Cool Season Mineralization of Recalcitrant Organic Nitrogen in Manured Soils

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Cool Season Mineralization of Recalcitrant Organic Nitrogen
in Manured Soils

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Nitrate is the predominant form of nitrogen (N) used by agricultural crops, but can contaminate water resources or denitrify to the greenhouse gas nitrous oxide (N_2O). Trends toward larger livestock farms and new legislation in developed countries have made N management increasingly important in manured fields. Recalcitrant organic N compounds in manure applied to agricultural fields mineralize slowly, contributing nitrate (NO_3^-) to the soil for years after application. With long-term manure application, the soil recalcitrant organic N pool may grow to the point that its annual mineralization generates significant masses of NO_3^-. Some of this recalcitrant organic N mineralization will occur during the cool season when crop N uptake is low and NO_3^- is especially prone to loss.

A simple model, RONDIMS, was developed to estimate the increase of recalcitrant organic N in manured soils over time. Using input values from the literature, RONDIMS predicted that recalcitrant organic N would approach a steady-state in 25 years if all crop N was supplied by manure. RONDIMS also predicted that cool season

recalcitrant organic N mineralization in manured fields could be an important contributor to leached N. In the RONDIMS simulations, cool season N mineralization was significant whether or not manure was applied at the correct rate and time.

This project used an *in situ* methodology, Ion Exchange Resin / Soil Cores (IER/SC), to measure cool season recalcitrant organic N mineralization in manured soils from Oregon's Willamette Valley. In five of seven soils studied, cool season organic N mineralization was equal to or greater than 20 mg N kg^{-1} soil by early February. By 18 May, all soils tested had mineralization exceeding 20 mg N kg^{-1}.

This project compared two methods of IER/SC: disturbed and undisturbed. Of 13 samples, three had N mineralization significantly greater ($p < 0.10$) in disturbed, as compared to undisturbed, cores. However, disturbed cores had less variable N mineralization, which allows the use of fewer cores in mineralization studies. Thus, this study indicates a trade-off in the two IER/SC methods: disturbed cores have lower variability but also have artificially increased N mineralization in some situations.

CHAPTER 1. INTRODUCTION

1.1 Overview

Nitrogen (N) is the most important mineral nutrient for most agricultural crops and nitrate (NO_3^-) is the predominant form of N used by crops. Nitrate can also be an environmental contaminant. Contamination occurs directly when NO_3^- leaches to groundwater (Heatwole et al., 1990) or runs off to surface water (Bushee et al., 1998), and indirectly when NO_3^- denitrifies to the greenhouse gas nitrous oxide (Lowrance et al., 1998). The aim of nitrogen management in agriculture is simple: supply enough NO_3^- to produce acceptable yields, but minimize the mass of nitrate available for export via surface water runoff, leaching and denitrification.

Although simple, this goal is not easily achieved, especially on fields fertilized with manure. Trends toward the concentration of livestock onto fewer farms with greater numbers of animals, and new legislation regulating the use of manure in the United States and Europe, have made N management goals increasingly important (USDA and EPA, 1999). One reason N management is difficult on livestock farms is that manure supplies N in a variety of forms that vary considerably in their availability to plants (Gilmour et al., 1977).

Ammonium (NH_4^+) and labile (quickly mineralized) organic forms of N in manure convert to NO_3^- and are essentially completely available to plants during the growing season in which they are applied. Applying manure to synchronize the availability of NH_4^+ and labile organic N compounds with crop N uptake is relatively straightforward (Hart et al., 1997).

However, manure also contains recalcitrant organic N compounds that mineralize[1] slowly and may not be converted to NO_3^- for many months or years after application. With long-term manure applications, the recalcitrant organic N pool may become large enough that even a slow mineralization rate can generate significant amounts of NO_3^-. During the cool season, when crop N uptake is low, any N that mineralizes is prone to contaminate ground and surface water or to denitrify into nitrous oxides (Hofman et al., 1994). This project seeks to examine the importance of cool season mineralization of recalcitrant organic N in manured soils and to compare two common methods of *in situ* N mineralization measurement. The project is organized into the following sections.

1.2 Literature review

It is important to note that the terms "recalcitrant" and "labile" organic N do not have universally accepted definitions. Also, the term "recalcitrant" itself often causes confusion because it implies a substance that does not mineralize at all. Still, these terms are used throughout this study because they are part of the commonly used language in the literature of N mineralization. The literature review provides examples of labile and recalcitrant organic compounds. This distinction between recalcitrant and labile is a simplification of actual biological systems in which mineralization occurs, but it has proven useful in the literature and in this project.

The first objective of the literature review was to summarize the peer-reviewed literature on the subject of N mineralization in manured soils. N mineralization in general has been the subject of numerous studies, many of which are cited in the literature review. However, cool season mineralization of recalcitrant organic N in manured soils has received little attention in the literature.

Several papers (Hofman et al., 1994; Zebarth et al., 1995; Ilsemann et al., 2001; Sullivan and Cogger, 2003) provide recommendations for maximum levels of residual soil NO_3^-, (i.e., that which remains in the soil profile at the end of the warm season.)

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[1] Throughout this document, the term "N mineralization" will be used to describe biologically-driven chemical reactions that produce NH_4^+ from organic compounds containing N.

Residual soil NO_3^- is prone to leaching, runoff and denitrification during the cool season when crop N uptake is low and precipitation exceeds evapotranspiration. There are no published recommendations for maximum levels of cool season N mineralization, however Sullivan and Cogger (2003) recommend changes in manure management practices if residual soil NO_3^- equals or exceeds 20 mg N kg^{-1} (approximately 84 kg N ha^{-1}) in western Oregon and Washington[2]. Because NO_3^- formed by recalcitrant organic N mineralization *during* the cool season is subject to the same loss pathways as residual soil NO_3^- present at the *beginning* of the cool season, this project used 20 mg N kg^{-1} as a benchmark for judging whether cool season N mineralization in the fields studied was excessive. The Sullivan and Cogger (2003) review also notes that soil NO_3^- in western Oregon is most vulnerable to loss before cool season grasses begin an accelerated uptake of N from the soil in late winter. This accelerated N uptake by grasses in Oregon's Willamette Valley begins on the "T-Sum 200" date in late January or early February[3].

The second objective of the literature review was to determine the conceptual/mathematical model best suited to understanding cool season N mineralization. The review concludes that a double pool first order equation using temperature-adjusted rate constants would be best suited because it is relatively simple, yet adequately captures the processes involved (Benbi and Richter, 2002).

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[2] Throughout this document, soil N concentrations are given in terms of mg N kg^{-1}, in which mg N refers to the mass of elemental N and kg^{-1} refers to the mass of dry soil.

[3] The T-Sum 200 date is calculated with Growing Degree Days (*GDD*), a measure of cumulative heat. *GDD* are calculated by summing the difference between each day's mean air temperature (ºC) and a given base temperature. If the mean daily temperature is less than or equal to the base temperature, no *GDD* accumulate for that date. For the purpose of estimating the date cool season grasses begin accelerated N uptake in late winter, the base temperature is 0ºC and calculations extend from 1 January until 200 *GDD* are reached (the T-Sum 200 date). In this study, *GDD* are sometimes used for purposes other than calculating the T-Sum 200 date. When *GDD* are used for other purposes, the base temperature and beginning date of calculations are noted.

The third objective of the review was to compare *in situ* methods for investigating cool season mineralization of recalcitrant organic N on numerous manured sites. The review concludes that the use of ion exchange resin / soil cores (IER/SC) is best suited to studying this process because IER/SC are relatively simple and inexpensive, have been widely used in warm-season studies and allow for exchange of gases and water while soils are incubated in natural settings (Kolberg et al., 1997). There are two common methods of preparing IER/SC (disturbed and undisturbed), but there are apparently no published studies comparing these two methods.

1.3 Recalcitrant Organic N Dynamics in Manured Soils (RONDIMS), a model

In order to quantitatively examine the role of recalcitrant organic N mineralization, a simple process-based model, the Recalcitrant Organic N Dynamics in Manured Soils (RONDIMS) was developed. It is a relatively simple spreadsheet model that is easily parameterized. Although RONDIMS focuses on recalcitrant organic N mineralization, it also includes modules that predict labile organic N mineralization, ammonia (NH_3) volatilization, crop N uptake and N leaching.

RONDIMS was used to simulate seven cropping scenarios: four with optimal manure application rates and timing and three based on farm records. The scenarios were set on a silt loam soil in Oregon's Willamette Valley. Weather data from Corvallis Oregon were used in the modeling simulations. Each RONDIMS modeling scenario was adjusted until recalcitrant organic N reached a steady-state level, simulating fields with long term manure applications. RONDIMS predicted that steady-state recalcitrant organic N pools would be approached after manure was applied to meet all crop N needs for 20 to 25 years.

The model predicted differences in hydrology for the seven scenarios. In RONDIMS the "cool season" is defined as the period during which the rolling 10-day average precipitation exceeds the rolling 10-day average evapotranspiration. Over the 10-year modeling period (1995 to 2005), corn cropping systems had a cool season of 24

September to 18 May and perennial grass systems had a cool season of 29 September to 17 April.

RONDIMS predicted that recalcitrant organic N mineralizing during the cool season was an important contributor to leached N. The optimized scenarios applied manure just before maximum crop N uptake and at rates that just supplied the necessary amount of N to produce high yields. The farm record scenarios generally applied manure too late in the year for optimal crop utilization and also tended to apply much more N than was needed by the crop. Because of this, the optimized scenarios had lower residual mineral N in the fall (11 to 31 kg ha^{-1}) than did the farm record scenarios (40 to 144 kg ha^{-1}). However, the cool season mineralization of recalcitrant organic N was high for both optimized (28 to 77 kg ha^{-1}) and farm record (33 to 52 kg ha^{-1}) scenarios. Thus, according to RONDIMS, cool season N mineralization is significant in these cropping systems whether or not manure is applied at the correct rate and time. Using the method outlined by Fried et al. (1976), RONDIMS predicts that mean leachate N concentrations from each of the farm record scenarios and the optimized corn-solid manure scenario would equal or exceed the 10 mg N L^{-1} drinking water standard.

RONDIMS also predicted that, with appropriate timing and methodology of fall soil collection, the labile organic N concentration in IER/SC could be minimized, thus allowing *in situ* studies that decouple the dynamics of labile versus *RON* mineralization.

1.4 Cool season mineralization of recalcitrant organic N in undisturbed cores of manured soils

The objectives of the *in situ* experiments described in this section were to (1) quantify N mineralization from recalcitrant organic N in soils with a long history of manure application; and (2) to examine the relationship between cool season recalcitrant organic N mineralization, a fall mineralizable N index, the % total soil N and residual fall soil mineral N.

Ion exchange resin / soil core (IER/SC) tubes were prepared with relatively undisturbed soils from five fields that had a history of long term manure application and one field that had not received manure in at least 10 years. The IER/SC method is an accepted procedure for measuring *in situ* soil N mineralization rates by incubating soil in tubes that are open to water and gas fluxes at the top and bottom (Eghball, 2000). Ion exchange resin placed in the bottom of each tube captures NO_3^- and NH_4^+ that leaches out of the soil. The soils for the IER/SC were collected in early October, a time that RONDIMS predicted minimal labile organic N concentrations in these manured systems. Thus, most of the N mineralization that occurred in the IER/SC was due to recalcitrant organic N.

The IER/SC experiments were conducted in the winter of 2003 to 2004 and again in the winter of 2004 to 2005. Soil was analyzed for mineral N, a mineralizable N index and total N before incubation. Incubation began in late October or early November. IER/SC were analyzed to determine N mineralization in February 2004, May 2004, December 2004 and February 2005. The February analyses were done at T-Sum 200. Nitrate is especially vulnerable to loss before T-Sum 200, because cool season grasses have little uptake of mineral N before that date.

All tested soils exceeded 20 mg N kg^{-1} residual fall NO_3^-, with values ranging from 27 to 138 mg N kg^{-1}. In five of the seven tested soils, organic N mineralization was equal to or greater than 20 mg N kg^{-1} by T-Sum 200. Values ranged from 5 to 37 mg N kg^{-1} and averaged 22.9 mg N kg^{-1}. By 18 May 2004, all soils tested had mineralization exceeding 20 mg N kg^{-1}. The N mineralization measurements in this experiment were conservative. Since the experimental design did not allow for measuring denitrification, it is likely that actual N mineralization was greater than the values reported here. Mineralizable N analyses conducted just before soils were incubated had no value in predicting mineralization rates in either year of the study. Also, neither the % total soil N nor the residual fall soil mineral N were good predictors of cool season mineralization.

In the fall, most of the mineral N was present as NO_3^- in the core soil. By T-Sum 200, most of this NO_3^- as well as most of the newly mineralized N had leached to the IER below the soil, affirming the concept that N mineralized before T-Sum 200 is highly vulnerable to loss. Much of the N that mineralized between February and May remained in the soil.

The mean cool season N mineralization (22.9 mg N kg^{-1}) from the beginning of incubation in the fall to T-Sum 200 in February was less than the mean residual soil mineral N concentration (59.7 mg N kg^{-1}) in the fall. Furthermore, cool season N mineralization was less than residual fall soil mineral N concentration in every field studied and in both years, although not significantly in all cases. These results demonstrate that, although cool season mineralization contributed a significant mass of NO_3^- prone to loss in the fields studied, residual soil mineral N contributed even more NO_3^-. These results are consistent with the predictions of RONDIMS in Chapter 3 of this project.

On manured fields, residual soil mineral N is best reduced by applying manure at the correct rate and time (Sullivan and Cogger, 2003). RONDIMS simulations (Chapter 3) demonstrated that perennial or cool season annual grass cover crops can reduce losses of N mineralized during the cool season. Thus, the results of this study suggest that correct rate and timing of manure applications *and* cool season grass crops may be needed to reduce losses of NO_3^- from manured fields during the cool season.

This project introduces the concept of “mineralization degree days” (*MDD*), a calculation similar to the widely used growing degree days, but which accounts for the exponential effect of temperature on mineralization predicted by the Arrhenius Equation (Vanotti et al., 1995). Nitrogen mineralization per *MDD* varied considerably between fields, which is consistent with the expected widely different recalcitrant organic N pool sizes between fields. Mineralization per *MDD* generally increased over time within fields, which is not consistent with the hypothesis that the recalcitrant organic N pool within a field does not change appreciably over one season. This indicates that the size of the recalcitrant organic N pool was not always the driving force in cool season net N mineralization. Other factors, such as denitrification rate or C:N ratio of substrates may have also played important roles.

1.5 Comparison of disturbed and undisturbed soil core methods

The objectives of this section were to compare the mean N mineralization, N mineralization variability, soil temperature and soil moisture in IER/SC filled with disturbed versus undisturbed soils to determine if the two methods produced different results. Theoretically, disturbed soils should exhibit greater N mineralization due to destruction of the protective capacity of soil aggregates (Franzluebbers and Arshad, 1997). The experiments to compare disturbed and undisturbed IER/SC were conducted concurrently with the experiments described above.

Of 13 field/incubation period combinations, 9 exhibited greater N mineralization in disturbed cores, as compared to undisturbed cores. Three of these were statistically significant ($p < 0.10$). The situations in which disturbed core mineralization exceeded undisturbed core mineralization were in Field A and in Trial period 3. Field A had a low (11.9%) clay content and low (1.20%) carbon content. A low clay content soil would be expected to have less protected organic matter, and less organic matter overall, than a high clay content soil (Van Veen et al., 1984). However, low clay soils may have a greater percentage of their protected organic N sequestered inside aggregates rather than adsorbed onto clay minerals (Franzluebbers, 1999). This could explain the increased N mineralization in Field A disturbed versus undisturbed cores. Trial period 3 was only 49 days long. Possibly, the short-term acceleration of N mineralization in disturbed cores during this period was due to the release of low C:N ratio compounds from inside soil aggregates (Hassink, 1992).

The disturbed cores had less variability in N mineralization than the undisturbed cores. Since reduced variability allows the use of fewer cores in mineralization studies and since the construction and analysis of cores is expensive, decreased variability is advantageous. Overall, this study indicates that there appears to be a trade-off in the use of disturbed versus undisturbed IER/SC incubations to study N mineralization: disturbed cores in this trial had lower variability, but experienced artificially increased N mineralization rates in some situations.

The mean core temperatures and the daily temperature ranges were not significantly different between disturbed and undisturbed cores at any time. There was also little difference between the mean core temperatures and the temperature of the field soil outside of the cores (at the same depth) at any time. During the winter incubations, there was little difference between the daily temperature ranges inside and outside of the cores. During the summer incubation, however, the daily temperature ranges inside the cores were 2 to 3ºC wider than the soil temperature at the same depth outside the cores.

The mean soil water potentials were similar for disturbed and undisturbed cores during both summer and winter incubations. In the summer incubation, the soil in the field outside the cores was drier (the water potential was more negative) than either the disturbed or undisturbed core soil, although this difference was not statistically significant. This tendency of IER/SC to be artificially moist compared with natural field soils has been noted by others (Myrold et al., 1992). During the winter incubation, this effect was negligible, due to the low evapotranspiration rates at that time.

1.6 Overall conclusions

a. Cool season recalcitrant organic N mineralization in manured soils can generate excessive amounts of soil NO_3^-, based on recommended maximum levels for fall residual NO_3^-.

b. The cool season recalcitrant organic N that mineralized in the soils examined *in situ* in this study was less than the fall residual mineral N in those soils, although not always significantly so.

c. Seeding winter grass crops may be an appropriate strategy to reduce the environmental impact of cool season N mineralization. However, grass crops take up little N before T-Sum 200 (November through January in Oregon's Willamette Valley). The results of this study suggest that, in some fields and some years, cool season mineralization of recalcitrant organic N may result in NO_3^- leachate concentrations that would exceed the 10 mg N L^{-1} drinking water standard whether or not manure was applied at the correct rate and time and whether or not a winter cover crop was grown.

d. The mineralizable N index described in the *in situ* experimental methodology, the % total soil N and the residual fall soil NO_3^- concentration were not useful predictors of cool season recalcitrant organic N mineralization Continued work is needed to develop a methodology to make accurate cool season N mineralization predictions.

e. Both disturbed and undisturbed IER/SC are effective means of measuring cool season recalcitrant organic N mineralization under the conditions described in this project. Disturbed IER/SC offered the advantage of less variability in N mineralization rates. However, disturbed IER/SC resulted in increased N mineralization compared to undisturbed cores in some situations.

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CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

Nitrogen (N) is the most important mineral nutrient for most agricultural crops and nitrate (NO_3^-) is the predominant form of N used by crops. Nitrate can also be an environmental contaminant. Contamination occurs directly when NO_3^- leaches to groundwater or runs off to surface water and indirectly when NO_3^- denitrifies to the greenhouse gas nitrous oxide. The aim of nitrogen management in agriculture is simple: supply enough NO_3^- to produce acceptable yields, but minimize the mass of NO_3^- available for export via surface water runoff, leaching and denitrification.

Although simple, this goal is not easily achieved, especially on fields fertilized with manure. Trends toward the concentration of livestock onto fewer farms with greater numbers of animals and new legislation regulating the use of fertilizer and manure in the United States and Europe have made N management goals increasingly important. One reason N management is difficult on livestock farms is that manure supplies N in a variety of forms that vary considerably in their availability to plants.

Ammonium (NH_4^+) and labile (quickly mineralized) organic forms of N in manure convert to NO_3^- and are essentially completely available to plants during the growing season in which they are applied. Applying manure to synchronize the availability of NH_4^+ and labile organic N compounds with crop N uptake is relatively straightforward.

However, manure also contains recalcitrant organic N compounds that mineralize slowly and may not be converted to NO_3^- for many months or years after application. With long-term manure applications, the recalcitrant organic N pool potentially can become large enough to generate significant amounts of NO_3^-. When crop N uptake is low during the cool season, any N that is mineralized is prone to contaminate ground and surface water or to denitrify into nitrous oxides.

Although many studies of N mineralization in soils have been completed, little attention in the scientific literature has been given to the mineralization of recalcitrant organic N during the cool season. Also, cool season mineralization of recalcitrant organic N is a process that is essentially ignored in public policy considerations of livestock agriculture.

2.2 Nitrogen on livestock farms

2.2.1 The N cycle

Figure 2.1 presents a simplified conceptual model of the N cycle on a farm field that receives applications of manure (Tisdale and Nelson, 1975). The highlighted cells are the focus of this study. In nature, N occurs as gases: dinitrogen (N_2), nitrous oxide (N_2O) and ammonia (NH_3); as ions: nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+); and as components of various organic compounds such as proteins, chitin, peptidoglycans and nucleic acids (Paul and Clark, 1989). In Figure 2.1, N oxidation states range from -3 (NH_4^+) to +5 (NO_3^-).

Because of its propensity to form gaseous compounds and readily leached anions, N is easily lost from soil ecosystems. At the same time, N is the mineral nutrient that is most likely to limit the growth of non-leguminous crop plants (Meisinger et al., 1992). Because it is both vital to plant nutrition and easily lost from soil ecosystems, soil N has been the subject of many studies, especially as related to manured soils. Few studies, however, have focused on the mineralization of organic N compounds during the cool season when crops are either not present or tend to be dormant.

Animal manure can be a good source of mineral N for crops (Gollehon et al., 2001) and manure applications can result in yields comparable to commercial N fertilization (Cherney et al., 2002). However, animal manure applications to cropland increase the likelihood of NO_3^- runoff to surface water (Cameron, 1986; Bushee et al., 1998), which may impact reservoirs used for drinking water, contribute to the eutrophication of some surface water bodies and lead to hypoxic zones in marine systems (EPA, 2002). Manure applications can increase leaching of NO_3^- to groundwater, which can impact aquifers used for drinking water (Heatwole et al., 1990; Holloway et al., 1996). For example, 13 to 28% of applied N was lost as NO_3^- leaching after cow (*Bos taurus*) slurry was applied in September to fallowed sandy loam cropland in the UK (Beckwith et al., 1998). The amount of NO_3^- that leaches following manure applications is highly variable and depends on many factors, including weather, soil, amount of N applied, timing of N applications and type of vegetation. For example, less than 1% of N was lost via NO_3^- leaching when dairy pond sludge was applied to perennial ryegrass (*Lolium perenne* L.) / white clover (*Trifolium repens*) pasture on a fine sandy loam soil in New Zealand (Cameron et al., 1996).

