter content, soil microbial C and N, as well as soil texture and pH (Franzluebbers et al., 2001; Senwo and Tabatabai, 2005; Ros et al., 2011b). Through comparison between mineralizable N and different soil physical and chemical properties across 98 agricultural soils, Ros et al. (2011b) concluded that soil organic matter variables are most important in predicting soil N
mineralization potential. Assuming 2% of soil N is mineralized each year (Foth and Ellis, 1996), soils with 3% of organic matter will release 60 lb N/acre, while soils with 1% organic matter will only supply 20 lb N/acre. So with a 2% difference in soil organic matter content, the difference in soil N supply credit can be as high as 40 lb N/acre. Further, even on the same field, large year to year variations within the optimum N rate for corn are observed. Soil N supply also varies greatly from year to year due to the varied rainfall amount and temporal distribution. Franzluebbers et al. (2001) indicated that in the field higher mean annual temperature resulted in greater soil mineralized N, while higher mean annual precipitation had inconsistent effects on soil N mineralization. Therefore, it is not reasonable to use one fixed value for the soil N supply credit when predicting the optimum N fertilizer rate for a variety of soils or for one soil under different weather conditions.

A large body of research has shown that fertilizer N requirement is poorly related to yield (Vanotti and Bundy, 1994; Bundy and Andraski, 1995; Kachonoski et al., 1996; Mamo et al., 2003; Lory and Scharf, 2003; Scharf et al., 2006; Bundy, 2006). Thus, a new fertilizer N recommendation strategy was developed and adopted in several states in the Midwest (Sawyer et al., 2006). Without considering the yield goal of the crops, this new approach generates fertilizer N recommendations based on the results of numerous N response trials conducted on different soils. After the N response trials are conducted, the overall goal is to find out the economic optimum N rate from the yield response curve derived from N response trial datasets while considering the cost of N fertilizer and the price of corn grain. However, yield response to N is highly dependent on soil type and weather. To convert a set of varying responses to N rate recommendations, the maximum return to N (MRTN) approach is used (Nafziger et al., 2004). The general steps are to fit the yield data collected at various N rates from many N response trials to a curve to obtain a mathematical equation of the curve, and then calculate the yield increase (above yield at zero N) from the response curve equation. The net return is yield increase times the
grain price, and minus the cost of the fertilizer. The MRTN rate is the N rate with the largest net return to N. Although soil N supply capacity is not directly included in the calculation, it has been integrated in the yield response curve. In general, this fertilizer recommendation strategy is more region- and soil-specific.

1.6.2 Application Methods

For granular fertilizers, typical N fertilizer application practices include broadcast, broadcast-incorporated, surface banded, and deep banded; while liquid fertilizers such as anhydrous ammonia and UAN are band-injected, or sprayed as foliar fertilizer (Jones and Jacobson, 2009). Although broadcasting is the easiest application practice to perform with less expensive equipment, it has been shown to be less effective than surface or subsurface banding due to NH₃ volatilization, especially for urea (Gould et al., 1986). Zero or minimal tillage management systems have been widely adopted in the Midwestern US (Phillips et al., 1980). No-till generally leads to greater soil moisture content, increased microbial activity and increased urease activity on the surface of crop residues. When urea is broadcast onto no-till fields, much of the fertilizer is in contact with crop residues and a greater amount of urea-N will be lost through NH₃ volatilization (Gould et al., 1986). However, when urea is banded at a depth of 2.5 cm, Bouwmeester et al. (1985) reported that NH₃ loss through volatilization was negligible.

1.6.3 Application Timing

Nitrogen fertilizer can be applied prior to seeding either in fall or spring, applied at the time of seeding as a starter, or side dressed after emergence (Jones and Jacobson, 2009). Fall application of N fertilizer results in N losses through leaching, denitrification and surface runoff prior to the next growing season. Research showed significantly lower corn grain yields from fall application compared with spring application (Vitosh, 1985; Vetsch and Randall, 2004), and often these yield reductions cannot be compensated for by greater N
application rates (Vitosh, 1985). However, in an 8-year study conducted on a Crosby silt loam soil in Ohio, nitrification inhibitors (nitrapyrin) with fall-applied N fertilizers increased crop yields compared to fall application without nitrification inhibitors (Stehouwer and Johnson, 1990).

Preplant applications of N fertilizers are common and easy to perform. However, under certain soil and weather conditions, like sandy soils with excessive rainfall early in the growing season, preplant applications can result in significant N losses before crop uptake (Vitosh et al., 1995). Side dress applications usually minimize these losses. However, side dress applications also carry the risk of suboptimal timing due to wet conditions during the application period or low N availability due to drought after side dressing. Therefore, it is reasonable to conclude that weather is probably the single most important factor that determines optimum fertilizer N application rates on a seasonal basis.

1.7 Concluding Remarks

Soil N is a primary resource for plant growth, and N mineralization plays an important role in soil N cycling. More accurate prediction of soil N mineralization would allow us to develop better N fertilizer recommendations to optimize crop yield and profit and reduce environmental pollution. Numerous methods, including biological incubations, chemical measurements and field estimates have been developed to estimate soil N mineralization. However, since N mineralization in soils is a complex process which can be affected by various factors, such as carbon input rates, cropping system, soil pH, temperature and water content, so far no single method has been widely accepted that can accurately quantify soil N mineralization. Thus, my research objectives are to compare different methods for estimating soil N mineralization, determine soil N mineralization potentials of different Indiana soils, and develop an N
transformation and loss model that couples a weather-driven crop growth model with soil surface and subsurface N mineralization algorithms with soil and fertilizer N transformation and loss processes to improve crop N fertilizer recommendations.
1.8 Reference


Table 1.1 Nitrogen uptake in the harvested portions of selected agronomic crops†.

<table>
<thead>
<tr>
<th>Crop</th>
<th>Unit of yield</th>
<th>N uptake per unit of yield (lb/unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>ton</td>
<td>60</td>
</tr>
<tr>
<td>Barley</td>
<td>bushel</td>
<td>1.6</td>
</tr>
<tr>
<td>Corn silage</td>
<td>ton</td>
<td>8.4</td>
</tr>
<tr>
<td>Wheat</td>
<td>bushel</td>
<td>1.8</td>
</tr>
</tbody>
</table>

† Adapted from Jones and Jacobsen, 2001.
Figure 1.1 Nitrogen uptake rate of corn and wheat as a function of crop growth over time. Adapted from University of California Water Resources Center (UCWRC), unknown publish year.
CHAPTER 2. ESTIMATING POTENTIALLY MINERALIZABLE NITROGEN IN INDIANA SOILS

2.1 Abstract

Soil nitrogen (N) supply is probably the single most important factor that causes observed differences in optimum fertilizer N rates for corn among soils in similar climatic conditions. Better estimates of soil mineralization would improve our ability to develop more accurate N rate recommendations for crop production. Through a preliminary study, we found a static incubation was better than a leaching incubation for predicting mineralized soil N under greenhouse conditions. Subsequently we used the static incubation method to assess N mineralization of seven major soils in Indiana at four different depths. The static incubation was conducted in centrifuge tubes at 25 °C with a moisture tension of 10 KPa for 16 weeks. Every four weeks soils were destructively sampled and extracted with 1 M KCl for the analysis of NO₃⁻-N and NH₄⁺-N soil N. The cumulative net N mineralization data were fitted to a first-order exponential model to determine potentially mineralizable soil N (N₀) and the N mineralization rate constant (k). The N₀ and k values estimated from this static incubation were related to some “quick” chemical indices for predicting N₀. The results showed that mineralizable N decreased with depth, but more than 50% of the total mineralizable N was contributed from a depth of 15 to 60 cm. The k values also varied with soil type and depth. Several chemical methods (Illinois Soil Nitrogen Test, anaerobic-N, hot KCl-N) were found to be related to the soil N mineralization potential with R² greater than 0.6. However, none of them was able to predict the mineralization rate constant k. Field soil N supply was also estimated through N response trials.
Results showed that on the same field the estimated soil N supply varied greatly from year to year with a standard deviation as high as 28 kg N ha\textsuperscript{-1}. In addition, mineralizable soil N estimated from the laboratory incubation was not correlated to the field measurements of soil N supply, which can be attributed to weather variations, landscape positions, etc. under field conditions.
2.2 Introduction

Nitrogen (N) is the most likely limiting essential nutrient for growth of non-legume crops. Soil N can typically provide 20 to 80% of the N required by crops (Broadbent, 1984), but in most soils and most situations fertilizer N must be added to maximize growth. Both under- and over- applications of N have economic consequences, so it is important to develop accurate N fertilizer application rate guidelines. Excessive N applications can lead to poor crop N uptake efficiency and may result in increased greenhouse gas emissions and nitrate loss to groundwater. Thus, the prediction of soil N mineralization gives us the ability to develop more accurate N fertilizer recommendations to optimize crop yields and profitability, and to reduce N losses to the environment.

Until recently, in Indiana and many midwest states, yield-based fertilizer recommendations were the most employed fertilizer management strategies. For example in in Indiana, Ohio, and Michigan the recommended N fertilizer rate for corn was based on the following relationship:

\[ \text{N application rate (lb/A)} = -27 + (1.36 \times \text{yield potential}) - \text{N credit} \]

where the N credit is given based on the previous crop (Vitosh et al., 1995). A 27 lb N/acre credit is given for soil N supply. However, the 27 lb N/acre credit underestimates N supply capacity of most Indiana soils, which often results in an excessive N fertilizer recommendation (Emmert, 2009). Further, soil N supplying capacity varies from soil to soil and year to year. Soil N supplying capacity is related to various soil properties including soil organic matter content, soil microbial C and N, as well as soil texture and pH (Franzluebbers et al., 2001; Senwo and Tabatabai, 2005; Ros et al., 2011). Based on comparisons among mineralizable soil N estimated through laboratory incubation and various soil physical and chemical properties across 98 agricultural soils, Ros et al. (2011a) concluded that soil organic matter is the most important variable in predicting soil N mineralization potential. Assuming 3.5% of soil N is mineralized each year
(Oberle and Keeney, 1990), soils with 3% of organic matter will release 105 lb N/acre, while soils with 1% organic matter will only supply 35 lb N/acre. So a 2% difference in soil organic matter content can produce as much as a 70 lb N/acre difference in soil N supply. In addition, the effect of temperature and moisture on soil N mineralization has been described by many researchers (Stanford et al., 1973; Stanford and Epstein, 1974; Antonopoulos, 1999). Franzluebbers et al. (2001) indicated that in the field higher mean annual temperature resulted in greater net N mineralization, while higher mean annual precipitation had inconsistent effects on net N mineralization. Because variations in soil N supply are related to weather variations, it is not reasonable to use one fixed value for soil N supply when predicting optimum N fertilizer rates for a variety of soils or for one soil under different weather conditions. If we are to improve N fertilizer recommendations, it is important that estimates of soil N supply consider both soil and weather parameters.

Numerous laboratory methods for predicting soil N availability have been proposed (Bremner, 1965; Keeney, 1980; Bundy and Meisinger, 1994; Griffin, 2008). Currently, the most satisfactory methods available for measurement of laboratory mineralizable N are biological methods that measure mineral N produced when soils are incubated under aerobic conditions. An approach developed by Stanford and Smith (1972) has been commonly accepted to predict the mineralized soil N from laboratory incubations using a first-order exponential model. Another laboratory incubation approach using static cups has been widely used as well (Keeney and Bremner, 1966; Zinati et al., 1997; Vernimmen et al., 2007; Schomberg et al., 2009), because it is easier to perform and requires less equipment. However, regardless of the method chosen, N mineralization estimates from disturbed soils under controlled laboratory conditions by themselves will not quantitatively predict soil N availability in the field, due to differences in soil disturbance and weather in the field compared to the laboratory (Cabrera and Kissel, 1988).
In addition to the relatively time consuming biological methods described previously, several more rapid chemical indices of soil N availability have been developed (Keeney and Bremner, 1966; Schomberg et al., 2009). However, none of these chemical methods closely simulate the microbial processes involved in soil N mineralization (Keeney and Bremner, 1966). The accuracy of these chemical methods is highly influenced by soil drying temperature prior to extraction, molarity of the extracting solution, soil-solution ratio, and extraction time and temperature (Ros et al., 2009). Some chemical indices including total carbon content, total N content, mineral N extracted by hot KCl, N mineralized under anaerobic conditions, and N mineralized in 24 days have been found to be highly correlated to soil N mineralization potentials estimated from long-term biological incubations (Schomberg et al., 2009).

Although soil N mineralization potentials can be easily measured and estimated from various laboratory procedures, limited work has been done to compare soil N mineralization estimated through laboratory procedures to soil N supply capacity under full field conditions. Schomberg et al. (2009) reported that the soil N mineralization potential estimated from laboratory incubations was as high as 500 mg kg\(^{-1}\), which is much greater than the total amount of N required for corn growth. However, because these laboratory results were not compared to field measures of crop N uptake or mineralization, it was not possible to determine whether a high estimate like this would result in optimum crop yields without additional fertilizer N applications. Therefore, it is more critical to find the relationship between laboratory mineralizable N and field soil N supply.

In addition, the importance of subsoil N mineralization to crop production has largely been overlooked. Most research on soil N mineralization has been limited to the plow layer, in spite of the fact that most plants also obtain N mineralized from deeper horizons (Cassmann and Munns, 1980). Cassmann and Munns (1980) found that up to 58% of the total estimated mineralized N could be attributed to the 18-108 cm soil depth. In 4 Moroccan soils studied by Soudi et al.
(1990), subsoil layers (below 20 cm) contributed 20 to 37% of total mineralized N. For more accurate N fertilizer recommendations, the potential contributions of N mineralized from subsoil should be considered.

The objectives of this study were to: (i) compare different biological methods used to quantify mineralized soil N; (ii) estimate potentially mineralizable soil N in Indiana soils at different depths using a long-term laboratory incubation method; (iii) relate soil N mineralization potential estimated from a long-term biological incubation method to some chemical N availability indexes; and (iv) determine the relationships between various laboratory estimates of mineralizable soil N and field soil N supply.

2.3 Materials and Methods

2.3.1 Comparison of Different Biological Methods used to Measure Mineralized Nitrogen

Eight soils were collected from four sites where corn N response trials were conducted following a previous soybean crop. The Chalmers and Raub soils were collected from the Purdue Agricultural Center for Research and Education (ACRE), the Blount and Pewamo soils were collected from the Davis-Purdue Agricultural Center (DPAC), the Pinhook and Tracy soils were collected from Pinney-Purdue Agricultural Center (PPAC), and the Cincinnati and Cobbsfork soils were collected from Southeast-Purdue Agricultural Center (SEPAC). After collection, all soils were screened under moist conditions to pass through a 1-cm sieve and stored at 4 °C. Selected properties of these soils are presented in Table 2.1.

2.3.1.1 Leaching incubation

Leaching incubation was performed according to Stanford and Smith (1972) with modifications. Subsamples of the eight soils were sieved to pass a 2-mm
screen. One hundred grams of moist soil were transferred to a leaching tube with a layer of glass wool placed in the bottom to prevent clogging of the porous bottom. A layer of glass wool was also placed over the soil to avoid dispersion during the process of leaching. Deionized water was then added to each tube to bring the soil water potential to 10 KPa. The tubes were weighed every four days to determine moisture loss and brought back to the proper moisture content with deionized water. The tubes were kept covered with perforated parafilm to reduce moisture loss and placed in an incubation chamber maintained at 25 °C for 16 weeks. Tubes were ranged in a randomized complete block design with three replications. Weekly leaching of mineral N was conducted using 100 mL 5 mM CaCl₂ solution in 30 to 50 mL increments. The leachate was collected and analyzed colorimetrically for mineral N (NH₄⁺-N and NO₃⁻-N) using an autoanalyzer (AQ2, Seal Analytical, Inc., UK).

2.3.1.2 Static Cup Incubation

Static cup incubation was conducted based on a modified approach of Schomberg et al. (2009). After sieving to pass a 2 mm screen, 25 g of moist soils were placed into plastic cups. Deionized water was added to bring them to 10 KPa water potential. Cups were loosely covered with lids to reduce moisture loss and placed in an incubation chamber with a constant temperature of 25 °C for 16 weeks. A randomized complete block design was used with soil type as the main factor and incubation time as a blocking factor. Each sample had three replications. These cups were weighed every four days to determine moisture loss and brought back to their proper moisture content with deionized water. At the end of each week, soils were sampled destructively by weighing 5 g soil out of each cup and equilibrating with 50 mL 2 M KCl for 1 hour. Soil extracts were analyzed for mineral N (NH₄⁺-N and NO₃⁻-N) as described above.
2.3.1.3 Greenhouse Experiment

One kilogram of each soil was mixed with a minus-N nutrient mixture (Allen et al., 1976) and placed in 2 L perforated pots. These pots were arranged on a greenhouse bench as a complete random block design with three replications. Soils were moistened to approximately 33 KPa. Fifteen winter wheat seeds were sown into each pot and thinned to 12 plants per pot after emergence. The greenhouse temperature was set to 27±5 °C and the photoperiod extended to 16 h with high pressure Na lamps.

Plants were watered with deionized water. Leachate was collected and returned to the pots to eliminate nutrient loss. Plants were harvested 2.5 cm above the soil surface every 28 d and stubble was left in the pots to regrow. After three harvests, soils were sieved again and all roots were recovered. A soil subsample was taken to determine the moisture content. We then mixed the remaining soil with the minus-N nutrient mixture and put the soil back into the pot for three more harvest cycles. This process was repeated until the plants stopped growing or died.

All of the plant tissues were dried at 60 °C, weighed, ground until they passed a 1mm sieve, and analyzed for total N using a dry combustion method with a CN analyzer (Flash 2000, CE Elantech, Inc., Lakewood, New Jersey). Mineral N content in soils before and after cropping were also measured as described above. Total nonexchangeable NH₄⁺-N content in soils before and after cropping were also measured using 7-d sodium tetraphenylboron extraction (Cox et al., 1996).

2.3.2 Estimation of Mineralizable Nitrogen in Indiana Soils at Different Depths

Soil samples were taken from seven sites (Agricultural Center for Research and Education (ACRE), Davis-Purdue Agricultural Center (DPAC), Northeast-Purdue Agricultural Center (NEPAC), Pinney-Purdue Agricultural Center (PPAC), Southeast-Purdue Agricultural Center (SEPAC), Southwest-Purdue Agricultural
Center (SWPAC), and Throckmorton-Purdue Agricultural Center (TPAC) in Indiana. The predominant soil series for ACRE are Chalmers and Raub (Chalmers-Raub), while Blount and Pewamo (Blount-Pewamo) for DPAC, Rawson and Haskins (Rawson-Haskins) for NEPAC, Sebewa for PPAC, Cobbsfork for SEPAC, Ade and Lyles (Ade-Lyles) for SWPAC, and Toronto for TPAC (Table 2.2). In each field composite soil samples were collected from depths of 0 to 15, 15 to 30, 30 to 45, and 45 to 60 cm. Samples were air-dried and sieved through a 2 mm screen after collecting them from the field. Soil water retention was determined for each sample using a pressure plate (Klute, 1986). Soil organic matter content was determined by the loss-on-ignition method (Ball, 1964). Soil pH was measured with a glass electrode from a 1:2 soil/water suspension. Soil texture was measured using the dispersion and sedimentation procedure described by Jackson (1958). Selected soil properties are presented in Table 2.3.

2.3.2.1 Static Cup Incubation

Five gram portions of sieved soil were placed into a plastic centrifuge tube for each sample. Cups were loosely covered by lids to reduce moisture loss and placed in a chamber with a constant temperature of 25 °C. A split-plot design was used with soil type as a whole-plot factor and soil depth as a sub-plot factor and each sample had three replications. Deionized water was added to bring soil moisture content to 10 KPa water potential. The cups were weighed every seven days to determine moisture loss and brought back to the proper moisture content with deionized water. Soil in cups was destructively extracted after 2, 4, 8, 12, and 16 weeks of incubation by using 50 mL 1 M KCl to rinse soil out of the cup into a 125 mL flask. After a one hour shaking (170 rpm), suspensions were filtered through a Whatman No. 1 filter paper and filtrates were collected for analysis of mineral N (NO$_3^-$-N and NH$_4^+$-N). The mineral N concentration in all the samples were analyzed colorimetrically using a continuous flow analyzer (Skalar Analytical B.V., The Netherlands).
2.3.2.2 Nitrogen Mineralization Indices

2.3.2.2.1 Illinois Soil Nitrogen Test (ISNT)

The ISNT was conducted according to Khan et al. (2001). One gram of soil was placed in a Mason jar along with 10 mL of 2 M NaOH. Samples were heated to 50 °C for 5 hours. The volatilized NH$_3$ gas was captured in the indicator solution H$_3$BO$_3$ and the amount of captured NH$_4^+$-N was quantified using acidimetric titration techniques.

2.3.2.2.2 Hot KCl Extractable NH$_4^+$ (Hot KCl-N)

Three grams of soil were placed in a 100 mL digestion tube and 20 mL of 2 M KCl were added to each tube. Each sample had three replicates. Tubes were placed on a block digester maintained at 100 °C for 4 hours. After removal from the block digester, the soil-solution mixture was filtered through a Whatman No. 1 filter paper and the filtrates were collected for further analysis of the NH$_4^+$-N. The NH$_4^+$-N concentration in all the samples were analyzed colorimetrically using a continuous flow analyzer (Skalar Analytical B.V., The Netherlands).

2.3.2.2.3 Short-term Anaerobic Incubation

To create an anaerobic condition, 5 g of soil sample were placed in the bottom of a screw cap test tube (17 ml) and 12.5 mL of water were added to fill the headspace inside the test tube. Samples were arranged in a chamber as a two-factor factorial design with three replicates. After incubation at 40 °C for 7 days, samples were then transferred into a 50 mL centrifuge tube. The remaining soil in the test tube was rinsed with 12.5 mL of 4 M KCl to ensure all the sample was transferred into the centrifuge tube. After 30 min shaking (180 epm), samples were filtered through a Whatman No. 1 filter paper and filtrates were collected and stored at 4 °C for further analysis of the NH$_4^+$-N. The NH$_4^+$-N concentration in all the samples were analyzed colorimetrically using a continuous flow analyzer (Skalar Analytical B.V., The Netherlands). The amount of mineralized N (anaerobic-N) during 7-d anaerobic incubation was calculated
by subtracting the initial \(\text{NH}_4^+\)-N concentration from the final \(\text{NH}_4^+\)-N concentration.

2.3.2.2.4 Three Day Flush of CO₂ (Fl_CO₂)

Forty grams of soil were placed in a 50 mL glass beaker. Deionized water was added to bring the soil moisture tension to 10 KPa. The glass beaker with soil samples was put in a Mason jar along with a vial of 10 mL deionized water and a vial of 10 mL 1 M NaOH. Lids were tightly fastened. Experimental design was a two-factor factorial design with three replicates. After 3 days incubation at 25 °C, the vials with 1 M NaOH were taken out of the jars. Barium chloride was added to the vials to precipitate carbonate. The quantity of CO₂ produced was determined by back-titrating excess NaOH with 1 M HCl. Controls (jars without soil) were set to measure background CO₂ concentration.