Manure applications can increase the rate of denitrification and result in emissions of the greenhouse gas N_2O, which has a global warming potential of 310 CO_2 equivalents per N_2O molecule (Six et al., 2002). Annual denitrification rates ranged from 11 to 37% of total N applied as liquid dairy manure at four application rates (246 to 802 kg N ha^{-1}) on a Georgia sandy loam (Lowrance et al., 1998). A silty clay loam planted to grain crops in the UK had farmyard manure treated plots with seasonal denitrification losses of up to 2 kg ha^{-1} day^{-1}, compared with denitrification losses of 0.6 kg ha^{-1} day^{-1} on plots receiving only inorganic N fertilizer (Goulding and Webster, 1989).

In planning manure and fertilizer applications, farmers must consider that no plant is perfectly efficient at absorbing N, or any other mineral, from the soil. This requires that some amount of N be applied in addition to that taken up by the crop, which results in residual NO_3^- remaining in the root zone at the end of the growing season. The amount of fall residual NO_3^- has been used to determine whether warm season N application rates were excessive (Sullivan and Cogger, 2003). Because precipitation rates are often high, evapotranspiration rates are low and plant N uptake is low during the cool season, residual soil nitrate is quite vulnerable to the leaching, runoff and denitrification losses discussed above. Some European states regulate permissible levels of residual soil NO_3^-

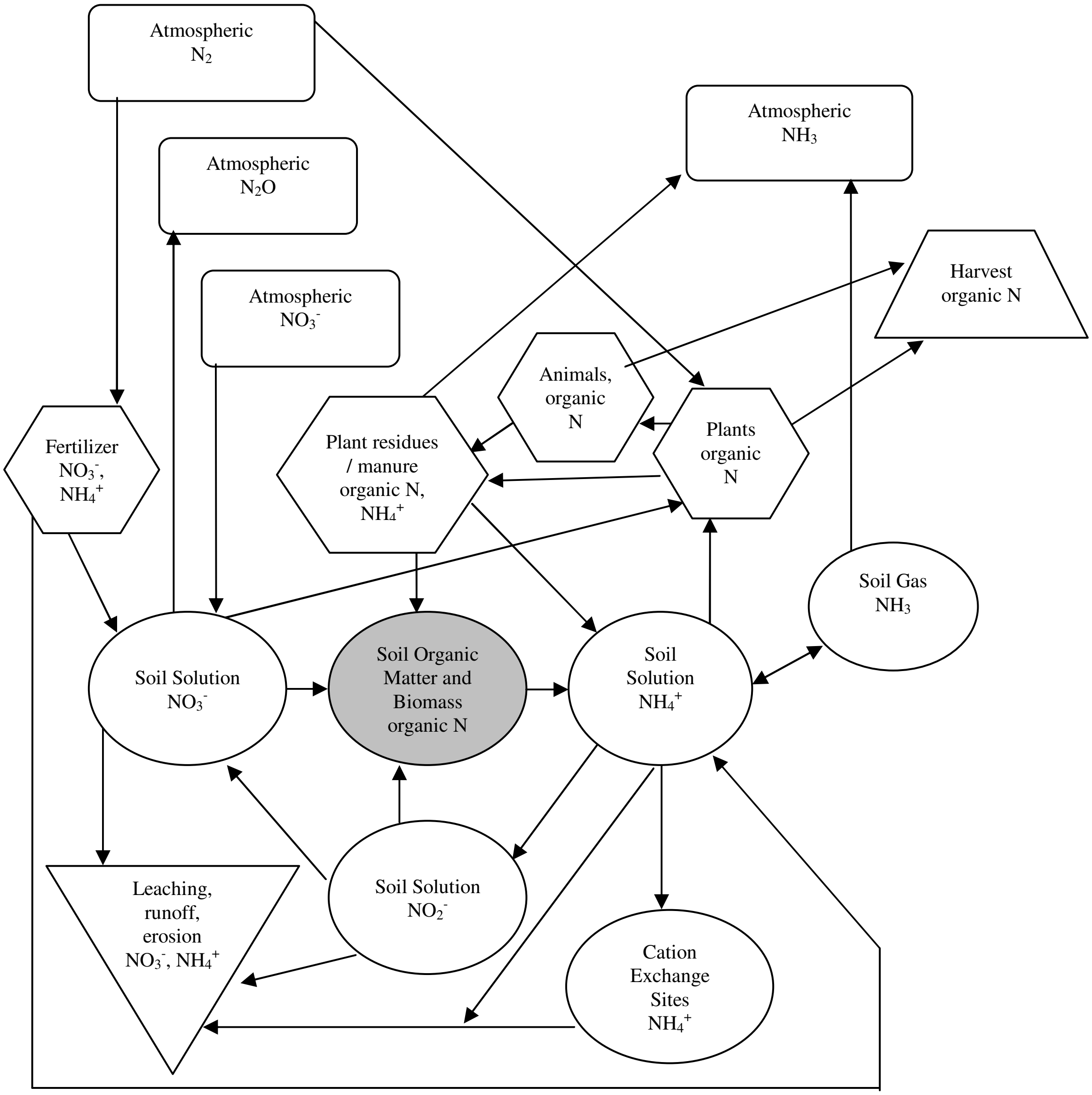

Figure 2.1. A simplified N cycle on a farm field receiving manure applications. Atmospheric components are rectangles, soil components are ovals, soil/atmosphere interfaces are hexagons, economically beneficial end products are trapezoids and water resources are triangles. Highlighted cell is subdivided into eight highlighted components in Figure 2.3. Adapted from Tisdale and Nelson (1975).

(Hofman et al., 1994). Presumably, NO_3^- that mineralizes during the cool season is also quite vulnerable to detrimental losses, however this process has not been well studied.

2.2.2 N balance

The efficiency of crop uptake of manure N sources tends to be low. One measurement of efficiency is to compare N recovered by crops to N applied via manure on small plots. On corn (*Zea mays* L.) plots in Wisconsin, only 15 to 18% of N applied via fresh dairy manure mixed with straw was recovered by the crop (Munoz et al., 2004). In a four-year trial on two UK perennial ryegrass (*Lolium perenne* L.) plots, the crop recovered 30 to 45% of applied N for fall applications and 38 to 72% for spring applications of cow manure slurry applied at 150 kg N ha^{-1}. For applications made at twice this rate, N recovery was 20 to 22% for fall applications and 32 to 64% for spring applications (Beckwith et al., 2002).

Examining the overall N balance on whole farms, rather than small plots, is another approach to understanding the inefficiencies of the N cycle in agriculture. Generally, the ratio of N output/input is greater on cash crop farms compared to livestock farms. For example, Barry et al. (1993) compared N efficiencies on a cash crop farm and a dairy farm in Ontario, Canada. The cash crop farm had total inputs of 140.2 kg N ha^{-1} yr^{-1} and grain outputs of 129.5 kg N ha^{-1} yr^{-1}, for an output/input ratio of 92%. The largest cash crop N inputs were N fertilizer and N fixation by the soybean crop. The dairy farm had total inputs of 129.5 kg N ha^{-1} yr^{-1} and milk, meat and grain outputs of 19.7 kg N ha^{-1} yr^{-1}, for an output/input ratio of 15%. The largest dairy farm N inputs were N fixation by legumes. The dairy farm imported no inorganic fertilizer.

Spears et al. (2003) used a spreadsheet model to compare N inputs and outputs on 41 dairy farms in Utah and Idaho. Inputs included N fixation by legume crops and imported feed, bedding, animals and fertilizer. Outputs included milk, meat and crops sold off the farm and any manure or compost trucked off the farm. Changes in the storage of organic N compounds in the soil were not addressed. The average output/input was 28.6% for farms that grew some of their own feed crops, 39.5% for farms that grew no crops and 35.8% for all farms in the study. Dairies that grew some of their own feed crops had a lower N efficiency because of inputs of fertilizer N and N fixation by legume crops.

Klausner et al. (1998) found a N output/input of 28% on a dairy farm in New York State, with total inputs of 267 kg N ha^{-1} yr^{-1} and total output of 76 kg N ha^{-1} yr^{-1}. In a case study of a dairy farm with 75 lactating Holstein cows (*Bos taurus*) in Nova Scotia, Canada, Lynch et al. (2003) found an N output/input of 25%. Of the 75% of N inputs that were unaccounted for, approximately 48% occurred in the barn (mostly due to NH_3 volatilization from stored manure) and 27% occurred in the field. This case study farm devoted 34% of its land area to intensively grazed pastures of perennial ryegrass (*Lolium perenne* L.), orchardgrass (*Dactylis glomerata* L.) and white clover (*Trifolium repens* L.).

The low efficiency of crop uptake of N from manure indicates a potential for environmental contamination of the atmosphere, groundwater and/or surface water. However, to the extent that some of the “lost” N is sequestered as recalcitrant organic compounds in the soil, the likelihood of environmental contamination could be reduced (Barry et al., 1993; Lynch et al., 2003). Soil organic N storage increased by approximately 73, 44 and 6 kg ha^{-1} yr^{-1} after tilled cropland was converted to permanent pasture during 0 to 10, 10 to 30 and 30 to 50 years following conversion, respectively, in the Southern Piedmont region of the United States (Franzluebbers et al., 2000).

Whether sequestration of N in recalcitrant organic compounds actually reduces the likelihood of NO_3^- leaching, runoff and denitrification depends on a number of factors. Because mineralization of organic N follows first order kinetics, soil organic N pools in stable farming systems will eventually approach a steady-state in which the mineralization rate of organic N will essentially equal the rate of organic N addition from crop residues, manure or other sources (Fried et al., 1976). The length of time required to reach that steady-state in manured soils, the size of the resulting N pools, the N mineralization rates which result and how much of the mineralization occurs during the cool season when leaching, runoff and denitrification losses are most likely has not been thoroughly investigated.

2.3 N uptake by plants

The reason that environmental contamination from NO_3^- is most likely during the cool season is that crop uptake of N is lowest at that time. The N uptake of most non-leguminous annual crops can be divided into three phases, as illustrated for corn (*Zea mays* L.) in Figure 2.2 (Ritchie et al., 1993). The first phase is the slow N uptake period during early vegetative growth. Phase II is rapid, almost linear, N uptake during late vegetative growth and early reproductive growth. Phase III is a period of little or no additional N uptake during late reproductive growth.

Although Figure 2.2 describes N uptake from a corn plant, this same type of sigmoid curve also fits the growth of other crops. Plots such as Figure 2.2 vary depending on species of crop, cultivar and environmental factors such as temperature, moisture and stresses from disease. Some crops, such as wheat, are harvested at plant maturity (phase III). Other crops, such as broccoli, are harvested earlier in the life cycle (phase II) (Sullivan et al., 1999).

Italian ryegrass (*Lolium multiflorum* L.) is often seeded as a fall cover crop to scavenge N after silage corn (Gangwer, 1999). However, Italian ryegrass accumulates only a limited mass of N during the coldest months of November through January (Griffith et al., 1997). Because of this, in Oregon's Willamette Valley, farmers are advised to begin applying N fertilizer to grass crops at T-Sum 200, just before Phase II accelerated N uptake by the crop begins (Pirelli et al., 2004). T-Sum 200 is based on Growing Degree Days (*GDD*) calculated by:

$$GDD_i = Ta - Tb \quad , \text{if } Ta >= Tb \qquad [2.1]$$

$$GDD_i = 0 \quad , \text{if } Ta < Tb \qquad [2.2]$$

$$GDD = \sum_{i=\Phi}^{\Omega} GDD_i \qquad [2.3]$$

where GDD_i is a single day's contribution to *GDD*, *Ta* is the mean air temperature for that day (°C), *Tb* is the base temperature, Φ is the date calculations begin and Ω is the date calculations end. For T-Sum 200 calculations, $Tb = 0°C$, $\Phi = 1$ January. T-Sum 200 is reached when $GDD = 200$. At T-Sum 200, Ω is usually between 30 January and 14 February in Oregon's Willamette Valley.

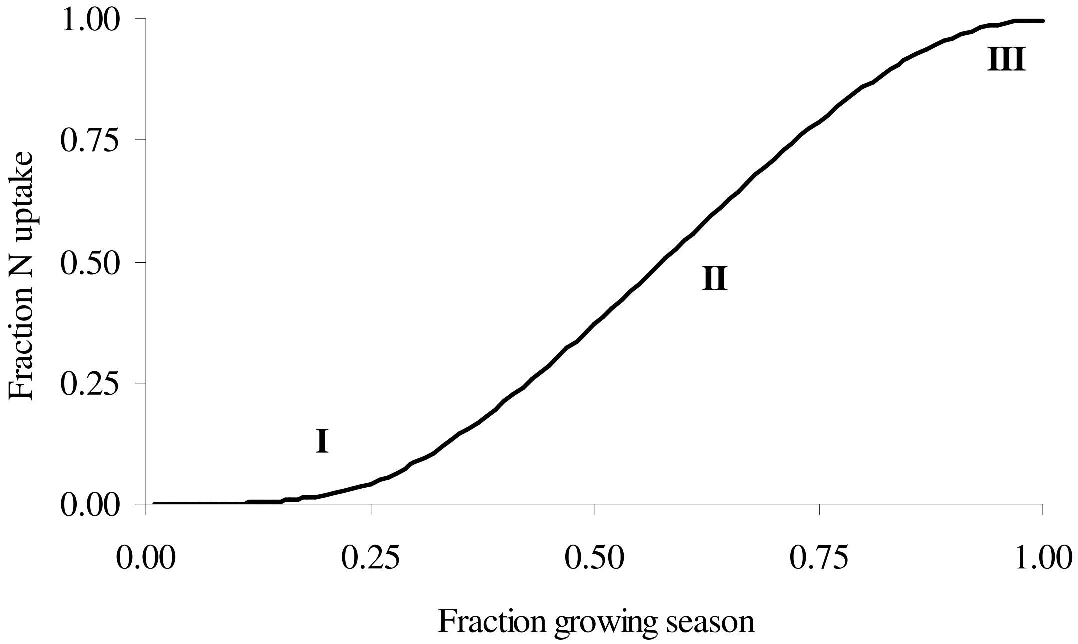

Figure 2.2. N uptake by a corn plant (*Zea mays* L.), with the three N uptake phases labeled. Adapted from Ritchie et al. (1993).

A simple mathematical model of crop growth, which simulates a smooth curve in Phase II was developed by Watts and Hanks (1978) and employs two functions:

$$FTNU = 8.878(FGS^{3.87}), \text{ when } 0 <= FGS <= 0.3 \quad [2.4]$$

$$FTNU = -0.660(FGS) + 3.485(FGS^2) - 0.930(FGS^3) - 0.899(FGS^4),$$

$$\text{when } 0.3 < FGS <= 1.0 \quad [2.5]$$

where *FTNU* is the fraction of total N uptake by a crop (dimensionless) and *FGS* is the fraction of the growing season (dimensionless). If N uptake and *FGS* data exist for crops, it is possible to fit polynomial equations such as Eq. [2.5] to those data.

Another relatively simple model of N uptake was developed by Whitmore and Addiscott (1987). This model has successfully modeled soil mineral N and N uptake in winter wheat grown in Great Britain. The N uptake component of the model is:

$$Y = (A^{-1/n} + \exp(-px))^{-q} \quad [2.6]$$

where *Y* is the N uptake on a given day, *A* is final N uptake, *q* is a shape constant that is empirically fitted, *p* is a constant that is related to the time it takes for soil moisture to reach field capacity after the wheat is seeded in the fall, *x* is a measurement of thermal time related to growing degree days and "exp" is the exponential function[1].

The farmer's goal is to produce a profitable harvest of plants and animals. With respect to N, this goal is achieved by applying fertilizer and manure in order to supply mineral nitrogen[2] at a sufficient rate to meet the crop's requirement at each stage of growth. During N uptake phase II, either the pool of soil NO_3^- must be large or the rate of NO_3^- formation from fertilizer, soil organic matter and manure must be rapid. If soil NO_3^- concentrations are high during phases I or III, because of residual soil NO_3^- or high rates of mineralization, there is increased potential for detrimental losses via surface runoff, leaching or denitrification.

2.4 N management planning

The United States Clean Water Act of 1972 authorized the U.S. Environmental Protection Agency (EPA) to develop rules regulating Concentrated Animal Feeding Operations (CAFOs). Most recently, the EPA revised these rules on 12 February 2003. The CAFO rules define an Animal Feeding Operation (AFO) as a livestock farm on which animals are confined to a non-vegetated facility (e.g. feedlot, barn or stable) for 45 or more days per year.

A "Large CAFO" is an AFO that confines a large number of livestock, for example 700 or more mature dairy cows (*Bos taurus*), 1,000 or more beef cattle (*Bos taurus*) or 2,500 or more swine (*Sus scrofa* L.) weighing more than 55 pounds each. A "Medium CAFO" is an AFO that meets two criteria. First, a Medium CAFO must confine a medium number of livestock, for example 200 to 699 mature dairy cows, 300 to 999 beef cattle or 720 to 2,499 swine weighing more than 55 pounds each. Second, a

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[1] Throughout this paper, "exp" is used to denote the natural exponential function in which the base of the natural logarithm (*e*) is raised to the power of the parenthetical value immediately following "exp."

[2] Although plants can also absorb NH_4^+ and urea, NO_3^- is the primary form of nitrogen absorbed by most crops.

Medium CAFO must discharge pollutants into waters of the United States either directly or via a man-made conveyance such as a pipe or ditch. An AFO with fewer livestock than Medium CAFOs may be designated as a Small CAFO if they are determined, on a case by case basis, to be a significant contributor of pollutants to waters of the United States (EPA, 2003).

CAFOs are required to obtain National Pollutant Discharge Elimination System (NPDES) permits. In some states, these permits are obtained directly from EPA. In other states, EPA has delegated the authority to issue permits to the state. Some states with the authority to issue NPDES permits to CAFOs have instituted regulations that are more restrictive than the Federal CAFO Rule, either in terms of which AFOs must obtain permits or what the permits require.

NPDES permits for CAFOs require the development of a Nutrient Management Plan (NMP). NMPs address nine components, including the storage of manure, the proper handling of animal mortalities, the diversion of clean water away from manure storage facilities, the exclusion of livestock from waters of the United States, proper handling and storage of chemicals, the reduction of erosion and nutrient runoff from cropland, protocols for testing manure and soil for nutrient content, record keeping and protocols for applying manure and wastewater to cropland. The protocols for applying manure and wastewater require that applications minimize the risk of pollutant runoff to waters of the United States. EPA references two United States Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS) documents for detailed guidance on applying manure and wastewater to meet CAFO Rule requirements: the Nutrient Management Standard (NRCS Practice Code 590) and the Waste Utilization Standard (NRCS Practice Code 633) (EPA, 2003).

The USDA Nutrient Management Standard requires that, in all situations, manure applications not exceed the N requirement of the crop (USDA-NRCS, 2002). The first step in applying the Nutrient Management practice is to estimate the N required by the crop[3]. This can be done by using fertilizer recommendations that are published by the

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[3] In some situations, manure is applied to meet the crop's phosphorus or potassium requirement, however only N calculations are discussed here for brevity.

Cooperative State Extension Service. If there are no published recommendations, then the N need is calculated by predicting crop yield and multiplying that yield by a published N content for the harvested portion of the crop.

After the initial step of determining crop need, there are various protocols for determining correct manure application rates. Table 2.1 summarizes the results of five such protocols, using silage corn (*Zea mays* L.) as an example. The calculations in Table 2.1 were based on assumptions that the corn was fertilized with only liquid manure, the corn crop required 224 kg ha^{-1} of available N, 71% of the manure N was NH_4^+-N (Hart et al., 1995), the manure was irrigated onto the field in the spring prior to planting corn and the manure was incorporated into the soil within one day of application. The calculations were made for two scenarios: one in which manure is applied to the field for the first time in recent years and one in which manure has been applied consistently for at least four years to the same field.

There is wide variation in the results of the five protocols illustrated in Table 2.1. The USDA National (USDA-NRCS, 1992), the USDA Oregon (USDA-NRCS, 2002) and the University of Nebraska (Koelsch and Shapiro, 2006) protocols all include specific calculations for estimating N losses due to NH_3 volatilization. The results of these calculations vary from 72 to 166 kg N ha^{-1} volatilized in this example. The Oregon State University (Hart et al., 1997) and Pennsylvania State University (Beegle, 1997) protocols do not include specific calculations to determine volatilization, although in the Pennsylvania State protocol volatilization appears to be included in “other losses.”

The other losses shown in Table 2.1 also include recalcitrant organic N that is not expected to mineralize during the growth of the crop and, presumably, losses due to denitrification and leaching. For all protocols shown, the other losses are less after repeated manure applications (Year 4 scenarios) because recalcitrant N that was applied in the previous years is assumed to mineralize during the current crop year. The USDA Oregon and Oregon State University protocols assume that the recalcitrant organic N pool has reached a steady-state by the fourth year of manure application, at which time the recalcitrant organic N that mineralizes annually during the corn growing season is assumed to equal the annual organic N addition via manure. Thus, these two protocols assume that recalcitrant organic N that mineralizes during the cool season when there is no corn crop growing is insignificant. The other three protocols assume other losses after four years of manure application, which could presumably include losses due to recalcitrant organic N mineralizing during the cool season. However, these cool season mineralization losses are not calculated explicitly.

Table 2.1. Five methods of determining manure application rates. The values shown assume liquid manure is applied to supply all N needed by a silage corn crop in Oregon's Willamette Valley.

Method	USDA National	USDA Oregon	Oregon State Univ.	Univ. Nebraska	Penn State Univ.
	kg N ha^{-1}				
Year 1					
NH_3 volatilization	75	166	0	81	‡
Crop need	224	224	224	224	224
Other §	470	274	448	71	336
Total to apply	769	664	672	376	560
Year 4					
NH_3 volatilization	75	75	0	72	‡
Crop need	224	224	224	224	224
Other §	353	0	0	37	122
Total to apply	652	299	224	333	346

§ "Other" may include organic N that does not mineralize, denitrification and leaching.

‡ Penn State Univ. combines NH3 volatilization with other losses.

Although the USDA National protocol (USDA-NRCS, 1992) allows for calculations that estimate denitrification and leaching losses, the other protocols do not address these losses specifically. None of the protocols specifically address losses of N to runoff, mineralization of soil organic N compounds not derived from manure, non-symbiotic atmospheric N fixation or atmospheric deposition of N. Insofar as these fluxes are similar for fields fertilized with either manure or inorganic fertilizer, they are implied in the Cooperative State Extension Service N recommendations. This is because those N recommendations are usually based on crop yield versus inorganic N application curves developed from randomized block experiments which are assumed to have typical N losses, mineralization and deposition (Donohue et al., 2005). One flux not accounted for in Extension Service N recommendations is cool-season N mineralization from recalcitrant organic N applied as manure, because this would occur after the crop was harvested. Thus, cool-season N mineralization is neither explicitly nor implicitly accounted for in the protocols shown in Table 2.1.