2.3.3 Field Experiment

Field experiments were conducted at the seven Purdue University Agricultural Centers from which soil samples were taken. Corn was grown after soybean in the same field in 2006, 2008 and 2010 at all locations. No-till practices were used at SEPAC and NEPAC, while conventional tillage practices were used elsewhere.

Starter fertilizer (urea ammonium nitrate, UAN) was applied 5 cm beside and below the seed at planting at a rate of 0 to 32 kg N ha⁻¹ (except one location, at SWPAC starter fertilizer was broadcast prior to planting in a form of diammonium phosphate at a rate of 20 kg N ha⁻¹). Nitrogen fertilizer was applied at 6 different rates from 0 to 224 kg ha⁻¹ in 45 kg ha⁻¹ increments. Fertilizer N was sidedressed with UAN when corn was at approximately V6 growth stage.

Field estimates of soil N supplying capacity were predicted from grain yield at a fertilizer N rate of 0 using a harvest index of 75% after subtracting the
amount of the starter fertilizer applied assuming the starter fertilizer use efficiency was 100%.

2.3.4 Data Analysis

All statistical analyses were performed with version 9.2 of SAS (SAS Institute Inc., 2008). Analysis of variance was conducted using the GLM procedure. Soil type was used as a class variable. The MEANS procedure with the LSD option was used for means separation. Relationships among the N mineralization data obtained through various methods were determined with the CORR procedure.

Linear regression was conducted to fit the cumulative net N mineralization data obtained from the laboratory incubation to a zero-order model with the REG procedure, and non-linear regression was performed to fit the N mineralization data to a first-order exponential model with the NLIN procedure. The zero-order kinetic model is of the form (Simard and N'dayegamiye, 1993):

\[ N_m = b_0 + kt \]

whereas the exponential equation is denoted by (Stanford and Smith, 1972)

\[ N_m = N_0 (1 - \exp(-kt)) \]

where \( N_m \) is cumulative net N mineralization in time \( t \), \( b_0 \) is the y-intercept, \( N_0 \) is the potentially mineralizable N, and \( k \) is rate constant of N mineralization. All results were adjusted to an oven-dry weight basis.
2.4 Results and Discussion

2.4.1 Comparison among Different Biological Methods for Measuring Mineralized Nitrogen

Results from both biological incubation methods showed more than 96% of the mineralized N was in the NO$_3^{-}$-N form after 16 weeks (Table 2.4), because NH$_4^{+}$-N was rapidly converted to NO$_3^{-}$-N by nitrifying bacteria under favorable conditions.

The amount of mineralized N varied among the different soils for both methods (Table 2.4). In the leaching incubation method, cumulative NH$_4^{+}$-N recovered was 0.3 to 0.7 mg N kg$^{-1}$ soil, and no significant differences in cumulative NH$_4^{+}$-N recovery were observed among soils (P>0.05). For total mineralized N, soils separated into 3 distinct groups, with the Blount, Pewamo, Tracy and Cincinnatti soils having the greatest mineralized N (42-45 mg N kg$^{-1}$ soil), the Chalmers, Pinhook and Cobbsfork having the next most mineralized N (33-35 mg N kg$^{-1}$ soil) and the Raub soil having the least mineralized N (29 mg N kg$^{-1}$ soil). With the static cup incubation method, soil mineralized N separated into more distinct groups. The cumulative NH$_4^{+}$-N recovered was 0.2 to 2.2 mg N kg$^{-1}$ soil. No significant difference in cumulative NH$_4^{+}$-N content was observed except between Raub and Cobbsfork soils. The Blount soil produced the greatest amount of total mineral N with a value of 73 mg N kg$^{-1}$ soil. Nitrogen mineralized in the Pewamo soil was not significantly different from that of the Blount soil. No significant difference in total mineralized N was observed among Cobbsfork, Tracy and Pinhook soils, however the total N mineralized in these soils were significantly less than the total N mineralized in Pewamo and greater than that in Raub, Cincinnati, and Chalmers. The Chalmers soil produced the least mineralized N with 47 mg N kg$^{-1}$ soil. Although the total mineralized N in Cincinnati soil (50 mg N kg$^{-1}$ soil) was greater than in Chalmers, the difference was not significant (P>0.05).
Nitrogen mineralization data obtained from the leaching incubation method showed that mineralized N steadily increased with time and had not slowed appreciably at 16 weeks (Figure 2.1). Therefore, the first-order kinetic model failed to fit the N mineralization data for 6 of the 8 soils studied. The smaller root mean square errors presented in Table 2.5 indicate that, compared with the first-order exponential model, a zero-order linear model was better fitted to the N mineralization data obtained for the leaching incubation method. In these zero-order models, the intercept \( b_0 \) ranged from -4.75 to 5.74 mg N kg\(^{-1}\) soil, and the rate constant \( k \) ranged from 1.86 to 2.95 mg kg\(^{-1}\) week\(^{-1}\). Tabatabai and Al-Khafaji (1980), reported the zero-order kinetic model was more appropriate to fit the N mineralization data for 12 surface soils from Iowa. In their study, \( b_0 \) of the fitted zero-order models were in a range of -6.6 to 17.7 mg N kg\(^{-1}\) soil, and the values of \( k \) were 1.7 to 4.2 mg kg\(^{-1}\) week\(^{-1}\). Simard and N'dayegamiye (1993) also found that mineralized N in seven Quebec meadow soils showed a linear increase with time through the whole incubation period using the leaching incubation method (388 days), and their estimated parameters for \( b_0 \) and \( k \) in the zero-order models ranged from -14.2 to 17.5 mg N kg\(^{-1}\) soil and 2.69 to 10.27 mg kg\(^{-1}\) week\(^{-1}\), respectively. The greater \( k \) values from the Quebec study are likely a result of the samples being collected from fields under pasture crops.

With the static cup incubation method, in all eight soils, N mineralization over the course of incubation was characterized by a linear increase in inorganic N for the first 8 to 12 weeks of incubation and followed by reduction in mineralization rate (Figure 2.2). The first order exponential model was a better fit to the N mineralization data obtained through the static cups incubation method as justified by smaller root mean square errors (Table 2.5). The N mineralization potential \( (N_0) \) and mineralization rate constant \( (k) \) were calculated for all eight soils. The range of values observed for \( N_0 \) was from 50 mg N kg\(^{-1}\) soil for Chalmers soil to 128 mg N kg\(^{-1}\) soil for Blount soil, and the average value for \( N_0 \) was 85 mg N kg\(^{-1}\) soil for eight soils. The rate constant \( k \) ranged from 0.0535 to 0.1687 week\(^{-1}\) with an average value of 0.0915 week\(^{-1}\). Schomberg et al. (2009)
estimated the N mineralization potentials for 44 soils collected from nine sites in the southern US with the static incubation method, and the values for $N_0$ reported in his study ranged from 35 to 488 mg N kg$^{-1}$ soil, while $k$ values ranged from 0.018 to 0.174 week$^{-1}$. Wang et al. (2003) also used the static cup incubation method for prediction of mineralizable N in 18 soils from Victoria, New South Wales, and Queensland in Australia and reported $N_0$ values ranged from 57 to 731 mg N kg$^{-1}$ soil, and $k$ values were in a range of 0.024 to 0.15 week$^{-1}$. Compared to the estimated values of N mineralization parameters from studies by Wang et al. (2003) and Schomberg et al. (2009), our $N_0$ values were generally at the lower end of the range while our $k$ values were generally at the higher end of the range.

Lower amounts of mineralized soil N were observed with the leaching incubation method compared to the static cup incubation method (Table 2.4). One possible explanation may be that substantial amounts of labile soluble organic N were removed by leaching in the leaching incubation (Smith et al., 1980; Parker and Sommers, 1983; Beauchamp et al., 1986; Wang et al., 2003). Wang et al. (2003) found that although the leached organic N accounted for only 0.7 to 2.4% of the total organic N of the soils, 22 to 90% of the leached organic N was mineralized after two weeks incubation because the soluble organic N had significantly greater mineralizability than the soil-bound organic N. Therefore, some researchers suggest the use of total leached N (soluble organic + inorganic N) rather than inorganic N alone for calculating $N_0$ and $k$ (Smith et al., 1980; Beauchamp et al., 1986). However, other researchers have reported that using total leached N to calculate $N_0$ and $k$ may overestimate the soil N mineralization potential (Parker and Sommers, 1983; Wang et al., 2003). Motavalli et al. (1995) suggested that the lower amount of mineralized N measured with the leaching incubation method, compared to the static cup incubation, was a result of the leaching solution failing to remove all of the NO$_3^-$-N from the soil. Results in their study showed that extraction efficiency for mineralized N using 0.01 M CaCl$_2$ or minus-N nutrient solution (containing 0.004 M CaCl$_2$) was lower (3 to 8 mg kg$^{-1}$
soil less for one extraction) compared with 2 M KCl, especially in smectitic soils or soils with a higher proportion of macroaggregates. In addition, for the leaching incubation method, within the 16 week incubation period, the mineralized N linearly increased with time and did not level off, which indicated that soil did not reach its mineralization potential within the 16 week incubation period; whereas for the static cup incubation method, after 16 weeks incubation, mineralized soil N was likely closer to the maximum potential value. Therefore, if the incubation period was extended, the cumulative mineralized N measured from these two incubation methods might not significantly differ. Motavalli et al. (1995) showed that the cumulative amount of N mineralized after a one year long incubation did not differ between leaching and non-leaching incubation methods.

The correlation between the amounts of mineralized N measured by these two incubation methods was poor (p=0.4; r=0.3). As discussed previously, for the leaching incubation method, 6 out of 8 soils did not reach their mineralization potential within the 16 weeks incubation period, and this may explain the poor relationship between mineralized N values measured for the two incubation methods. However, we were able to estimate the N₀ and k values for the Raub and Cincinnati soils through both methods. Results showed that k values estimated from leaching incubation were lower compared with that estimated from the static cup incubation for both soils, indicating a slower mineralization rate as determined using the leaching incubation method. The N₀ values estimated from both methods were similar for the Raub soil, but for the Cincinnati soil, the leaching incubation method was approximately 12 mg N kg⁻¹ soil greater than for the static cup incubation method. The greater mineralizable N value estimated from the leaching incubation method for the Cincinnati soil might be attributed to leaching effects, which would increase soil pH if the initial soil pH was very low (Wang et al., 2003).

The results for observed net N mineralized (N₀ᵇ) by 8 different soils measured by exhaustive cropping under greenhouse conditions showed that the
soils separated into three groups. These data are presented in Table 2.6. The higher N_{ob} group included the Cobbsfork and Blount soils with cumulative net mineralized N values of 62 and 61 mg N kg^{-1} soil, respectively. The lower N_{ob} group included the Raub, Pinhook, and Chalmers soils with the amount of cumulative net mineralized N ranging from 45 to 47 mg N kg^{-1} soil. The N_{ob} values for Pewamo, Tracy, and Cincinnati soils (50 to 58 mg N kg^{-1} soil) was not significantly different from either group. No significant difference in total nonexchangeable NH_{4}^{+}-N content was observed for soil samples taken before planting and after harvesting. By comparing mineralized N estimated from the two laboratory incubation methods to mineralized soil N supply under greenhouse conditions, the static cup incubation method was found to better predict N mineralization from exhaustive cropping under greenhouse conditions (Figure 2.3), which was expected because mineralized soil N measured using the static cup incubation method was closer to the potential soil N mineralization value through 16 weeks incubation.

In general, the static cup incubation method has more advantages for estimating soil mineralizable N compared to the leaching incubation method as it is an easier test to perform and soils approach soil N mineralization potential more quickly.

2.4.2 Estimation of Mineralizable Nitrogen in Indiana Soils at Different Depths

2.4.2.1 Nitrogen Mineralization Potential Estimated by Static Cup Incubation

Similar to the previous experiment, recovered NH_{4}^{+}-N in soil samples was low throughout the entire incubation period in all samples. The inorganic N was mainly in the form of NO_{3}^{-}-N, especially in the top soil layers due to nitrification.

An initial flush of mineralized N was observed in the surface soils during the two weeks of incubation (Figure 2.4) and was likely due to the rewetting of pretreated soil samples that increases the initial rate of N mineralization (Cabrera and Kissel, 1988; Wang et al., 2003). Some researchers developed a two-pool
model that separates the mineralizable N into two pools, a large one that mineralizes slowly and a small one that mineralizes rapidly (Molina et al., 1980; Beauchamp et al., 1986; Cabrera and Kissel, 1988). However, this initial pool of rapidly mineralizable N is generally small and usually does not significantly affect the final results, so researchers tend to ignore it to simplify the model (Cabrera and Kissel, 1988; Schomberg et al., 2009). A one-pool model was used to fit the N mineralization data in our study to calculate N₀ and k. Following the initial flush, the N mineralization pattern of the seven soils was characterized by a steady increase in inorganic N which began to level off after 8 or 12 weeks of incubation. Cumulative mineralized N actually decreased after 12 weeks incubation in the surface layer of the Toronto soil (Figure 2.4). Similar observations were made by Schomberg et al. (2009) for 6 of 44 soil samples collected from nine sites in the southern US, which they suggested might have resulted from denitrification and/or immobilization of NO₃⁻-N in the soil.

For the surface soil (0-15 cm), Cobbsfork had the greatest N mineralization potential with a N₀ value of 68 mg N kg⁻¹ soil, while Toronto soil had the least N₀ value of 50 mg N kg⁻¹ soil (Table 2.7). Soils separated into three groups, with greater N₀ values (68 to 63 mg N kg⁻¹ soil) for Cobbsfork, Sebewa, and Ade-Lyles surface soils, and significantly lower N₀ values for Toronto surface soil. However, the difference between N₀ values (61 to 57 mg N kg⁻¹ soil) for Blount-Pewamo, Rawson-Haskins and Chalmers-Raub surface soils and N₀ values for soils in the other two groups was not significant (P>0.05). Soil mineralization potential values were also reported by Campbell et al. (1984; 66 to 185 mg N kg⁻¹), and Walley et al. (2002; 9 to 401 mg N kg⁻¹) for soils of Saskatchewan (heavily manured soils excluded), and Carter and MacLeod (1987; 44 to 247 mg N kg⁻¹) for soils from Prince Edward Island. Schomberg et al. (2009) reported that the N mineralization potentials for 44 soil samples collected from 9 sites in the southern USA were in a range of 35 to 488 mg N kg⁻¹ soil. Wang et al. (2003) reported the N mineralization potentials for 18 soils collected from Victoria, New South Wales, and Queensland in Australia were from 57 to 731 mg N kg⁻¹ soil.
Although the measured values for $N_0$ in our study were in the range of $N_0$ values reported in these previous studies, they were in the lower end of the range. The lower values of $N_0$ in this study compared with previous studies could be due to the selection of nonmanured, cultivated soils, lower incubation temperature ($25^\circ C$ vs. $35^\circ C$), or shorter incubation time (16 weeks vs. 41 weeks).

The mineralization rate constant, $k$, also varied among soils. Blount-Pewamo soil had the greatest mineralization rate (0.2153 week$^{-1}$). The $k$ values for Rawson-Haskins and Toronto soils (0.1710 and 0.1702 week$^{-1}$) were less than the $k$ value for Blount-Pewamo soil, but the difference was not statistically significant ($P>0.05$). The $k$ values for Chalmers-Raub, Sebewa, Cobbsfork and Ade-Lyles soils (0.1589 to 0.1190 week$^{-1}$) were significantly less than the $k$ value for Blount-Pewamo soil ($P<0.05$) (Table 2.7). The large variation in $k$ values of different soils was in agreement with other studies (Paustian and Bonde, 1987; Dendooven et al., 1995; Curtin and Wen, 1999; Wang et al., 2003; and Schomberg et al., 2009). The averaged $k$ value among all the samples in our study was about 0.1594 week$^{-1}$, which was greater than the $k$ values reported by Wang et al. (2003, 0.069 week$^{-1}$) and Schomberg et al. (2009; 0.070 week$^{-1}$), and this difference might be related to the lower estimated $N_0$ values and shorter incubation times.

The relationship between estimated $N_0$ and $k$ values has been discussed by Wang et al. (2003). They found a significant inverse relationship between $N_0$ and $k$ values. They also indicated that lower values of $N_0$ were observed if the inorganic N production rate leveled off with time. This study was in agreement with our observed results of relatively low $N_0$ values and relatively high $k$ values compared to the studies mentioned previously. To provide a reliable benchmark for comparing N mineralization capacities among different soils, Wang et al. (2003) also suggested using a fixed value for mineralization rate constant $k$ (0.054 week$^{-1}$) to determine the mineralization potential $N_0$. However, due to the large difference between the $k$ values we calculated and Wang et al. (2003)
suggested, it might be not reasonable to use the fixed k value for the estimation of the N mineralization potential in our study.

Soil mineralizable N measured in the laboratory generally decreased with depth (Table 2.7). This observation could be attributed to a decrease in the availability of organic N (amino acid N) to microorganisms with soil depth, as reported by Hadas et al. (1986). The magnitude of the decrease generally declined with soil depth. Averaged across seven soils, the estimated N₀ values significantly decreased from 0-15 cm depth to 15-30 cm depth and from 15-30 cm depth to 30-45 cm depth, but the difference between the two bottom depths was small and not significant (P>0.05). The k value also varied with soil depth. However, the variations in k with depth were not consistent because of the confounding relationship between N₀ and k. So as suggested by Mary and Remy (1979), we also calculated the product of N₀ × k to explore the effect of depth on N mineralization. The results showed that N₀ × k decreased with soil depth, with values 11 for 0-15 cm, 7 for 15-30 cm, 4 for 30-45 cm, and 3 for 45-60 cm. Similarly, the values of N₀ × k among the top three layers were significantly different while the values of N₀ × k for the bottom two layers were statistically not different (P>0.05). Similar results were found in previous studies. Cabrera and Kissel (1988) fit the cumulative net N mineralization data to a two-pool model, and both N₁ and k₁ values estimated for the large mineralizable N pool tended to decrease with depth. Soudi et al. (1990) indicated the effect of depth on N mineralization rate could be expressed by a model: mineralization rate = 0.54 exp(-0.040D) where D is the depth in cm, while our data showed the relationship between averaged N₀ value and depth was expressed as N₀ = 72 exp(-0.020D) where D is the depth in cm.

The percentage of the total mineralizable N in the surface layer (0-15 cm) varied from 33 to 48% (Table 2.7). Averaged among all seven soils, the surface soil (0-15 cm) contributed approximately 42% of total mineralizable soil N, thus about 58% of potentially mineralizable soil N can be supplied from the subsoil.
This result was consistent with the study by Cassmann and Munns (1980), who showed that 58% of the total mineralized N was contributed from 18 to 108 cm depth of soils. Cabrera and Kissel (1988) also indicated that 35 to 48% of the total mineralizable soil N came from the surface layer (0-15 cm) in three Kansas soils to a depth of 120 cm. Persson and Wiren (1995) found that the contribution of the soil surface layer was as high as 74% of the total net soil N mineralization, but their study was conducted on nonfertilized forest soils with organic horizons.

2.4.2.2 Chemical Indices of Nitrogen Availability

For the surface soil, the ISNT ranged from 123 to 218 kg N ha\(^{-1}\) (average of 170 kg N ha\(^{-1}\)) with the greatest ISNT value for Sebewa soil and the least ISNT value for Ade-Lyles soil (Table 2.8). The anaerobic-N value for Cobbsfork soil was the greatest (61 mg N kg\(^{-1}\) soil). The anaerobic-N values for Toronto, Chalmers-Raub, and Sebewa were not statistically different, but all significantly less than that for Cobbsfork soil (P<0.05). Rawson-Haskins had the lowest anaerobic-N value (38 mg N kg\(^{-1}\) soil) and it was significantly lower than all the other soils except Blount-Pewamo (P<0.05). The hot KCl-N for seven surface soils varied from 7 to 11 mg N kg\(^{-1}\) soil. Although the range was small, the hot KCl-N values were separated into more distinct groups as shown in Table 2.8. The Fl\(_{CO2}\) values for seven surface soils ranged from 44 to 107 mg C kg\(^{-1}\) soil (average of 67 mg C kg\(^{-1}\) soil). However, no significant difference in Fl\(_{CO2}\) values was observed (P>0.05), since the standard deviations of three replicates of samples were really large. The N availability indices ISNT, anaerobic-N, and hot KCl-N all generally decreased with depth. However, depth did not have significant effect on Fl\(_{CO2}\) values.

Of the four N availability indices, ISNT, anaerobic-N, and hot KCl-N showed promise in predicting potentially mineralizable N with R\(^2\) > 0.60 (Figure 2.5). Among these three indices, ISNT and hot KCl-N can be determined in a relatively short period of time (4 or 5 hours) compared to the 7 days needed for the anaerobic N test. None of the indices were correlated to the mineralization rate
constant $k$ (Figure 2.6). Our results are consistent with the results from Schomberg et al. (2009) who found that total C, total N, N mineralized by hot KCl, anaerobic N, and N mineralized in 24 d were reasonable predictors of $N_0$, but none were predictors for $k$. The ISNT was developed as a quick and simple alternative to determine amino sugar N as hydrolysable amino sugar N has been shown to predict mineralizable soil N (Bushong et al., 2008).

However, arguments still exist. Curtin and Wen (1999) found that hot KCl-N was poorly correlated to laboratory mineralizable N ($R^2=0.13$) but mineralization rate $k$ can be predicted with a function of hot KCl-N/$N_0$ ($R^2=0.64$). Sharifi et al. (2007a) also reported a poor relationship between hot KCl-N and $N_0$ with a $R^2$ value of 0.26.

### 2.4.3 Nitrogen Mineralization Potential from Field Estimates

Field studies suggest that soil N supply varies from soil to soil and year to year (Table 2.9). In 2006, field soil N supply ranged from to 23 kg N ha$^{-1}$ (Cobbsfork soil) to 96 kg N ha$^{-1}$ (Toronto soil). In 2008, soil N supply was greatest in Sebewa soil with a value of approximately 64 kg N ha$^{-1}$ and least in Cobbsfork soil with a value of 24 kg N ha$^{-1}$. In 2010, field soil N supply was in a range of 25 kg N ha$^{-1}$ (Ade-Lyles soil) to 53 kg N ha$^{-1}$ (Rawson-Haskins soil). Averaged across three years, Soil N supply in Toronto soil (76 kg N ha$^{-1}$) was greater than soil N supply in all other soils except Chalmers-Raub and Sebewa. The difference in soil N supply in Chalmers-Raub, Sebewa, Rawson-Haskins, and Blount-Pewamo soils (61-36 kg N ha$^{-1}$) was not statistically different ($P>0.05$). The average soil N supply was least in Ade-Lyles and Cobbsfork soils with values of 30 kg N ha$^{-1}$ and 27 kg N ha$^{-1}$, respectively. The total amount of laboratory mineralizable N of all four layers ranged from 115 to 183 mg kg$^{-1}$ N in the seven soils (Table 2.7). Compared with soil N supply estimated from the field, clearly, laboratory mineralization potentials overestimate potentially plant-available soil N supply. This result was in agreement with Cabrera and Kissel (1988), who showed that mineralizable N estimated from laboratory incubations
overpredicted the amount of the mineralized N in the field by 67 to 343%. Delphin (2000) also compared net N mineralization estimated by calculating the N balance sheet in the field to the amount of mineralized N measured from laboratory incubation as well as from an outdoor incubation. Results of this study showed that, although the amount of mineralized N measured from laboratory incubation was in good agreement with the values measured through outdoor incubation, both methods over predicted net N mineralization in the field.

Relationships between laboratory soil N mineralization estimates and soil N supply in the field were poor (Figure 2.7). The poor relationship between laboratory mineralizable N and field soil N supply can be attributed to the consistent moisture and temperature conditions as well as minimal N loss under laboratory conditions when compared to the inherent variability of these factors in the field. Within the range of 5 to 35 °C, an Arrhenius function describes the relationship between temperature and N mineralization, as a 10-degree increase in temperature increases the mineralization rate two times (Cassman and Munns, 1980; Kladivko and Keeney, 1987). In our research, 25 °C was used as the laboratory soil incubation temperature, and the temperature variation was within 1°C. In the field, fluctuation in temperature from 0 to 35 °C are common and can lead to large variations in soil N mineralization. The optimum soil moisture tension for N mineralization is between 10 and 30 KPa (Stanford and Epstein, 1974; Myers et al., 1982). At greater moisture contents, soil N mineralization is limited due to oxygen deficiency (Foth and Ellis, 1997). Mineralized N also decreases linearly with moisture tension from 30 to 150 KPa (Stanford and Epstein, 1974). In our study, soil samples were incubated with moisture tension of 10 KPa. Under such conditions, soil N mineralization was maximized. In the field, excessively wet or dry conditions significantly decrease soil N mineralization rates. In addition, field soil N availability is also affected by other N transformation and loss mechanisms such as denitrification and leaching, which are driven by temperature and moisture as well. For example, heavy precipitation results in large mineral N loss through leaching. In Indiana the average annual
nitrate-N loss from drainage tiles was as high as 70 kg ha\(^{-1}\) (Kladivko, 2001) which is approximately one third of the typical N fertilizer application rate. When a heavy rainfall happens after several weeks of high temperature (>25 °C), large amounts of mineralized soil N and fertilizer N can be lost from the crop root zone via leaching and or denitrification, resulting in a significant loss of soil N supply in the field. Some studies suggest that combining soil N mineralization potential and pre-plant soil mineral N content increased correlation coefficients between laboratory mineralization estimates and field soil N supply indices (Stanford et al., 1977; Kuo et al., 1996; Carpenter-Boggs et al., 2000). However, pre-plant soil mineral N content is highly sensitive to the sampling date (McTaggart and Smith 1993; Zebarth and Paul 1997). Therefore, it might not be reliable to use the pre-plant soil mineral N content as a predictive test for fertilizer recommendations, especially in humid environments where the NO\(_3^-\)-N concentrations in the soil change rapidly over time (Sharifi et al., 2007b).

Figure 2.7 also clearly showed for most soils the variability in soil N supply measured in the field was greater than the variability in soil N supply measured in the laboratory. The variability of field soil N supply among years indicates that weather is the most important factor that impacts soil N mineralization in the field. In a study established in potato trials located in New Brunswick and Prince Edward Island, Canada and Maine, USA. Sharifi et al. (2007b) compared \(N_0\), \(k\), and \(N_0 \times k\) predicted from laboratory incubation methods with the field soil N supply estimated from plant N uptake without fertilizer application (PNU\(_{0N}\)), PNU\(_{0N}\) plus mineral N content in the top 30cm depth of soil at harvest (PNU\(_{0N}+SMNh\)), or relative yield. Similar to our results, they found little correlation between \(N_0\) and any field-based indices of soil N supply. Although the \(k\) and \(N_0 \times k\) were significantly correlated with PNU\(_{0N}\) and PNU\(_{0N}+SMNh\) \((r=0.54–0.67)\) for the 2004-2005 data, the relationship between these mineralization parameters and the indices of field soil N supply was weak \((r=0.13-0.39)\) due to the large yearly variation in field soil N supply.
2.5 Conclusions

When comparing two long-term aerobic incubation methods, the static cup incubation method required less incubation time for the prediction of soil N mineralization potential, and the measured mineralized N with this method was better correlated to plant N uptake measured under greenhouse conditions. Several short-term chemical indices showed promises in predicting soil N mineralization potentials as well, most notably ISNT, hot KCl and anaerobic N. However, there were difficulties in extrapolating results from laboratory incubations to field scale where weather factors and other N transformation and loss processes play a more important role in controlling soil N supply. Therefore, to better predict field soil N supply, a weather-driven model should be developed to incorporate soil surface and subsurface N mineralization potentials with crop growth and N uptake parameters and N transformation and loss mechanisms.
2.6 Reference


Table 2.1 Selected properties of eight Indiana soils collected at 0-30 cm depth of the Ap horizon.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Taxonomic class</th>
<th>pH†</th>
<th>OM‡</th>
<th>Texture§</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers</td>
<td>Fine-silty, mixed, superactive, mesic Typic Endoaquoll</td>
<td>6.7</td>
<td>42 g kg⁻¹</td>
<td>410, 470, 120</td>
</tr>
<tr>
<td>Raub</td>
<td>Fine-silty, mixed, superactive, mesic Aquic Argiudoll</td>
<td>6.4</td>
<td>27 g kg⁻¹</td>
<td>270, 490, 240</td>
</tr>
<tr>
<td>Blount</td>
<td>Fine, illitic, mesic Aeric Epiaqualf</td>
<td>6.4</td>
<td>26 g kg⁻¹</td>
<td>330, 490, 150</td>
</tr>
<tr>
<td>Pewamo</td>
<td>Fine, mixed, active, mesic Typic Argiaquoll</td>
<td>6.3</td>
<td>39 g kg⁻¹</td>
<td>490, 410, 100</td>
</tr>
<tr>
<td>Pinhook</td>
<td>Coarse-loamy, mixed, superactive, mesic Mollic Endoaqualfs</td>
<td>6.5</td>
<td>24 g kg⁻¹</td>
<td>190, 310, 500</td>
</tr>
<tr>
<td>Tracy</td>
<td>Coarse-loamy, mixed, active, mesic Ultic Hapludalfs</td>
<td>6.3</td>
<td>16 g kg⁻¹</td>
<td>170, 270, 560</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>Fine-silty, mixed, active, mesic Oxyaquic Fragiudalf</td>
<td>5.3</td>
<td>17 g kg⁻¹</td>
<td>250, 430, 320</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>Fine-silty, mixed, active, mesic Fragic Glossaqualf</td>
<td>5.9</td>
<td>19 g kg⁻¹</td>
<td>210, 570, 220</td>
</tr>
</tbody>
</table>

† Measured with a glass electrode from a 1:1 soil/water suspension
‡ OM = Soil organic matter determined by loss-on-ignition method (Ball, 1964).
§ Determined using the dispersion and sedimentation procedure described by Jackson, 1958
Table 2.2 Predominant soil series and taxonomic class of soils for seven sites

<table>
<thead>
<tr>
<th>Location</th>
<th>Soil Series and Taxonomic class</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACRE</td>
<td>Chalmers: Fine-silty, mixed, superactive, mesic Typic Endoaquoll</td>
</tr>
<tr>
<td></td>
<td>Raub: Fine-silty, mixed, superactive, mesic Aquic Argiudoll</td>
</tr>
<tr>
<td>DPAC</td>
<td>Blount: Fine, illitic, mesic Aeric Epiaqualf</td>
</tr>
<tr>
<td></td>
<td>Pewamo: Fine, mixed, active, mesic Typic Argiaquoll</td>
</tr>
<tr>
<td>NEPAC</td>
<td>Rawson: Fine-loamy, mixed, active, mesic Oxyaquic Hapludalf</td>
</tr>
<tr>
<td></td>
<td>Haskins: Fine-loamy, mixed, active, mesic Aeric Epiaqualf</td>
</tr>
<tr>
<td>PPAC</td>
<td>Sebewa: Fine-loamy over sandy or sandy-skeletal, mixed, superactive, mesic Typic Argiaquoll</td>
</tr>
<tr>
<td>SEPAC</td>
<td>Cobbsfork: Fine-silty, mixed, active, mesic Fragic Glossaqualf</td>
</tr>
<tr>
<td>SWPAC</td>
<td>Ade: Coarse-loamy, mixed, superactive, mesic Lamellic Argiudoll</td>
</tr>
<tr>
<td></td>
<td>Lyles: Coarse-loamy, mixed, superactive, mesic Typic Endoaquoll</td>
</tr>
<tr>
<td>TPAC</td>
<td>Toronto: Fine-silty, mixed, superactive, mesic udollic Epiaqualf</td>
</tr>
</tbody>
</table>
Table 2.3 Properties of soils collected at four depths (0 to 15, 15 to 30, 30 to 45, and 45 to 60 cm) from seven sites in Indiana.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth</th>
<th>pH†</th>
<th>OM‡</th>
<th>Texture§</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td></td>
<td>g kg⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalmers-Raub</td>
<td>0-15</td>
<td>6.5</td>
<td>36</td>
<td>350</td>
<td>470</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>7.6</td>
<td>37</td>
<td>380</td>
<td>440</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>6.2</td>
<td>25</td>
<td>400</td>
<td>450</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>6.4</td>
<td>25</td>
<td>360</td>
<td>450</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Blount-Pewamo</td>
<td>0-15</td>
<td>7.1</td>
<td>36</td>
<td>410</td>
<td>430</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>7.8</td>
<td>31</td>
<td>450</td>
<td>400</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>7.9</td>
<td>30</td>
<td>440</td>
<td>400</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>8.0</td>
<td>25</td>
<td>500</td>
<td>330</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Rawson-Haskins</td>
<td>0-15</td>
<td>6.4</td>
<td>25</td>
<td>270</td>
<td>320</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>6.8</td>
<td>21</td>
<td>340</td>
<td>290</td>
<td>380</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>7.3</td>
<td>17</td>
<td>380</td>
<td>230</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>7.9</td>
<td>19</td>
<td>420</td>
<td>220</td>
<td>370</td>
<td></td>
</tr>
<tr>
<td>Sebewa</td>
<td>0-15</td>
<td>6.6</td>
<td>32</td>
<td>270</td>
<td>280</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>6.4</td>
<td>31</td>
<td>320</td>
<td>280</td>
<td>410</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>6.6</td>
<td>23</td>
<td>320</td>
<td>300</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>6.9</td>
<td>17</td>
<td>300</td>
<td>280</td>
<td>430</td>
<td></td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>0-15</td>
<td>6.2</td>
<td>23</td>
<td>240</td>
<td>630</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>5.8</td>
<td>20</td>
<td>320</td>
<td>580</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>5.7</td>
<td>19</td>
<td>320</td>
<td>580</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>5.5</td>
<td>19</td>
<td>310</td>
<td>540</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>Ade-Lyles</td>
<td>0-15</td>
<td>6.4</td>
<td>14</td>
<td>110</td>
<td>200</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>6.9</td>
<td>10</td>
<td>100</td>
<td>210</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>7.0</td>
<td>04</td>
<td>100</td>
<td>190</td>
<td>710</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>7.0</td>
<td>06</td>
<td>120</td>
<td>190</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Toronto</td>
<td>0-15</td>
<td>6.2</td>
<td>24</td>
<td>230</td>
<td>580</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>5.7</td>
<td>22</td>
<td>310</td>
<td>540</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>5.6</td>
<td>19</td>
<td>320</td>
<td>430</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>5.6</td>
<td>22</td>
<td>370</td>
<td>410</td>
<td>230</td>
<td></td>
</tr>
</tbody>
</table>

† Measured with a glass electrode from a 1:1 soil/water suspension.
‡ OM = Soil organic matter determined by loss-on-ignition method (Ball, 1964).
§ Determined using the dispersion and sedimentation procedure described by Jackson (1958).
Table 2.4 The cumulative amount of nitrogen (NO$_3^-$-N and NH$_4^+$-N) mineralized by eight soils during the 16 week incubation for the leaching incubation and static cup incubation methods.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Leaching incubation</th>
<th>Static cup incubation</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH$_4^+$-N</td>
<td>NO$_3^-$-N</td>
<td>Total</td>
<td>NH$_4^+$-N</td>
<td>NO$_3^-$-N</td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mg kg$^{-1}$ soil</td>
<td>mg kg$^{-1}$ soil</td>
<td></td>
<td>mg kg$^{-1}$ soil</td>
<td>mg kg$^{-1}$ soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalmers</td>
<td>0.4a†</td>
<td>34c</td>
<td>35b</td>
<td>0.7ab</td>
<td>46e</td>
<td>47e</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raub</td>
<td>0.7a</td>
<td>28d</td>
<td>29c</td>
<td>2.2a</td>
<td>53d</td>
<td>55d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blount</td>
<td>0.3a</td>
<td>44a</td>
<td>45a</td>
<td>1.0ab</td>
<td>72a</td>
<td>73a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pewamo</td>
<td>0.6a</td>
<td>41b</td>
<td>42a</td>
<td>0.6ab</td>
<td>67ab</td>
<td>68ab</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pinhook</td>
<td>0.3a</td>
<td>34c</td>
<td>35b</td>
<td>0.6ab</td>
<td>61c</td>
<td>62c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tracy</td>
<td>0.5a</td>
<td>42ab</td>
<td>42a</td>
<td>1.4ab</td>
<td>63bc</td>
<td>65bc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cincinnati</td>
<td>0.5a</td>
<td>43ab</td>
<td>44a</td>
<td>0.7ab</td>
<td>49de</td>
<td>50de</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>0.6a</td>
<td>33c</td>
<td>33b</td>
<td>0.2b</td>
<td>66bc</td>
<td>66bc</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Numbers followed by the same letter are not significantly different (p>0.05).

Table 2.5 Root mean square errors for zero-order and first-order models fitted to N mineralization data obtained for the leaching incubation and static cup incubation methods.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Leaching incubation</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zero-order</td>
<td>First-order</td>
<td>Zero-order</td>
<td>First-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalmers</td>
<td>0.7</td>
<td>1.6</td>
<td>3.3</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raub</td>
<td>0.9</td>
<td>0.7</td>
<td>2.8</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blount</td>
<td>1.7</td>
<td>5.3</td>
<td>3.6</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pewamo</td>
<td>0.4</td>
<td>1.6</td>
<td>3.1</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pinhook</td>
<td>1.2</td>
<td>2.9</td>
<td>3.8</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tracy</td>
<td>1.6</td>
<td>4.1</td>
<td>2.3</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cincinnati</td>
<td>0.7</td>
<td>0.4</td>
<td>1.9</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>0.5</td>
<td>1.9</td>
<td>4.4</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.6 Plant uptake nitrogen, mineral nitrogen in soils before and after cropping, and observed net nitrogen mineralized under greenhouse conditions (unit: mg kg\(^{-1}\)).

<table>
<thead>
<tr>
<th>Soil</th>
<th>(N_{\text{uptake}})</th>
<th>(N_r)</th>
<th>(N_{\text{min}})</th>
<th>(N_{\text{ob}})</th>
<th>(\text{Nonex}<em>N</em>{b})</th>
<th>(\text{Nonex}<em>N</em>{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers</td>
<td>54d§§</td>
<td>4</td>
<td>11</td>
<td>47b</td>
<td>177A</td>
<td>186A</td>
</tr>
<tr>
<td>Raub</td>
<td>58cd</td>
<td>2</td>
<td>15</td>
<td>45b</td>
<td>146A</td>
<td>140A</td>
</tr>
<tr>
<td>Blount</td>
<td>69ab</td>
<td>4</td>
<td>12</td>
<td>61a</td>
<td>226A</td>
<td>209A</td>
</tr>
<tr>
<td>Pewamo</td>
<td>69ab</td>
<td>5</td>
<td>16</td>
<td>58ab</td>
<td>282A</td>
<td>278A</td>
</tr>
<tr>
<td>Pinhook</td>
<td>62bc</td>
<td>2</td>
<td>17</td>
<td>46b</td>
<td>126A</td>
<td>126A</td>
</tr>
<tr>
<td>Tracy</td>
<td>73a</td>
<td>2</td>
<td>18</td>
<td>57ab</td>
<td>126A</td>
<td>127A</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>59cd</td>
<td>2</td>
<td>11</td>
<td>50ab</td>
<td>125A</td>
<td>126A</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>74a</td>
<td>4</td>
<td>16</td>
<td>62a</td>
<td>110A</td>
<td>128A</td>
</tr>
</tbody>
</table>

\(^1\)\(N_{\text{uptake}}\) is the total N taken up by plants at harvest.
\(^2\)\(N_r\) is measured soil mineral N in the soils after two cropping sequence.
\(^3\)\(N_{\text{min}}\) is the measured soil mineral N in the soils before planting.
\(^4\)\(N_{\text{ob}}\), the observed net N mineralized in soils, was determined using the following equation: \(N_{\text{ob}}=(\text{Mineral } N_r + \text{ Plant } N_{\text{uptake}}) - \text{ Mineral } N_{\text{min}} + N_{\text{loss}}\). \(N_{\text{loss}}\) is considered as the amount of N leached from the soil, which is negligible, because we returned the leachate back to the pots.
\(^\dagger\dagger\)\(\text{Nonex}_N_{b}\) is the measured total nonexchangeable \(\text{NH}_4^+\)-N content in the soils before planting.
\(^\dagger\dagger\)\(\text{Nonex}_N_{a}\) is the measured total nonexchangeable \(\text{NH}_4^+\)-N content in the soils after two cropping sequence.
\(^\S\S\)Capital letters indicate the difference in total nonexchangeable \(\text{NH}_4^+\)-N content before planting and after harvesting. Lower case letters indicate difference in N amount as affected by soil type. Numbers followed by the same letter are not significantly different (\(p>0.05\)).
Table 2.7 Predicted $N_0$ and $K$ values of four depth for seven soils $^\dagger$. The relative contribution from the top soil (0-15cm) was indicated.

<table>
<thead>
<tr>
<th>Soil</th>
<th>0-15cm</th>
<th>15-30cm</th>
<th>30-45cm</th>
<th>45-60cm</th>
<th>Sum of $N_0$</th>
<th>% in top layer§</th>
<th>Ave. k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_0$</td>
<td>$k$</td>
<td>$N_0$</td>
<td>$k$</td>
<td>$N_0$</td>
<td>$k$</td>
<td></td>
</tr>
<tr>
<td>Chalmers-Raub</td>
<td>57ab‡</td>
<td>0.2083</td>
<td>12</td>
<td>47</td>
<td>0.1240</td>
<td>6</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1077</td>
<td>3</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0361</td>
<td>1</td>
<td>175ab</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33</td>
<td>0.1190b</td>
</tr>
<tr>
<td>Blount-Pewamo</td>
<td>61ab</td>
<td>0.2469</td>
<td>15</td>
<td>47</td>
<td>0.2394</td>
<td>11</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1876</td>
<td>8</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1873</td>
<td>7</td>
<td>183a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33</td>
<td>0.2153a</td>
</tr>
<tr>
<td>Rawson-Haskins</td>
<td>60ab</td>
<td>0.1651</td>
<td>10</td>
<td>29</td>
<td>0.2009</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2240</td>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0941</td>
<td>3</td>
<td>151bc</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>41</td>
<td>0.1710ab</td>
</tr>
<tr>
<td>Sebewa</td>
<td>67a</td>
<td>0.1118</td>
<td>7</td>
<td>31</td>
<td>0.1897</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1379</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1016</td>
<td>2</td>
<td>141c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48</td>
<td>0.1352b</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>68a</td>
<td>0.2286</td>
<td>16</td>
<td>30</td>
<td>0.2077</td>
<td>6</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0724</td>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0762</td>
<td>1</td>
<td>142c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48</td>
<td>0.1462b</td>
</tr>
<tr>
<td>Ade-Lyles</td>
<td>63a</td>
<td>0.1520</td>
<td>10</td>
<td>30</td>
<td>0.2542</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0830</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1851</td>
<td>3</td>
<td>131cd</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48</td>
<td>0.1589b</td>
</tr>
<tr>
<td>Toronto</td>
<td>50b</td>
<td>0.1408</td>
<td>7</td>
<td>30</td>
<td>0.2165</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1709</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1525</td>
<td>2</td>
<td>115d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44</td>
<td>0.1702ab</td>
</tr>
<tr>
<td>Average</td>
<td>61A</td>
<td>0.1791α</td>
<td>35B</td>
<td>0.1991α</td>
<td>7b</td>
<td>27C</td>
<td>0.1405β</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4c</td>
<td>25C</td>
<td>0.1190β</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3c</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42</td>
<td>0.1594</td>
</tr>
</tbody>
</table>

$^\dagger$ $N_0$ is the potentially mineralizable N with a unit of mg kg$^{-1}$, and $k$ is the first order rate constant (week$^{-1}$).

$^\ddagger$ Numbers followed by the same notation symbol are not significantly different (p>0.05).

§ Top layer: 0-15 cm depth; % in top layer=$N_0$(0-15 cm)/sum of $N_0$ × 100%
Table 2.8 Results from various indices for predicting potentially mineralizable nitrogen in seven soils of four depths.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth (cm)</th>
<th>ISNT (kg ha(^{-1}))</th>
<th>Anaerobic-N (mg N kg(^{-1}))</th>
<th>Hot KCl-N (mg N kg(^{-1}))</th>
<th>FL_CO(_2) (mg C kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers-Raub</td>
<td>0-15</td>
<td>217</td>
<td>47BC(^a)</td>
<td>10.5AB(^a)</td>
<td>66Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>203</td>
<td>23b</td>
<td>7.8b</td>
<td>49ab</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>109</td>
<td>8c</td>
<td>5.6c</td>
<td>60a</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>65</td>
<td>4d</td>
<td>4.5d</td>
<td>25b</td>
</tr>
<tr>
<td>Blount-Pewamo</td>
<td>0-15</td>
<td>166</td>
<td>43CD(^a)</td>
<td>7.7DE(^a)</td>
<td>107Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>128</td>
<td>14b</td>
<td>3.8b</td>
<td>60a</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>98</td>
<td>11b</td>
<td>3.7b</td>
<td>55a</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>78</td>
<td>9b</td>
<td>3.0c</td>
<td>66a</td>
</tr>
<tr>
<td>Rawson-Haskins</td>
<td>0-15</td>
<td>150</td>
<td>38Da</td>
<td>8.5CD(^a)</td>
<td>52Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>76</td>
<td>16b</td>
<td>4.9b</td>
<td>49a</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>55</td>
<td>10c</td>
<td>3.4c</td>
<td>33a</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>26</td>
<td>6d</td>
<td>2.5d</td>
<td>33a</td>
</tr>
<tr>
<td>Sebewa</td>
<td>0-15</td>
<td>218</td>
<td>47BC(^a)</td>
<td>11.1Aa</td>
<td>96Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>138</td>
<td>18b</td>
<td>7.1b</td>
<td>74ab</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>55</td>
<td>6c</td>
<td>4.6c</td>
<td>47ab</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>31</td>
<td>4d</td>
<td>3.7d</td>
<td>25b</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>0-15</td>
<td>165</td>
<td>61Aa</td>
<td>10.0B(^a)</td>
<td>58Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>86</td>
<td>17b</td>
<td>5.8b</td>
<td>33a</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>77</td>
<td>5c</td>
<td>3.0c</td>
<td>35a</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>38</td>
<td>3c</td>
<td>3.5c</td>
<td>44a</td>
</tr>
<tr>
<td>Ade-Lyles</td>
<td>0-15</td>
<td>123</td>
<td>46Ca</td>
<td>7.2E(^a)</td>
<td>77Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>78</td>
<td>25b</td>
<td>4.8b</td>
<td>63a</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>28</td>
<td>5c</td>
<td>2.7c</td>
<td>68a</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>20</td>
<td>3c</td>
<td>2.8c</td>
<td>55a</td>
</tr>
<tr>
<td>Toronto</td>
<td>0-15</td>
<td>147</td>
<td>51Ba</td>
<td>9.2Ca</td>
<td>44Aa</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>126</td>
<td>27b</td>
<td>7.0b</td>
<td>71a</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>88</td>
<td>12c</td>
<td>5.0c</td>
<td>41a</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>60</td>
<td>7d</td>
<td>4.6c</td>
<td>41a</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Capital letters indicate difference in values as affected by soil type, while lower case letters indicate difference in values as affected by depth. Numbers followed by the same notation symbol are not significantly different (p>0.05).
Table 2.9 Estimated field soil nitrogen supply (in kg ha\(^{-1}\)) for seven soils in 2006, 2008, and 2010.