The nutrient management planning protocols described above involve a number of estimates and thus may lead to significant errors in calculations of acceptable manure application rates. In some parts of the United States, the USDA Nutrient Management Standard requires the use of residual soil nitrate testing in the fall to aid in the evaluation of N application rates (USDA-NRCS, 2002a). In western Oregon, if residual soil NO_3^- concentrations exceed 15 mg N kg^{-1} soil for perennial grass (various species) or 20 mg N kg^{-1} soil for silage corn (*Zea mays* L.), farmers are advised that manure applications during the growing season were excessive and should be reduced in future years (Sullivan and Cogger, 2003). Assuming a soil sampling depth of 30 cm and soil bulk density of 1.4 g cm^{-3}, then 15 to 20 mg N kg^{-1} equals approximately 63 to 84 kg N ha^{-1}.

These western Oregon recommendations are consistent with those from other agricultural regions. For example, some states in Germany and the Netherlands have set goals for residual soil NO_3^- on cropland to be below 45 to 70 kg N ha^{-1} to reduce the potential for NO_3^- losses to the environment (Hofman et al., 1994; Ilsemann et al., 2001). Zebarth et al. (1995) estimated an acceptable upper limit of residual soil NO_3^- at 100 kg N ha^{-1} in south-coastal British Columbia to safeguard groundwater in this region where annual water flow through the soil profile is approximately 1,000 mm.

The literature reports no recommendations for maximum levels of cool season N mineralization in Europe, Canada or the United States. Because N mineralized *during* the cool season is subject to the same loss pathways as NO_3^- present at the *beginning* of the cool season, this project will use the western Oregon residual soil NO_3^- benchmark of 20 mg N kg^{-1} soil as an approximate standard for cool season N mineralization. That is, in this study, cool season mineralization of 20 mg N kg^{-1} soil or greater will be considered excessive.

High residual soil NO_3^- accumulates when farmers apply fertilizer N or manure in excess of agronomic recommendations. This happens for a variety of reasons, including: (a) the desire to ensure good yields (Huang et al., 2000), (b) the need to reduce manure hauling costs (Ma and Ogilvie, 1998), (c) the lack of adequate waste storage facilities (USDA-NRCS, 1992) and (d) the mineralization of organic N compounds after harvest (Hofman et al., 1994). Factors (a) through (c) may result in manure applications that are in excess of the N needs of a crop and thus are possible to address without hurting crop yields. Factor (d), the mineralization of organic N compounds after harvest, may contribute to residual soil NO_3^- even when only enough manure is applied to meet crop N needs.

The recalcitrant organic N pool is generally larger than the labile organic N pool and has slower mineralization rates. This combination of a large pool plus slow mineralization rate makes recalcitrant organic N difficult to manage. It could take years to manipulate the size of the recalcitrant organic N pool, and thus the mass of recalcitrant organic N that mineralizes annually. Recalcitrant organic N mineralization after the growing season could contribute significantly to N losses to the environment, but the rates of this mineralization on farms receiving manure applications have received little attention in research or in public policy.

The literature recommends management practices that can reduce residual soil nitrate losses: a) modify N fertilizer and/or manure application rates and timing; b) use nitrification inhibitors; and c) plant fall cover crops (Beckwith et al., 1998). However, the literature contains no recommendations for practices to reduce loss of N mineralized after the growing season, although it is reasonable to assume that reduced manure application rates, nitrification inhibitors and fall cover crops would have some effectiveness.

2.5 Organic N mineralization processes

2.5.1 Soil N pools

Figure 2.3 illustrates a more detailed conceptual model of the highlighted cells in Figure 2.1 (Van Veen et al., 1984; Paul and Clark, 1989).

2.5.2 Chemical factors influencing N mineralization

In Figure 2.3, organic N pools 2, 3, 4, 8, 9, 10 and 11 all mineralize to form NH_4^+ via Eq. [2.7] and [2.8] below. This is a catabolic reaction that provides heterotrophic microbes with energy, C and N. NH_4^+ is nitrified in Eq. [2.9] and [2.10]. Nitrification provides autotrophic bacteria with energy to reduce CO_2 (Atlas and Bartha, 1993).

$$\text{Organic N compounds} \rightarrow \text{R-NH}_2 + CO_2 \quad [2.7]$$

$$\text{R-NH}_2 + 2H_2O \rightarrow NH_4^+ + OH^- + \text{R-OH} \quad [2.8]$$

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad [2.9]$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad [2.10]$$

The relative rates of the above equations are: [2.10] > [2.9] >= [2.8] > [2.7], which results in soil N tending to be mostly in the form of organic compounds or NO_3^- (Tisdale and Nelson, 1975). NO_2^- is not shown in Figure 2.3 because its concentration is generally much lower than either NO_3^- or NH_4^+. The ratio of NH_4^+ held on cation exchange sites to NH_4^+ in soil solution ranges up to 10:1 (Barber, 1984) and thus NH_4^+ is resistant to leaching. The anion NO_3^-, however, exists mostly in the soil solution and can fairly easily leach below root zones where it is no longer available for plant growth and may contaminate groundwater.

Eq. [2.11] depicts the mineralization of urea, a common inorganic fertilizer. This spontaneous exothermic reaction proceeds rapidly under favorable soil temperatures, moisture levels and urease concentrations. Urease is an enzyme naturally present in the soil that catalyzes the first part of Eq. [2.11]. Most urea is converted to NH_4^+ within days of application to soil:

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{-2} \quad [2.11]$$

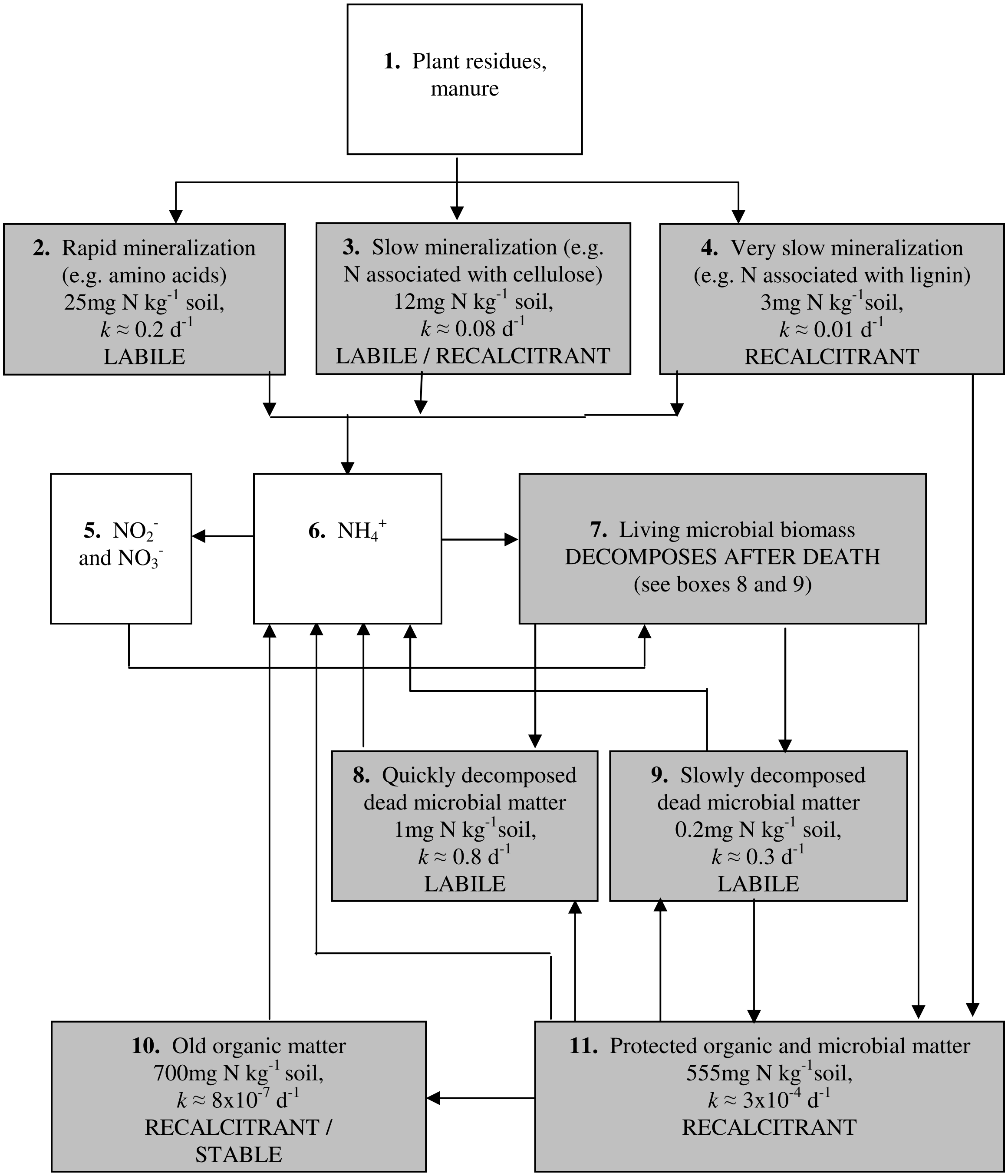

Figure 2.3. Conceptual model of N mineralization in soil. Arrows represent N flux between pools in a modeled decomposition of straw added to soil in a single application of 40 mg N kg^{-1} soil. This fresh organic N is partitioned into cells 2 through 4. Pools 8 through 11 represent dead organic N at the time of straw addition. N concentrations in the inorganic and living pools (5 through 7) are not provided because these pools change quickly. First order mineralization rate constants (*k* values for mineralization to NH_4^+) are given. The eight shaded cells above are components of the shaded cell in Figure 2.1 (Van Veen et al., 1984; Paul and Clark, 1989).

Mineralization models generally do not attempt to distinguish between more than three organic N pools. The convention is to label these pools “labile,” “recalcitrant” and “stable” based on their mineralization rates. Labile organic N mineralizes relatively quickly and includes Pools 2, 8 and 9 in Figure 2.3. Labile organic N includes proteins, nucleic acids, amino acids and other compounds easily degraded by microbes.

Recalcitrant organic N includes Pools 4, 10 and 11 in Figure 2.3. Pool 4 is lignin and associated N compounds, which mineralize slowly. Pool 10 is old organic matter (humus), a mixture of high molecular weight organic compounds such as lignin and polyphenols that are resistant to microbial attack and can have half-lives of thousands of years (Jenny, 1983; Six et al., 2002). Some compounds in Pool 10 can be considered recalcitrant, but other compounds can be considered so stable as to essentially not mineralize at all. Pool 11 is protected from mineralization because of its association with soil particles rather than its chemical composition. Pool 3, N associated with cellulose and hemi-cellulose, could be considered labile, recalcitrant or some combination of both.

Most of the organic N in soil is recalcitrant or stable (Paul and Clark, 1989). However, empirically determined values for the concentration of organic N compounds in the pools shown in Figure 2.3 are not available in the literature because there are no analytical techniques to measure all seven of the dead organic N pools shown in Figure 2.3 (Stevenson, 1996; Swift, 1996). Deans et al. (1986) determined, in an analysis of mineralization data collected by others, that recalcitrant organic N accounted for 75 to 97% of the “potentially mineralizable N” in 20 soils from Connecticut, Maryland and Minnesota. This is an underestimate of the total organic N concentration, however, because the term “potentially mineralizable N” does not include stable organic N in Pool 10. For example, recalcitrant organic mineralization rates in this study ranged from 6×10^{-4} to 1×10^{-2} d^{-1}. Comparing these mineralization rates to those suggested for Pools 10 and 11 in Figure 2.3, it is clear that much of Pool 10 (and perhaps some of Pool 11) were not considered potentially mineralizable in the Deans et al. (1986) data.

Although living microbes (Pool 7 in Figure 2.3) and other soil fauna drive the mineralization of organic N, the microbes are also a sink for mineral N. The rate at which N mineralization occurs, and whether the mineralization will result in a net increase in the soil mineral N pools, is affected by both the complexity of the organic substrate and by the C:N ratio of the organic matter.

Bacterial cells have a C:N ratio of 3:1 to 5:1, fungi have C:N ratios of 4.5:1 to 15:1 and soils have an average C:N ratio of 10:1 (Paul and Clark, 1989). Knowing a microbe's C:N ratio, its substrate utilization efficiency and the substrate C:N ratio allows an estimation of the net N mineralization that will occur. For example, suppose a bacterial population with a C:N ratio of 5:1 attacks a rapidly mineralized substrate. If the utilization efficiency is 50%, the bacteria will incorporate 50 g of C into biomass for every 100 g of C mineralized. The bacteria will require 10 g of N to maintain its C:N ratio in this new biomass. If the substrate yields more than 10 g of N (i.e. if its C:N ratio is less than 10:1), then there will be a net N mineralization (the mineral N pool will increase). If the substrate C:N is more than 10:1, the bacteria will take mineral N out of the soil solution to satisfy its needs and there will be a net immobilization of mineral N.

Another approach to the same type of estimation is given mathematically in Eq. [2.12] (Whitmore and Handayanto, 1997):

$$N_f = C_O((1/z) - (E/y)) \qquad [2.12]$$

where N_f is the mass of N mineralized once all mineralization is complete, C_O is the mass of carbon in the initial substrate, z is the C:N ratio of the initial substrate, E is the microbial utilization efficiency and y is the C:N ratio of the organic end product of mineralization.

2.5.3 Biotic factors influencing N mineralization

Although bacteria and fungi drive N mineralization, other soil organisms have significant effects on the process. Estimates of dry faunal biomass composition in an agricultural field of alfalfa (*Medicago sativa*) were 2%, 2%, 15% and 81% for earthworms, protozoa, bacteria and fungi, respectively (Lofs-Holmin and Bostrom, 1982). Hassink et al. (1993) reported biomasses of <1%, 3%, 95% and 1% for nematodes, protozoa, bacteria and fungi, respectively, in grass pasture soils.

Fungi and bacteria are able to mineralize soil organic matter as a source of both energy and nutrients. These micro-organisms can be lumped into two broad physiological categories: k-strategists and r-strategists (Atlas and Bartha, 1993). R-strategists have high growth rates and depend on labile organic matter. Many r-strategists are bacteria (e.g. *Pseudomonas* , *Aspergillus*, *Penicillium* and *Bacillus*), however some are fungi (e.g. *Mucor* and *Rhizopus*). K-strategists have slower growth rates but are able to utilize more recalcitrant organic compounds. Many k-strategists are fungi (e.g. Basidiomycota), however some are bacteria (e.g. *Cytophaga* and *Agrobacterium*) (Clarholm, 1985). It is possible that the two mineralization rates described by the double-pool model to be described later (Eq. [2.21]) are attributable both to a difference in physiology between bacteria and fungi and to a difference in chemistry between labile and recalcitrant organic N (Bonde and Rosswall, 1987).

Clarholm (1985) demonstrated successively greater N mineralization in autoclaved soil inoculated with bacteria by adding glucose, glucose plus protozoa or growing wheat plus glucose and protozoa. This suggests that soil bacterial activity (and thus N mineralization rate) can be limited by lack of available C. This limitation may be overcome in the rhizosphere by the following cycle: new root tissues secrete labile C compounds; localized bacterial populations expand, using the root exudates as a C source; these bacteria mineralize adjacent organic matter (Pools 2, 3, 4, 10 and 11 in Figure 2.3) as a N source; protozoa (predominantly amoebae) consume the bacteria; the protozoa excrete NH_4^+; the roots absorb this mineral N and continue to grow.

In addition to protozoa, earthworms (*Lumbricus terrestris* and *Aporrectodea tuberculata*) and some nematode species also graze on bacteria. Because grazers tend to have high C:N ratios compared with their bacterial food sources, they excrete mineral N and thereby directly contribute to mineralization. Hassink et al. (1993) demonstrated greater N mineralization with increased nematode and protozoan grazing. Bohlen and Edwards (1995) inoculated microcosms with *L. terrestris* and *A. tuberculata* after addition of inorganic N fertilizer, dairy manure or vetch (*Vicia vellosa*) residue. Earthworm addition decreased microbial biomass and increased N mineralization in all plots. Earthworms increased N mineralization the most in plots treated with manure. The authors suggest that the earthworms ingested microbial biomass and excreted mineral N.

In addition to this direct effect on N mineralization, earthworms can also indirectly increase N mineralization rates in soil by physical tunneling (increased soil aeration) and excretion of organic matter (casts) that has a lower C:N ratio than the ingested organic matter. Earthworm casts stimulate microbial activity and N mineralization. Willems et al. (1996) demonstrated that earthworms can increase N mineralization by up to 90 kg N ha^{-1} $year^{-1}$ and that stimulation of microbial activity was more important than physical tunneling in this effect. Thus, earthworms can directly increase N mineralization through consuming bacteria and excreting mineral N in some situations and can also increase N mineralization through stimulation of bacterial activity in other situations.

When cattle manure was applied to a sandy soil, bacterial biomass increased immediately, protozoa numbers increased over a period of days and nematodes and soil NO_3^- concentrations increased over a period of weeks (Opperman et al., 1989). In this study, plots with added earthworms showed increased bacteria levels to depths of 17.5 cm as well as increased N mineralization rates.

The papers cited above illustrate the complexity of soil biology. Certainly, bacteria and fungi play a dominant role in soil N mineralization. However, protozoa, nematodes, earthworms, plants and vertebrates also affect N mineralization in soil ecosystems. Because populations of soil organisms have seasonal variability, especially when subjected to freeze-thaw cycles (Biederbeck and Campbell, 1971), *in vitro* N mineralization studies under optimal temperature and moisture conditions may not represent biotic processes that occur during the cool wet season. To adequately capture the effects of organisms on cool season N mineralization, it may be necessary to conduct *in situ* experiments during that time of year.

2.5.4 Physical factors influencing N mineralization

The microbial species involved in N mineralization of manure applied to soils are assumed to be predominately mesophiles (organisms with an optimal growth temperature of 20 to 45°C) (Gilmour et al., 1977; Atlas and Bartha, 1993). A short-hand notation, Q_{10}, is often used for the change in reaction rates per each 10°C rise in temperature.

Some experimental data suggest that N mineralization Q_{10} values may vary significantly depending on the type of organic matter being decomposed, the temperature range over which experiments are run and the soil type (MacDonald et al., 1995; Vigil and Kissel, 1995).

Compared to temperature, less is known about the effects of moisture on N mineralization rate constants. Some data suggest that at 30 to 60% of a soil's water holding capacity, N mineralization rate is linearly related to soil moisture content (Gilmour et al., 1977). As soil moisture increases beyond 90% of the fillable pore space, the decreased diffusion of O_2 can limit mineralization.

Because temperature and moisture effects on N mineralization are profound, there have been many efforts to accurately measure N mineralization under field conditions (Dowdell and Webster, 1980; Raison, 1987; Subler et al., 1995; Kolberg et al., 1997; Sullivan et al., 1999; Eghball, 2000). Most efforts at measuring N mineralization *in situ*, however, have been made during the warm season because that is the time period when crop demand for N is greatest. One notable exception is Myrold et al. (1992), who examined year-round N mineralization in pasture soils receiving manure. This study did not distinguish between labile and recalcitrant organic N mineralization, however.

Soil texture and structure characteristics also influence N mineralization. The protected organic matter (pool 11 in Figure 2.3) contains some organic compounds and microbial matter of a chemical composition that should be subject to moderate or rapid mineralization, but that is protected from mineralization by physical association with soil particles. For example, protected organic matter tends to have a lower C:N ratio than unprotected organic matter and thus tends to mineralize quickly after the protective capacity is reduced by soil disturbance (Hassink, 1992). Clay particles have an especially high capacity for protecting organic matter from mineralization (Paul and Clark, 1989).

The protective capacity of clay partially explains why mineralization rates in sandy soils exceed those of clay soils. Van Veen et al. (1984) successfully modeled C mineralization by assigning preservation capacities of 700 ug C g^{-1} soil for a clay soil and 300 ug C g^{-1} soil for a sandy soil. In this model, the preservation capacity "protected" the organic matter from decomposition until the organic carbon concentration exceeded the preservation capacity. These results are contradictory to the Stanford and Smith (1972) findings of consistent mineralization rates for widely different soils. The discrepancy is partially explained by the method by which Stanford and Smith sieved soil prior to incubation, which would have destroyed some of the soil structure providing protection.

Protective mechanisms include soil aggregates that isolate organic compounds and bacteria from grazers and clay surfaces that adsorb organic compounds. The idea of sorption as a protective mechanism is supported by evidence that clay mineralogy affects its protective capacity. For example, 2:1 clays, such as illite, montmorillonite and smectite, with high cation exchange capacity (CEC) provide more protective capacity than 1:1 clays, such as kaolinite, with relatively low CEC (Six et al., 2002).

Evidence supporting protection inside soil aggregates is given by Hassink et al. (1993), who demonstrated good correlation between bacterial biomass and soil pore volume in the 0.2 to 1.2 μm diameter range. This size of pores is sufficiently large for the many bacteria less than 0.3 μm in diameter but excludes protozoa, which are limited to soil pores greater than 8 μm, and nematodes, which are mostly 15 to 60 μm in diameter. Thus, soil aggregates appear to reduce N mineralization by protecting bacteria from grazers.

Surprisingly, some low clay content soils have exhibited greater organic carbon mineralization than high clay content soils after aggregates are crushed (Franzluebbers and Arshad, 1997). In that study, perhaps much of the protective capacity of the high clay content soils was due to adsorption, which would not be affected by aggregate crushing. Another possible mechanism to explain these results is that the coarse-textured soils formed weaker aggregates than the clays. These weaker aggregates may have been more thoroughly destroyed by crushing.

Although mineralogy of soil changes only over geologic time periods, soil aggregates can be changed quickly by management practices. Farming systems based on no-till planting rather than annual tillage increase soil aggregates, protective capacities and soil organic matter (Six et al., 2002).

Numerous studies demonstrate that soil tillage causes increased N mineralization (for example, (El-Haris et al., 1983; Doran, 1987; Tracy et al., 1990; Franzluebbers et al., 1995)). This is due at least partially to disturbance of soil aggregates and thus the reduction of protective capacity. Aggregate protection is likely to reduce mineralization rates more during the cool, wet season when there is usually no tillage of agricultural fields than during the growing season when farmers till the soil to produce their crops.