<table>
<thead>
<tr>
<th>Soil</th>
<th>2006</th>
<th>2008</th>
<th>2010</th>
<th>Mean</th>
<th>STD†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers-Raub</td>
<td>86</td>
<td>50</td>
<td>46</td>
<td>61ab</td>
<td>22</td>
</tr>
<tr>
<td>Blount-Pewamo</td>
<td>28</td>
<td>45</td>
<td>N/A‡</td>
<td>36bc</td>
<td>12</td>
</tr>
<tr>
<td>Rawson-Haskins</td>
<td>40</td>
<td>34</td>
<td>53</td>
<td>42bc</td>
<td>10</td>
</tr>
<tr>
<td>Sebewa</td>
<td>70</td>
<td>64</td>
<td>44</td>
<td>59ab</td>
<td>13</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>23</td>
<td>24</td>
<td>35</td>
<td>27c</td>
<td>7</td>
</tr>
<tr>
<td>Ade-Lyles</td>
<td>35</td>
<td>31</td>
<td>25</td>
<td>30c</td>
<td>5</td>
</tr>
<tr>
<td>Toronto</td>
<td>96</td>
<td>57</td>
<td>N/A</td>
<td>76a</td>
<td>28</td>
</tr>
</tbody>
</table>

† STD=standard deviation.
‡ Data is not available.
Figure 2.1 Time course of N mineralization of eight Indiana soils through 16 weeks for the leaching incubation method. The cumulative N values obtained as a sum of NO$_3^-$-N and NH$_4^+$-N were mean of three replicates. Error bars indicate the standard deviation of the mean of three replicates.
Figure 2.2 Time course of N mineralization of eight Indiana soils through 16 weeks for the static cup incubation method. The cumulative N values obtained as a sum of NO₃⁻-N and NH₄⁺-N were mean of three replicates. Error bars indicate the standard deviation of the mean of three replicates.
Figure 2.3 The linear relationship between mineralized nitrogen estimated from two laboratory incubation methods to greenhouse measurements of plant nitrogen uptake.
Figure 2.4 Time course of N mineralization of four depths of soils from seven locations. The cumulative N values obtained as a sum of NO$_3^-$-N and NH$_4^+$-N were mean of three replicates. Error bars indicate the standard deviation of the mean of three replicates. Letters indicate difference in cumulative mineralized N as affected by different incubation times. Points labeled by the same letter are not significantly different (p>0.05).
Figure 2.5 Correlation between nitrogen indices and mineralizable N estimated from long-term static cups incubation.
Figure 2.6 Correlation between nitrogen indices and mineralization rate constant $k$ estimated from long-term static cups incubation.
Figure 2.7 The relationship between laboratory soil N mineralization estimates and predicted soil N supply in the field. The horizontal error bars are the standard deviation of the mean of triplicate measurements of lab mineralization and the vertical error bars are the standard deviation of the mean of three years of observations in the field.
3.1 Abstract

The year to year variability in optimum fertilizer nitrogen (N) rate for corn grown on the same field clearly indicates that weather drives soil and fertilizer N transformations and crop N availability. To better predict in-season optimum N rates in the field, we developed an N model that couples soil surface and subsurface N mineralization algorithms with soil and fertilizer N transformation and loss processes. Processes considered in the model include soil N mineralization, nitrification, denitrification, and nitrate leaching, and the model is driven by air temperature, soil moisture and pH, and a crop growth model. Readily available data including soil texture, pH and organic matter, daily air temperature and precipitation/irrigation, fertilizer N source, placement and timing, and crop planting/emergence date are used as model inputs. Through simple regression analyses from existing N response studies (6 site years) we found that yearly plant N uptake simulated from this model was highly correlated to yield data under field conditions ($R^2 > 0.95$ for any site year, $R^2 > 0.80$ for combined site years). Thus, we believe that this model has the potential to improve the prediction of optimum in-season fertilizer N rates compared to traditional fertilizer N recommendation strategies.
3.2 Introduction

Nitrogen (N) fertilizer applications are critical for optimum corn yield and profitability. Too little N results in suboptimal yield while excessive N fertilizer applications result in significant N losses and negative environmental consequences. Therefore, optimizing fertilizer N application rates has always been one of the most researched topics in agricultural history. In Indiana, a yield based fertilizer recommendation strategy had been used for decades using the following relationship: N application rate (lb/A) = -27 + (1.36*yield potential)-N credit, where the N credit is given based upon the previous crop (Vitosh et al., 1995). A 27 lb/acre credit was given for soil N supply. However, numerous studies have shown that fertilizer N requirement is poorly related to yield (Vanotti and Bundy, 1994; Bundy and Andraski, 1995; Kachonoski et al., 1996; Mamo et al., 2003; Lory and Scharf, 2003; Scharf et al., 2006; Bundy, 2006). As a result, a new fertilizer N recommendation strategy was developed, and has been adopted in several states in the Midwest (Sawyer et al., 2006). Without considering the yield goal of the crops, this new approach generates fertilizer N recommendations based on the results of numerous N response trials conducted on different soils. This approach requires yield data from many N response trials and many site-years. While this approach is conclusive based on past field results it may not be useful to predict the optimum N rate for the upcoming growing season due to large year to year variations in optimum N rate for corn grown on the same field due to variable weather factors (temperature, precipitation, etc.). Weather variables play an important role in regulating N dynamics in the soil-water-plant system. In addition, this approach only generates N recommendations for optimum management scenarios where most of the N is applied as a sidedress application when corn is near the V6 growth stage. Thus, the development of a N simulation model which is driven by weather factors and integrates various transformation and loss processes of soil and fertilizer N could lead to a better understanding of N dynamics in agricultural ecosystems and improve the prediction of optimum in-season fertilizer N rates.
compared to the fertilizer N recommendation strategies currently used in the cornbelt of the Midwestern US.

Numerous models that simulate soil N transformations and transport have been developed. However, most of them models one single N transformation or transport process. For example, N mineralization under field conditions has been simulated through a modeling approach that considers field fluctuations in temperature and moisture (Cameron and Kowalenko, 1976; Myers et al., 1982; Antonopulos, 1999). Parton et al. (1996) developed a model to simulate the production of nitrogen (N₂) and nitrous oxide (N₂O) from nitrification and denitrification. They found that N₂O fluxes from both mechanisms are a function of soil temperature, soil pH, and soil water-filled pore space. Good agreement between simulated and measured data was observed in this study with r² greater than 0.62. Johnsson et al. (1991), developed a denitrification model that included a field potential denitrification rate and functions for the effect of soil aeration status, soil temperature, and soil NO₃⁻-N content. The denitrification rates simulated by this model were within 20% of the mean of the measured values for two seasons. For ammonia (NH₃) volatilization, some models simulate NH₃ volatilization by dealing with the transformations between different species of ammoniacal N in the soil, as well as the movement of ammoniacal N and water within the soil profile and between the soil surface and the atmosphere (Rachhpal-Singh and Nye, 1986; Kirk and Nye, 1991; Genermont and Cellier, 1997). Sogaard et al. (2002) described the volatilization process by a Michaelis-Menten-type equation, with the volatilization loss rate as a function of various factors that significantly affect volatilization, including soil water content, air temperature, wind speed, fertilizer type, application method, and rate, etc.

In addition, there are some models that integrate various N transformation and transport processes to simulate different mineral-N dynamics. For example, a model named SOILN was developed for the simulation of soil N dynamics, in which processes such as plant uptake, mineralization/immobilization, nitrification,
denitrification, and leaching are considered (Bergstrom et al., 1991). However, the results showed the simulated N-uptake tended to overestimate the field measurements for some site-years. Another model, the Danish simulation model DAISY, simulated soil N dynamics and biomass production by considering a number of modules including a hydrological model for soil water dynamics, a soil temperature model, a soil N model, and a crop model for crop N uptake (Hansen et al., 1991). The model failed to accurately estimate the amount of N in the soil-plant system in heavily fertilized treatments due to the underestimation of the denitrification rate. Another N simulation model, DRAINMOD–N II, was developed to model different N transformation and transport processes including atmospheric deposition, application of mineral N fertilizers including urea and anhydrous ammonia, soil amendment with organic N sources including plant residues and animal waste, plant uptake, organic C decomposition and associated N mineralization/immobilization, nitrification, denitrification, NH$_3$ volatilization, and N losses via subsurface drainage and surface runoff (Youssef et al., 2005). Although some studies have tested this model and found this model showed promise in predicting N losses from drained agricultural lands (Youssef et al., 2006; Slazar et al., 2009; Thorp et al., 2009), no research was reported on the use of this model to predict soil available N or to relate the model-simulated results to crop production.

Our model, driven by environmental factors including temperature, soil moisture and pH, etc., couples soil surface and subsurface N mineralization algorithms with soil and fertilizer N transformation and loss processes and crop N uptake to improve the prediction of optimum in-season fertilizer N rates. Currently, processes considered in the model include soil N mineralization, nitrification, denitrification, and nitrate leaching.
3.3 Model Description

3.3.1 Estimation of Soil Moisture and Temperature

In the first step, soil temperature and moisture are simulated, and then the outputs are utilized as driving factors for the N model. Soil temperature is estimated from the 7 day running average air temperature. However, time lags and damping effects with depth are not yet accounted for, which may result in the overestimation of the topsoil temperature and underestimation of the subsoil temperature. Soil moisture content is estimated from irrigation scheduling software (www.purdue.edu/agsoftware/irrigation), which is based on FAO irrigation and drainage paper No. 56: Crop Evapotranspiration (Allen et al. 1998). Precipitation, evapotranspiration, crop water uptake, and contribution from prior irrigation events are included in the soil moisture model. The evapotranspiration rate is determined based on the Penman-Monteith equation.

3.3.2 Soil Nitrogen Transformation and Loss Processes

Nitrogen transformation and loss processes considered in the model include soil N mineralization, nitrification, denitrification, nitrate leaching and so on (Figure 3.1). This daily time step model currently calculates crop N uptake and N transformations and losses as follows:

1. Determine amount of organic N that will mineralize;
2. Determine applied fertilizer ammonium \((\text{NH}_4^+)\) and nitrate \((\text{NO}_3^-)\) N;
3. Determine amount of \(\text{NH}_4^+\)-N converted to \(\text{NO}_3^-\)-N;
4. Determine amount of N taken up by crop;
5. Determine amount of \(\text{NO}_3^-\)-N lost due to denitrification;
6. Determine amount of \(\text{NO}_3^-\)-N lost through leaching.
3.3.2.1 Mineralization

Nitrogen released through mineralization is able to provide 20 to 80% of the N required by crops (Broadbent, 1984). Accurate prediction of soil N mineralization is crucial for developing accurate N fertilizer recommendations.

To simulate N mineralization, first-order kinetic models are often used to quantify the process (Sanford and Smith, 1972; Cameron and Kowalenko, 1976), where the mineralization rate is proportional to the amount of potentially mineralizable soil N, and is defined by the equation:

\[ \frac{dN}{dt} = -kN_0 \]

where \(N_0\) is the amount of soil mineralizable N and \(k\) is the mineralization rate constant. This equation can also be expressed as:

\[ N_m = N_0 \left(1 - \exp(-kt)\right) \]

where \(N_m\) is cumulative net N mineralization at time \(t\), \(N_0\) is the potentially mineralizable soil N, and \(k\) is the first order rate constant. Potentially mineralizable soil N is the fraction of organic N in the soil which is readily mineralized. Ros et al. (2011) indicated that the size of soil organic matter pools and fractions is the primary factor that controls soil N mineralization potential. So in our model, the mineralization potential is a function of soil organic matter content.

To incorporate weather factors into the equation, the mineralization rate constant \(k\) is adjusted by soil temperature and moisture factors, and based on a model presented by Antonopoulos (1999) the equation is expressed as:

\[ k_1 = ke_t e_w \]
where $\epsilon_t$ is a temperature factor, and $\epsilon_w$ represents the effect of water content. Johnsson et al. (1987) suggested to use the $Q_{10}$ relationship to define the effect of temperature on soil mineralization as follows:

$$\epsilon_t = Q_{10}^{(T_1 - T_2)/10}$$

where $T_1$ is the soil temperature, $T_2$ is the incubation temperature at which $\epsilon_t$ equals to 1, and $Q_{10}$ represents the changes in rate when temperature is changed 10 degrees. $Q_{10}$ of N mineralization is approximately 2 (Stanford et al., 1973; Kladivko, and Keeney, 1987) in the temperature range of 5 to 35 °C. The soil moisture factor $\epsilon_w$ is a function of the soil water filled pore space (WFPS) (Antonopoulos, 1999).

$$\epsilon_w = \frac{1}{\theta} - \frac{1}{\theta_w} \quad \text{when } \theta < \theta_{lo};$$
$$\epsilon_w = 1 \quad \text{when } \theta_{lo} \leq \theta \leq \theta_{ho};$$
$$\epsilon_w = 0.6 + (1-0.6) \frac{1}{\theta_s} - \frac{1}{\theta} \quad \text{when } \theta > \theta_{ho};$$

where $\theta_s$, $\theta_{ho}$, $\theta_{lo}$, and $\theta_w$ are WFPS at saturation, WFPS=0.6, WFPS=0.5, and WFPS at wilting point, respectively.

### 3.3.2.2 Nitrification

Nitrification is a process through which $NH_4^+$ is oxidized by chemoautotrophic bacteria, and converted to $NO_2^-$, and eventually to $NO_3^-$ (Foth and Ellis, 1996). Two steps are involved in this process. The first step is to oxidize the $NH_4^+$ to $NO_2^-$ as follow:

$$2\text{NH}_4^+ + 3\text{O}_2 = 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+$$

Bacteria of the genus *Nitrosomonas* and several other bacteria are responsible for this conversion. This step produces protons and is considered a natural soil acidification process. The second step is conversion from $NO_2^-$ to $NO_3^-$ by *Nitrobacter* as follows:
\[2\text{NO}_2^- + \text{O}_2 = 2\text{NO}_3^-\]

Nitrification can be calculated by:

\[N_{\text{nitrification}} = k e_t e_m e_{\text{pH}} e_{\text{NH}_4}\]

in which \(k\) is the potential nitrification rate (\(\mu g\) N \(g^{-1}\) soil day\(^{-1}\)) and \(e_t, e_m, e_{\text{pH}},\) and \(e_{\text{NH}_4}\) are response functions accounting for the effects of soil temperature, soil water content, soil pH and initial \(\text{NH}_4^+\) content, respectively.

Generally, nitrification rate increases with temperature from 0 to 30 °C. The activities of nitrifying bacteria cease below 0 °C (Sabey et al., 1959; Malhi and McGill, 1981) and perform very slowly when the soil temperature is below 5 °C (Brady and Weil, 2008). The optimum temperature for nitrification is generally between 20 to 30 °C (Brady and Weil, 2008). The temperature effect can be expressed as following algorithm:

\[e_t = -0.06 + 0.13 e^{0.07 \cdot T}\] (Parton et al., 1996)

The optimum soil moisture content for nitrifying bacteria is about the same as the most favorable moisture for plant growth, which is about 60% WFPS (Brady and Weil, 2008). However, the optimum moisture for nitrification differs slightly with soil texture (Parton et al., 1996). Below the optimum soil moisture, nitrification rate declines as soil moisture decreases (Malhi and McGill, 1982; Gilmour, 1984; Parton et al., 1996). When soil is too wet, due to the shortage of \(\text{O}_2\) in the soil system, nitrification is not appreciable (Miller and Johnson, 1964; Malhi and McGill, 1982). Parton et al. (1996) used following algorithm to model the effect of moisture on nitrification:

\[e_m = \left(\frac{\theta - b}{a - b}\right)^d \left(\frac{b - a}{a - c}\right)^d\]

\(\Theta\) is the actual value of soil WFPS. For sandy soil, the estimated values of \(a, b, c,\) and \(d\) are 0.55, 1.70, -0.007, and 3.22, respectively, while for medium-textured
soils, the estimated values of $a$, $b$, $c$, and $d$ are 0.60, 1.27, 0.0012, and 2.84, respectively.

The effect of soil pH on nitrification rate is significant. Nitrification generally increased with soil pH over the range of 4.9 to 7.2 (Gilmour, 1984). Dancer et al. (1973) reported that nitrification rates were similar for pH from 5.3 to 6.6, but were substantially less at pH 4.7. Besides temperature, moisture, and soil pH, the abundance of $\text{NH}_4^+$ present in the soil also plays an important role in the activity of nitrifying microorganisms. Malhi and McGill (1982) indicated that an increase in nitrification rate was observed when $\text{NH}_4^+$-N concentration increased from 50 to 200 µg·g$^{-1}$ soil, but nitrification rate decreased when the $\text{NH}_4^+$-N content was up to 300 µg·g$^{-1}$ soil due to the combined effect of low pH and high salt content. The algorithms for pH and $\text{NH}_4^+$-N content effects are described as:

$$
\epsilon_{\text{pH}} = 0.56 + \frac{\arctan(pH+0.45*(-5+pH))}{pi} \text{(Parton et al., 1996)}
$$

$$
\epsilon_{\text{NH}_4} = 1 - e^{-0.105*\text{NH}_4} \text{(Parton et al., 1996)}
$$

3.3.2.3 Denitrification

Denitrification is the process of reducing $\text{NO}_3^-$ to gaseous forms such as nitric oxide (NO), nitrous oxide ($\text{N}_2\text{O}$), and nitrogen gas ($\text{N}_2$). This process occurs under an anaerobic environment, where bacteria use $\text{NO}_3^-$ as a terminal electron acceptor in respiration in the absence of $\text{O}_2$. Denitrification is favored in anaerobic, warm, near-neutral soils containing adequate carbon and substrate sources (Keeney, 1980).

Denitrification can be calculated from an equation presented by Johnsson et al. (1991):

$$
N_{\text{denitrification}} = ke_t e_m e_{\text{NO}_3}
$$
Where $k$ is a potential rate ($\mu g \, N \, g^{-1} \, soil \, day^{-1}$) and $e_t$, $e_m$, and $e_{NO3}$ are response functions based on the effects of soil temperature, soil water content and NO$_3$-N content, respectively.

The effect of temperature on denitrification rates follows the Arhenius equation:

$$e_t = Q_{10}^{(T_1 - T_2)/10}$$

where $T_1$ is the soil temperature, $T_2$ is the temperature at which $e_t$ equals 1, and $Q_{10}$ represents the changes in rate when temperature is changed 10 degrees. $Q_{10}$ is approximately 3 (Johnsson et al., 1991) when the temperature is above 5 °C.

The moisture effect on denitrification rates is highly dependent on a critical soil moisture threshold value. Above this value, denitrification rates increased sharply with increased soil moisture content. Below that, soil moisture content appeared not to be the predominant control factor (Pilot and Patrick, 1972; Klemedtsson et al., 1991). Such moisture effects can be described as:

$$e_m = \left(\frac{\theta - \theta_d}{\theta_s - \theta_d}\right)^2$$

where $\Theta_d$ is a threshold point of soil water content with a value of approximately 60% water-filled pore space (Johnsson et al., 1991). The soil water threshold point differs with soil texture (Barton et al., 1999). Generally, greater threshold soil moisture content is observed in coarse-textured soils than in fine-textured soils with reported values of 74% to 83% WFPS for sandy and sandy loam soils, 62% to 83% WFPS for loam soils, and 50% to 74% for clay loam soils. $e_m$ increases from the threshold point and reaches maximum at saturation ($\theta_s$).
Denitrification is favored when there are adequate substrate sources (Keeney, 1980). So the effect of $\text{NO}_3^-$ concentration in the soil is also considered in our model.

$$e_{\text{NO}_3} = \frac{C_{\text{NO}_3}}{C_{\text{NO}_3} + C_s}$$

In this equation, the half-saturation constant, $C_s$, is the concentration of $\text{NO}_3^-$ at which the reduction factor $e_{\text{NO}_3}$ is 50% of maximum. The estimated half-saturation constant is 2.45 $\mu$g N g$^{-1}$soil (Klemmedtsson et al., 1991).

### 3.3.2.4 Crop Nitrogen Uptake

Simulation of crop N uptake is based on the thermal unit concept that crop growth can be described as a temperature sum (growing degree days). Calculation of the growing degree days (GDD) using the modified formula suggested by the National Oceanic and Atmospheric Administration in 1971, and the temperature limit for corn growth is not lower than 10 °C or higher than 30 °C. Four or more crop specific N uptake rates are utilized according to crop development and the length of the growing season (Table 3.1). Both $\text{NO}_3^-$-N and $\text{NH}_4^+$-N are assumed equally available for crop uptake. When the amount of mineral N present in the soil is insufficient to satisfy the crop demands, the actual crop N uptake is the available mineral N content in the soil.

### 3.3.2.5 Nitrate Leaching

Nitrate leaching is calculated based on water flow and $\text{NO}_3^-$-N concentration in each soil layer. For a given layer with water outflow to the layer below, $\text{NO}_3^-$-N amount is reduced proportionately, while for each layer with water inflow from layers above, water's $\text{NO}_3^-$-N is added to its $\text{NO}_3^-$-N amount. New $\text{NO}_3^-$-N concentration is then recalculated for each soil layer.
3.4 Model Application

3.4.1 Field Site

The experimental field was located at Purdue University’s Agronomy Center for Research and Education (ACRE) in West Lafayette, Indiana. The climate in the region is temperate and humid with an average annual precipitation of about 889 mm and an average annual temperature of about 10.6 °C. The parent material in this area consists of loess deposits and underlying till. The soil taxonomic class is Typic Endoaquolls, characterized as a poorly drained soil with silty clay loam texture and high in organic matter content. The top surface soil (0-30 cm) has about 35% clay, 3.6% organic matter, and a pH of 6.5-7.6, while in the subsurface soil (30-60 cm) organic matter content decreased by approximately 1%. The cropping system was corn-soybean rotation. In each year, 28 kg ha\(^{-1}\) N was applied as a starter fertilizer at planting, with 0, 45, 90, 134, 179, or 224 kg ha\(^{-1}\) sidedressed in early June as urea ammonium nitrate (UAN). The yield data were obtained in this field experiment from 2006 to 2011 for all N treatments. These data were used to validate the N simulation model.

3.4.2 Input Data

The input data used in this model (Table 3.1) include soil texture with depth, and soil pH and organic matter (OM), and daily high and low air temperature, and precipitation/irrigation as well as fertilizer N source, placement and timing, and crop planting/emergence date, while humidity and wind speed are optional. Soil and weather data can be obtained based on location. Weather data can be imported from web services such as U.S. National Weather Service Forecast, and iMETOS ag Weather Station Data.

3.4.3 Simulation Results and Discussion

The \(\text{NH}_4^+\)-N and \(\text{NO}_3^-\)-N pools as well as cumulative mineralized N, cumulative crop N uptake, cumulative denitrified N, and cumulative leached N are simulated through the model. In Figure 3.2, an example of model output
showed simulated soil N accumulation and loss and crop N uptake resulted from an application of a total of 252 kg ha\(^{-1}\) fertilizer N (as UAN) in 2008 at ACRE. The peak of the NH\(_4^+\)-N happened early in May from the application of fertilizer N. After that, the NH\(_4^+\)-N content in the soil slowly decreased, and converted to NO\(_3^-\)-N through nitrification indicated by a gradual increase in NO\(_3^-\)-N concentration in soil. The simulated N mineralization rate did not elevate until late March because of the low temperature during winter time (<10 °C), and it reached the soil mineralization potential late in September with a value of 173 kg N ha\(^{-1}\). This field received totally 1090 mm of rain from October 2007 to October 2008. The model estimates that these rainfall events resulted in a loss of 39 kg ha\(^{-1}\) N through leaching and the high soil moisture content resulted from the rainfall events caused loss of 29 kg ha\(^{-1}\) N through denitrification. Excess NO\(_3^-\)-N was predicted at the end of the growing season which may be lost through leaching in the coming year. Together leaching loss, denitrification loss, as well as the excess NO\(_3^-\) in the soil, the total simulated N loss was as high as 112 kg ha\(^{-1}\) resulted from application of 252 kg ha\(^{-1}\) fertilizer N. The model predicted 313 kg ha\(^{-1}\) N was taken up by plants.

Table 3.2 shows a summary of model-simulated NO\(_3^-\)-N, NH\(_4^+\)-N, cumulative denitrified N, cumulative leached N, cumulative mineralized N, and cumulative crop N uptake at various fertilization rates from 2006 to 2011 at ACRE. In the table, it indicates that the NH\(_4^+\)-N estimated by the model generally decreases with the increasing fertilizer application rates, but the concentration of the NH\(_4^+\)-N left in the soil at the end of the growing season is very low. Excessive amounts of NO\(_3^-\)-N are only predicted when fertilizer rate is higher than 208 kg ha\(^{-1}\). In 2006, the model estimates the NO\(_3^-\)-N left in the soil at the end of the growing season is as high as 56 kg ha\(^{-1}\). In this case, high amounts of NO\(_3^-\)-N will be detected in the tile drainage if there are rainfall events during the winter or early spring. Otherwise, in arid areas, the excess NO\(_3^-\)-N left in the soil can also be available for the growth of crops in the coming growing season.
The model estimates the accumulative denitrified N generally increases with the increasing fertilizer application rates (Table 3.2). The N loss through denitrification and leaching are also highly dependent on rainfall in that year. For example, in both 2009 and 2011, 28 kg ha\(^{-1}\) N was applied at planting, with 179 kg ha\(^{-1}\) sidedressed in early June. In 2011 the field received over 76 mm of rain on June 20th and another 51 mm on July 1st. These rainfall events resulted in rapid losses of over 34 kg ha\(^{-1}\) N due to leaching based on the estimation of the model. The total simulated N loss through denitrification and leaching was 123 kg ha\(^{-1}\) in 2011. In 2009, the field received a 66 mm rain on June 1st, but this occurred prior to sidedressing. So the model estimates 75 kg ha\(^{-1}\) N lost through denitrification and leaching in 2009. Less N loss results in higher crop N uptake. The model’s estimate of crop N uptake is 304 kg ha\(^{-1}\) in 2009 and only 258 kg ha\(^{-1}\) in 2011, while the field-measured grain yield was 14 Mg ha\(^{-1}\) in 2009 and 12 Mg ha\(^{-1}\) in 2011.

The relationship between modeled corn N uptake and measured corn grain yield was strong (R\(^2\) > 0.8) across 6 years (Figure 3.4). For each individual site year, the R\(^2\) value was greater than 0.97 (Figure 3.3). Additionally, the relationships between the simulated corn N uptake and measured corn grain yield were nearly linear with the coefficient for the quadratic term in the equations lower than 0.0004.

3.5 Conclusion

In general, the strong correlation between the model-simulated N uptake and field-measured crop yield validated the performance of this N transformation and loss model. Thus, we believe this N model has the potential to improve the prediction of optimum in-season fertilizer N rates compared to traditional fertilizer N recommendation strategies. However, more work still has to be done to
improve and further validate this model under different soil, weather, and management conditions.

Further programming is underway to i) incorporate NH$_3$ volatilization and manure N mineralization into the model, ii) calculate net rainfall infiltration based on variations in topography and soils, iii) test the model across different soil and climatic conditions and iv) add more crops (corn and winter wheat are the only crops currently programmed).
3.6 Reference


dependence of nitrogen mineralization rate constant: A theoretical approach.
Soil Sci. 159: 294-300.

Boca Raton, FL.

ammonia volatilization from slurry applied to bare soil. Agric. For. Meteorol.

Gilmour, J.T. 1984. The effects of soil properties on nitrification and nitrification

nitrogen dynamics and biomass production in winter wheat using the Danish
simulation model DAISY. Fert. Res. 27: 245-259.

Simulation of field scale denitrification losses from soils under grass ley and

corn response to applied fertilizer: application in site-specific crop
International Conference on Precision Agriculture. Precision Agriculture,
425-432. Madison, WI, ASA, CSSA, and SSSA.

Madison, WI.


Table 3.1 Summary of model parameter inputs.

<table>
<thead>
<tr>
<th>Soil Parameter†</th>
<th>Depth in</th>
<th>Clay %</th>
<th>Silt %</th>
<th>H₂Owp ‡</th>
<th>AWC§</th>
<th>Bulk Density mg cm⁻³</th>
<th>OM %</th>
<th>Soil pH</th>
<th>Ksat um sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13</td>
<td>31</td>
<td>59</td>
<td>0.23</td>
<td>0.19</td>
<td>1.4</td>
<td>4.5</td>
<td>6.7</td>
<td>9.17</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>34</td>
<td>56</td>
<td>0.23</td>
<td>0.19</td>
<td>1.5</td>
<td>2</td>
<td>7.2</td>
<td>9.17</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>19</td>
<td>40</td>
<td>0.13</td>
<td>0.14</td>
<td>1.6</td>
<td>0.75</td>
<td>7.2</td>
<td>9.17</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>15</td>
<td>40</td>
<td>0.11</td>
<td>0.14</td>
<td>1.8</td>
<td>0.75</td>
<td>7.9</td>
<td>0.92</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crop and Management Parameter</th>
<th>Crop N Uptake Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop</td>
<td>Corn</td>
</tr>
<tr>
<td>Growing Season</td>
<td>120 days</td>
</tr>
<tr>
<td>Projected Yield</td>
<td>200 units/A</td>
</tr>
<tr>
<td>Rooting Depth</td>
<td>3 feet</td>
</tr>
<tr>
<td>Starting Residue</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitrogen Transformation Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>k Day⁻¹</td>
</tr>
<tr>
<td>Mineralization</td>
</tr>
<tr>
<td>Nitrification</td>
</tr>
<tr>
<td>Denitrification</td>
</tr>
</tbody>
</table>

† Source of soil parameter data is NRCS Soil Data Mart.
‡ Volumetric soil water content at wilting point.
§ Available water capacity.
¶ Crop N uptake rates are in kg ha⁻¹ of N per centigrade growing degree.

---

"cle considered in this model."
Table 3.2 Nitrogen model predictions at various fertilizer nitrogen rates from 2006 to 2011 at ACRE (Unit: kg ha\(^{-1}\)).

<table>
<thead>
<tr>
<th>Year</th>
<th>Ferti.N(^\dagger)</th>
<th>Min.N(^\dagger)</th>
<th>UptakeN(^\dagger)</th>
<th>Denitri.N(^\dagger)</th>
<th>LeachN(^\dagger)</th>
<th>Nitrate(^\dagger)</th>
<th>Ammonium(^\dagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>28</td>
<td>173</td>
<td>149</td>
<td>12</td>
<td>39</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2006</td>
<td>73</td>
<td>173</td>
<td>196</td>
<td>15</td>
<td>34</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2006</td>
<td>118</td>
<td>173</td>
<td>239</td>
<td>17</td>
<td>34</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2006</td>
<td>163</td>
<td>173</td>
<td>282</td>
<td>20</td>
<td>34</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2006</td>
<td>207</td>
<td>173</td>
<td>310</td>
<td>22</td>
<td>34</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>2006</td>
<td>252</td>
<td>173</td>
<td>310</td>
<td>25</td>
<td>34</td>
<td>56</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>28</td>
<td>173</td>
<td>158</td>
<td>13</td>
<td>29</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2007</td>
<td>73</td>
<td>173</td>
<td>205</td>
<td>16</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>118</td>
<td>173</td>
<td>247</td>
<td>19</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>163</td>
<td>173</td>
<td>291</td>
<td>20</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>207</td>
<td>173</td>
<td>310</td>
<td>21</td>
<td>25</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>2007</td>
<td>252</td>
<td>173</td>
<td>310</td>
<td>22</td>
<td>25</td>
<td>68</td>
<td>0</td>
</tr>
<tr>
<td>2008</td>
<td>28</td>
<td>173</td>
<td>148</td>
<td>8</td>
<td>44</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2008</td>
<td>73</td>
<td>173</td>
<td>195</td>
<td>11</td>
<td>40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2008</td>
<td>118</td>
<td>173</td>
<td>236</td>
<td>16</td>
<td>39</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2008</td>
<td>163</td>
<td>173</td>
<td>276</td>
<td>21</td>
<td>39</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2008</td>
<td>207</td>
<td>173</td>
<td>313</td>
<td>26</td>
<td>39</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>2008</td>
<td>252</td>
<td>173</td>
<td>313</td>
<td>29</td>
<td>39</td>
<td>44</td>
<td>0</td>
</tr>
<tr>
<td>2009</td>
<td>28</td>
<td>173</td>
<td>135</td>
<td>5</td>
<td>58</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>2009</td>
<td>73</td>
<td>173</td>
<td>182</td>
<td>9</td>
<td>53</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2009</td>
<td>118</td>
<td>173</td>
<td>222</td>
<td>14</td>
<td>53</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2009</td>
<td>163</td>
<td>173</td>
<td>263</td>
<td>18</td>
<td>53</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2009</td>
<td>207</td>
<td>173</td>
<td>304</td>
<td>22</td>
<td>53</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2009</td>
<td>252</td>
<td>173</td>
<td>304</td>
<td>27</td>
<td>53</td>
<td>41</td>
<td>2</td>
</tr>
<tr>
<td>2010</td>
<td>28</td>
<td>173</td>
<td>153</td>
<td>8</td>
<td>34</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2010</td>
<td>73</td>
<td>173</td>
<td>194</td>
<td>10</td>
<td>36</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2010</td>
<td>118</td>
<td>173</td>
<td>224</td>
<td>14</td>
<td>48</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2010</td>
<td>163</td>
<td>173</td>
<td>254</td>
<td>22</td>
<td>54</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2010</td>
<td>207</td>
<td>173</td>
<td>280</td>
<td>36</td>
<td>59</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2010</td>
<td>252</td>
<td>173</td>
<td>303</td>
<td>53</td>
<td>64</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>2011</td>
<td>28</td>
<td>173</td>
<td>141</td>
<td>13</td>
<td>46</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2011</td>
<td>73</td>
<td>173</td>
<td>175</td>
<td>17</td>
<td>54</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2011</td>
<td>118</td>
<td>173</td>
<td>206</td>
<td>25</td>
<td>61</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2011</td>
<td>163</td>
<td>173</td>
<td>233</td>
<td>35</td>
<td>67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2011</td>
<td>207</td>
<td>173</td>
<td>258</td>
<td>50</td>
<td>73</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2011</td>
<td>252</td>
<td>173</td>
<td>280</td>
<td>66</td>
<td>79</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^\dagger\)Ferti.N is fertilizer N application rate. Min.N is model predicted cumulative mineralized N. UptakeN is model simulated crop N uptake. Denitri.N is model predicted cumulative denitrified N. LeachN is model predicted total leached N. Nitrate and Ammonium are predicted NO\(_3\)-N and NH\(_4\)+-N concentrations in soils at the end of each year.
Figure 3.1 The N cycle considered in this model.
Figure 3.2 An example of model output showing soil N accumulation and loss and crop N uptake resulting from an application of 224 kg ha\(^{-1}\) fertilizer N (as UAN) in 2008 at ACRE.
Figure 3.3 Relationship between model-simulated corn N uptake and measured corn grain yield for each individual site year.
Figure 3.4 Relationship between model-simulated corn N uptake and measured corn grain yield (A) and relative corn grain yield (B) across 2006 to 2011.
CHAPTER 4. POTASSIUM IN SOILS: A LITERATURE REVIEW

4.1 Introduction

Potassium (K) is an essential element for the growth and development of all plants. After nitrogen (N) and phosphorus (P), K is the third nutrient most likely to limit crop productivity. Plants take up K in its ionic form ($K^+$) and it is not incorporated into the structure of organic compounds, but remains in the ionic form in solution in the cells. In addition to serving as an osmotic regulator, $K^+$ is an activator for over 80 different enzymes which are responsible for various metabolic processes including protein formation, energy metabolism, sugar degradation and so on (Brady and Weil, 2008).

Potassium is the seventh most abundant element and accounts for 2.6% of the earth’s crust. The average total K content in the plow layer is approximately 0.83%, or 15,000 kg ha$^{-1}$ (Foth and Ellis, 1996). Most commercial crops require 100 to 300 kg K ha$^{-1}$ for good growth (Haby et al., 1990). Therefore, when soils have high amounts of plant-available K, the requirement for K fertilizer is low or nonexistent. However, good K nutrition is critical to increase plants’ adaptability to environmental stresses and to improve the quality of flowers, fruits, and vegetables.

Due to the increasing recognition of the importance of K, extensive research has been carried out worldwide to investigate soil K availability to plants and numerous comprehensive literature reviews have summarized K chemistry in soils (Martin and Sparks, 1985; Sparks and Huang, 1985; Sparks, 1987; Kirkman et al., 1994).
4.2 Forms of Potassium

Potassium exists in soil in four forms: structural K, nonexchangeable K, exchangeable K, and solution K. Although these four forms can be measured separately with different analytical techniques, they are not clearly defined in the soil.

4.2.1 Structural Potassium

Structural or mineral K is defined as K that is bonded within the crystalline structure of K-bearing minerals. The mineral K content of soils depends on the structure and composition of parent rocks (Malavato, 1985; Sparks and Huang, 1985). Generally, igneous rocks have greater mineral K contents than sedimentary rocks. Among igneous rocks, the early formed basalts have mineral K contents of approximately 7 g K kg\(^{-1}\), while later-formed igneous rocks such as micas and K-feldspars are the primary sources of K-bearing minerals with more than 70 g K kg\(^{-1}\) (Malavato, 1985). The mineral K content of sedimentary rocks also varies, from approximately 6 g K kg\(^{-1}\) in limestone to about 30 g K kg\(^{-1}\) in clayey shale (Malavato, 1985).

Indiana soils are developed under different parent materials, so the K content varies according to the nature of the parent rocks. The northern area of Indiana, affected by either the Wisconsin or Illinois glaciation, has high amounts of micaceous clay minerals. However, in the southern area of Indiana, the parent rocks are mainly limestone and sandstone, and therefore have lower K contents in the soil.

4.2.2 Nonexchangeable Potassium

Nonexchangeable K, often referred to as fixed K or interlayer K, is held between the layers of micaceous clay minerals. Although nonexchangeable K is not immediately accessible for plant uptake, it is still considered as the main K reserve of the soil, because nonexchangeable K can become an important K
source for crop nutrition when exchangeable and solution K are depleted by crop uptake or leaching.

The amount of nonexchangeable K in soil is influenced by the types and quantities of clay minerals, particle size, and fixation or release of K in the minerals (Kirkman et al., 1994). Clay type is considered the dominant factor affecting the nonexchangeable K content in the soil. Generally, micas and vermiculites contain greater amounts of nonexchangeable K than kaolinites and smectites (Arifin et al., 1973; Shaviv et al., 1985; Goli-Kalanpa et al., 2008). A significant positive relationship between nonexchangeable K and illite content was found by Rezapour et al. (2009). Particle size also has an impact on nonexchangeable K content (MacLean and Brydon, 1963; Munn et al., 1976). The average amount of nonexchangeable K in the clay fraction can be 16 times greater than in the silt or sand fractions (Al-Kanani et al., 1984). Thus, most K fixation studies have focused on the clay fraction. However, Murashkina et al. (2007) argued in their study that the silt fraction could also dominate fixation of added K.

4.2.3 Exchangeable Potassium

Exchangeable K is held by electrostatic bonds at the edge and surface positions of clay minerals as well as humus colloids. The exchange sites on clay minerals resulting from isomorphic substitution are relatively constant. Due to the protonation or deprotonation of reactive functional groups such as phenols and carboxylic acids, the negative charges on humus colloids are pH dependent.

Exchangeable K is closely related to soil cation exchange capacity (CEC) with a range of 10 to 400 mg K kg\(^{-1}\) (Kirkman et al., 1994). Soils with large amounts of vermiculite or mica, and high organic matter content are generally high in exchangeable K content.
4.2.4 Solution Potassium

Solution K is the form that can be readily used by plants or leached. Solution K level is low (3 to 170 μg mL\(^{-1}\)) when compared to soil total K (Kover and Barber, 1990; Brouder et al., 2003) and it is also subject to leaching. In many soils, solution K content is not sufficient for plants to grow. However, solution K can be replenished from exchangeable and nonexchangeable K forms. The release of K to the surrounding soil water is characterized as a rapid release from the exchange sites followed by a slow release from the edge and interlayer (Dihillon and Dhillon, 1990; Jalali, 2006). Cox and Joern (1997) found that nonexchangeable K release by NaBPh\(_4\) occurred in 96 h. Martin and Sparks (1983) reported that, when equilibrated with H-saturated resin, K release from soils was complete in about 40 days.

4.3 The Potassium Cycle

The amount of K present in each form at a given period of time is not fixed. Changes among K forms occur with plant uptake, fertilizer addition, leaching losses, release/fixation processes and so on. However, only solution K is readily available for plant uptake. Thus, many studies have investigated the transformation processes that determine K availability to plants.

4.3.1 Weathering/Formation

Mineral K is the primary form of K occurring in the soil and is not instantly available for plant uptake. Release of K from these parent rocks follows the process of weathering. The weathering process is influenced by the composition and structure of the primary minerals, particle size distribution, environmental factors, biological activity, etc. (Sparks and Huang, 1985). For example, biotites weather easily, while feldspars weather slowly (Kirkman et al., 1994). The K release rate from larger particles is greater than from smaller particles unless at later stages of K depletion or from clay-size micas (Sparks and Huang, 1985).
Both high temperature and biological activity increase K release rate (Sparks and Huang, 1985).

The general weathering sequence of K-bearing minerals is that mica weathers to illite (hydrous mica), and eventually vermiculite or smectite. Along this weathering sequence, water content, specific surface area and cation exchange capacity increase, while K content decreases from approximately 10% to less than 1% in these minerals (Kirkman et al., 1994). Potassium releases from the mineral crystalline structure into the surrounding soil water.

4.3.2 Release/Fixation

Potassium ions can be entrapped in the ditrigonal cavities of the facing interlayer oxygens between the unit cells of 2:1 layer silicates due to the geometry of the fixation sites and the size of K\(^+\) ions. This fixation can decrease the amount of K immediate availability to the plants. However, it is not permanent, because interlayer K release occurs when exchangeable K and solution K are depleted by crop uptake or leaching.

The release or fixation of K is a complex process, and its mechanism is not well understood. According to Steffen and Sparks (1997), factors that affect fixation and release of soil K include the type of clay, the occurrence of wetting/drying and freezing/thawing, and factors that can affect solution K levels such as fertilizer input, plant uptake, and leaching loss.

4.3.2.1 Type of Clay

The type of clay mineral is considered to be the dominant factor that determines the extent of K fixation. Many researchers have indicated that soils with more illites and vermiculites have greater K fixation capacity (Arifin et al., 1973; Shaviv et al., 1985; Goli-Kalanpa et al., 2008). Goli-Kalanpa et al. (2008) found that in soils with large amounts of smectites, a greater quantity of added K remained in solution. Sorption of K\(^+\) by vermiculite causes the collapse in the
alternate layers and results in the formation of regularly interstratified mica-vermiculite layers (Sawhney, 1971). Interstratification in clay minerals is known as more than one kind of layer silicates that stack along the direction perpendicular to the basal plane (Sawhney, 1989). The interstratified clay minerals are abundant in the clay and silt fraction of soils and sediments.

The kinetics of nonexchangeable K release also depends on the relative amounts of different K-bearing minerals. The nonexchangeable K release rate from mica and vermiculite is diffusion-controlled (Dhillon and Dhillon, 1989; Cox and Joern, 1997; Jalali, 2006), while the K release rate from biotite fits a first-order model or a zero-order model depending on the extraction methods (Martin and Sparks, 1983; Dhillon and Dhillon, 1989). Additionally, the release rate of nonexchangeable K was found to be particle size dependent (Cox and Joern, 1997).

4.3.2.2 Wetting/Drying and Freezing/Thawing Effects

Drying of soils has been found to cause both fixation and release of K. Vitko et al. (2009) investigated the effects of different drying methods (moist, air-dry, and oven-dry) on the soil test K (STK) level of soil samples under different K fertilizer rate treatments. Soil samples with an initial STK level greater than 100 mg kg\(^{-1}\) showed a significant decrease in STK after both air- and oven-drying, which indicated fixation of K upon drying. Jones et al. (1960) dried samples at 110°C for 24 hours, and found the amount of exchangeable K either increased or decreased depending on the soil type. Cook and Hutcheson (1960) concluded that drying effects on STK levels depend on the initial exchangeable K concentrations in the soil. When the initial exchangeable K was high, fixation occurred upon drying; while when the initial exchangeable K was low, release was observed.