2.5.5 Limitations of conceptual model

The conceptual model represented in Figure 2.3 is well-accepted in the scientific literature. Numerous studies of the chemical, biotic and physical factors of N mineralization support the usefulness of this conceptual model. However, the seven non-living soil organic N pools (2, 3, 4, 8, 9, 10, 11) in Figure 2.3 are arbitrary distinctions. Soil ecosystems have innumerable organic compounds containing N, ranging from simple urea up to high molecular weight humus compounds with chemical structures not yet enumerated. Efforts to construct process-based models of the soil N cycle with seven pools would grossly simplify reality. Still, most process-based N mineralization models have only one to five organic N pools due to difficulties in parameterizing pools that cannot be directly measured and that differ along a continuum rather than discretely (Ma and Shaffer, 2001).

Jenny (1983) described efforts to predict N mineralization as follows: “So crucial is soil nitrogen for biomass production that agriculturists have searched for a century for tests and equations that would link the two. Legions of soil analyses and field and greenhouse trials unfold endless complexities, and a myriad of climatic, plant and soil variables is involved. Daily or weekly monitoring of nitrates in the field has not been found practicable. Instead, soil samples are taken to the laboratory and are incubated for weeks.”

More recently, Vigil et al. (2002) spoke to the same subject: “The real need is for a ‘simple functional model’ that can be easily manipulated and that takes into account climate, soils and management, an old idea that has not yet been achieved.”

As work continues on more accurate process-based models, the need still exists to predict N mineralization rates of manure-amended soil. The models and measurement methods described in the following sections primarily were developed to address N mineralization of labile organic matter during the growing season. However, with some adaptations, they can be used to better understand mineralization of recalcitrant organic N during the cool season.

2.5.6 Mineralization kinetics

There are four categories of mathematical models used to describe nitrogen mineralization kinetics in manured soils: decay series, hyperbolic/parabolic equations, first order equations and second order equations. Mathematical representations are important both in understanding the underlying mechanisms of N mineralization and in predicting the growth and decay of recalcitrant organic N pools.

2.5.6.1 Decay series

This model employs a set of empirically determined percentages of the total N in manure that is mineralized each year following manure application. For example, Pratt et al. (1973) give the decay series for fresh bovine (*Bos taurus*) waste (3.5% N by dry weight) as 0.75, 0.15, 0.10, 0.05. If this manure is applied at a rate of 100 kg N ha^{-1}, then the decay series model predicts that 75% of the total N (75 kg ha^{-1}) will be mineralized in the first year and 25 kg ha^{-1} of recalcitrant organic N will remain in the soil. In the second year, 15% of the remaining N (0.15 x 25 kg ha^{-1} = 3.75 kg ha^{-1}) will be mineralized. In the third year, 10% of the remaining N (0.10 x 21.25 kg ha^{-1} = 2.125 kg ha^{-1}) will be mineralized. In the fourth and subsequent years, the decay series model predicts a first order mineralization with 5% of the remaining manure N mineralizing each year.

The decay series approach is widely cited in the literature because it was an early attempt to quantify manure mineralization rates and because decay series are one of the methods recommended by USDA to approximate the mineralization rates of N from manure applications (USDA-NRCS, 1992).

2.5.6.2 Hyperbolic and parabolic equations

Before nonlinear curve fitting programs were available, N mineralization was often predicted with a hyperbolic equation (Eq. [2.13]) and the Lineweaver-Burk double reciprocal method as shown in Eq. [2.14] (Deans et al., 1986; Paul and Clark, 1989). The hyperbolic function is called the "Michaelis-Menten" equation in enzyme chemistry, the "Monod" equation when used to describe microbial growth and the "Langmuir" equation in adsorption chemistry. The basic function is the same, regardless of the name:

$$N_{min} = (t)N_O / (B + t) \qquad [2.13]$$

$$1/N_{min} = B/(t)N_O + 1/N_O \qquad [2.14]$$

where N_{min} is the amount of N mineralized (kg ha^{-1}) after elapsed time t, N_O is the initial potentially mineralizable organic N (kg ha^{-1}) and B is the slope of the linear plot of $1/N_{min}$ as a function of $1/(t)N_O$. B has units of time and is equal to the time at which half of the potentially mineralizable organic N is mineralized. Time t is typically reported either in days or weeks.

When t is very large in Eq. [2.13], N_{min} approaches N_O. When t is very small, $\mathrm{d}N_{min}/\mathrm{d}t$ approaches N_O/B. Sometimes, Eq. [2.13] is written as:

$$N_{min} = (t)N_O/(BN_O + t) \qquad [2.15]$$

In this form, $\mathrm{d}N_{min}/\mathrm{d}t$ approaches $1/B$ as t becomes very small. Parabolic functions such as Eq. [2.16] have also been successfully fitted to N mineralization data, but are not generally used in modeling because the coefficients have no physical meaning (Benbi and Richter, 2002):

$$N_{min} = (a)t^b \qquad [2.16]$$

where a and b are coefficients fitted to N_{min} versus t data.

2.5.6.3 First order equations

This group of models is based on the assumption that the concentration of one or more primary substrates controls a reaction and therefore the reaction rate depends on the concentrations of those substrates. There are a number of variations on first order models.

2.5.6.3.1 Single pool first order

This is the simplest form of the first order reaction and assumes that only one organic N pool mineralizes, as represented in Eq. [2.17] (Stanford and Smith, 1972; Watts and Hanks, 1978; Paul and Clark, 1989; Serna and Pomares, 1991).

$$\mathrm{d}N/\mathrm{d}t = -k(N) \qquad [2.17]$$

where k is a first order mineralization constant with units of inverse time and N is the potentially mineralizable organic N. Integrating Eq. [2.17] results in:

$$N_t = N_O \exp(-kt) \qquad [2.18]$$

where N_t is the potentially mineralizable organic N (kg ha^{-1}) after elapsed time t. Since it is often more important to know the amount of N mineralized rather than the amount of potentially mineralizable organic N remaining, Eq. [2.19] is often used:

$$N_{min} = N_O(1 - \exp(-kt)) \qquad [2.19]$$

Dividing both sides of Eq. [2.18] by N_O, setting N_t equal to one half of N_O and then taking the natural logarithm of both sides of the equation gives the half life, $t_{1/2}$, of the potentially mineralizable N (Gilmour et al., 1977):

$$t_{1/2} = 0.693/k \qquad [2.20]$$

2.5.6.3.2 Double pool first order

A double pool model that splits the potentially mineralizable organic N into labile and recalcitrant pools often offers a better fit to experimentally determined data (Molina et al., 1980; Deans et al., 1986; Bonde and Rosswall, 1987; Vanotti et al., 1995; Gilmour et al., 1996). The double pool model lumps pools 2, 8 and 9 in Figure 2.3 into the “labile” pool. Pools 4, 10 and 11 in Figure 2.3 are lumped together into the “recalcitrant” pool. Pool 3 in Figure 2.3 may be included in either labile or recalcitrant or split between the two pools. A double pool model is represented mathematically as:

$$N_{min} = N_O S(1 - \exp(-ht)) + N_O(1 - S)(1 - \exp(-kt)) \qquad [2.21]$$

where S is the initial fraction of potentially mineralizable organic N that is labile, h is the mineralization rate constant for the labile organic N (units of inverse time) and k is the mineralization rate constant for the recalcitrant N (units of inverse time).

2.5.6.3.3 Multiple pool first order

Recognizing that Figure 2.3 arbitrarily divides soil organic N compounds into seven pools, it is logical to accept that first order mineralization models could have three or more pools of potentially mineralizable organic N (Seligman and van Keulen, 1980; Benbi and Richter, 2002). Mathematically, this would be represented similarly to Eq. [2.21], but with additional fractions of N_O, each with its own rate constant. However, using more than two potentially mineralizable pools does not necessarily increase a mathematical model's predictive capacity (Willigen and Neeteson, 1985).

2.5.6.3.4 Simplified double pool

In a double pool model, the recalcitrant organic N is generally a larger pool than the labile. For example, a study of 37 soils in the United States found that $(1 - S)$, the fraction of recalcitrant organic N, varied from 0.75 to 0.99 (Deans et al., 1986). Because the recalcitrant pool is large and because it mineralizes slowly, it can often be effectively modeled with a zero-order equation (Bonde and Rosswall, 1987; Vanotti et al., 1995). This simplifies Eq. [2.21]:

$$N_{min} = N_O S(1 - \exp(-ht)) + C(t) \qquad [2.22]$$

where C is a zero-order mineralization rate constant (kg ha^{-1}d^{-1}).

2.5.6.4 Second order equations

Whitmore (1996) found that a second order equation was superior to a first order equation in describing CO_2 production from sugar beet and vegetable residues in pot experiments. In terms of N mineralization:

$$\mathrm{d}N/\mathrm{d}t = -k_2(\alpha)(1 - \alpha)(N)^2 \qquad [2.23]$$

where k_2 is a second order constant and α is the fraction of potentially mineralizable organic N (N) that is incorporated into the microbial biomass. The theory behind Eq. [2.23] is that the mineralization rate will be proportional to both the amount of N in the substrate, $(1 - \alpha)(N)$, and the amount of N that has been incorporated into the microbial biomass, $(\alpha)(N)$.

Any of the first order or the second order equations shown above could be used to model recalcitrant organic N during the cool season, however Eq. [2.21] is best suited for this task because it combines simplicity with a reasonable approximation of the physical processes involved. However, the mineralization rate constants for Eq. [2.21] (k and h) are generally determined by in vitro experiments at relatively high temperatures (30 to 40°C) and optimal moisture conditions. Therefore, any attempt to model the mineralization of recalcitrant organic N during the cool season would require modifying the rate constants for temperature and, perhaps, moisture.

2.5.6.5 Temperature and moisture factors

As previously discussed, the mineralization rate of organic N compounds in manure is widely assumed to follow the Van't Hoff rule, based on the Arrhenius equation, that mineralization rates double with every 10ºC increase in temperature[4] (Gilmour et al., 1977). With this assumption, first order mineralization rate constants may be adjusted for actual temperature conditions using Eq. [2.24] (Vanotti et al., 1995):

$$k = k_{Tr}(0.933^{(Tr-T)}) \qquad [2.24]$$

where k is the rate constant (units of inverse time) adjusted for actual temperature, k_{Tr} is the rate constant at reference temperature Tr, 0.933 is a constant that applies when the reaction rate halves with every 10°C decrease in temperature and T is the mean soil temperature (°C). Because soil temperatures do not fluctuate greatly in agricultural fields during the growing season, some models simplify the temperature effect to a linear equation. For example, the CERES-N model uses Eq. [2.25]:

$$k = k_{Tr}(T - 5)/Tr \qquad [2.25]$$

where Tr is assumed to be 35°C.

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[4] The commonly used shorthand abbreviation for this rule is "$Q_{10} = 2$", where Q_{10} is the factor by which mineralization rates increase for every 10ºC rise in temperature.

Some models employ annual heat units for adjusting N mineralization rate constants. Annual heat units are a special case of Eq. [2.1] through Eq. [2.3] and equal the cumulative *GDD* for an entire year. Annual heat units can be used to adjust *k* values using Eq. [2.26]:

$$k = (k_{Tr})(0.933^{-((AHU/365) - (Tr - Tz))}) \qquad [2.26]$$

where *AHU* are annual heat units, *Tz* is a temperature below which no mineralization occurs and all other variables are as previously defined. In the literature, *Tz* for Eq. [2.26] is often set equal to 5°C.

Crohn (2006) introduced the concept of "temperature adjusted time," which is based on a more exact application of the Arrhenius equation than Eq. [2.24]:

$$k = k_{Tr}(Q_{10})^{(1+(Tr/10))(1-(Tr/T))} \qquad [2.27]$$

where all variables are as previously defined, except units of ºK are used rather than ºC.

As noted previously, temperature effects on mineralization are at least partially related to the kind of organic substrate being mineralized. For example, Nicolardot et al. (1994) found that glucose decomposed 4.6 times faster than hollocellulose at 28ºC and 17.6 times faster at 5 ºC. This phenomenon has led some to suggest that temperature should be used to modify the size of the potentially mineralizable organic N pools rather than the mineralization rate constants (MacDonald et al., 1995). Others suggest modifying models to include an activation energy for mineralization reactions (Whitmore and Handayanto, 1997).

As previously discussed, compared to temperature, less is known about the effects of moisture on N mineralization rate constants. Some data suggest that when soil water holding capacity is between 30 to 60%, k is linearly related to soil moisture content (Gilmour et al., 1977). As soil moisture increases beyond 90% of the fillable pore space (*FPS*), the decreased diffusion of O_2 can limit mineralization. A mathematical representation of this effect is given by Watts and Hanks (1978):

$$N_{min} = (R_m)(N_{opt}) \qquad [2.28]$$

$$R_m = 1.111(FPS) \qquad \text{for } FPS < 0.9 \qquad [2.29]$$

$$R_m = 10.0 - 10.0(FPS) \qquad \text{for } FPS >= 0.9 \qquad [2.30]$$

where N_{min} is the mass of N mineralized over a given time (kg ha^{-1}), adjusted for soil moisture, N_{opt} is the mass of N mineralized over a given time (kg ha^{-1}) at optimum soil moisture of 0.9 FPS, R_m is a factor to adjust for actual soil moisture (no units) and FPS is the fraction of the soil fillable pore space containing water (no units).

Although first order models such as Eq. [2.17] through Eq. [2.22] may be adequate for describing N mineralization under controlled temperature and moisture conditions in a laboratory, a model predicting actual N mineralization of recalcitrant organic N compounds in cool, wet fields would need to incorporate terms such as Eq. [2.24] through Eq. [2.30] for temperature and moisture effects.

2.5.7 Process-based computer models

There are a number of process-based computer models for N mineralization. Models generally employ first order kinetics for mineralization, but some processes are modeled with zero-order or hyperbolic equations. Effects of temperature, moisture and other factors are either simulated with equations such as Eq. [2.24] through Eq. [2.33] or with modifiers that assume a value of 0.0 to 1.0 to adjust rate coefficients (Ma and Shaffer, 2001). A summary of nine mineralization models is provided in Table 2.2. Although most, if not all, of the models shown in Table 2.2 are capable of simulating recalcitrant organic N mineralization on manured fields during the cool season, there is no evidence in the literature that this has been done.

Table 2.2. N mineralization models. These models generally employ first order kinetics to simulate N mineralization.

Model name	Organic N pools	Objectives	Institution	Reference
NTRM (Nitrogen, Tillage and crop Residue Management)	1	Examine soil management strategies and the effect of climate change on crop yields and nitrate leaching.	USDA-ARS	(Shaffer and Larson, 1987)
NLEAP (Nitrate Leaching and Economic Analysis Package)	3	Quantify agricultural nitrate leaching and economic factors resulting from management strategies.	USDA-ARS	(Shaffer et al., 1991)
RZWQM (Root Zone Water Quality Model)	5	Simulation of agricultural management on water quality, including nitrogen and pesticides.	USDA-ARS	(Ahuja et al., 2000)
CENTURY	5	Simulate long-term effects on soil and carbon dynamics.	Colorado State University	(Parton et al., 1994)
CERES (Crop Estimation through Resource and Environment Synthesis)	4	A family of models that simulate crop growth and various soil functions.	Various U.S. and European universities	(Hanks and Ritchie, 1991)
GLEAMS (Groundwater Loading Effects of Agricultural Management Systems)	3	Evaluate the effect of management practices on pesticide and nutrient leaching.	Univ. of Georgia, USDA-ARS	(Leonard et al., 1987)
LEACHM (Leaching Estimation and Chemistry Model)	3	Simulates vertical movement of water, pesticides, nitrogen and phosphorus.	Cornell Univ.	(Hutson, 2000)
NCSOIL	4-6	Study the mechanisms of N and C cycling, using modeled N and C tracers.	Univ. of Minnesota	(Molina et al., 1983)
EPIC (Environmental Policy Integrated Climate)	3	Study the effects of erosion on crop yield, plus simulate nitrogen leaching and phosphorus runoff.	Texas A&M Univ.	(Williams, 1995)

2.6 Measuring organic N mineralization

2.6.1 In vitro determinations

The usual experimental approach to determine N_O and k for an organic N pool is to incubate the soil or soil/waste mixture *in vitro* under controlled conditions and then measure the concentration of mineral N (NH_4^+ plus NO_3^-) that evolves over time. Considerations must be made for soil preparation, temperature, moisture and mineral N extraction. These factors are treated somewhat differently, depending on experimental objectives.

Generally, soil is air dried and then ground to pass through a 2 mm sieve (Stanford and Smith, 1972; Antil et al., 2001). Sometimes, the soil is mixed with washed sand or vermiculite to provide a more physically homogeneous mixture and to prevent particle size segregation during packing (Stanford and Smith, 1972; Bonde and Rosswall, 1987). The soil is then incubated at a constant temperature, usually in the dark. Temperatures used for incubation vary from 25°C (Smith et al., 1998; Gilmour and Skinner, 1999) to 37°C (Antil et al., 2001). Serna and Pomares (1991) incubated soils in chambers with a 16 h photoperiod.

The soil is usually incubated at constant moisture content, ranging from a potential of -80 kPa (Stanford and Smith, 1972; Bonde and Rosswall, 1987) to saturated (Antil et al., 2001). When soils are incubated in a saturated condition, they become anaerobic and nitrification (Eq. [2.9] and Eq. [2.10]) does not occur. This simplifies analysis because only evolved NH_4^+ needs to be measured rather than both NH_4^+ and NO_3^-.

Mineral N can be extracted from *in vitro* incubations by either operating the incubation as a series of batch experiments or as a chemostat. In the batch method, some number (x) of time periods to sample is chosen. Initially, a set of nx incubation batches is begun simultaneously, where n is the number of replications. A value of $n = 3$ is typical (Serna and Pomares, 1993; Gilmour and Skinner, 1999). If more than one treatment is desired (for example one soil with two or more manure amendments), then the total number of batches is nxy, where y is the number of treatments. At the end of each time period, ny batches are harvested, the soil is homogenized and a subsample of soil is analyzed for NH_4^+ and NO_3^-. Harvested batches are discarded after sampling. An example of the batch incubation method is provided by Antil et al. (2001).

In the chemostat method, *ny* incubations are started in containers open at both the top and bottom. A glass wool pad at the bottom of each container holds soil in place, while another glass wool pad at the top of the container prevents the dispersion of soil when extractant solution is added (Bonde and Rosswall, 1987). At each sampling time, mineral N is extracted from each container. After extraction, a minus-N nutrient solution is added to replace minerals that may have been leached out of the chemostats during extraction. The chemostats are then returned to the incubation chamber until the next sampling time. An example of the chemostat method is provided by Stanford and Smith (1972).

The extraction of mineral N from *in vitro* incubations is usually accomplished by adding 2M KCl solution to the sample, shaking for 1 h and then filtering. Sometimes, a $CaCl_2$ solution is used in place of KCl (Bonde and Rosswall, 1987). The KCl solution to soil ratio varies from 4.5:1 to 10:1 (mass basis) and the extraction can be accomplished either in one step or several washes (Cabrera and Kissel, 1988). The filtrate is analyzed for NH_4^+ and NO_3^- via a variety of methods. Non-linear regression is used to determine both the potentially mineralizable N and the mineralization rate constant for first order models. A description and analysis of this technique is given by Robinson (1985).

There are a number of drawbacks to using *in vitro* techniques to determine mineralization rates in agricultural situations. First, the methods often require over 60 days, making them expensive and logistically difficult for routine farm use (Gilmour et al., 1996). Second, *in vitro* incubations are conducted under controlled light, temperature and soil moisture conditions that are not characteristic of actual soil conditions in the field (Smith and Peterson, 1982). The soil disturbance (i.e. drying, grinding, sieving and re-wetting) that is necessary for preparing *in vitro* trials may result in artificially inflated N_O and mineralization rate values (Cabrera and Kissel, 1988). This may be due to the destruction of the protective capacity of clays and thus the movement of organic matter out of the protected organic matter pool and into a pool with a higher mineralization rate (see Figure 2.3) (Benbi and Richter, 2002). *In vitro* mineralization experiments do not account for important farm field parameters such as tillage, irrigation, the growth of crops, freeze-thaw cycles, wetting-drying cycles or the action of macro-invertebrates such earthworms. There do not appear to be any *in vitro* attempts to determine the mineralization rates of recalcitrant organic N during the cool season.

These drawbacks have led to a number of efforts to perfect a rapid analysis index to predict the amount of potentially mineralizable nitrogen in soils, bio-solids and manure (Serna and Pomares, 1993; Bundy and Meisinger, 1994; Gilmour et al., 1996). Soil N mineralization indices are correlated to N_O and can sometimes be used to adjust nitrogen fertilizer rates to account for expected N mineralization. For example, the N mineralization index recommended by Oregon State University for winter wheat employs a two week anaerobic incubation of soil samples, followed by NH_4^+ analysis (Hart et al., 2006). However, no rapid analytical technique has been found that accurately predicts nitrogen mineralization potential at the farm field level under a variety of conditions that include recalcitrant organic N derived from manure that mineralizes during the cool season. The task of developing such a technique is complicated by the high variability of manure and soil characteristics, climate and management between farms and regions (Vigil et al., 2002).

2.6.2 In situ determinations based on crop response

Four *in situ* methods for determining suitable manure (or other organic amendment) application rates are fertilizer equivalence (FE), apparent N recovery (ANR), relative N recovery (RNR) and ^{15}N recovery. These methods measure the response of crops to changes in pools 1 through 4 in Figure 2.3. Because of the costs involved in trying to excavate entire plants from soil, these methods generally only measure above-ground portions of the crops and so are based on an assumption that above-ground N uptake is well correlated to root N uptake.

2.6.2.1 Fertilizer equivalent (FE)

With *FE*, a series of crop plots are fertilized with two or more rates of inorganic N fertilizer while adjacent plots are treated with one or more rates of organic amendment (e.g. manure). One or more parameters (e.g. total above-ground crop N uptake) are regressed as a function of inorganic N fertilizer rate. That parameter is also measured for a given rate of organic amendment. To solve for *FE*, data from the plot receiving the organic amendment is entered into the regression curve for the inorganic N fertilizer to determine the amount of inorganic fertilizer that is equivalent to that rate of organic amendment. The *FE* method is based on an assumption that the only effect the organic amendment has on the measured crop parameter is due to the amendment's available N. For example, the *FE* method is unreliable if the organic amendment significantly stimulates growth of the crop because it improves soil structure and water holding capacity. Interesting examples of the *FE* method can be found in Gale (2004).