However the mechanisms driving wetting/drying effects on STK have not been well studied. Sparks and Huang (1985) postulated that the degree of
rotation of soil minerals changed upon drying, which caused changes in the K-O bond. Cook and Hutcheson (1960) found that soils with low K-supplying potential required more heating temperature for the clay minerals to collapse, which explained why release occurred upon drying when the initial exchangeable K was low (Cook and Hutcheson, 1960).

Similar effects of freezing/thawing on soil exchangeable content were found by Fine et al. (1941). They concluded that soils of low fertility that received small amounts of K fertilizer had an increase in exchangeable K content after freezing treatment; however, exchangeable K content decreased after the freezing treatment in soils with a high exchangeable K level.

4.3.2.3 Soil Solution K⁺ and NH₄⁺

When the concentration of K in the soil solution increases from the addition of fertilizer K or the release of the K from primary minerals by weathering, the shift in equilibrium may result in the fixation of K by clay minerals. On the other hand, when the concentration of K in soil solution decreases due to crop removal or leaching losses, release of K occurs to balance the shift in equilibrium.

Applying N fertilizer in the ammonium (NH₄⁺) form as salts or as anhydrous ammonia (AA) may also affect the fixation or release of K, because NH₄⁺ has a similar ionic radius as K⁺, and can also be fixed in the interlayer region of 2:1 clay minerals. Thus, NH₄⁺ ions compete with K⁺ for specific fixation sites, as well as block the release of K. Previous studies found that the order of fertilizer application is important for the competition of NH₄⁺ and K⁺ for similar fixation sites (Zhang et al., 2010). If NH₄⁺ is applied after K⁺, a decrease in NH₄⁺ fixation and a reduction in the release of nonexchangeable K was observed (Welch and Scott, 1961; Kilic et al., 1999). However, application of NH₄⁺ prior to or at the same time of K⁺ has been shown to decrease K fixation and increase exchangeable K concentration in the soil near the fertilizer placement site (Acquaye and Mclean, 1966; Bartlett and Simpson, 1967; Stehouwer and Johnson, 1991; Brouder and
Cassman, 1994; Kilic et al., 1999). The exchangeable and fixed K concentrations in soils are also influenced by fertilizer rates. In a study by Chen and Mackenzie (1992), combinations of four N rates (0, 1, 2, and 3 cmol N kg\(^{-1}\) as NH\(_4\)Cl) and four K rates (0, 1, 2, and 3 cmol K kg\(^{-1}\) as KCl) were added to soil samples. Results showed K fixation was enhanced by increased K rates and decreased by increased N rates. At greater rates of both NH\(_4\)\(^+\) and K fertilizer additions, NH\(_4\)\(^+\) fixation was favored over K\(^+\). However, from a long-term standpoint, high K fertilization rates would decrease soil fixation capacities for both NH\(_4\)\(^+\) and K (Liu et al., 1997; Zhang et al., 2007). The effect of NH\(_4\)\(^+\)-N fertilizer application on K fixation and release is also influenced by soil clay content. Fine-textured soils generally have a greater capacity to absorb NH\(_4\)\(^+\) than coarse-textured soils (Jenny et al., 1945; Martin and Chapman, 1951; Stanley and Smith, 1956). Stehouwer and Johnson (1991) found that the effect of simultaneous injection of AA and KCl on the distribution of exchangeable and fixed K\(^+\) was more pronounced in a silty clay loam soil than in a silt loam soil. In the silty clay loam soil, compared to injection of KCl alone, injection of AA + KCl significantly increased exchangeable K\(^+\) concentration and decreased fixed K\(^+\) concentration at the injection point, whereas in the silt loam soil, little effect of the interactions between AA and KCl fertilizers was shown. Chen and Mackenzie (1992) also reported variations in fixed K amounts in different soils affected by added NH\(_4\)Cl and KCl fertilizers, as the fixed proportion of added K increased with soil clay content. In addition, the competitive fixation of NH\(_4\)\(^+\) and K\(^+\) is also affected by the dominate type of clay present in the soil. Bajwa (1987) found that montmorillonitic clays fix more NH\(_4\)\(^+\) compared to K\(^+\), while vermiculitic clays fix both in relatively equal proportions.

4.3.3 Crop K Uptake

Crop K uptake plays an important role in K cycling because large amounts of K are removed by crops during growth and development. In general, the amount of K taken up by crops is second only less than N (Korb et al., 2002). For sugar
beets, K removal can be as high as 515 kg ha\(^{-1}\) (CFA, 1995). The K removal rate varies among crops, ranging from 1.4 to 60 lb per unit of yield (Table 4.1). However, the K concentrations in small grains are much less than that in the straw and roots (Vitosh et al., 1995). Thus, if the crop straw and chaff are left in the field after harvest, a large portion of K removed by the crop will be returned to the soil for crops grown the following season.

Mass flow and diffusion are the two dominant mechanisms accounting for K delivery to crop roots. In soils naturally high in solution K or where fertilizer K has been applied, considerable amounts of K move to crop roots with water flow. However, when solution K concentrations are low, mass flow contributes only about 10% of the required K (Tisdale et al., 1993). Diffusion occurs when there is a K concentration gradient. Although diffusion only takes place in a small distance (1 to 4 mm) around roots or out of clay interlayers, it accounts for 88 to 96% of K absorption (Tisdale et al., 1993).

Regardless of the transportation mechanisms, K moving to crop roots requires sufficient water (Korb et al., 2002). Therefore, moisture is one of the most important factors that influences crop K uptake. Skogley and Haby (1981) showed that the quantity of K absorbed by crop roots increased 175% when soil moisture increased from 10 to 28%. However, when soil moisture is too high, crop roots cannot function normally due to low O\(_2\) concentrations in the soil and K uptake can be reduced by 70% (Tisdale et al., 1993). Temperature also significantly influences K uptake due to its effects on root activity and plant physiological processes (Korb et al., 2002). Ching and Barber (1979) reported that total K uptake by corn was 2.6 times greater at 29 °C compared with total K uptake at 15 °C. In the same study, root growth significantly increased with increased temperature. Deeper rooted crops can greatly improve the turnover of available K in the soil by removing K from the subsoil and depositing it at the surface when roots are left in the field after harvest (Korb et al., 2002).
4.4 Methods of Assessing Nonexchangeable Potassium

Various methods have been used to determine the nonexchangeable K content in soils, including boiling nitric acid (HNO₃), extraction with sodium tetraphenylboron (NaBPh₄), exhaustive cropping of soil in the greenhouse.

4.4.1 Boiling Nitric Acid Extraction

The quickest and easiest way to assess nonexchangeable K is to use boiling HNO₃. This method, described by Pratt (1965), is to boil the soil in 1N HNO₃ over a flame for 10 minutes, filter the slurry, leach the soil with dilute HNO₃, and determine the K content in the filtrate. This method has been modified in several ways based on the boiling temperature or the boiling time (Pratt and Morse, 1954; Conyers and Mclean, 1969). However, the main problem with boiling HNO₃ method is its potential to dissolve K in primary minerals, resulting in an overestimation of available K, and also the inability of HNO₃ to completely extract interlayer K, resulting in an underestimation of nonexchangeable K.

4.4.2 Sodium Tetraphenylboron Extraction

Scott et al. (1960) developed the NaBPh₄ method to extract interlayer K in soils. The BPh₄⁻ anion combines with solution K and forms a potassium tetraphenylboron (KBPh₄) precipitate, while Na⁺ exchanges with interlayer K. After the extraction period, the KBPh₄ precipitate is dissolved by boiling water and the precipitate K is recovered by using Hg²⁺ to destroy BPh₄⁻. Smith and Scott (1966) optimized this method to obtain maximum K extraction. However, it was not suitable for routine lab measurement due to the high volatility and toxicity of Hg. Cox et al. (1996) modified this method by using Cu²⁺ as a replacement for Hg²⁺ to make it more suitable for routine lab work. In their research, it was found that NaBPh₄ extraction removed much more nonexchangeable K than the boiling HNO₃ method and that NaBPh₄ is able to more closely simulate the release mechanism of nonexchangeable K by plant roots.
4.4.3 Exhaustive Cropping of Soil in the Greenhouse

Exhaustive cropping has also been used to determine plant-available nonexchangeable K (Pratt, 1951; Cox et al., 1999). Soils are cropped with plants in the greenhouse and fertilized with a K-minus nutrient mixture. Cropping and harvesting sequences are repeated until the plants become K deficient or die. Total plant biomass and root uptake is measured along with the exchangeable K concentration in the soils before and after cropping. The difference between initial and final exchangeable soil K is attributed to crop K uptake, with the balance of K removal attributed to nonexchangeable K uptake. However, to accurately assess the quantities of nonexchangeable K uptake by plants, soil chemical and mineralogical measurements must be performed as exchangeable K is in dynamic equilibrium with nonexchangeable K.

4.5 Potassium Fertilizer Management

4.5.1 Application Rate

Currently, soil test-based K fertilizer recommendations are widely used. Through a soil test, the quantity of available K level in the soil is measured. The current soil test K level is compared with the K demands of crops to determine if additional fertilizer input is necessary and how much K fertilizer has to be applied. The soil test level demanded by the crop for optimum growth is termed the critical level. Any soil test level below the critical level indicates the nutrient in the soil is deficient for crop growth (Vitosh et al., 1995). When the soil test level is above the critical level, addition of fertilizer may also be necessary to maintain a high level of the nutrient content in the soil to prevent future deficiencies and to guard against nutrient deficiencies due to suboptimal environmental factors.

Soil test critical levels are the key to K fertilizer recommendations and they are commonly determined by long-term field studies. For Indiana, Michigan and
Ohio, Vitosha et al. (1995) predicted the exchangeable K soil test critical levels (mg K kg\(^{-1}\) soil) through an algorithm:

\[ K \text{ Critical level} = 75 + 2.5 \times CEC \]

Cox et al. (1999) also reported that critical levels (mg K kg\(^{-1}\) soil) can be well predicted (\(R^2 = 0.986\)) in greenhouse studies using the model:

\[ K \text{ Critical level} = 34.5 - 3.41 \times \text{Illite K} + 3.52 \times CEC, \]

where illite K is the nonexchangeable K concentration in the soil measured by NaBPh\(_4\) extraction after a 7-d incubation.

4.5.2 Application Timing

Many farmers in the Midwest US apply enough K in the fall prior to planting corn to fertilize both the upcoming corn crop and the soybean crop grown in the following year, because application of K fertilizers once for two years of crop production saves on application costs, reduces traffic over the field, and fits a 2-year or 4-year soil testing cycle (PPI and PPIC, 1999). Fall application of K is typical because of time, workload, dry soils, available fertilizers, and application before fall tillage (Sawyer and Mallarino, 2009). For soils with high amounts of mica and vermiculite clay minerals and greater cation exchange capacity, added K will be bonded to the exchange sites of organic matter and clay minerals or fixed in the interlayer of clay minerals. This K can then be released back to the soil solution when solution K is depleted by crop uptake. Although there is a long time between fertilizer application and crop use, added K is assumed to be readily available for the crops to be grown next year or for multiple years.

In a corn-soybean rotation, all K fertilizers can be applied after soybean harvest and ahead of the corn. Enough K will be returned to the soil from corn residues for the growth of the soybean crop in the following year. Soybean removes greater quantities of K than corn does (PPI and PPIC, 1999; Korb et al.,
2002; IPNI, 2010) (Table 4.1), so it may be more efficient to assess soil test K levels after soybean harvest due to both the greater K uptake and greater demand of K late in the growing season for soybean compared to corn. In addition, K fertilizer application after soybean harvest and ahead of corn instead of after corn harvest and ahead of soybean fits better into most soil testing cycles. However, as long as enough K fertilizer is applied to maintain a high soil test K level, application time of K fertilizer is less critical.

4.6 Concluding Remarks

In this chapter we reviewed the different forms of K in soils, the various factors that control K dynamics among each form, as well as different assessment methods for nonexchangeable K. The most important aspect of nonexchangeable K is how it releases to exchangeable and solution K forms, which are readily accessible for plant uptake. However, the release or fixation of K is a complex process, depending on a number of factors and this mechanism is not well understood. Thus, my research objectives were (i) to assess the effect of AA injection on K fixation around the injection point over time; and (ii) to evaluate the effect of different soil moisture conditions (moist, air-dry, oven-dry) on soil test K levels.
### 4.7 Reference


Table 4.1 The amount of potassium removed in harvest portions of selected agronomic crops†

<table>
<thead>
<tr>
<th>Crop</th>
<th>Unit of yield</th>
<th>K$_2$O removed per unit of yield (lb/unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>ton</td>
<td>60</td>
</tr>
<tr>
<td>Barley‡</td>
<td>bushel</td>
<td>1.6</td>
</tr>
<tr>
<td>Corn silage</td>
<td>ton</td>
<td>8.4</td>
</tr>
<tr>
<td>Soybean</td>
<td>bushel</td>
<td>1.4</td>
</tr>
<tr>
<td>Wheat‡</td>
<td>bushel</td>
<td>2.0</td>
</tr>
</tbody>
</table>

† Adapted from Korb et al., 2002.
‡ Wheat and barley harvest include grain and straw.
CHAPTER 5. IMPACT OF BAND INJECTION OF ANHYDROUS AMMONIUM ON SOIL POTASSIUM CONCENTRATION

5.1 Abstract:

In most studies on competitive ammonium (NH$_4^+$) and potassium (K$^+$) fixation, NH$_4^+$ is applied as a salt. However, band-injection of anhydrous ammonia (AA) has been widely used in corn production for decades. We conducted a laboratory study to assess the effect of band-injected AA on exchangeable and nonexchangeable K concentrations near the injection point over time in four soils. Soils were packed in rectangular boxes with AA injected in the center at a rate equivalent to 170 kg N ha$^{-1}$. Following injection, soils were incubated in a chamber at a moisture tension of 0.05 MPa and 22 °C. Exchangeable and nonexchangeable K concentrations were analyzed in soil samples collected from 7 concentric zones at various distances from the injection point at 7, 14, and 28 days after AA injection. The effect of AA injection was more pronounced on nonexchangeable K than on exchangeable K. In the two soils with higher clay content and cation exchange capacity, there was a steep gradient of decreasing nonexchangeable K content up to 4.5 cm away from the injection point. This effect lasted through 14 days. However, in the other two soils, AA injection did not affect exchangeable or nonexchangeable K concentrations.

Without large increase in exchangeable K concentration, the reduction in nonexchangeable K indicated the K was fixed more deeply in the clay mineral interlayer. This study changes our perspectives on the blocking effect of NH$_4^+$ on K release and explains K deficiency symptoms that occasionally result following AA injection.
5.2 Introduction

Potassium (K) is an essential nutrient for plant growth. After nitrogen (N) and phosphorus, K is the third most likely nutrient to limit crop productivity. Good K nutrition is critical to increase plants’ adaptability to environmental stresses and to improve the quality of flowers, fruits, and vegetables. Lack of K results in stunted crop growth, poorly developed root systems, weak stalks, as well as severe yield loss (Brady and Weil, 2008). Due to the increasing recognition of the importance of K, extensive research has been carried out worldwide to investigate soil K and its availability to plants. Researchers found that K+ ions can be trapped between the layers of 2:1 clay minerals in the soil due to the geometric structure of the fixation sites and the size of the K+ ions. This fixation decreases K availability for plant uptake (Martin and Sparks, 1985; Sparks and Huang, 1985; Sparks, 1987; Kirkman et al., 1994). Although many studies on soil K fixation have been conducted, problems associated with soil K management have often been ignored in the last decade. This is especially true in Asian countries where N fertilizers have been over-applied while K fertilizer application has been ignored, resulting in a continual depletion of soil K (Zhang et al., 2010). In addition, under organic farming practices, soils also suffer from negative K field balances, which may deplete soil exchangeable K if K release from soil minerals does not replace the amount of K that is harvested.

In the northern two thirds of Indiana, soil parent material was affected by either the Wisconsin or Illinois glaciation. Soils in this area of the state have large quantities of K-bearing micaceous clay minerals. Many researchers have indicated that soils with more micaceous clay minerals have greater K fixation capacity (Arifin et al., 1973; Shaviv et al., 1985; Goli-Kalanpa et al., 2008). However, these soils also can release fixed K when exchangeable and solution K are depleted by crop uptake or leaching. Therefore, understanding K fixation and release dynamics is critical in soils with greater quantities of micaceous clay minerals, especially when K fertilization is less than crop K removal.
The release or fixation of K is a complex process affected by numerous factors including clay type, the occurrence of wetting/drying and freezing/thawing, fertilizer input, etc. (Steffen and Sparks, 1997). Among these factors, application of N fertilizer in an ammonium (NH\textsubscript{4}\textsuperscript{+}) form can significantly impact the K nutrition of crops. Ammonium ions have a similar ionic radius and energy of hydration as K\textsuperscript{+} ions, so they can also be fixed in the interlayer of 2:1 clay minerals. The competitive relationship between NH\textsubscript{4}\textsuperscript{+} and K\textsuperscript{+} fixation has been reported in numerous studies (Welch and Scott, 1961; Scherer, 1982; Stehouwer and Johnson, 1991; Kilic et al., 1999; Zhang et al., 2010). Previous studies found that the order of fertilizer application is important for the relative competition of NH\textsubscript{4}\textsuperscript{+} and K\textsuperscript{+} for fixation sites (Zhang et al., 2010). Simultaneous application of NH\textsubscript{4}\textsuperscript{+} and K\textsuperscript{+} decreased K fixation and increased exchangeable K concentration in the soil near the fertilizer placement site (Stehouwer and Johnson, 1991; Brouder and Cassman, 1994; Kilic et al., 1999). Potassium applied before NH\textsubscript{4}\textsuperscript{+} addition decreased NH\textsubscript{4}\textsuperscript{+} fixation and resulted in a large reduction in the release of nonexchangeable K (Welch and Scott, 1961; Kilic et al., 1999). However, in these studies, both N and K fertilizers were applied. Fewer studies have been conducted to investigate the effect of N fertilizer alone on soil K fixation.

In most studies on competitive NH\textsubscript{4}\textsuperscript{+} and K\textsuperscript{+} fixation, NH\textsubscript{4}\textsuperscript{+} is applied as a salt. However, band-injection of anhydrous ammonium (AA) is widely used. Research has found that AA injection results in greater fixation of NH\textsubscript{4}\textsuperscript{+} compared with other forms of NH\textsubscript{4}\textsuperscript{+} salt fertilizers (Young and Cattani, 1962). The injection of AA initially increases soil pH. The charge of soils generated from the broken edges of clay minerals or on soil organic matter is pH-dependent and increases as soil pH increases, resulting in greater retention of NH\textsubscript{4}\textsuperscript{+} (Nommick, 1957). Additionally, an increase in dissolved organic carbon is observed for a short time after AA injection (Tomasiewicz and Henry, 1985; Clay et al., 1995). Organic compounds adsorbed on the surface of clay minerals have been shown to have a blocking effect on NH\textsubscript{4}\textsuperscript{+} release and fixation (Greenland, 1965; Dudas and Pawluk, 1970; Syers et al., 1970). Removal of organic matter from the clay surface increases
the amounts of NH$_4^+$ fixed with the application of ammonium-based N fertilizers (Hinman, 1966).

In addition, in most previous studies, the amounts of fixed NH$_4^+$ and K$^+$ in the soil were analyzed separately with different methods. For nonexchangeable NH$_4^+$, the HF/HCl digestion method developed by Silva and Bremner (1966) is commonly used; whereas for nonexchangeable K$^+$, the most commonly used method is the boiling nitric acid (HNO$_3$) extraction method developed by Pratt (1965). The mechanism of the HF/HCl digestion method is to destroy the structure of soil minerals with a very strong acid to dissolve the NH$_4^+$ in soil minerals into the digestion solution. On the other hand, the HNO$_3$ method replaces the exchangeable and nonexchangeable K$^+$ with H$^+$ ions, in addition to some K$^+$ released by the dissolution of K-bearing minerals. Due to the difference in mechanisms of the two analytical methods, it might not be reasonable to directly compare the quantity of nonexchangeable NH$_4^+$ and K$^+$ analyzed by these methods. Additionally, research showed the HF/HCl digestion method overestimated the amount of nonexchangeable NH$_4^+$ that is available for plants (Nieder et al., 2011), while the boiling HNO$_3$ method did not completely extract interlayer K (Cox et al., 1996).

Scott et al. (1960) developed the sodium tetraphenylboron (NaBPh$_4$) method to extract interlayer K in soils. The BPh$_4^-$ anion combines with solution K and forms a potassium tetraphenylboron (KBPh$_4$) precipitate, while Na$^+$ exchanges with interlayer K. After the extraction period, the KBPh$_4$ precipitate is dissolved by boiling water and the precipitate K is recovered by using Hg$^{2+}$ to destroy BPh$_4^-$. Smith et al. (1994) found that a 7-d extraction with NaBPh$_4$ was also suitable for the measurement of the nonexchangeable NH$_4^+$ in different soils. Therefore, the NaBPh$_4$ method can be used to extract both NH$_4^+$ and K$^+$ at the same time. Cox et al. (1996) modified this method by using Cu$^{2+}$ as a replacement for Hg$^{2+}$ to make it more suitable for routine lab work. In their research, it was found that NaBPh$_4$ extraction extracted 71% of NH$_4^+$ released by the conventional HF/HCl
method and removed up to 10 times more nonexchangeable K than the boiling HNO₃ method because the NaBPh₄ extraction is able to more closely simulate the release mechanism of the nonexchangeable NH₄⁺/K⁺ uptake by plant roots as it simply depletes solution NH₄⁺/K⁺.

The objective of this study was to simulate the band injection of AA under laboratory conditions, and assess the effect of AA injection on K fixation around the injection point over time in four soils with the modified NaBPh₄ extraction method.

5.3 Materials and Methods

5.3.1 Sample Treatment

Four soils were collected from 3 conventional tillage field sites. At each site soils were sampled to a depth of 30 cm and stored in a field-moist condition at 4 °C until used. Pertinent soil properties are presented in Table 5.1.

Soil samples were passed through a 2 mm sieve and packed into 30×30×5 cm boxes at a bulk density of 1.3 g cm⁻³. Deionized water was added to bring water potential to 0.05 MPa and soil samples were allowed to equilibrate for 10 days at 20 °C prior to fertilizer application. Using an apparatus similar to that developed by Stehouwer and Johnson (1991), AA was added at a rate of 23 g box⁻¹ (equivalent to 170 kg ha⁻¹ N). The AA was injected into the center of each soil box. After the injection of AA, all boxes were incubated in a growth chamber for 7, 14, or 28 days at 22 °C. Boxes were arranged in a split-plot design with different soil types as the main plots and different incubation times as subplots and each treatment combination was replicated three times. The boxes were weighed every 3 or 4 days to determine moisture loss, and brought back to their original water content with deionized water. After each incubation time, boxes were removed from the growth chamber for destructive sampling. Soil material
around the injection point was divided into seven concentric zones with diameters of 0-4, 4-6, 6-9, 9-12, 12-15, 15-18, and 18-21 cm. Soils taken from the same zone were pooled and mixed as one sample before any analysis.

5.3.2 Sample Analysis

Soil pH was measured with a glass electrode from a 1:2 soil:water suspension. A 1-g subsample was used to determine exchangeable K after extraction with Mehlich-3 solution. Total nonexchangeable K was extracted with NaBPH₄ using a 7-d extraction period according to Cox et al. (1996). We also used the boiling HNO₃ extraction method (Pratt, 1965), which is more widely used to determine the total nonexchangeable K content in some samples in which large reductions in nonexchangeable K content were observed with the 7-d NaBPH₄ extraction. All extracts were stored in sealed vials at 4 °C before determination of K⁺ concentration using a flame emission spectrophotometer.

5.3.2.1 Sodium Tetraphenylboron Extraction Procedure

Soil samples weighing 0.5 g were placed in Folin Wu tubes and 3 ml of extracting solution (0.2 M NaBPH₄-1.7 M NaCl-0.01 M EDTA) were added. After 7 d of incubation, 25 ml of quenching solution (0.5 M NH₄Cl-0.11 M CuCl₂) was added to the tubes to stop K extraction. The tubes were then placed on a digestion block preheated to 130 °C for 45 minutes. After removal from the digestion block, the suspension in the tubes was diluted to 50 ml with deionized water, mixed, and then left undisturbed for 2 hours to allow the soil to settle. We transferred 20 ml of the top clear solution to vials containing 3 drops of concentrated HCl. These solutions were stored at 4 °C before analysis.

5.3.2.2 Boiling Nitric Acid Extraction Procedure

We placed 2.5 g of air-dried, ground soil into digestion tubes. After adding 25 ml 1.0 M HNO₃, these tubes were placed on a hot digestion block and gently boiled for 10 minutes once boiling began. The suspension in the tubes was filtered into a 100 ml volumetric flask. Soils in the funnel were rinsed with four 15-
ml aliquots of 0.1 M HNO₃. Then flasks were brought to volume with 0.1 M HNO₃. Solutions in the flasks were stored at 4 °C before analysis.

5.3.3 Data Analysis

All statistical analyses were performed with version 9.2 of SAS (SAS Institute Inc., 2008). Analysis of variance was conducted using the GLM procedure. Soil type was considered as the main plot and used as a class variable, while incubation time and distance were subplots. The MEANS procedure with the LSD option was used for means separation.

5.4 Results and Discussion

5.4.1 Soil pH

Initial soil pH was in a range of 5.6 to 6.0. In all four soils, seven days after injection of AA, soil pH within 6 cm of the point of AA injection increased significantly (Figure 5.1). This increase in pH can be attributed to the reaction between NH₃ and H₂O, through which OH⁻ ions are produced. High pH (>8) near the point of AA injection persisted through 14 days of incubation and at day 28 it decreased likely due to nitrification. In the Chalmers and Pewamo soils, soil pH had little change at the outer zones 9 to 11.5 cm away from the AA injection point indicating that the injected AA did not move beyond 9 cm from the injection point. In the Raub soil, the effect of AA injection on soil pH was significant up to 7.5 cm from the injection point, whereas in Pinhook soil, a large decrease in pH was observed at day 28 up to 11.5 cm away from the injection point. The impacted area after AA injection was larger in the Pinhook soil than in the other three soils, which might be due to the higher sand content in the Pinhook soil. Eno and Blue (1954) found that soil pH was initially increased by AA injection but decreased with time, and this effect was restricted to a 7.6 cm zone centered on the injection row in sandy soil. Stanley and Smith (1956) reported a gradual
decrease in soil pH from center to 15 cm away from the injection point two
months after applying 6 g of AA (equivalent to 20 kg ha\(^{-1}\) N) in a silt loam soil.

5.4.2 Soil Exchangeable and Nonexchangeable Potassium Content

The average exchangeable K concentrations in each untreated soil
decreased in following order: Pewamo (258 mg kg\(^{-1}\)) > Pinhook (242 mg kg\(^{-1}\)) >
Raub (209 mg kg\(^{-1}\)) > Chalmers (170 mg kg\(^{-1}\)). These soils differed little in
exchangeable K and there was only a slight effect of AA injection on
exchangeable K (Figure 5.2).

In Indiana, K fertilizer recommendations are made based on soil test results
(Mehilich-3 or ammonium acetate, pH 7.0, exchangeable K content). Any soil test
K level below the critical soil test level indicates that the soil is K deficient for
optimum crop growth (Vitosh et al., 1995). When soil test K level is above the
critical level, addition of fertilizer may also be necessary to maintain the soil test
K level at or slightly above the critical level, even though no yield response to the
applied K will be observed.

The soil test K critical level can be calculated through an algorithm
developed by Vitosh et al. (1995):

\[
K \text{ Critical level} = 75 + 2.5 \times \text{CEC}
\]

Based on this algorithm, soil critical levels are 123 mg K kg\(^{-1}\), 118 mg K kg\(^{-1}\), 98
mg K kg\(^{-1}\), and 103 mg K kg\(^{-1}\) for soils Chalmers, Pewamo, Pinhook and Raub,
respectively. Cox et al. (1999) also reported that soil K critical levels can be well
predicted \(R^2=0.986\) using the model:

\[
K \text{ Critical level} = 34.5 - 3.41 \times \text{Illite K}^+ + 3.52 \times \text{CEC}
\]

where illite K is the nonexchangeable K concentration (g K\(^+\) kg\(^{-1}\)) in the soil
measured by NaBPh\(_4\) extraction after a 7-d incubation. Since CEC and K-bearing
minerals contents are the two major properties controlling K-buffering capacity in
the soil (Mengel and Busch, 1982), these two factors are both considered in the equation. Based on Cox et al. (1999) model, Soil critical levels are 91 mg K kg\(^{-1}\), 70 mg K kg\(^{-1}\), 62 mg K kg\(^{-1}\), and 67 mg K kg\(^{-1}\) for the Chalmers, Pewamo, Pinhook and Raub soils, respectively. Comparing soil test K levels and soil K critical levels, in all four soils, soil test K levels are much greater than the soil K critical levels, so no K fertilizer application is required. However, after solution K and exchangeable K is depleted by crop uptake and leaching, the blocking effect of NH\(_4^+\) on fixed K release might result in K-deficiency in crops in late-season. Therefore, it is important to determine the effect of AA injection on soil exchangeable and nonexchangeable K content.

The total nonexchangeable K analyzed with NaBPh\(_4\) 7-d extraction decreased in the following order: Pewamo (7428 mg kg\(^{-1}\)> Chalmers (3228 mg kg\(^{-1}\)> Raub (2019 mg kg\(^{-1}\)> Pinhook (1485 mg kg\(^{-1}\)), and the total nonexchangeable K concentrations in these four soils are positively correlated to soil clay content. The positive relationship between soil nonexchangeable K concentration and clay content is consistent with the results found in many previous studies (McEwen and Matthews, 1957; MacLean and Brydon, 1963; Munn et al., 1976). However, K fixation can also occur in silt or fine-sand size fractions of the soil with the presence of silt or fine-sand size vermiculite minerals (Murashkina et al., 2007).

In the Chalmers and Pewamo soils, the total nonexchangeable K concentration decreased significantly in the soil up to 4.5 cm from the injection point 7 days after the injection of AA, and this decrease persisted through 14 days of incubation, but after 28 days the effect was no longer apparent (Figure 5.3). Seven days after AA injection, a large variation in total nonexchangeable K concentration was observed at the center zone (4.5-6 cm), which indicated that the effect of AA injection on total nonexchangeable K concentration in soils 4.5-6 cm away from the injection point was not consistent among all three replications.
In the Pinhook and Raub soil, injection of AA had no significant effect on total nonexchangeable K concentration.

Although greater movement of ammonia (NH$_3$) was observed in the sandy Pinhook soil, the injected AA had a more pronounced effect on exchangeable K and nonexchangeable K concentrations in the Chalmers and Pewamo soils than in Raub and Pinhook soils. This result may be attributed to the different textures of soil samples. McDowell and Smith (1958) found that NH$_3$ moved up to 7.5 cm away from AA injection point in sandy and silt loam soils, while only moving 5 cm in a clay soil. Their observations were similar to the results found in our study. The reduced NH$_3$ movement in the higher clay soils in both studies likely due to the greater capacity of fine-textured soils to sorb NH$_3$ compared coarser ones (Jenny et al., 1945; Martin and Chapman, 1951; Stanley and Smith, 1956). This also explains why AA injection had a more pronounced effect on K distributions in the two soils with higher clay content. Similar results were observed by other researchers. Stehouwer and Johnson (1991) found that the effect of simultaneous injection of AA and KCl on the distribution of exchangeable and fixed NH$_4^+$ and K$^+$ were more pronounced in a silty clay loam soil than in a silt loam soil. Chen et al. (1992) also reported that the variation in the quantity of fixed K after adding N and K fertilizers was related to soil texture.

In addition to the amount of clay, the type of clay mineral is also considered to be a dominant factor that determines the extent of K fixation and release. Many researchers have shown that soils with more illites and vermiculites have greater K fixation capacity (Arifin et al., 1973; Shaviv et al., 1985; Goli-Kalanpa et al., 2008). Bajwa (1987) found that montmorillonitic clays fix more NH$_4^+$ and less K$^+$, while vermiculitic clays fix both. In soils with large amounts of smectites, a greater quantity of added K remained in the form of solution K (Goli-Kalanpa et al., 2008). Therefore, the effect of AA injection on K distribution in soils may be explained by both differences in clay content and clay mineralogy.

Our results showed that the exchangeable and nonexchangeable K contents
in the Raub and Pinhook soils did not change much after the injection of AA, whereas in Chalmers and Pewamo soils, AA injection significantly decreased the nonexchangeable K content near the injection point, surprisingly without increases in the exchangeable K concentration. This observation indicated that some nonexchangeable K was fixed more deeply in the clay mineral interlayer and became not extractable by NaBPh$_4$. To the best of our knowledge, this observation has not been reported previously. Stanley and Smith (1956) evaluated the effect of AA injection on the availability of soil exchangeable K in a Putnam silt loam soil. They showed that the effect of AA injection on the amount of readily available K was not pronounced, with 10 mg kg$^{-1}$ of HCl-extractable K in the soil 0 to 3 cm away from the injection point and 7.9 mg kg$^{-1}$ of HCl extractable K in the untreated soils. Tung et al. (2009) evaluated K concentrations in groundwater under different fertilizer application treatments. They found that without the application of K fertilizer, K concentrations in the groundwater decreased following the application of N fertilizer (at a rate of 3.75 kg ammonium chloride per palm per year equivalent to about 180 kg N ha$^{-1}$), however this decrease was not statistically significant because in the absence of K application, soil solution K concentrations were very low, ranging from 1.3 to 10.7 mg L$^{-1}$. Unfortunately, total nonexchangeable K content was not measured in either of these studies. While the initial exchangeable K concentrations were greater in the soils used in our studies, we also did not observe a pronounced change in exchangeable K concentration upon AA injection.

Although the blocking effect of NH$_4^+$ on release of fixed K from clay minerals has been observed in many studies (Welch and Scott, 1961; Springob, 1999), the way in which AA application decreases nonexchangeable K content near the injection point is not clear. We proposed two mechanisms to explain the “disappearance” of K after AA injection: one is the deprotonation of clay minerals due to the high pH resulting from AA injection; the other is the dehydration of interlayer water caused by the reaction between NH$_3$ and water. After AA injection, the magnitude of soil pH generally increased by 2 (pH > 8.0), indicating
a large production of OH⁻ groups, which reacts with the H⁺ ions on the surface of clay minerals resulting in increased soil charge on the clay minerals and the corresponding deprotonation can then lead to the collapse of the clay mineral interlayer. The effect of pH changes on K fixation has been reported in some early studies (Volk, 1934; Martin et al., 1946). Generally, K fixation increased with soil pH. When soil pH value is as low as 2.5, no fixation occurred. As soil pH value increased to 5.5, K fixation increased rapidly, and when soil pH was above 5.5, the increase in K fixation tended to slow down. The increased K fixation resulted from the decreased amount of H⁺ ion present in the soil that competes with K⁺ on the fixation sites at low pH (2.5 to 5.5) and the decreased number of interlayer hydroxyl aluminum polymer cations when soil pH is between 5.5 and 8.0 (Thomas and Hipp, 1968). On the other hand, the water fixed in between the 2:1 clay mineral interlayers is more acidic (Mortland, 1966). The reaction between NH₃ and such “acidic” water is enhanced by the injection of AA. Removal of the interlayer water fixed in clay minerals can potentially collapse the clay mineral interlayer and reduce the amount of K extracted by all current analytic methods. Further study on these two mechanisms will improve our understanding of the blocking effect of NH₄⁺ on soil K release.

5.4.3 Comparison between Two Nonexchangeable Potassium Extraction Methods

Nonexchangeable K was extracted with both NaBPh₄ and boiling HNO₃. Although nonexchangeable K levels using boiling HNO₃ were 10 times less than nonexchangeable K levels using NaBPh₄, both methods showed large reductions in nonexchangeable K concentrations near the injection point 7 days after AA injection (Figure 5.4).

So far no chemical extraction method is regarded as ideal for predicting the total nonexchangeable K content in soil. The boiling HNO₃ extraction is a widely accepted method because it is the quickest and easiest way of measuring the
amount of nonexchangeable K. However, the role of $\text{H}_3\text{O}^+$ in nonexchangeable K release is questioned. Only within a certain range of pH or with a weak acid concentration does $\text{H}_3\text{O}^+$ behave as an exchanger to replace the interlayer K. With a higher concentration of acid, $\text{HNO}_3$ may also dissolve structural forms of K (Martin and Sparks, 1985). The NaBPh$_4$ extraction method more closely simulates the mechanism of nonexchangeable K release brought by uptake of K by plant roots. The BPh$_4^-$ anion combines with released solution K and precipitates, while Na$^+$ exchanges with the interlayer K (Scott et al., 1960). This method is not widely used by commercial soil testing laboratories because of its cost and mammalian toxicity of NaBPh$_4$. In our research, we found that the NaBPh$_4$ method extracted 10 times more nonexchangeable K than the boiling $\text{HNO}_3$ extraction, which agrees with the study of Cox et al. (1996). The total nonexchangeable K referred in our study was actually NaBPh$_4$ extractable K. However, neither of these methods was able to extract the nonexchangeable K in soils near the injection point 7 days after AA injection.

### 5.5 Conclusion

In conclusion, injection of AA did not have a pronounced effect on exchangeable K content in the soil, but dramatically decreased nonexchangeable K contents by 40 to 60% near the injection point in Chalmers and Pewamo soils for approximately 14 days.

From a mechanistic point of view, this result complicates the modeling of release kinetics of nonexchangeable K in soils. Many studies found the parabolic diffusion equation could be used to better explain the K release kinetics (Dhillon and Dhillon, 1989; Cox and Joern, 1997; Jalali, 2006). However, they were only studying the release of K from the nonexchangeable K pool to the exchangeable K pool. When AA is injected, both exchangeable and nonexchangeable K concentrations may decrease. Therefore, the parabolic diffusion equation is not
suitable for accurately predicting the release of K in the presence of blocking ions. From a practical point of view, high K fixation potentials are observed in soils that have large amounts of micaceous or vermiculitic clay minerals (Arifin et al., 1973; Shaviv et al., 1985; Goli-Kalanpa et al., 2008). Injection of AA could exacerbate K fixation in these soils and lead to K deficiency in crops, unless the grower applied additional K fertilizer.

As we discussed above, the types and amounts of clay minerals are believed to be the most important factors that determine K fixation and release. Future studies should be conducted to evaluate the changes in clay mineral properties after injection of AA, which we hope could further explain our observations of reduced nonexchangeable K near the AA injection point in some soils, but not others.
5.6 Reference:


Mortland, M.M. 1966. Ammonia interactions with soil minerals. pp. 188-197. In M.H. McVikar et al. (ed.) Agricultural anhydrous ammonia technology and use. AAI, ASA, and SSSA, Madison, WI.


Table 5.1 Soil characteristics in the upper 30 cm of the Ap horizon of the Chalmers, Pewamo, Pinhook, and Raub soil samples.

<table>
<thead>
<tr>
<th>Soil Series</th>
<th>Soil Classification†</th>
<th>Sand (g kg⁻¹)</th>
<th>Silt (g kg⁻¹)</th>
<th>Clay (g kg⁻¹)</th>
<th>OM‡ (g kg⁻¹)</th>
<th>CEC§ (cmol kg⁻¹)</th>
<th>pH¶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalmers</td>
<td>Fine-silty, mixed, superactive, mesic Typic Endoaquoll</td>
<td>120</td>
<td>470</td>
<td>410</td>
<td>42</td>
<td>19.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Pewamo</td>
<td>Fine, mixed, active, mesic Typic Argiaquoll</td>
<td>100</td>
<td>410</td>
<td>490</td>
<td>39</td>
<td>17.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Pinhook</td>
<td>Coarse-loamy, mixed, superactive, mesic Mollic Endoaqualfs</td>
<td>500</td>
<td>310</td>
<td>190</td>
<td>24</td>
<td>9.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Raub</td>
<td>Fine-silty, mixed, superactive, mesic Aquic Argiudoll</td>
<td>240</td>
<td>490</td>
<td>270</td>
<td>27</td>
<td>11.1</td>
<td>5.9</td>
</tr>
</tbody>
</table>

†Mineral classifications are mixed for all soils.
‡OM = Soil organic matter content determined by loss-on-ignition method (Ball, 1964).
§CEC = Cation exchange capacity determined by summation of basic cations measured with Mehlich-3 extraction and acid cations extracted by Barium Acetate.
¶Soil pH was measured with a glass electrode in a 1:2 soil:water suspension.
Table 5.2 Protected LSD\(_{0.05}\) values for sources of variance in exchangeable (Ex\_K) and nonexchangeable (NonEx\_K) K levels (mg kg\(^{-1}\)) in Chalmers, Pewamo, Pinhook, and Raub soils.

<table>
<thead>
<tr>
<th>Source</th>
<th>Chalmers</th>
<th>Pewamo</th>
<th>Pinhook</th>
<th>Raub</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ex_K</td>
<td>NonEx_K</td>
<td>Ex_K</td>
<td>NonEx_K</td>
</tr>
<tr>
<td>Distance</td>
<td>8</td>
<td>246</td>
<td>7</td>
<td>791</td>
</tr>
<tr>
<td>Time</td>
<td>5</td>
<td>161</td>
<td>4</td>
<td>518</td>
</tr>
<tr>
<td>Distance ×Time</td>
<td>13</td>
<td>427</td>
<td>12</td>
<td>1369</td>
</tr>
</tbody>
</table>
Figure 5.1 Soil pH over 28 days after injection of anhydrous ammonia as affected by distance from the anhydrous ammonia injection point in Chalmers, Pewamo, Pinhook, and Raub soil. Dash lines indicate initial soil pH. Soil pH values were obtained from a 1:2 slurry as mean of three replicates. Error bars indicate the standard deviation of the means. Letters indicate the difference in soil pH as affected by distance from the injection point. Points labeled by the same letter are not significantly different (p>0.05).
Figure 5.2 Distribution of exchangeable K over time and distance from the anhydrous ammonia injection point in a Chalmers, Pewamo, Pinhook, and Raub soil after injection of anhydrous ammonia. Dash lines indicate the exchangeable K concentration in untreated soils. The exchangeable K values are means of three replicates. Error bars indicate the standard deviation of the means.
Figure 5.3 Distribution of total nonexchangeable $K$ over time and distance from the anhydrous ammonia injection point in a Chalmers, Pewamo, Pinhook, and Raub soil after injection of anhydrous ammonia. Dash lines indicate the total nonexchangeable $K$ concentration in untreated soils. The nonexchangeable $K$ values are means of three replicates. Error bars indicate the standard deviation of the means. Letters indicate the difference in total nonexchangeable $K$ content as affected by distance from the injection point. Points labeled by the same letter are not significantly different ($p>0.05$).
Figure 5.4 Distribution of total nonexchangeable K over distance from the anhydrous ammonia injection point in Pewamo soil seven days after injection of anhydrous ammonia. Total nonexchangeable K was extracted with boiling nitric acid and by 7-d incubation in sodium tetraphenylboron (STPB). The nonexchangeable K values are means of two replicates. Error bars indicate the standard deviation of the means.
CHAPTER 6. IMPACT OF MOISTURE ON SOIL TEST POTASSIUM LEVELS

6.1 Abstract

Soil testing results are critical to determine accurate soil fertilizer application rates. Soil samples collected under different moisture contents can cause variations in soil test K (STK) levels. Additionally, soil testing labs oven dry soil samples at low temperature, which might not result in the best assessment of soil available K because previous studies have found that soils may fix or release K upon drying. This study was conducted to evaluate the impacts of moisture content on STK levels and the relationship between STK level changes and soil K critical values. Five field sites were established throughout Indiana from 1998 to 2002. Sites were cropped in a soybean-corn rotation. Four different rates of K fertilizer (0, 67, 134, 202 kg K₂O ha⁻¹) were applied annually. Several soil samples from each site were picked to provide a range in Mehlich-3 STK values from 30 to 200 mg kg⁻¹. The dry soil samples were rewetted to field capacity and incubated at 25 ºC for 21 days before splitting into three subsamples for different drying methods (moist, air-dry, and oven-dry at 40 ºC). Each sample was extracted with Mehlich-3 to assess soil available K. The results showed that mehlich-3 STK levels did not differ between the air-dried and oven-dried treatment. Soils with low STK levels released K, while soils with high STK levels fixed K upon drying. The equilibrium concentration of soil exchangeable K (at which no change occurs in STK upon drying) varied with soils (104 to 241 mg kg⁻¹), and was positively related to the predicted soil K critical value.
6.2 Introduction

Currently, soil-test based K fertilizer recommendations are widely used throughout the US. Through a soil test, the quantity of available K in the soil is measured. The current soil test K (STK) level is compared with the K demands of crops to determine if additional fertilizer input is necessary and, if so, how much K fertilizer should be applied. Therefore, soil test results are critical to determine accurate soil fertilizer application rates. However, current studies often suggest poor relationships between STK levels and yield response (McLean, 1976; Cassman et al., 1990), indicating possible existing errors in soil K testing.

Soil testing labs typically oven-dry soil samples for convenience, which might not be a best assessment of soil available K. Previous studies have found that soil moisture content has a dramatic impact on soil K dynamics (Thomas and Hipp, 1968), because drying soil samples changes the soil solution’s ionic strength and solution K concentration which results in fixation or release of soil K (Brouder, 2010). For example, assuming a soil has a gravimetric moisture content of 0.28 ml H₂O g⁻¹ soil and a solution K concentration of 30 mg L⁻¹, after soil moisture content is reduced to a 0.20 ml H₂O g⁻¹ soil, soil solution K concentration would be 42 mg L⁻¹ given that no K adsorption on the soil particles occurred. This increase in soil solution K will shift the equilibrium condition among different forms of soil K. However, the nature of this shift is still not well understood.