2.6.2.2 Apparent N recovery (ANR)

ANR compares crop N uptake from plots receiving the organic amendment with control plots receiving no amendment. *ANR* is also called the "difference method" because it is based on the assumption that N mineralized from pools 7 through 11 in Figure 2.3 and then taken up by the crop will be the same whether or not organic amendments (pools 1 through 4) are added. *ANR* is calculated by:

$$ANR = (\text{treatment N harvest} - \text{control N harvest})/(\text{applied N}) \quad [2.31]$$

where treatment N harvest is the N (kg ha^{-1}) harvested in the above-ground portion of the crop treated with organic amendment, control N uptake (kg ha^{-1}) is that harvested from the non-amended plot and applied N is the total N (kg ha^{-1}) applied to the treatment plots. An example of the *ANR* method can be found in Beckwith et al. (2002).

2.6.2.3 Relative N recovery (RNR)

RNR is similar to *ANR*, except N uptake from control plots is not subtracted. *RNR* overestimates N recovery compared with *ANR* (Cherney et al., 2002).

$$RNR = \text{(treatment N harvested)/(applied N)} \qquad [2.32]$$

2.6.2.4 ^{15}N recovery

^{15}N recovery is similar to *ANR*, but uses isotopic N. It is calculated by measuring the percentage of ^{15}N recovered in the above-ground portion of the crop. For this method, one set of plots receives an organic amendment treated with ^{15}N and another set of plots receives the same rate and type of organic amendment that is not treated with ^{15}N. The calculation is:

$$^{15}\text{N recovery} = U(c - d)/f(m - g) \qquad [2.33]$$

where U is the above-ground crop N harvested (kg ha^{-1}), c is the atom % ^{15}N in the treated crop, d is the atom % ^{15}N in the control crop, f is the total organic amendment N applied (kg ha^{-1}), m is the atom % ^{15}N in the treated organic amendment and g is the atom % ^{15}N in the untreated organic amendment.

Increases in U relative to f indicate that either a high percentage of the manure N became available and was used by the crop or the pre-existing soil N pools supplied a large amount of available N to the crop. Because the atom % ^{15}N of the pre-existing soil N pools is assumed to be significantly less than that of the labeled organic amendment, c will be smaller than m if the pre-existing soil N pool supplies any N to the crop. If all other factors remain constant, an increase in c indicates an increase in the relative contribution of N from the organic amendment versus N from pre-existing soil pools. The d and g terms are included to account for potential differences in the atom % ^{15}N between the untreated manure and the pre-existing soil N pools.

The atom ^{15}N recovery method does not rely on the assumptions needed for the *FE* and the *ANR* methods. An example of the ^{15}N recovery method can be found in Munoz et al. (2004). *ANR* and ^{15}N recovery both estimate the fraction of N in the organic amendment that is actually taken up by the crop. *FE* compares the response of a crop to the organic amendment versus inorganic N fertilizer. Because inorganic N fertilizer is never completely taken up by a crop, *FE* estimates tend to be higher than *ANR* and ^{15}N recovery. In a trial comparing the three methods, Munoz et al. (2004) found that the ^{15}N recovery method had less variability than the other methods, however it involved more time and expense to plan, set up and conduct the ^{15}N recovery experiment.

The *ANR*, *RNR*, *FE* and ^{15}N recovery methods generally focus on determining N mineralization from an organic amendment during the first growing season after addition. Because these methods all rely on crop uptake, they are not well suited for measuring cool season mineralization of recalcitrant organic N when crop uptake is low or no crops are growing.

2.6.3 In situ determinations based on mineral N measurement

The four methods described above are not designed to estimate net N mineralization because they do not account for losses of N to the environment. Estimating net N mineralization requires measuring changes in mineral N (pools 5 to 6 in Figure 2.3) and may include manipulations of some of the organic N pools. *In situ* net N mineralization measurement requires methods such as closed-container incubations, lysimeters and ion exchange resin / soil cores (IER/SC).

2.6.3.1 Closed-containers

Closed-container incubations eliminate or greatly reduce movement of water through incubating soil. This is accomplished by containing the soil in a sealed plastic bag or a polyvinyl chloride (PVC) tube that is capped at the top to prevent precipitation or irrigation water from entering. The soil can be collected in bulk, mixed and then packed into the containers by hand or it can be collected in intact soil cores which are placed into the container with minimal disturbance. Because little or no water enters or leaves the container, insignificant mineral N leaches out. Thus, net N mineralization can be estimated by subtracting the initial mineral N concentration in the soil from the final mineral N concentration. Closed-container incubations generally do not allow the moisture level of the incubating soil to fluctuate naturally with precipitation events, however Subler et al. (1995) reported no significant differences between moisture contents in PVC tubes and the surrounding bulk soil. For long incubations in soils with high N mineralization rates, there is a concern that mineral N concentrations can build inside closed-containers to the point that N mineralization rates are altered.

2.6.3.2 Lysimeters

Lysimeters are monoliths of soil, generally collected with minimal disturbance and contained in structures that are sealed on the sides but open at the top and bottom. Soil water exiting the bottom of lysimeters is collected and analyzed to measure water volumes and concentrations of dissolved compounds of interest. Lysimeter walls extend above the soil surface to prevent inflow or runoff of surface water and usually extend deep enough to allow vegetation to grow with minimal root restrictions.

Depending on objectives, measurements made with lysimeters can include mineral N leaching, N uptake by plants, NH_3 volatilization, denitrification and fluxes in soil mineral N or organic N pools. To distinguish between mineral N supplied by amendments versus pre-existing soil N pools, amendments can be labeled with ^{15}N (Dowdell and Webster, 1980). Labor and material costs to construct lysimeters are high.

2.6.3.3 Ion exhange resin / soil cores (IER/SC)

The use of IER/SC is an *in situ* approach to measuring N mineralization rates and, in some situations, NO_3^- losses from soils. IER/SC address the concerns noted above for the closed-container methods but are much less expensive than lysimeters. IER/SC use tubes made of PVC, aluminum or galvanized pipe that typically measure approximately 5 cm inner diameter by 15 to 50 cm long (Myrold et al., 1992; Kolberg et al., 1997; Sullivan et al., 1999; Eghball, 2000). IER/SC are open at both the top and the bottom to allow exchange of gases and water. However, the bottom of each IER/SC is fitted with ion exchange resins (IER) that capture NO_3^- and NH_4^+ leached from the captured soil column.

IER/SC are either filled with disturbed soil by hand-packing or with relatively undisturbed soil by pounding the tubes into the soil and then extracting intact cores.

When filled by hand-packing, the IER/SC soil can be homogenized to reduce the high variability inherent in the spatial distribution of soil N. Also, the addition of manure N to IER/SC can be more highly controlled when IER/SC are hand-packed. There do not appear to be published studies directly comparing the hand-packed versus undisturbed methods of IER/SC.

IER/SC exclude living plant roots, thus allowing a fairly direct measurement of net N mineralization, because there is no plant uptake of NO_3^-. On the other hand, the lack of living plants makes it difficult to mimic soil moisture conditions in the field. For example, some IER/SC experiments have demonstrated that soil moisture inside the core can be higher than that outside the core. Thus, the core mineralization rates may be higher than under field conditions (Myrold et al., 1992). Root exclusion could negate the bacterial stimulation of root growth as previously noted (Clarholm, 1985), which would tend to decrease N mineralization in IER/SC relative to natural soil. Soil disturbance inherent in hand-packed IER/SC preparation may alter N mineralization rates (Raison, 1987). Presumably, this is because disturbing the soil destroys some of the protective capacity of clay, thereby converting protected organic and microbial N into more labile organic N compounds (see Figure 2.3). However, Sullivan et al. (1999a) collected data from hand-packed IER/SC and adjacent field soils and concluded that the effect of soil disturbance in hand-packed IER/SC may be insignificant.

Living plant roots are severed when the IER/SC are filled, whether the disturbed or undisturbed soil approach is used. These severed plant roots may change net mineralization rates, although Raison (1987) indicates this is unlikely.

IER/SC may be set up in a batch type experiment in which *n* cores are installed initially and then *n/x* cores are harvested for each of *x* time periods. Another method is to install the cores serially: *n/x* cores are installed initially and then harvested at the end of the first time period, at which time a fresh set of *n/x* cores are installed.

Both lysimeters and IER/SC most closely mimic actual field moisture and temperature conditions. Because moisture and temperature factors are critical for measuring cool season mineralization of recalcitrant organic N, these techniques are best suited for this task. Due to their expense, lysimeters are generally limited to detailed studies of a specific site. IER/SC are better suited to studies of cool season recalcitrant organic N mineralization from a range of sites.

2.7 Summary

N is the mineral nutrient most likely to limit the growth of non-leguminous agricultural crops. In soils, N occurs as both organic and inorganic compounds. Organic N compounds vary considerably in form from simple amino acids that are quickly mineralized to humus compounds that are exceedingly complex and can have half-lives of thousands of years. Most of the inorganic N in soil solutions occurs as NO_3^- or NH_4^+.

NO_3^- is a common environmental pollutant because its negative charge limits its adsorption to soil particles and allows it to leach to ground water or be transported via runoff to surface water. Excessive levels of NO_3^- in drinking water can harm human health; excessive levels of NO_3^- in marine systems can lead to hypoxic zones. Under anaerobic soil conditions, NO_3^- can denitrify, generating the greenhouse gas N_2O.

Manure produced on livestock farms has long been used as a source of N (and other nutrients) for crop production. However, the efficiency of manure N utilization, as measured by the mass of crop N harvested divided by the mass of manure N applied, tends to be low. This can result in high levels of residual soil NO_3^- at the end of the growing season. Residual soil NO_3^- is highly prone to runoff, leaching and denitrification. Due to the environmental risks involved, which are compounded by the trend toward the concentration of greater numbers of livestock on fewer farms, the application of manure is regulated on large livestock farms (CAFOs) in the United States. These regulations are based in part upon standards developed by the United States Department of Agriculture (USDA).

One of the reasons that manure N has low utilization efficiency is that it is difficult to manage the mineralization of recalcitrant organic N compounds contained in manure. The mineralization of organic N compounds in manure during the growing season has been the subject of numerous studies. However, there has been little effort to investigate the mineralization of recalcitrant organic N compounds from manure during the cool season, the time period when crops are either not grown or are often dormant, precipitation typically exceeds evapotranspiration and NO_3^- runoff, leaching and denitrification are most likely. Cool season recalcitrant organic N mineralization is neither addressed in United States CAFO regulations nor in the protocols for determining appropriate manure application rates.

Numerous models, mostly based on first order mineralization kinetics, have been developed to simulate N mineralization in soils. Apparently, no modeling studies have investigated the potential for cool season recalcitrant organic N mineralization in manured fields.

In vitro and *in situ* techniques have been developed to measure N mineralization, but these techniques have never been used to measure the mineralization of recalcitrant organic N in manured fields. The process of organic N mineralization in soils is affected by spatially and temporally variable chemical, biotic and physical factors. To capture the effect of these processes, especially during the cool season, it is reasonable to use *in situ* ion exchange resin / soil cores (IER/SC).

IER/SC can be prepared either by homogenizing and hand-packing soil samples into tubes, or by collecting relatively undisturbed cores. Both techniques have been described in peer-reviewed publications, but there do not appear to be any studies that directly compare the results of these two techniques.

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CHAPTER 3. RECALCITRANT ORGANIC N DYNAMICS IN MANURED SOILS (RONDIMS), A MODEL

3.1 Abstract

Nitrogen (N) is both the most often limiting mineral nutrient for non-leguminous crop growth and a common environmental contaminant, especially on farms that apply manure to soils. Manure applications tend to increase the recalcitrant organic nitrogen (*RON*) pool in soils and the subsequent mineralization of this *RON* can be significant. Some *RON* will mineralize during the cool season when crop N uptake is minimal and leaching and denitrification may be high due to precipitation that exceeds evapotranspiration. In this project, a simple model, Recalcitrant Organic Nitrogen Dynamics In Manured Soils (RONDIMS) was developed to investigate the effects of management practices on the seasonal mineralization of *RON* in manured soils.

Simulations were based on 10 years of weather data (1995 to 2005) at Corvallis, Oregon and assumed that *RON* had reached a steady-state after a long prior period of manure application. Simulations included four cropping systems with optimal manure and irrigation application and three cropping systems based on farm records. RONDIMS predicted that manure was a more important source of *RON* than crop residue in these systems, especially for annual crops or when manure was applied in solid form. The model predicted that N efficiency (crop harvested N / applied N) ranged from 38 to 78%.

The optimized scenarios applied manure just before maximum crop N uptake and at rates that supplied just enough N to meet crop demands. The farm record scenarios applied too much manure too late in the year for optimal crop utilization. Because of this, the farm record scenarios had higher residual mineral N (49 to 135 kg ha^{-1}) in the fall than did the optimized scenarios (9 to 19 kg ha^{-1}).

However, the cool season mineralization of *RON* was high for both optimized (29 to 73 kg ha^{-1}) and farm record (31 to 52 kg ha^{-1}) scenarios. In five of the seven scenarios, cool season mineralization of *RON* was greater than the concentration of residual mineral N in the fall. RONDIMS predicted that each of the farm record scenarios and one of the optimized scenarios would have average annual leachate concentrations equal to or greater than the 10 mg N L^{-1} drinking water standard and that cool season mineralization of *RON* contributed from 9 to 55% of the leached N. RONDIMS also predicted that cool season mineralization of labile organic N (*LON*) contributed from 10 to 60% of the leached N. The cool season *LON* pool was formed primarily from crop residues in the optimal scenarios and by both crop residues and late season manure applications in the farm record scenarios.

These RONDIMS predictions are consistent with current public policy that promotes applying manure at optimal times and rates in order to reduce residual mineral N concentrations in the fall. However, RONDIMS predicted that even when manure is applied at optimal times and rates, the mineralization of *RON* and *LON* during the cool season may still result in excessive levels of NO_3^- leaching to groundwater. Cool season *RON* mineralization was especially high in the simulated farming system that applied solid manure, according to RONDIMS. RONDIMS predicted that a perennial grass crop (*Dactylis glomerata* L.) or an annual grass cover crop (*Lolium multiflorum* Lam.) could capture mineral N formed by the cool season mineralization of *RON* and *LON*, and thus reduce NO_3^- leaching.

RONDIMS predicted that, with proper timing of soil collection, the labile organic N concentration in ion exchange resin / soil core experiments can be minimized, thus allowing field studies that decouple the dynamics of labile versus recalcitrant organic N.

3.2 Introduction

Because of its propensity to form gaseous compounds and anions, N is easily lost from soil ecosystems. At the same time, N is the mineral nutrient that is most likely to limit the growth of non-leguminous crop plants (Meisinger et al., 1992). Because it is both vital to plant nutrition and easily lost from soil ecosystems, soil N has been the subject of many studies, especially as related to manured soils.

Animal manure applications can result in yields comparable to commercial N fertilization (Cherney et al., 2002). However, animal manure applications to cropland increase the likelihood of NO_3^- runoff to surface water (Cameron, 1986; Bushee et al., 1998), which may impact reservoirs used for drinking water, contribute to eutrophication and lead to hypoxic zones in marine systems (EPA, 2002). Manure applications can increase leaching of NO_3^- to groundwater, which can impact aquifers used for drinking water (Heatwole et al., 1990; Holloway et al., 1996). Manure applications can increase the rate of denitrification and result in emissions of the greenhouse gas N_2O, which has a global warming potential of 310 CO_2 equivalents per N_2O molecule (Six et al., 2002).

These N losses are consistent with the low efficiency of crop N uptake from manure sources. On corn (*Zea mays* L.) plots in Wisconsin, only 15 to 18% of N applied via fresh dairy manure mixed with straw was recovered by the crop (Munoz et al., 2004). In a four-year trial on two UK perennial ryegrass (*Lolium perenne* L.) plots, the crop recovered 30 to 45% of applied N for fall applications and 38 to 72% for spring applications of cow manure slurry at 150 kg N ha^{-1}. For applications made at twice this rate, N recovery was 20 to 22% for fall applications and 32 to 64% for spring applications (Beckwith et al., 2002).

Although some mineral N leaches or denitrifies during the growing season, mineral N not taken up by crops often remains as residual soil NO_3^- at the end of the growing season. In many agricultural regions, the end of the growing season marks the beginning of a cool season in which precipitation rates are high, evapotranspiration rates are low and plant N uptake is low. During this cool season, residual soil NO_3^- is vulnerable to the leaching, runoff and denitrification losses discussed above. The concentration of residual soil NO_3^- has been used to evaluate manure application rates and application timing (Sullivan and Cogger, 2002) and some European states regulate permissible levels of residual soil NO_3^- (Hofman et al., 1994).

One reason the goal of reducing cool season losses of N on manured fields is difficult to achieve is that manure supplies N in a variety of forms that vary considerably in their availability to plants (Gilmour et al., 1977). Ammonium and labile (quickly mineralized) organic N in manure convert to NO_3^- and are essentially completely available to crops during the growing season in which they are applied. Applying manure to synchronize the availability of NH_4^+ and labile organic N (*LON*) compounds with crop N uptake is relatively straightforward (Hart et al., 1997). However, manure also contains recalcitrant organic N (*RON*) that mineralizes slowly and may not be converted to NO_3^- for many months or years after application.

Because mineralization of organic N follows first order kinetics, *RON* in stable farming systems will eventually approach a steady-state in which the *RON* mineralization rate will essentially equal the rate of *RON* addition from crop residues, manure or other sources (Fried et al., 1976). Nitrate resulting from *RON* mineralization *during* the cool season may leach, runoff or denitrify just like residual soil NO_3^- that is formed *before* the cool season. However, the length of time required to reach a *RON* steady-state in manured soils, the size of the resulting N pools and the cool season N mineralization rates that result are unknown.

Nine process-based computer models that can simulate N mineralization in manured fields are described in Table 3.1 (Ma and Shaffer, 2001). Although these models all use first-order N mineralization equations, they differ in the number of organic N pools they employ and also differ in the objectives for which they were developed. Apparently, no N mineralization modeling studies have focused on the mineralization of *RON* in manured soils during the cool season. The models shown in Table 3.1 are complex, require considerable parameterization and were not designed to compare cool season mineralization of *RON* in different cropping systems.

Table 3.1. Computerized N mineralization models. These models generally employ first order kinetics to simulate N mineralization (Ma and Shaffer, 2001).

Model name	Organic N pools	Objectives	Institution	Reference
NTRM (Nitrogen, Tillage and crop Residue Management)	1	Examine soil management strategies and the effect of climate change on crop yields and nitrate leaching.	USDA-ARS	(Shaffer and Larson, 1987)
NLEAP (Nitrogen Loss and Environmental Assessment Package)	3	Quantify agricultural nitrate leaching and economic factors resulting from management strategies.	USDA-ARS	(Shaffer et al., 1991)
RZWQM (Root Zone Water Quality Model)	5	Simulation of agricultural management on water quality, including nitrogen, pesticides.	USDA-ARS	(Ahuja et al., 2000)
CENTURY	5	Simulate long-term effects on soil and carbon dynamics.	Colorado State University	(Parton et al., 1994)
CERES (Crop Estimation through Resource and Environment Synthesis)	4	A family of models that simulate crop growth and various soil functions.	Various U.S. and European universities	(Hanks and Ritchie, 1991)
GLEAMS (Groundwater Loading Effects of Agricultural Management Systems)	3	Evaluate the effect of management practices on pesticide and nutrient leaching.	Univ. of Georgia, USDA-ARS	(Leonard et al., 1987)
LEACHM (Leaching Estimation and Chemistry Model)	3	Simulates vertical movement of water, pesticides, nitrogen and phosphorus.	Cornell Univ.	(Hutson, 2000)
NCSOIL	4-6	Study the mechanisms of N and C cycling, using modeled N and C tracers.	Univ. of Minnesota	(Molina et al., 1983)
EPIC (Environmental Policy Integrated Climate)	3	Study the effects of erosion on crop yield, plus simulate nitrogen leaching and phosphorus runoff.	Texas A&M Univ.	(Williams, 1995)

A simple N mineralization model for manured soils, Recalcitrant Organic Nitrogen Dynamics In Manured Soils (RONDIMS), was developed here to simulate the contribution of manure to soil *RON* and the subsequent mineralization of *RON* during the cool season. Seven cropping systems were compared: four with optimized manure applications made at agronomically optimal rates and timing and three with manure application rates and timing based on records from farms participating in the ion exchange resin / soil core (IER/SC) studies described in other chapters of this document. The IER/SC farms chosen for modeling were the locations for Fields B, E and G described in other chapters.

3.3 Materials and methods

RONDIMS minimizes the number of parameters needed to model manured soils, but focuses on the dynamics of *RON*. RONDIMS is written in Microsoft Excel©, version 2003. RONDIMS uses a daily time step, has one input screen and six modules: weather, mineral N, *LON*, *RON*, crops and soil water. In this study, RONDIMS was used to simulate steady-state conditions for *RON*, based on the concept of Fried et al. (1976) that constant manure additions to the soil will eventually approach a steady-state at which time the mass of *RON* mineralized annually will essentially equal the annual mass of *RON* added. Organic N mineralization calculations are based on the double pool exponential model widely described in the literature (Molina et al., 1980; Deans et al., 1986; Bonde and Rosswall, 1987; Vanotti et al., 1995; Gilmour et al., 1996).

3.3.1 Input screen

In the RONDIMS input screen, the user enters a variety of data concerning soil, manure, crops and irrigation. Although these data may be entered in any sequence, the approach used in this study was as follows.

3.3.1.1 LON and RON mineralization rates

The *LON* mineralization rate constant was set at 0.1 d^{-1} at 35 ºC. The *RON* mineralization rate constant was set at 0.001 d^{-1} at 35 ºC. These values are consistent with values reported in the literature. For example, Deans et al. (1986) found *LON* mineralization rate constants of approximately 0.3 d^{-1} and *RON* mineralization rate constants of 0.004 d^{-1} in an analysis of soil data from Minnesota, Maryland and Connecticut. Paul and Clark (1989) estimated N mineralization rates for the labile portion of manure and crop residue (e.g. amino acids) at 0.2 d^{-1} and rates for the recalcitrant portions ranging from 0.08 d^{-1} (for N associated with cellulose) to 0.0003 d^{-1} (for clay protected N compounds). Gilmour et al. (1996) found *LON* mineralization rate constants of approximately 0.17 d^{-1} and *RON* mineralization rate constants of 0.003 d^{-1} with biosolid amended soil in Arkansas. Quemada et al. (1997) estimated N mineralization rate constants for carbohydrate and protein (the labile portion of crop residue) to range from 0.14 to 0.67 d^{-1} and for lignin and cellulose (the recalcitrant portion of crop residue) to range from 0.00095 d^{-1} to 0.021 d^{-1}.

3.3.1.2 Available water holding capacity of the soil.

This was set at 0.2 cm water cm^{-1} soil for all scenarios modeled in this study. This capacity is suitable for silt loam soils in Oregon's Willamette Valley (Green et al., 1982). The initial water balance on 1 October 1995 was set to 50% of the available water holding capacity for all scenarios because that was the target moisture level for irrigation in the optimized cropping systems that were modeled and also corresponded well with early fall soil moisture levels measured for these soil/crop systems in the ion exchange resin / soil core *in situ* experiments conducted as part of the overall *RON* project.

3.3.1.3 Crops and planting dates

In this study, three cropping systems were examined: continuous corn (*Zea mays* L.), corn followed by an annual ryegrass (*Lolium multiflorum* Lam.) cover crop and perennial orchardgrass (*Dactylis glomerata* L.). The corn was planted on 14 May.

Annual ryegrass was planted on 1 October and harvested as silage or greenchop on 30 April. The perennial grass was assumed to be an established crop at the beginning of the simulations and to remain as a perennial crop throughout the simulations. Planting and harvesting dates for the optimized scenarios were based on a study by Moberg and Rambo (2000).

3.3.1.4 Irrigation

For the optimized cropping systems, 2.5 to 5.0 cm of irrigation was applied when the soil moisture in the root zone dropped to 50% of the available water holding capacity during the irrigation season (June through September). RONDIMS predicted soil moisture deficiencies during October through May to be minor. A June through September irrigation season, with 5 cm average irrigation amounts corresponds to actual irrigation practices for these crops in Oregon's Willamette Valley (Moberg and Rambo, 2000). With this irrigation regime, RONDIMS predicted that soil moisture in the root zone would occasionally drop below 50% available water holding capacity during some summers in 1996 through 2005. For the farm record scenarios, irrigation was applied based on farmer records for typical irrigation frequency and rate during average years. These farmers reported less frequent irrigation than would be optimal for crop growth, due to a shortage of labor and irrigation equipment on these farms.

3.3.1.5 Applications of manure to soil

For the optimized cropping systems, manure applications to each field were simulated at rates and times that minimized N deficiency for the corn and perennial grass crops. "Minimize" was defined in this study to mean that RONDIMS predicted less than 10 kg N ha^{-1} deficiency for corn during an average growing season, and less than 10 kg N ha^{-1} deficiency for perennial grass during the main N uptake period of February through October RONDIMS predictions of N deficiency for perennial grass during November through January were ignored as N uptake during this period is low and it is logistically difficult for farms to apply manure during this time of year due to high rainfall conditions.

RONDIMS predictions of N deficiency for annual ryegrass at any time were ignored as the objective for this crop is to utilize residual soil N (Shipley et al., 1992; Gangwer, 1999).

Manure applications were scheduled in RONDIMS beginning in the spring. The minimum application made was 25 kg N ha^{-1} and applications were adjusted upward in 5 kg N ha^{-1} increments until the objectives outlined above were achieved. There were no constraints placed on manure timing other than described above. Consequently, in the optimized cropping scenarios, numerous manure applications were made to match N supply to crop need, thus minimizing both leaching and crop N deficiency. For example, in the optimized continuous corn liquid manure scenario, manure was applied four times, beginning on 15 June and ending on 15 July.

Manure NH_4^+-N and organic N concentrations for the optimized simulations were based on Hart et al. (1995) estimates for dairy manure. For the simulations based on farm records, manure test data from the respective farms were used to determine manure NH_4^+-N and organic N fractions. For both optimized and farm record simulations, the organic N was estimated to be 44% labile / 56% recalcitrant for liquid manure and 35% labile / 65% recalcitrant for solid manure. These estimates were derived by using an iterative solution for a double pool exponential mineralization equation with a *LON* mineralization rate constant of 0.1 d^{-1}, a *RON* mineralization rate constant of 0.001 d^{-1} and estimates from work by Koelsch and Shapiro (2006) for dairy manure organic N mineralization over time. These estimates are reasonably consistent with the 25% *LON* / 75% *RON* fractionation estimated by Gilmour et al. (1996) for biosolids.

3.3.1.6 Beginning mineral N, LON and RON concentrations

These values were established with an iterative process in which initial guesses for 1 October 1995 values were input and a 10-year simulation was made. The ending value was then used as the new beginning value, and this process was repeated until the beginning and final N pools matched (within 1 kg N ha^{-1}) and crop N availability goals were reached. Thus, for both the optimized and farm record simulations, the systems were assumed to have reached a steady-state level of *RON* prior to the start of the simulation. For the farm record simulations, this is a significant departure from the soil/crop systems on the farms used for IER/SC trials. The farm records used for the simulations on these fields were from only one or two year's data (depending on the field). These farm records were approximate, imprecise and not verifiable. For the purposes of the simulations described below, the farm records are accurate enough to achieve the objectives of this study. However, none of the IER/SC farms had precise records extending back in time far enough to determine whether *RON* had approached a steady-state. Indeed, the simulations described below assume that only one crop was grown repeatedly on these farm record fields, which was not the case. In summary, the farm record scenarios were useful to contrast the optimized scenarios with more typical farming systems, but did not attempt to truly model the N dynamics in those actual fields.

3.3.2 Weather module

The weather module uses data from the Agrimet (Bureau of Reclamation, 2005) service for Corvallis, Oregon (44.5°N, 123.3°W) for 1 October 1995 through 30 September 2005. These 10 years of data can easily be changed in RONDIMS to other locations or time periods, however this was not done in this study. Initial weather data include mean daily soil temperature (ºC) at 4 inch depth (approximately 10cm), mean daily air temperature (ºC), daily precipitation (cm), and reference evapotranspiration (cm). The Agrimet reference evapotranspiration (ET) is based on alfalfa (*Medicago sativa* L.). Conversion of this reference ET to daily predictions for a given crop is made in the soil moisture module. RONDIMS converts daily weather data into temperature-adjusted *LON* mineralization rate constant (d^{-1}) and temperature-adjusted *RON* mineralization rate constant (d^{-1}).

The daily temperature-adjusted mineralization rate constants are calculated with Eq. [3.1] (Vanotti et al., 1995):

$$k = k_{Tr}(0.933^{(Tr-Ts)}) \qquad [3.1]$$

where k is the rate constant (d^{-1}) adjusted for soil temperature, k_{Tr} is the rate constant at the reference temperature of 35ºC (0.1 d^{-1} for *LON* and 0.001 d^{-1} for *RON* in these simulations), 0.933 is a constant that applies when the reaction rate halves with every 10°C decrease in temperature and *Ts* is the mean soil temperature (°C) at 10 cm depth. RONDIMS also calculates the average annual mineralization rate constants for *LON* and *RON* for the 10 year simulation.

RONDIMS tallies Growing Degree Days (*GDD*) for use in modeling crop growth, using Eq. [3.2] through Eq. [3.4] (Pirelli et al., 2004):

$$GDD_i = Ta - Tb \quad \text{, if } Ta >= Tb \qquad [3.2]$$

$$GDD_i = 0 \quad \text{, if } Ta < Tb \qquad [3.3]$$

$$GDD = \sum_{i=\Phi}^{\Omega} GDD_i \qquad [3.4]$$

where GDD_i is a single day's contribution to *GDD*, *Ta* is the mean air temperature for that day (°C), *Tb* is the base temperature, Φ is the date calculations begin and Ω is the date calculations end. For RONDIMS crop modeling, *Tb* is 6°C for cool season grasses (annual ryegrass and orchardgrass) and 10°C for corn. For annual crops, Φ is the planting date and Ω is the harvest date. For perennial crops, Φ is 1 October and Ω is 30 September. RONDIMS uses *GDD* to calculate crop N uptake, using Eq. [3.10] through Eq. [3.14].

RONDIMS does not calculate T-Sum 200 (see Eq. [2.1] through Eq. [2.3]). T-Sum 200 is a good estimate of the date that cool season grasses begin accelerated N uptake from the soil in late winter (Pirelli et al., 2004). However, this estimate of one specific date on which N uptake accelerates is not necessary in RONDIMS because RONDIMS simulates N uptake on a daily basis.

The RONDIMS weather module also tracks irrigation applications and calculates the 10 day rolling average precipitation, ET and precipitation plus irrigation.

3.3.3 Mineral N module

Mineral N for RONDIMS is defined as NO_3^--N plus NH_4^+-N. RONDIMS calculates mineral N (kg N ha^{-1}) in five soil layers. For all scenarios, the surface soil (root zone 1) was 25 cm deep. RONDIMS forecasts the deepest rooting crop in a simulation and evenly divides root zones 2 through 5 between the deepest rooting depth and the bottom of root zone 1. Rooting depths are described in the soil moisture section. For the scenarios described here, root zones 2 through 5 were each 23.75 cm deep. Sources of mineral N in root zone 1 include direct addition of NH_4^+ via manure, and mineralization of *LON* and *RON*. The only source of mineral N for root zones 2 through 5 is assumed to be leaching from root zone 1. Sinks of mineral N include crop uptake from all root zones, NH_3 volatilization from root zone 1 and leaching from root zone 5. RONDIMS assigns all NH_3 volatilization to occur on the day manure is applied. Volatilization rates depend on type of manure and application method as shown in Table 3.2 (USDA-NRCS, 1992).

Mineral N leaches based on the fraction of percolation on a given day divided by the available water holding capacity of the root zone. For example, if there is 20 kg mineral N ha^{-1} in root zone 1, the root zone currently holds its full capacity of 6.0 cm water and 3.0 cm of precipitation falls, then half of the root zone water (3.0 cm / 6.0 cm) is assumed to percolate and RONDIMS will move half of the mineral N (10 kg N ha^{-1} in this example) down to root zone 2. Mineral N leaching from the root zone 5 is lost from the system. Thus, RONDIMS assumes mineral N leaching is via advection (plug flow), with no disperson. This simplification of hydrology is consistent with the project's goals for a simple model that focuses on N mineralization. Calculations of N concentrations in leachate were based on similar hydrologic simplifications described by Zebarth (1995).

RONDIMS tracks four pools of mineral N in each of the five root zones: that derived from direct addition of NH_4^+, mineral N derived from *LON* mineralization, mineral N derived from *RON* mineralization during the cool season and mineral N derived from *RON* mineralization during the warm season. RONDIMS does not distinguish between NO_3^--N and NH_4^+-N, which may cause RONDIMS to overestimate leaching, since NH_4^+ is not generally prone to leaching (Brady and Weil, 1996). RONDIMS does not have a routine to predict denitrification, which may also lead to overestimations of N leaching.

Table 3.2. NH_3 volatilization parameters used in RONDIMS, based on USDA estimates (USDA-NRCS, 1992). The values shown are the percent of NH_4^+ in manure that RONDIMS predicts will volatilize after spreading. All volatilization in RONDIMS occurs on the application date.

	Oct-April	May-Sept
Liquids sprinkled	25%	25%
Solids broadcast		
incorporated within 4 days	5%	40%
incorporated after 4 days	10%	50%

3.3.4 Labile organic N (LON) module

In the simulations described here, RONDIMS defines *LON* as organic N compounds with a mineralization rate constant, k_{Tr} from EQ. [3.1], of approximately 0.100 d^{-1} at 35ºC. *LON* mineralization is calculated by a first order equation (Stanford and Smith, 1972; Paul and Clark, 1989; Serna and Pomares, 1991):

$$d(LON)/dt = -k(LON) \qquad [3.5]$$

where k is the temperature-adjusted rate constant (d^{-1}) as defined in Eq. [3.1]. Integrating Eq. [3.5] results in:

$$LON_t = LON_O \exp(-kt) \qquad [3.6]$$

where LON_t is *LON* (kg ha^{-1}) after elapsed time t, LON_O is initial *LON* and "exp" is the natural exponential function[1].

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[1] Throughout this paper, "exp" is used to denote the natural exponential function in which the base of the natural logarithm (e) is raised to the power of the parenthetical value immediately following "exp."

RONDIMS adds all manure and crop residue *LON* to root zone 1. Crop residue is added on the harvest date for annual crops and on 30 September for perennial grass. RONDIMS tracks daily *LON* mineralization and cumulative *LON* mineralization for each water year (1 October through 30 September).

3.3.5 Recalcitrant organic N (RON) module

In the simulations described here, RONDIMS defines *RON* as organic N compounds with a mineralization rate constant, k_{35} from EQ. [3.1], of approximately 0.001 d^{-1} at 35ºC. *RON* mineralization is calculated with the same method as *LON* mineralization, except that the rate constant is smaller (Stanford and Smith, 1972; Paul and Clark, 1989; Serna and Pomares, 1991):

$$d(RON)/dt = -k(RON) \qquad [3.7]$$

where k is the temperature-adjusted rate constant (d^{-1}) as defined in Eq. [3.1]. Integrating Eq. [3.5] results in:

$$RON_t \;=\; RON_O \exp(-kt) \qquad [3.8]$$

where RON_t is *RON* (kg ha^{-1}) after elapsed time t and RON_O is initial *RON*.

RONDIMS adds all manure and crop residue *RON* to root zone 1. Crop residue is added on the harvest date for annual crops and on 30 September for perennial grass. Although RONDIMS maintains a running total of *RON* in root zone 1, it also tracks each yearly addition of *RON* separately (as well as the *RON* specified at the beginning of the simulation). This allows the user to monitor the relative ages of the *RON* fractions. As with *LON*, RONDIMS tracks both daily *RON* mineralization and cumulative mineralization for each water year (1 October through 30 September). The main RONDIMS model runs for 10 years. However, the *RON* module also predicts the size of the *RON* pool for 50 years, based on the mean annual *RON* additions and the mean annual temperature-adjusted *RON* mineralization rate constant.

The mineralization module used in RONDIMS is a simplified calculation compared with the models listed in Table 3.1, which typically include calculations of C:N ratio in organic residues in order to determine net mineralization rates (McGill et al., 1981; Sharpley and Williams, 1990; Vigil and Kissel, 1991). This simplification was used because RONDIMS is designed to predict organic N dynamics over long periods of time, over which C:N ratios are likely to be of minor importance. RONDIMS is also simplified, compared to models in Table 3.1, in that it does not track a stable organic matter pool (humus). RONDIMS assumes that humus materials in the soil have reached a steady state and that neither the mass of humus that mineralizes nor the mass of new humus created is significant.

3.3.6 Crop module

RONDIMS allows the user to specify crop parameters including maximum potential N uptake (kg ha^{-1} yr^{-1}), length of growing season (d), % of total crop N that is harvested, fractionation of crop residue between *LON* and *RON*, root depth at maturity and crop N uptake function. Values are shown in Table 3.3.

Table 3.3. Crop parameters used in RONDIMS simulations. Corn N uptake in the farm record scenario with continuous corn was 282 kg ha^{-1}. Corn N uptake in the farm record scenario in which corn was followed by annual ryegrass was 313 kg ha^{-1}.

	Growing season (d)	**Potential crop N uptake (kg ha-1)**	**Total N harvested (%)**	**Fraction labile organic N in residue**	**Rooting depth (cm)**	**Base temperature for GDD (ºC)**	**N Uptake equation**
Optimized crop systems							
continuous corn	133	282	83	0.68	120	10	Watts & Hanks
annual ryegrass	212	131	74	1.00	30	6	polynomial
perennial grass	365	272	77	0.25	120	6	polynomial
Actual crop systems							
continuous corn	133	282-313	83	0.68	120	10	Watts & Hanks
annual ryegrass	212	162	74	1.00	30	6	polynomial
perennial grass	365	155	77	0.25	120	6	polynomial

Recalcitrant organic N in residue = 1 - labile organic residue

The RONDIMS crop module calculates total potential crop N uptake with Eq. [3.9]:

$$C_{NU} = ((C_{BH})\ (C_{FN}))\ /\ ((C_{AH})\ (C_{FT})) \qquad [3.9]$$

where C_{NU} is the potential crop N uptake (kg ha^{-1}). C_{BH} is the harvested crop dry matter (kg ha^{-1}), determined for the optimized scenarios with published yield data (Green et al., 1982; Gangwer, 1999; Moberg and Rambo, 2000) and for the farm record scenarios using farmer records. C_{FN} is the fraction of N in C_{BH}, based on livestock feed data (Cullison and Lowrey, 1987). C_{AH} is the fraction of the above-ground crop that is harvested, based on USDA estimates for various harvesting methods (Foster et al., 2003). C_{FT} is the fraction of the total crop N that is above the ground, and was based on estimates of 75 to 90% of the biomass of annual crops being above ground (Harvey, 1939; Gangwer, 1999; Sullivan et al., 1999). For perennial crops, C_{FT} is the fraction of crop N turnover that is above ground, where crop N turnover is the sum of the harvested above-ground crop N plus above-ground crop residue N that is added to the soil annually plus root N that is added to the soil annually via root die-off, as estimated by USDA (Foster et al., 2003).

The product (C_{AH}) (C_{FT}) is "% total N harvested" in Table 3.3. This convoluted method of determining potential crop N uptake was necessary because there are little or no published data for total N uptake by both roots and above-ground portions of crops grown to maturity in field conditions.

The RONDIMS crop module assumes the fraction of crop residue N that is associated with *RON* compounds equals the sum of the cellulose, hemicellulose and lignin concentration in the residue (Quemada and Cabrera, 1995; Quemada et al., 1997), based on published feed analyses of crops and crop residues (Cullison and Lowrey, 1987). RONDIMS assumes no crop N is NH_4^+, so the remaining fraction of N is assumed to be *LON*.

Effective crop rooting depths and maximum allowable moisture depletion were based on recommended values from the Bureau of Reclamation Agrimet weather service (Bureau of Reclamation, 2005). In keeping with the goal of simplifying model parameterization, RONDIMS assumes that crops achieve their maximum rooting depths immediately after planting. For the perennial grass simulations, maintaining a constant rooting depth is consistent with real crop/soil relationships. For the corn simulations, using the maximum rooting depth immediately did not change the RONDIMS N leaching prediction significantly in the scenarios modeled here because these scenarios had little percolation of water below root zone 5 during the corn growing season. Any mineral N leached below the shallow root zone of a young corn crop was eventually captured by roots as growth continued into the summer. This assumes that irrigation water is not over-applied, which was the case for both the optimized and farm record modeling scenarios. For the annual ryegrass simulations, the use of an immediate mature root system on the 1 October planting date may result in a slight over-prediction of residual soil mineral N captured by the ryegrass. This effect seems to be negligible, however, since RONDIMS predicted 34 to 43 kg N ha^{-1} uptake by ryegrass between planting and 1 January, which is consistent with the 43 kg N ha^{-1} uptake measured for ryegrass cover crops in Willamette Valley trials (Sattell et al., 1999).

RONDIMS simulates daily potential N uptake for corn (*Zea mays* L.), a warm season annual grass, with a model developed by Watts and Hanks (1978):

$$FTNU = 8.878(FGS^{3.87}), \text{ when } 0 <= FGS <= 0.3 \qquad [3.10]$$

$$FTNU = -0.660(FGS) + 3.485(FGS^2) - 0.930(FGS^3) - 0.899(FGS^4), \text{ when } 0.3 < FGS <= 1.0 \qquad [3.11]$$

$$FGS = GDD / GDD_T \qquad [3.12]$$

where $FTNU$ is the fraction of total N uptake by a crop (dimensionless) by a given date, FGS is the fraction of the growing season (dimensionless) that has transpired by that date. GDD are the growing degree days accumulated by that date and GDD_T are the total GDD accumulated by crop harvest for annual crops or 30 September for perennial crops (see Eq. [3.2] through Eq. [3.4]).

RONDIMS uses fifth order polynomials as shown in Eq. [3.13] to estimate daily potential N uptake by perennial grass and in Eq. [3.14] for annual ryegrass:

$$FTNU = 62.8(\mathrm{FGS}) + 632(FGS)^2 - 1219(FGS)^3 + 690(FGS)^4 - 69.1(FGS)^5 \qquad [3.13]$$

$$FTNU = -5.43(FGS) + 603(FGS)^2 - 2011(FGS)^3 + 2730(FGS)^4 - 1217(FGS)^5 \qquad [3.14]$$

where *FTNU* and *FGS* are as defined above. The constants in Eq. [3.13] and Eq. [3.14] were determined by non-linear regression of data for perennial grass growth published by USDA-NRCS (2002) and for annual ryegrass by Gangwer (1999) and Sattell et al. (1999).

Equations [3.10] through [3.14] were chosen because they have few variables that need to be parameterized and can be easily fitted to local data. These RONDIMS N uptake equations are much simpler than the process-based algorithms used in most of the models shown in Table 3.1. For example, EPIC has a crop growth model that depends on solar radiation, leaf area index, day length, the efficiency of crops in converting radiation to biomass, crop height, root weight, rooting depth, optimal crop N concentrations, mass flow of N to roots and various stress factors (Williams, 1995). However, the goal of RONDIMS was to model the dynamics of *RON* during the cool season. The crop N uptake equations were only included to provide an approximate indication of how N mineralization timing relates to generalized values of crop uptake. Thus, the simplified N uptake equations in RONDIMS were more appropriate for this study. The potential N uptake for the 2001 to 2002 season in the optimized scenarios is illustrated in Figure 3.1.

Actual daily N uptake by crops is simulated by comparing the mineral N mass in the current crop root zone to the potential daily crop N uptake as calculated above. If the mineral mass in the current crop root zone is equal to or greater than the potential daily crop N uptake, then the actual crop N uptake equals the potential crop N uptake. Otherwise, the actual crop N uptake equals the mass of mineral N in the current crop root zone. Because of this, the actual N uptake curves for modeled crops were somewhat different than the potential N uptake curves shown in Figure 3.1. This was especially true for annual ryegrass, which was N deficient in February through April for all simulations.