In addition, soil samples taken in a dry season may also provide misleading results for STK levels. Many studies have shown that STK levels vary for soil samples collected at different times. Liebhardt and Teel (1977) measured STK levels in soil samples taken periodically after crop harvest from 28 unfertilized plots in Delaware. They found that STK values gradually increased from October until late May. Childs and Jencks (1967) reported low available soil K levels in September, which increased and reached a maximum during the winter months (November to February), then decreased in the spring, and reached the lowest
STK level in early summer. Seasonal differences in STK levels were also reported by Vitko et al. (2010). They found the difference between STK levels in samples collected in fall versus in spring varied greatly from site to site and year to year. Mallarino et al. (2011) also indicated that the effect of sample date on STK levels was not consistent but site-specific. Large variations of STK across fields were observed in this study as well. These observations may be partially attributed to the variations in soil moisture content at the time the soil samples were collected.

Another aspect of making accurate K fertilizer recommendations is to determine the STK level that coincides with optimum crop growth, which is also called the critical level. Any STK level below the critical level indicates that the nutrient in the soil is deficient for optimum crop growth (Vitosh et al., 1995). When the soil test level is above the critical level, fertilizer additions may still be necessary to maintain the soil test level, even though no yield response will be observed.

Accurate soil test critical levels are the key to optimizing fertilizer recommendations. Soil test K critical levels are commonly determined from long-term field studies. Vitosh et al. (1995) predicted STK critical levels for Indiana, Michigan and Ohio through the following algorithm:

\[ K \text{ Critical level} = 75 + 2.5 \times CEC \]

where CEC is the abbreviation for soil cation exchange capacity. However, this model may not be reliable to predict the K critical level in soils with appreciable amounts of non-exchangeable K. Cox et al. (1999) reported critical levels can be well predicted \((R^2=0.99)\) using the model:

\[ K \text{ Critical level} = 34.5 - 3.41 \times \text{Illite K}^+ + 3.52 \times CEC, \]

where illite K is the nonexchangeable K concentration \((\text{g K kg}^{-1})\) in the soil measured by sodium tetraphenylboron (STPB) extraction after a 7-d incubation.
This model has not been widely accepted for the prediction of soil K critical levels, since the STPB extraction is not widely used by commercial soil testing laboratories and it has not been tested in the field.

Previous studies have found that the impact of sample drying on STK level changes is highly depending on the equilibrium concentration of soil exchangeable K. At this level no changes in exchangeable K concentration would be observed upon drying. The equilibrium level of K varies among soils (196 mg K kg$^{-1}$ in Cook and Hutchenson, 1960; 175 mg K kg$^{-1}$ in Dowdy and Hutchenson, 1963; 420 mg K kg$^{-1}$ in Haby et al., 1988), and is related to soil mineralogical properties (Haby et al., 1990). Barbagelata (2006) also indicated that the difference between exchangeable K levels in dried soils and moist soils had a positive linear relationship with soil CEC when it was expressed in absolute values. However, no study has been conducted to investigate the relationship between the equilibrium concentration of K and soil K critical level.

The objectives of this study are to i) find out how Mehlich-3 extractable K content varies under different soil moisture conditions (moist, air-dry, oven-dry) in five soils; and ii) evaluate the relationship between the equilibrium level of K and the soil K critical level.

6.3 Materials and Methods

Five field sites were established at Davis-Purdue Agricultural Center (DPAC), Northeast-Purdue Agricultural Center (NEPAC), Pinney-Purdue Agricultural Center (PPAC), Southeast-Purdue Agricultural Center (SEPAC), and Throckmorton-Purdue Agricultural Center (TPAC) from 1998 to 2002 by Sylvie Brouder. The soil taxonomic class and selected soil chemical and physical properties for each location are presented in Table 6.1. All sites were cropped in a soybean-corn rotation and received four different rates of K fertilizer (0, 67, 134, 202 kg K$_2$O ha$^{-1}$) for 4 years.
Soil samples were collected at two depths, 0-10 cm and 10-20 cm. After taking the samples back to the laboratory, they were air dried, sieved to 2 mm, and stored at room temperature before any analysis. According to prior Mehlich-3 STK results, we selected 91 samples to provide a range of STK values from 30 to 200 mg kg\(^{-1}\). These samples were rewetted to field capacity, placed in plastic cups and incubated for 21 days at 25 °C.

After 21 days of incubation, soil samples were split to undergo different drying methods. One third of the sample was kept moist, one third was air-dried and one third was oven-dried at 40 °C for 16 hours. All samples were extracted by Mehlich-3 solution to assess soil available K. All K concentrations were determined using a flame photometer.

All statistical analyses were performed with version 9.2 of SAS (SAS Institute Inc., 2008). Analysis of variance was conducted using the GLM procedure. The relationship between the equilibrium concentrations of soil exchangeable K and predicted soil K critical values was determined with the CORR procedure. A curve was fitted with version 11.0 of SigmaPlot (Systat Software Inc., 2008) for data showing the relationship between the Mehlich-3 STK level in moist soil and the percent change in STK upon drying in each soil.

6.4 Results

No significant differences (p>0.05) in Mehlich-3 STK level were observed between air-dried and oven-dried samples except for PPAC soil in which fixation of K was observed in most samples, however the amount fixed was all less than 10% (Figure 6.1). Therefore, Soil test K levels after drying are presented as the average value of air- and oven-dried samples.

Four of five soils with low STK levels released K upon drying, while soils with high STK levels fixed K upon drying. Among these soils, the highest amount of released K was 24%, while up to 15% was fixed. In Figure 6.2, a logarithmic
regression line (Y=a + b log(x)) was drawn for each soil to show the relationship. With higher R² values, soils from NEPAC and SEPAC were best fitted to this model. Unlike the soils from the other locations, soils from PPAC fixed K upon drying at both low and high STK levels; however the amount fixed was generally less than 10% (Figure 6.3).

The equilibrium concentration of soil exchangeable K (the level at which no change in STK upon drying) varied greatly among soils and it decreased in the following order: TPAC (241 mg kg⁻¹) > DPAC (173 mg kg⁻¹) > NEPAC (127 mg kg⁻¹) > SEPAC (106 mg kg⁻¹). Soils from PPAC fixed K upon drying regardless of STK level. Soil K critical levels were predicted using the models developed by Vitosh et al. (1995) and Cox et al. (1999). Calculated from the Vitosh model, the predicted soil K critical values were 106, 96, 87.5, 88, and 105 mg kg⁻¹ for soils from DPAC, NEPAC, PPAC, SEPAC, and TPAC, respectively, whereas according to the Cox model, the predicted soil K critical values were 64, 49, 45, 48, and 66 mg kg⁻¹ for soils from DPAC, NEPAC, PPAC, SEPAC, and TPAC, respectively. The equilibrium STK levels were well correlated to the critical STK values predicted by both the Cox model (r=0.92) and Vitosh model (r=0.87). Both soil CEC and clay mineralogy are important for controlling K-buffering capacity in the soil (Mengel and Busch, 1982) and most soils in Indiana are relatively high in micaceous clay minerals.

6.5 Discussion

The effect of drying on STK levels observed in our study was consistent with other research. Cook and Hutcheson (1960) concluded that the effects of drying on STK levels depend on the initial exchangeable K concentrations in the soil. When the initial exchangeable K is high, fixation occurred upon drying; while when the initial exchangeable K is low, release was observed. Jones et al. (1960) dried samples at 110°C for 24 hours, and found that the amount of exchangeable
K either increased or decreased depending on the soil type. Vitko et al. (2009) investigated the effects of different drying methods (moist, air-dry, and oven-dry) on STK level of soil samples under different K fertilizer rate treatments. Their results showed that soil samples with an initial STK level greater than 100 mg kg\(^{-1}\) showed a significant decrease in STK after both air- and oven-drying, which indicated the fixation of K upon drying. However, in some early studies (Luebs et al., 1956; Hanway and Scott, 1959), they found that the ammonium acetate extractable K concentrations in the soil tend to increase upon drying. The results found in these previous studies might be due to initially lower exchangeable K concentrations (less than 100 mg kg\(^{-1}\)) in the soils they tested, as well as using different extractants for measuring exchangeable K, as Hanway and Scott (1959) found that different extractants have different sensitivities to drying.

In our study, we found that the effect of air-drying on STK level was similar to oven-drying. However, many previous studies found that changes in exchangeable K content were greater upon oven-drying than air-drying (Cook and Hutcheson, 1960; Haby et al., 1988; Barbagelata, 2006). Jones et al. (1960) also reported that air-drying always resulted in a release of K from nonexchangeable form to exchangeable form, whereas oven-drying might increase or decrease soil exchangeable K concentration depending on soil properties. Vitko et al. (2009) found that, compared with air-drying, oven-drying significantly increased the Bray-1 STK value in only one soil out of five, so the effects of air-drying and oven-drying on soil exchangeable K level is dependent on soil type, STK level and the extractant used.

Although many studies have been conducted to investigate the effect of drying on STK levels, the mechanism(s) that controls K release or fixation in soils is still not well understood. Different mechanisms were proposed to explain such observation that soils with low STK levels released K upon drying, while soils with high STK levels fixed K upon drying. Some researchers found soils with low K-supplying potential required greater temperatures for clay minerals to collapse,
which may explain why release occurred when the initial exchangeable K was low (Cook and Hutcheson, 1960). Dowdy and Hutcheson (1963) found that soil clay mineralogy determined K release or fixation upon soil sample drying. They found that illite appeared to be the source of K release when soil is dried, while vermiculite and montmorillonite were related to K fixation. In addition, McLean and Watson (1985) stated that the release of nonexchangeable K upon drying when the STK level is low can be attributed to the expansion of layers at the edge of the micaceous clay that happened upon soil drying; while when the STK level is high, interlayer water is dried out upon soil drying, resulting in the collapse of clay minerals and fixation of K.

6.6 Conclusion

In conclusion, STK levels varied with moisture content in soils with 2:1 clay minerals. When the soil was low in K, an increase in STK occurred upon drying. However, when the soil was high in K, STK decreased upon drying. This indicated that the practice of drying prior to soil analysis used by most soil test laboratories may not be appropriate for assessing STK levels. Additionally, under dry conditions in the field, K availability will likely be overestimated in low testing soils and underestimated in high testing soils. Luebs et al. (1956) reported that crops could absorb 67 to 134 kg ha\(^{-1}\) more K when soils are moist compared to dry soils. This study also helps explain observed K deficiencies in crops during moisture stress, even on soils with relatively high STK levels.
6.7 References:


Table 6.1 Soil characterization of a bulk soil sample collected from five field sites.

<table>
<thead>
<tr>
<th>Location</th>
<th>Soil series</th>
<th>Soil taxonomic class</th>
<th>CEC $^\text{†}$ cmol$_c$ kg$^{-1}$</th>
<th>Illite K $^\text{‡}$ g kg$^{-1}$</th>
<th>Texture g kg$^{-1}$§</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPAC</td>
<td>Blount</td>
<td>Fine, illitic, mesic Aeric Epiaqualf</td>
<td>12.4</td>
<td>4.19</td>
<td>350 110 540</td>
</tr>
<tr>
<td>NEPAC</td>
<td>Glynwood</td>
<td>Fine, illitic, mesic Aquic Hapludalfs</td>
<td>8.4</td>
<td>4.39</td>
<td>270 390 340</td>
</tr>
<tr>
<td>PPAC</td>
<td>Tracy</td>
<td>Coarse-loamy, mixed, active, mesic Ultic Hapludalfs</td>
<td>5.0</td>
<td>2.13</td>
<td>180 500 320</td>
</tr>
<tr>
<td>SEPAC</td>
<td>Cobbsfork</td>
<td>Fine-silty, mixed, active, mesic Fragic Glossaqualf</td>
<td>5.2</td>
<td>1.37</td>
<td>220 150 630</td>
</tr>
<tr>
<td>TPAC</td>
<td>Toronto</td>
<td>Fine-silty, mixed, superactive, mesic Udollic Epiaqualf</td>
<td>12.0</td>
<td>3.06</td>
<td>320 80 600</td>
</tr>
</tbody>
</table>

$^\text{†}$CEC = Cation exchange capacity determined by summation of basic cations measured with Mehlich-3 extraction and acid cations extracted by Barium Acetate

$^\text{‡}$Illite K = Nonexchangeable K extracted using 7-day incubation in 0.2 M NaBPh$_4$

$^\text{§}$Determined using the dispersion and sedimentation procedure described by Jackson, 1958
Figure 6.1 The relationship between Mehlich-3 soil test K levels of oven-dried soils vs. Mehlich-3 soil test K levels of air-dried soils from five locations.
Figure 6.2 Relationship between the Mehlich-3 soil test K levels of moist soils from four locations (DPAC, NEPAC, SEPAC, and TPAC) and the percent change in soil test K upon drying as described by the logarithmic model \([Y=a + b\times\log(x)]\). Soil test K levels upon drying were presented as the mean of air- and oven-dried samples. The vertical lines showed soil K critical levels predicted using model: Critical K = 75 + 2.5×CEC (Vitosh et al., 1995). The vertical dash lines showed soil K critical levels predicted using model: Critical K = 34.5 - 3.41×illite K + 3.52×CEC (Cox et al., 1999) where illite K is measured by NaBPh₄⁺ extraction after soil was incubated in it for seven days.
Figure 6.3 Relationship between the Mehlich-3 soil test K levels of moist soils from PPAC and the percent change in soil test K upon drying. Soil test K levels upon drying were presented as the mean of air- and oven-dried samples. The vertical line showed soil K critical levels predicted using model: Critical K = 75 + 2.5×CEC (Vitosh et al., 1995). The vertical dash line showed PPAC soil K critical level predicted using model: Critical K = 34.5 - 3.41×illite K + 3.52×CEC (Cox et al., 1999) where illite K is measured by NaBPh₄⁺ extraction after soil was incubated in it for seven days.
APPENDICES
Figure A.1 Locations of seven study sites where soil sample was collected
Table A.1 Geographic coordinates of study sites for chapter 2, 3 and 5.

<table>
<thead>
<tr>
<th>Site</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACRE</td>
<td>40.48428</td>
<td>-87.00816</td>
</tr>
<tr>
<td>DPAC</td>
<td>40.24583</td>
<td>-85.15053</td>
</tr>
<tr>
<td>NEPAC</td>
<td>41.11578</td>
<td>-85.44312</td>
</tr>
<tr>
<td>PPAC</td>
<td>41.45119</td>
<td>-86.93895</td>
</tr>
<tr>
<td>SEPAC</td>
<td>39.04344</td>
<td>-85.52725</td>
</tr>
<tr>
<td>SWAPC</td>
<td>38.74530</td>
<td>-87.48169</td>
</tr>
<tr>
<td>TPAC</td>
<td>40.26856</td>
<td>-86.87787</td>
</tr>
</tbody>
</table>
## Appendix B  Summary of Analysis of Variance Tables

Table B.1 Analysis of variance for mineralized N evaluated by different incubation methods

<table>
<thead>
<tr>
<th>Incubation method</th>
<th>Source of Var.</th>
<th>DF ‡</th>
<th>NO3⁻</th>
<th>NH4⁺</th>
<th>Total P value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leaching incubation</td>
<td>Soil</td>
<td>7</td>
<td>0.0021</td>
<td>0.8329</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.2987</td>
<td>0.3083</td>
<td>0.2659</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cups incubation</td>
<td>Soil</td>
<td>7</td>
<td>&lt;0.0001</td>
<td>0.4905</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.6170</td>
<td>0.2173</td>
<td>0.2865</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Greenhouse</td>
<td>Soil</td>
<td>7</td>
<td>N/A</td>
<td>N/A</td>
<td>0.0002§</td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>N/A</td>
<td>N/A</td>
<td>0.1439</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

† Var.-variance
‡ DF - degrees of freedom
§ Total plant uptake N under greenhouse conditions
Table B.2 Analysis of variance for laboratory predicted mineralizable N (N₀), mineralization rate constant (k) and products of N₀⨉k

<table>
<thead>
<tr>
<th>Variable</th>
<th>Source of Variance</th>
<th>DF</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₀</td>
<td>Soil</td>
<td>6</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Depth</td>
<td>3</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Soil×Depth</td>
<td>18</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.9305</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>54</td>
<td>-</td>
</tr>
<tr>
<td>k</td>
<td>Soil</td>
<td>6</td>
<td>0.0306</td>
</tr>
<tr>
<td></td>
<td>Depth</td>
<td>3</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>Soil×Depth</td>
<td>18</td>
<td>0.1269</td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.7238</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>54</td>
<td>-</td>
</tr>
<tr>
<td>N₀×k</td>
<td>Soil</td>
<td>6</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Depth</td>
<td>3</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Soil×Depth</td>
<td>18</td>
<td>0.0108</td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.5442</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>54</td>
<td>-</td>
</tr>
</tbody>
</table>

† DF-degrees of freedom
Table B.3 Analysis of variance for pH, exchangeable (Ex_K) and nonexchangeable K (Nonex_K) levels in Chalmers, Pewamo, Pinhook, and Raub soils after injection of anhydrous ammonia.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Source of Variance</th>
<th>DF†</th>
<th>pH</th>
<th>Ex_K</th>
<th>Nonex_K</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance</td>
<td>6</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>Chalmers</td>
<td>Time</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0711</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance×Time</td>
<td>12</td>
<td>0.0016</td>
<td>0.0029</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.6289</td>
<td>0.9891</td>
<td>0.7507</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance</td>
<td>6</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>Pewamo</td>
<td>Time</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance×Time</td>
<td>12</td>
<td>0.0006</td>
<td>0.0014</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.6426</td>
<td>0.0630</td>
<td>0.2928</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance</td>
<td>6</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.8484</td>
<td></td>
</tr>
<tr>
<td>Pinhook</td>
<td>Time</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0047</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance×Time</td>
<td>12</td>
<td>&lt;0.0001</td>
<td>0.0004</td>
<td>0.4278</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.0048</td>
<td>0.3075</td>
<td>0.4115</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance</td>
<td>6</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.2074</td>
<td></td>
</tr>
<tr>
<td>Raub</td>
<td>Time</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.0022</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distance×Time</td>
<td>12</td>
<td>&lt;0.0001</td>
<td>0.2120</td>
<td>0.1340</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.1957</td>
<td>0.3131</td>
<td>0.1694</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

† DF-degrees of freedom
Table B.4 Analysis of variance for soil test K levels as affected by drying.

<table>
<thead>
<tr>
<th>Location</th>
<th>Source of Variance</th>
<th>DF†</th>
<th>Air-dry vs Oven-dry</th>
<th>Moist vs Oven-dry</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat</td>
<td>1</td>
<td>0.4921</td>
<td>0.0064</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample</td>
<td>19</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Sample</td>
<td>19</td>
<td>0.3857</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0070</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Block</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0080</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>76</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>DPAC</td>
<td>Treat</td>
<td>1</td>
<td>0.3989</td>
<td>0.0184</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample</td>
<td>16</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Sample</td>
<td>16</td>
<td>0.3498</td>
<td>0.0042</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.0046</td>
<td>0.2646</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Block</td>
<td>2</td>
<td>0.0012</td>
<td>0.0409</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NEPAC</td>
<td>Treat</td>
<td>1</td>
<td>0.0132</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample</td>
<td>18</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Sample</td>
<td>18</td>
<td>0.7879</td>
<td>0.1055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>0.0314</td>
<td>0.2245</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Block</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0078</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PPAC</td>
<td>Treat</td>
<td>1</td>
<td>0.3934</td>
<td>0.4847</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample</td>
<td>14</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Sample</td>
<td>14</td>
<td>0.1187</td>
<td>0.0157</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Block</td>
<td>2</td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SEPAC</td>
<td>Treat</td>
<td>1</td>
<td>0.7990</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample</td>
<td>19</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Sample</td>
<td>19</td>
<td>0.9036</td>
<td>0.1119</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Block</td>
<td>2</td>
<td>&lt;0.0001</td>
<td>0.0135</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treat×Block</td>
<td>2</td>
<td>0.0015</td>
<td>0.0306</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>73</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

† DF-degrees of freedom
Table C.1 Soil moisture contents at water retentions of 10 kPa, 33 kPa, 50 kPa, and 100 kPa for selected soils (unit: g g$^{-1}$).

<table>
<thead>
<tr>
<th>Soil</th>
<th>10 kPa</th>
<th>33 kPa</th>
<th>50 kPa</th>
<th>100 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blount</td>
<td>0.27</td>
<td>0.25</td>
<td>0.24</td>
<td>0.22</td>
</tr>
<tr>
<td>Chalmers</td>
<td>0.31</td>
<td>0.28</td>
<td>0.26</td>
<td>0.23</td>
</tr>
<tr>
<td>Cincinnati</td>
<td>0.24</td>
<td>0.21</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>0.26</td>
<td>0.23</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td>Pewamo</td>
<td>0.34</td>
<td>0.30</td>
<td>0.30</td>
<td>0.24</td>
</tr>
<tr>
<td>Pinhook</td>
<td>0.24</td>
<td>0.20</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>Raub</td>
<td>0.27</td>
<td>0.23</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>Tracy</td>
<td>0.20</td>
<td>0.18</td>
<td>0.16</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Table C.2 Soil moisture contents at water retention of 10 kPa for selected soils at four depths.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth</th>
<th>10 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>g g$^{-1}$</td>
</tr>
<tr>
<td>Chalmers-Raub</td>
<td>0-15</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.37</td>
</tr>
<tr>
<td>Blount-Pewamo</td>
<td>0-15</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.38</td>
</tr>
<tr>
<td>Rawson-Haskins</td>
<td>0-15</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.28</td>
</tr>
<tr>
<td>Sebewa</td>
<td>0-15</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.30</td>
</tr>
<tr>
<td>Cobbsfork</td>
<td>0-15</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.35</td>
</tr>
<tr>
<td>Ade-Lyles</td>
<td>0-15</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.18</td>
</tr>
<tr>
<td>Toronto</td>
<td>0-15</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>15-30</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>30-45</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>45-60</td>
<td>0.37</td>
</tr>
</tbody>
</table>
VITA

Chun Zhao earned her Bachelor of Science degree in Soil and Agrochemistry at Northwest Agriculture and Forestry University in China in 2007. She started her postgraduate study at Purdue University in August, 2007 to work with Dr. Brad Joern and Dr. Jim Camberato in the area of Soil Fertility and Chemistry. She received the Marvin and Barbara Phillips Scholarship as recognition of her research work. Chun’s interests and enthusiasm in Soil Science not only showed through her research but also her active involvement in teaching activities. She assisted in the instruction of the courses AGRY 255 (Introduction to Soil Science) and AGRY 365 (Soil Fertility) and received the outstanding graduate teaching award in 2012.