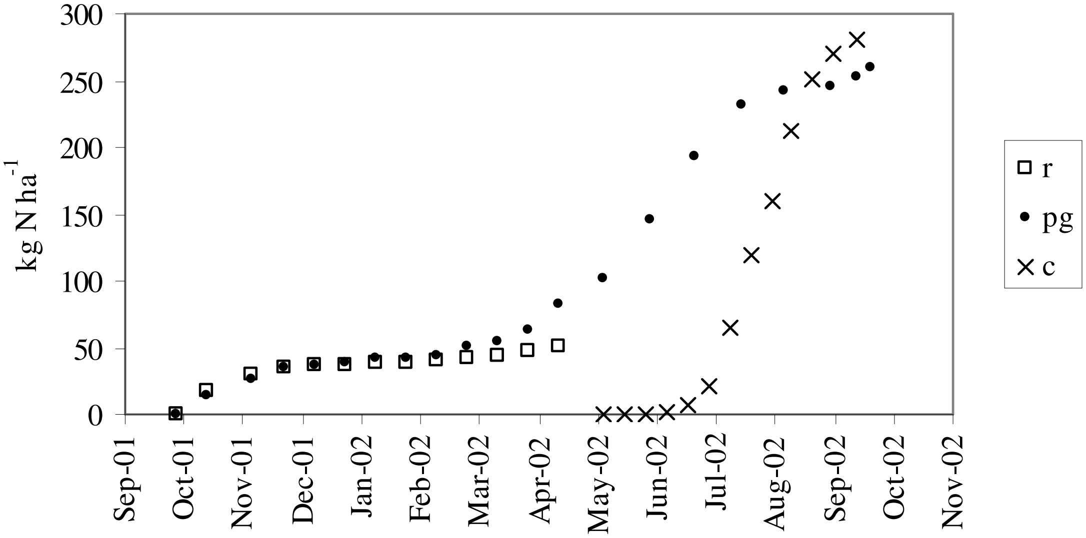

Figure 3.1. Potential cumulative N uptake by three crops, as predicted by RONDIMS for October 2001 through September 2002. c = corn, r = annual ryegrass, pg = perennial grass.

3.3.7 Soil moisture module

RONDIMS tracks moisture in all five soil layers. Root zone 1 is the layer extending from the soil surface to a depth of 25 cm. Root zones 2 through 5 extend from the bottom of root zone 1 down to the depth of the deepest rooted crop in the rotation. The crop draws soil moisture from root zone 1 until the available water drops to zero for that layer. Then the crop begins to draw moisture from root zone 2. When root zone 2 is dry, the crop draws moisture from root zone 3. This process continues until root zone 5 is dry. At that point, no further water withdrawal occurs until precipitation or irrigation recharges one or more root zones.

As discussed in the mineral N module description above, percolation out of a root zone occurs when precipitation or irrigation causes soil moisture to exceed the available water holding capacity of that root zone. Percolation from a root zone recharges soil moisture in the next lower root zone. Percolation from root zone 5 is lost from the system.

RONDIMS modifies the Agrimet alfalfa reference evapotranspiration by multiplying it by a crop coefficient factor that changes as the crop grows (Bureau of Reclamation, 2005). This is based on the principal that evapotranspiration for most crops is correlated to the amount of evapotranspiration for alfalfa on a given day. If the previous five days of precipitation exceeds the previous five days of evapotranspiration, then the soil surface is assumed to be wet and the crop coefficient is set to 1.0 for that day.

3.4 Results and Discussion

3.4.1 Hydrology

As stated previously, the objectives of this study were to use RONDIMS to estimate the contribution of manure to the *RON* pool and the mineralization of the *RON* pool during the cool season. The hydrology module of RONDIMS was important in defining the cool season for different cropping systems. All RONDIMS simulations described here assumed a silt loam soil with an available water holding capacity of 0.2 cm water cm^{-1} soil.

Table 3.4 displays several hydrologic parameters. RONDIMS predictions for water percolating below the deep root zone varied by cropping system and irrigation amount. Continuous corn had the most water percolating on the most days while perennial grass had the least, for both the optimized and farm record scenarios. Optimized scenarios applied more irrigation water in the summer and had higher moisture levels going into the fall. Thus, the optimized scenarios had more percolation days than the farm record scenarios, which generally irrigated at rates below the crop potential consumptive water use.

In this study, “cool season” was defined as the time period when precipitation exceeded evapotranspiration each year. Based on a 10-day rolling average for the 10-year scenarios modeled here, RONDIMS predicted that the corn and corn-annual ryegrass systems had cool seasons beginning 24 September and ending 18 May. Annual ryegrass transpiration of soil moisture in February through April reduced the mean annual percolation days and mean annual percolation amounts for corn-annual ryegrass compared to continuous corn. However, once the ryegrass was harvested on 30 April, RONDIMS predicted that evapotranspiration would drop below precipitation until 18 May. The perennial grass cool season began slightly later than the annual crops (29 September) due to greater late season evapotranspiration for this crop. The perennial grass cool season ended a full month earlier (17 April) than the annual crop cool season due to strong evapotranspiration in the spring.

Table 3.4. RONDIMS predictions of various hydrologic parameters. "Percolation days" are the average days per year that water percolated below the deepest root zone. "Cool season begins" is the average fall date when precipitation first exceeds evapotranspiration. "Cool season ends" is the average spring date when precipitation last exceeds evapotranspiration. O = optimized simulation, A = simulation based on farm records, cc = continuous corn, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure, S = solid manure.

	O-cc-L	O-cc-S	O-cr-L	O-pg-L	A-cc-L	A-cr-L	A-pg-L
Mean annual percolation days (d)	210	210	193	176	205	180	169
Mean annual percolation amount (cm)	79	79	76	69	74	68	64
Mean annual irrigation (cm)	40	40	41	47	20	23	19
Cool season begins	24-Sep	24-Sep	24-Sep	29-Sep	24-Sep	24-Sep	29-Sep
Cool season ends	18-May	18-May	18-May	17-Apr	18-May	18-May	17-Apr

3.4.2 Estimation of time to steady-state

Figure 3.2 illustrates RONDIMS predictions of the *RON* pool over time for the seven cropping systems examined. All other RONDIMS predictions in this study assume that the systems began at steady-state for *RON*, but this chart assumes that *RON* additions began at year 0 and remained constant over time. As demonstrated by Fried et al. (1976), the *RON* pool increases until a steady-state is approached, at which time the mineralization rate essentially equals the rate of *RON* addition. RONDIMS predicted that the optimized system with solid manure applications would create the largest *RON* pool.

This was due to 45% of the solid manure N being recalcitrant compared to only 16% of the liquid manure N. RONDIMS also predicted relatively high *RON* pools for the continuous corn and perennial grass systems that were based on farm records. This was due to high liquid manure application rates on these farms.

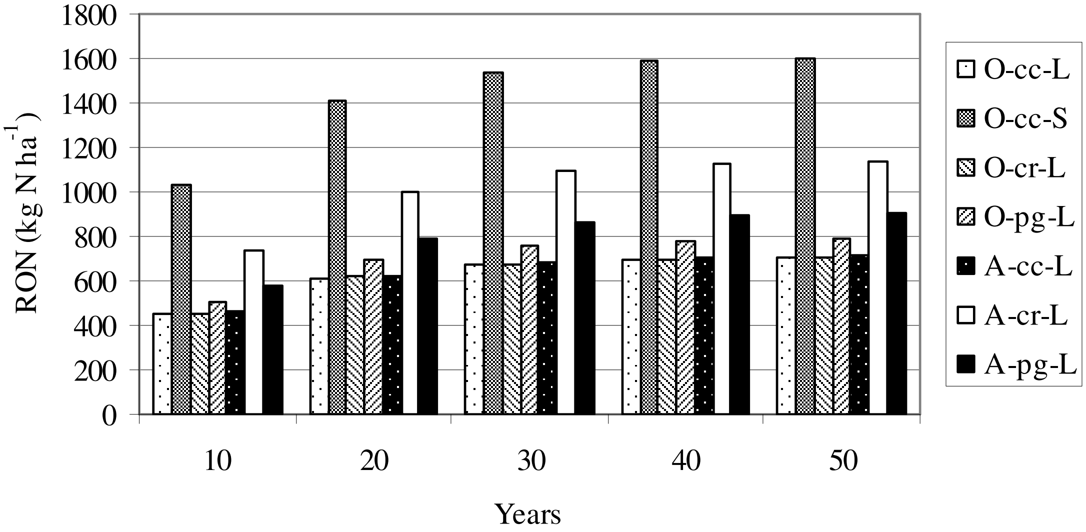

Figure 3.2. Recalcitrant organic N pools in different cropping systems, as predicted by RONDIMS. O = optimized simulation, A = simulation based on farm records, cc = continuous corn, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure, S = solid manure.

Table 3.5 shows a mathematical representation of *RON* growth, assuming constant annual applications of RON_A (kg N ha^{-1} yr^{-1}) to the soil. Immediately after *RON* is applied in any year, the *RON* pool is composed of that recent addition (which has not yet begun to mineralize) plus the *RON* that remains from previous years. The *RON* remaining from previous years is as predicted by Eq. [3.8], except that an annualized mineralization rate constant, β (yr^{-1}), is used in place of the daily rate constant (*k* from Eq. [3.1]).

A true calculation of β is:

$$\beta = -(\ln(RON_\lambda / RON_O))/t \qquad [3.15]$$

where RON_λ is the *RON* concentration on the final day of the modeled mineralization and t is the number of years modeled. Eq. [3.15] assumes that no *RON* is added during a modeled scenario.

Since RON was added repeatedly during each modeling run, Eq. [3.15] could not be used and instead β was approximated by annualizing the average daily rate constant:

$$\beta = 365\left(\frac{\sum_{i=1}^{\lambda} k_i}{\lambda}\right) \qquad [3.16]$$

where λ is the total number of days that the model runs and k_i is each day's temperature-adjusted rate constant

Table 3.5 illustrates that the increase in *RON* for any one year, n, in this system is approximated by:

$$\Delta RON = RON_A \exp(-n\beta) \qquad [3.17]$$

where ΔRON is the increase in *RON* over the previous year. In other words, the annual increase in *RON* in this system of constant annual *RON* additions is approximately equal to the mineralization rate of the *RON* added in the first year.

RON never truly reaches steady-state. However, some operational definition of "steady-state" may be made and the time needed to reach that state can be approximated mathematically:

$$(1 - y)RON_A = RON_A \exp(-n\beta) \qquad [3.18]$$

where y is some arbitrarily large fraction of RON_A that mineralizes at "steady-state." As n grows very large, y approaches 1.0.

Eq. [3.17] and [3.18] are approximations because they are based on the assumptions that both RON_A and β will remain constant from year to year. For RON_A to remain constant, the same rate of manure and crop residue must be applied each year. For β to remain constant, the chemical, biological and physical factors influencing mineralization rate (see Chapter 2) must remain constant.

Table 3.5. Calculation of recalcitrant organic N at the beginning of each year (*RON_T*). Assumes constant annual recalcitrant organic N additions (RON_A) that begin at time $t = 0$ and a temperature-adjusted annualized first order mineralization rate constant, β (yr^{-1}).

Time (yr)	RON_T
0	RON_A
1	$RON_A + RON_A\,(\exp(-\beta))$
2	$RON_A + RON_A\,(\exp(-\beta)) + RON_A\,(\exp(-2\beta))$
3	$RON_A + RON_A\,(\exp(-\beta)) + RON_A\,(\exp(-2\beta)) + RON_A\,(\exp(-3\beta))$
n-1	$RON_A + RON_A\,(\exp(-\beta)) + RON_A\,(\exp(-2\beta)) + RON_A\,(\exp(-3\beta)) + \ldots + RON_A\,(\exp(-(n-1)\beta))$
n	$RON_A + RON_A\,(\exp(-\beta)) + RON_A\,(\exp(-2\beta)) + RON_A\,(\exp(-3\beta)) + \ldots + RON_A\,(\exp(-(n-1)\beta)) + RON_A\,(\exp(-n\beta))$

Solving Eq. [3.18] for n:

$$n = -(\ln(1-y)) / \beta \qquad [3.19]$$

For example, in the RONDIMS simulations described in this study, β was 0.0972 yr^{-1}. If steady-state is defined as the time at which $y = 0.90$, then Eq. [3.19] results in $n =$ 23.7 years. Thus, after approximately 23 years of constant *RON* addition, a mass equal to 90% of the annual *RON* application mineralizes each year. For $y = 0.99$, RONDIMS estimated steady-state during the 47th year of constant RON_A applications. The time periods needed to approach steady-state, as predicted by RONDIMS, are reasonably consistent with results of Franzluebbers et al. (2000), who determined that soil organic N storage increased by approximately 73, 44 and 6 kg N ha^{-1} yr^{-1} after tilled cropland was converted to permanent pasture during 0 to 10, 10 to 30 and 30 to 50 years following conversion, respectively, in the Southern Piedmont region of the United States.

Eq. [3.19] illustrates that n does not depend on RON_A. The size of the RON pool at the operationally defined steady-state, however, does depend on RON_A, as shown in Eq. [3.20]:

$$RON_{ss} = ((y)\,(RON_A)) / \beta \qquad [3.20]$$

where RON_{ss} is RON at the defined steady-state. For the above example, with continuous corn and constant solid manure applications, RON_A was 157 kg N ha^{-1} and RON_{ss} equaled 1454 kg N ha^{-1} for $y = 0.90$.

3.4.3 Sources and sinks of RON

The sources of N for the modeled scenarios are shown in Table 3.6. The RONDIMS simulations assumed that the only primary N input into these systems was N applied via manure, although 9 to 17% of the total annual N flux was cycled from the soil to the crop and then back to the soil via crop residue. See Sections 3.3.4 and 3.3.5 for descriptions of how crop residue is added to the soil in RONDIMS. For the optimized perennial grass with liquid manure application, 52% of the *RON* was supplied by the manure and 48% was supplied by crop residue. This relatively high contribution of perennial grass residue to the *RON* pool is consistent with widely accepted findings of increased soil organic matter in perennial grass versus annual crop systems (Doran, 1987).

Manure applications supplied 78 to 85% of the *RON* for each of the other liquid manure scenarios. When manure was applied as a solid, it supplied 90% of the average annual *RON*. As explained previously, this is due to the relatively high fraction of solid manure N being *RON*.

Table 3.7 displays the sinks of N in the RONDIMS simulations. N harvested in the crop accounted for 38 to 78% of the N lost from the system and, for most scenarios, was the largest sink. Field studies of N capture by growing crops vary widely. For example, on corn (*Zea mays* L.) plots in Wisconsin, only 15 to 18% of N applied via fresh dairy manure mixed with straw was recovered by the crop in the first year (Munoz et al., 2004). In a four-year trial on two UK perennial ryegrass (*Lolium perenne* L.) plots, the crop recovered 30 to 45% of applied N for fall applications and 38 to 72% for spring applications of cow manure slurry applied at 150 kg N ha^{-1}. For applications made at twice this rate, N recovery was 20 to 22% for fall applications and 32 to 64% for spring applications (Beckwith et al., 2002).

Table 3.6. Sources of annual N for the RONDIMS modeled scenarios. Manure was the most important source of both total N and recalcitrant organic N in these systems. For O-pg-L, crop residue was also a large percentage of the recalcitrant organic N. O = optimized simulation, A = simulation based on farm records, cc = continuous corn, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure, S = solid manure.

N Source	**O-cc-L**	**O-cc-S**	**O-cr-L**	**O-pg-L**	**A-cc-L**	**A-cr-L**	**A-pg-L**
	kg N ha^{-1} yr^{-1}						
Via manure							
NH_4-N	238	95	238	178	384	327	143
Labile organic N	44	79	44	33	40	74	53
Recalcitrant organic N	54	142	54	40	55	94	69
Manure total	**335**	**315**	**335**	**250**	**479**	**496**	**265**
Via crop residue							
NH_4-N	0	0	0	0	0	0	0
Labile organic N	32	32	45	12	32	69	6
Recalcitrant organic N	15	15	15	37	15	17	19
Crop residue total	**47**	**47**	**61**	**49**	**48**	**86**	**26**

For the farm record perennial grass and continuous corn simulations, predictions of N leaching below the root zone were high due to applications of manure N at the wrong times and at rates that were too high. RONDIMS predicted relatively high N leaching for the optimized continuous corn with solid manure simulation, due to *RON* that mineralized during the cool season when there was no growing crop.

Table 3.7. Sinks of annual N for the RONDIMS modeled scenarios. Harvested crop N was the largest N sink for most scenarios. O = optimized simulation, A = simulation based on farm records, cc = continuous corn, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure, S = solid manure.

N Sink	O-cc-L	O-cc-S	O-cr-L	O-pg-L	A-cc-L	A-cr-L	A-pg-L
				kg N ha^{-1}			
Leach below root zone	51 (15%)	85 (27%)	12 (4%)	12 (57%)	157 (33%)	672 (14%)	125 (48%)
NH_3-N volatilization	59 (18%)	5 (1%)	59 (18%)	44 (18%)	96 (20%)	82 (16%)	36 (14%)
Harvest	225 (67%)	225 (72%)	263 (78%)	188 (77%)	226 (47%)	347 (70%)	98 (38%)

3.4.4 Residual soil mineral N and cool season RON mineralization

In western Oregon, if residual soil NO_3^- concentrations exceed 20 mg N kg^{-1} after silage corn (*Zea mays* L.) harvest, farmers are advised that manure applications during the growing season were excessive and should be reduced in future years (Sullivan and Cogger, 2003). Assuming a soil sampling depth of 30 cm and soil bulk density of 1.4 g cm^{-3}, 20 mg N kg^{-1} equals approximately 84 kg N ha^{-1}.

These western Oregon recommendations are reasonably consistent with those from other agricultural regions. For example, some states in Germany and the Netherlands have set goals for residual soil NO_3^- on cropland to be below 45 to 70 kg N ha^{-1} to reduce the potential for NO_3^- losses to the environment (Hofman et al., 1994; Ilsemann et al., 2001). Zebarth et al. (1995) estimated an acceptable upper limit of residual soil NO_3^- at 100 kg N ha^{-1} in south-coastal British Columbia to safeguard groundwater in this region where annual water flow through the soil profile is approximately 1,000 mm. For the analyses below, the Western Oregon benchmark of 84 kg N ha^{-1} was used to determine if residual soil NO_3^- concentration or cool season N mineralization was excessive.

For example, Table 3.8 compares cool season *RON* mineralization to residual soil mineral N. The residual soil mineral N exceeded 84 kg N ha^{-1} in the farm record continuous corn with liquid manure and the farm record perennial grass RONDIMS predictions. In the continuous corn scenario, the high residual soil mineral N value was due mostly to poor manure timing: a liquid manure application of 163 kg N ha^{-1} on 10 October when no growing crop was in the field.

The high residual soil mineral N in the farm record perennial grass scenario was due to both poor manure timing and excessive manure amount: a 20 May liquid manure application of 265 kg N ha^{-1}. Not only was this rate of manure more than the annual potential crop uptake (155 kg N ha^{-1}), but the application occurred well after the perennial grass early season N uptake period shown in Figure 3.1. Consequently, RONDIMS predicted this crop to be N deficient but also predicted a very high residual soil mineral N concentration in September.

For the farm record corn with annual ryegrass cover crop scenario, manure timing was fairly good, with some manure applied in March for the ryegrass and some manure applied in June for the corn. However, the March application was excessively high (248 kg N ha^{-1} applied versus potential annual ryegrass uptake of 162 kg N ha^{-1}). This resulted in 23 kg N ha^{-1} leaching between March and July. Thus, RONDIMS predicted that both excessive manure application rates and non-optimal manure application timing can cause high residual soil mineral N.

Table 3.8. RONDIMS predictions of residual soil mineral N and cool season recalcitrant organic N mineralized. All residual mineral N concentrations are on 30 September, except A-cc-L, which is on 30 October because manure was applied in October in this scenario. See Table 3.4 for the definition of cool season. O = optimized simulation, A = simulation based on farm records, cc = continuous corn, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure, S = solid manure.

	O-cc-L	O-cc-S	O-cr-L	O-pg-L	A-cc-L	A-cr-L	A-pg-L
	kg N ha^{-1}						
Mean residual mineral N	10	19	10	9	110 §	49	135
Cool season recalcitrant organic N mineralized	32	73	32	29 †	33	52	31 †
Sum	42	92	42	38	143	101	166

§ For A-cc-L, the mean residual mineral N is on 30 Oct. All other values are on 30 Sept.

† The cool season for perennial grass systems is 29 Sept - 17 Apr. All other system cool seasons are 24 Sept - 18 May.

In each of the optimal RONDIMS scenarios, the mean residual mineral N (Table 3.8) is considerably less than 84 kg N ha^{-1}, illustrating that good manure management can minimize residual soil mineral N. However, the sum of cool season *RON* mineralization plus residual mineral N exceeded 84 kg N ha^{-1} in the optimal continuous corn with solid manure application and in each of the farm record scenarios. Also, RONDIMS predicted cool season *RON* mineralization to exceed residual soil mineral N in five out of seven scenarios. In the modeled scenarios, residual soil mineral N only exceeded cool season *RON* mineralization when manure was grossly over-applied or applied at the wrong time.

3.4.5 N leaching

Table 3.9 displays mineral N concentration (mg N L^{-1}) in predicted average annual leachate below root zone 5. The drinking water standard for NO_3^- is 10 mg N L^{-1} (EPA, 2001). RONDIMS predicted that four of the seven scenarios resulted in average annual leachate of 10 mg N L^{-1} or greater. Only two of the seven scenarios, the optimized corn-ryegrass and the optimized perennial grass, had predicted average annual leachate below 5 mg N L^{-1}. The contribution of cool season *RON* mineralization to leachate was greatest for the solid manure scenario, due to the relatively high ratio of *RON* to NH_4^+ in this manure source.

RONDIMS predicted that, in the optimized scenarios, *RON* that mineralized during the cool season contributed 21 to 55% of all N leached. For the scenarios based on farm records, *RON* that mineralized during the cool season contributed 9 to 16% of all N leached. *LON* mineralization contributed an additional 10 to 60% of the leached N. Most of the *RON* pool originated from manure (see Table 3.6). Most of the *LON* that mineralized and then leached originated from crop residue added to the soil in the fall. Neither the *RON* mineralization nor the crop residue *LON* mineralization can be controlled by manipulating manure applications in any one year.

These predictions, coupled with the observations of manure timing and rates offered above, suggest several best management practices that could reduce N leaching in manured fields. First, because the optimal scenarios had substantially less N leached than the farm record scenarios, applying manure at appropriate rates and timing can significantly reduce N leaching. Second, winter grass crops (either perennial or annual) can reduce leaching both of N remaining as residual at the end of the growing season and N mineralizing from *RON* and *LON* during the cool season. Third, on some farms (especially those with high solid manure application rates), it may be beneficial to reduce manure application in order to reduce the build-up of large *RON* pools. This can be accomplished by trucking manure to non-livestock farms. If manure application rates are reduced below the N needs of the crop, then inorganic N fertilizer would be needed to maintain yields.

Table 3.9. RONDIMS predictions of sources of leached N. *RON* = recalcitrant organic N, O = optimized simulation, A = simulation based on farm records, cc = continuous corn, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure, S = solid manure.

	O-cc-L	**O-cc-S**	**O-cr-L**	**O-pg-L**	**A-cc-L**	**A-cr-L**	**A-pg-L**
Total N leached (kg N ha^{-1})	51	85	12	12	157	67	127
Annual percolation (cm)	79	79	76	69	74	68	64
Average N in leachate (mg N L^{-1})	6.5	10.8	1.5	1.7	21.3	10.0	19.8
N in leachate due to NH_4^+ (mg N L^{-1})	0.0	0.5	0.0	1.1	11.6	5.2	8.8
N in leachate due to LON (mg N L^{-1})	3.9	4.0	0.8	0.2	6.7	2.6	4.5
N in leachate due to cool season RON (mg N L^{-1})	2.5	5.9	0.7	0.4	2.9	1.8	2.1
N in leachate due to warm season RON (mg N L^{-1})	0.1	0.4	0.0	0.1	0.1	0.4	4.5

Figures 3.3 through 3.6 illustrate the predicted average monthly contributions of various sources of mineral N to leachate below root zone 5. Note that the scales are different for different scenarios to make relative contributions easier to discern. Also note that the charts depict sources of mineral N. For example, the bars labeled "cool season *RON*" represent NO_3^--N that was mineralized from *RON* during the cool season and then leached.

In the optimal continuous corn scenario (Figure 3.3), essentially no mineral N that originated as manure NH_4^+ leached. This is because it was relatively easy in a modeling exercise to apply manure so that the readily available NH_4^+ did not exceed the crop's needs. It was not, however, as easy to control the amount of *LON* and *RON* that mineralized. In October, the predicted mineral N concentration in leachate was approximately 7 mg N L^{-1}, with 5 mg N L^{-1} supplied by *LON* mineralization and 2 mg N L^{-1} supplied by *RON* that mineralized during the cool season. Leachate N concentrations increased to 20 mg N L^{-1} in November as fall rains increased percolation, pushing mineral N downward through root zone 5. By December, root zone mineral N originating from *LON* had been partially depleted by leaching. During January through May, most of the N in leachate was derived from cool season *RON* mineralization, with increasing amounts each month as the soils warmed and mineralization increased. By June, percolation below root zone 5 ceased as evapotranspiration exceeded precipitation plus irrigation. Thus, RONDIMS predicted that, even when manure was applied to supply the summer crop with the correct amount of N at the correct time, the cool season mineralization of *LON* (from crop residue) and *RON* (mostly from manure) caused November leachate concentrations to exceed 10 mg N L^{-1}.

When manure was applied as a solid rather than a liquid (bottom chart in Figure 3.3), RONDIMS predicted two important changes in the leachate pattern. First, leachate from cool season *RON* mineralization was greater throughout the year due to the larger *RON* pool in the solid manure scenario (also see Figure 3.2). This resulted in a predicted mean annual leachate concentration of 10.8 mg N L^{-1} for the solid manure scenario, compared to only 4.5 mg N L^{-1} for the liquid scenario. In November, the predicted leachate N concentration from cool season *RON* alone exceeded 10 mg N L^{-1} for the solid manure scenario.

Second, RONDIMS predicted greater N leachate concentration in May (11.6 mg N L^{-1}, equivalent to 7.6 kg N ha^{-1}) for the solid manure scenario. This relatively high concentration was due to logistical limitations that farmers face in applying solid manure to corn. Liquid manure can be applied before corn is planted and also irrigated onto the crop throughout the growing season, allowing for multiple small applications of N. Solid manure, however, must be applied only before corn is planted. In this scenario, solid manure was applied at a rate sufficient to supply the entire crop's N requirement. RONDIMS predicted this single application would produce a large amount of soil mineral N before the crop was planted, and also predicted that some of this mineral N would leach during rainfall events in May[2].

Figure 3.4 illustrates predicted benefits of seeding a cover crop of annual ryegrass (*Lolium multiflorum* Lam.). The November leachate concentration for the corn – annual ryegrass scenario was greatly reduced (6.1 mg N L^{-1}) compared with the continuous corn with no cover crop (20.1 mg N L^{-1}). RONDIMS predicted a high leachate concentration for the corn – annual ryegrass scenario in August. This was due to a small (less than 0.5 kg N ha^{-1}) mass of N leaching in a small volume (less than 0.3 cm) of percolate and was caused by the rules for irrigation used in the modeling exercises (see Section 3.3.1) rather than any significant physical events being simulated.

The predicted fall N leachate concentrations for the optimal perennial grass scenario in Figure 3.4 were quite low due to N uptake by the perennial grass crop in November through January. Most of the N leaching occurred in February through May. The source of most of this leached N was NH_4^+ from four manure applications between 15 February and 1 May. In this case, the perennial grass N uptake kept pace with the slow release of N from *RON* mineralization. The NH_4^+ in the manure supplied enough mineral N to cause predicted leachate concentrations to reach 6.5 mg N L^{-1} in March but to never reach the 10 mg N L^{-1} drinking water standard in any month.

Figure 3.5 displays RONDIMS predictions for the farm record corn-annual ryegrass and perennial grass scenarios. Predicted November leachate concentrations exceeded 28 mg N L^{-1}, due to NO_3^- remaining in the soil profile after excessive (496 kg N ha^{-1}) manure applications in March through June. Some of this residual fall soil NO_3^-

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[2] As explained in Section 3.3.5, RONDIMS does not include a module to adjust mineralization rates due to C:N ratios in manure or residue. It is likely that the spike in leachate concentrations predicted for May in the solid manure scenario would be less significant, or may not occur at all, if mineralization rates were adjusted for C:N ratios (Whitmore and Handayanto, 1997).

continued to leach in December. By January and February, the residual fall soil NO_3^- had been depleted and only small amounts of NO_3^- (less than 5 mg N L^{-1}) leached in those months. In March through May, leaching increased again due to the excessive spring manure applications. The apparently high leachate concentrations in June and July were due to a relatively small mass (4.6 kg N ha^{-1}, which was only 7% of the total annual N leached) that RONDIMS predicted would leach in a small volume (1.0 cm) of percolate. The predicted mean annual leachate concentration was 10.0 mg N L^{-1} for this farm record corn-annual ryegrass scenario.

Also in Figure 3.5, the farm record perennial grass scenario had a predicted high leachate N concentration in May due to an excessive (265 kg N ha^{-1}) application of manure that month. Not only was this N application more than the crop's potential N uptake (155 kg N ha^{-1}), but it occurred too late in the crop's N uptake curve for optimal use. This resulted in a large predicted fall mineral N pool, mostly originating from manure NH_4^+, that subsequently leached over the winter. Although in this scenario the predicted leachate N originating from cool season *RON* mineralization is low relative to that originating from NH_4^+, it is comparable in total to other scenarios and contributed 7 mg N L^{-1} to the leachate in November.

As shown in Figure 3.6, the predicted leachate N exceeded 90 mg N L^{-1} in November for the farm record continuous corn scenario. This was due mostly to an application of 163 kg N ha^{-1} on 10 October that contributed large amounts of mineral N from NH_4^+ and *LON* mineralization. A combination of NH_4^+, *LON* mineralization and *RON* mineralization caused predicted N leachate to exceed 10 mg N L^{-1} in four additional months in this scenario. As in other scenarios, the June leachate concentration shown in Figure 3.6 is misleading as it resulted from only 4.1 kg N ha^{-1} (approximately 3% of the annual leachate N mass) in only 1.8 cm of percolate.

RONDIMS predicted no October percolation of water beneath root zone 5 in any of the farm record scenarios. In these farm record scenarios, the low summer irrigation rates (see Table 3.4) resulted in very low soil moisture in October and a subsequent delay in the onset of percolation below root zone 5 until November.

To summarize Figures 3.3 through 3.6, RONDIMS predicted that leachate from all but the optimal perennial grass scenario would exceed the 10 mg N L^{-1} drinking water standard during at least one month. In the optimal scenarios, RONDIMS predicted that the leached N mostly originated from the cool season mineralization of *LON* and *RON*. In the farm record scenarios, RONDIMS predicted that most of the leached N originated from manure NH_4^+, but cool season *LON* and *RON* mineralization also contributed significant amounts of the leached N.

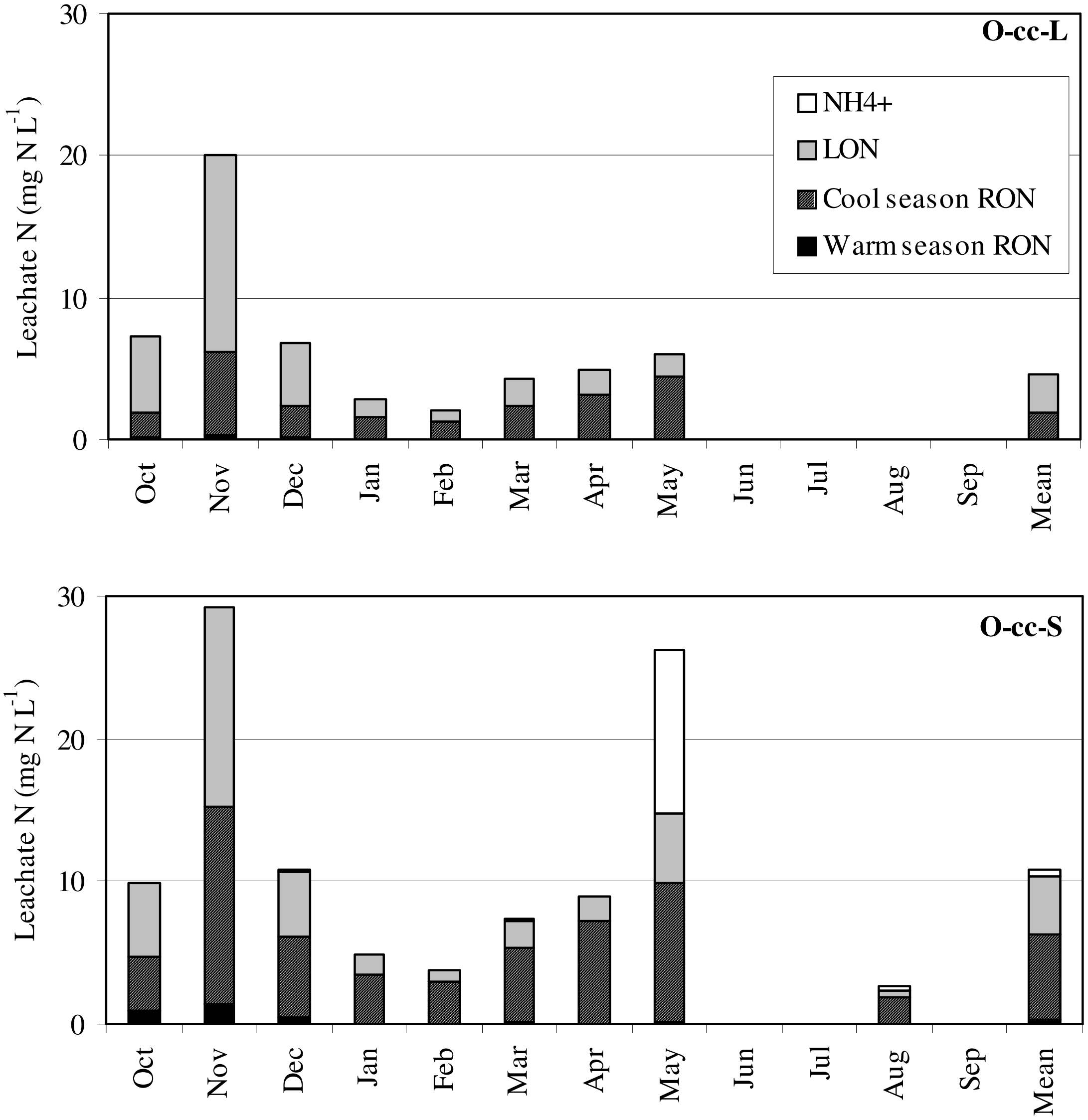

Figure 3.3. Average monthly contributions of N sources to N leachate as predicted by RONDIMS for two optimized continuous corn scenarios. O = optimized simulation, cc = continuous corn, L = liquid manure, S = solid manure.

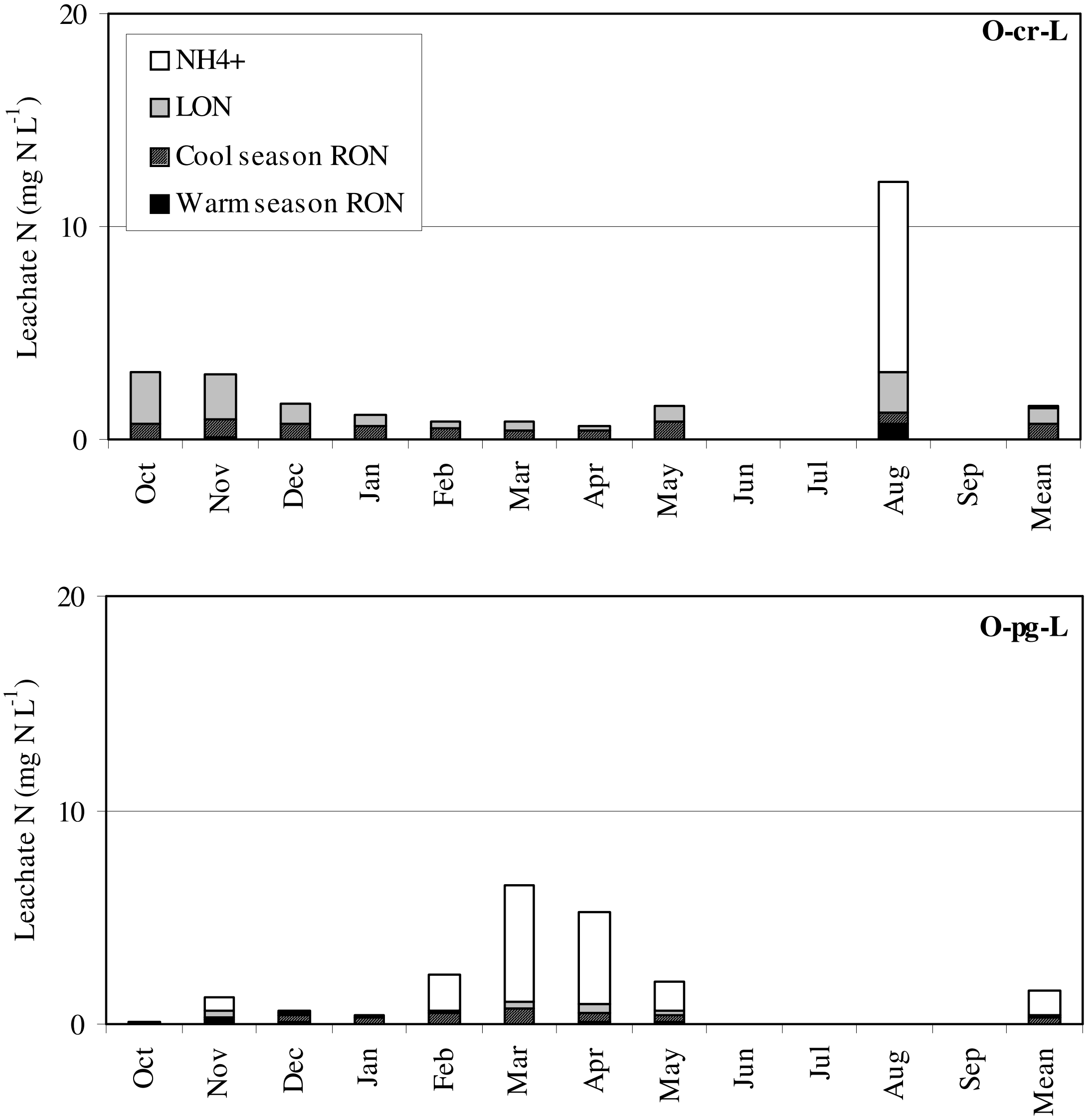

Figure 3.4. Average monthly contributions of N sources to N leachate as predicted by RONDIMS for two optimized scenarios with grass crops. O = optimized simulation, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure.

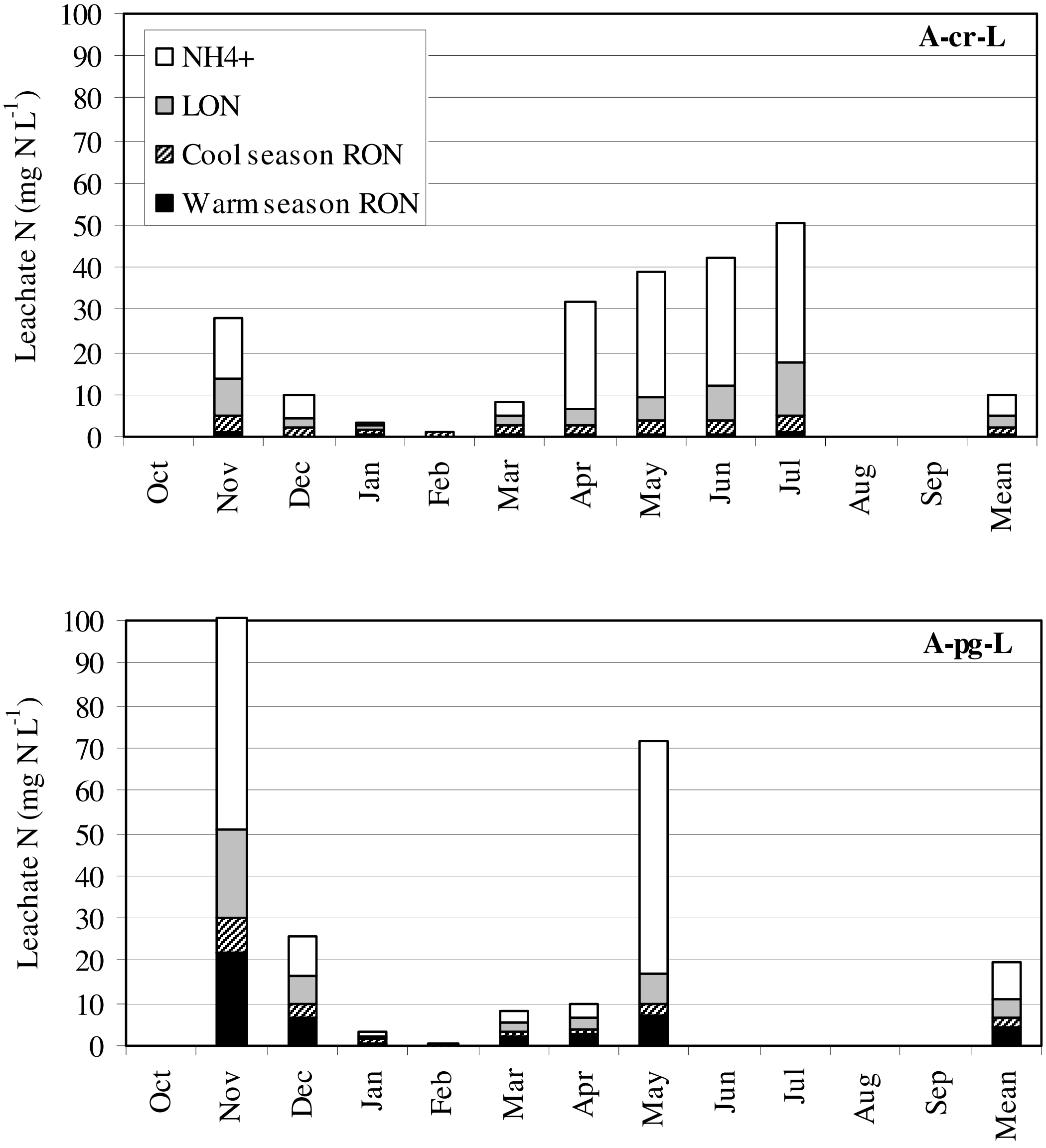

Figure 3.5. Average monthly contributions of N sources to N leachate as predicted by RONDIMS for two farm record scenarios with grass crops. A = farm record simulation, cr = corn-annual ryegrass, pg = perennial grass, L = liquid manure.

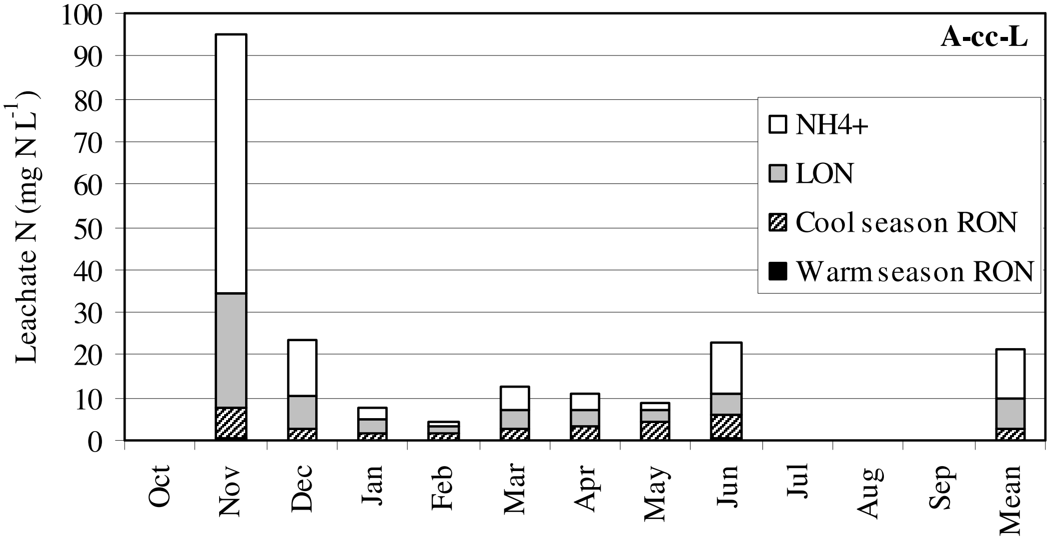

Figure 3.6. Average monthly contributions of N sources to N leachate as predicted by RONDIMS for the farm record continuous corn scenario. A = farm record simulation, cc = continuous corn, L = liquid manure.

3.4.6 Ion exhange resin / soil core considerations

The ion exhange resin / soil core (IER/SC) method is an *in situ* approach to measuring N mineralization rates and, in some situations, NO_3^- losses from soils. IER/SC use tubes made of PVC, aluminum or galvanized pipe that typically measure approximately 5 cm inner diameter by 15 to 50 cm long (Myrold et al., 1992; Kolberg et al., 1997; Sullivan et al., 1999; Eghball, 2000). IER/SC are open at both the top and the bottom to allow exchange of gases and water, however the bottom of each IER/SC is fitted with ion exchange resins (IER) that capture NO_3^- and NH_4^+ leaching from the captured soil column.

IER/SC are either filled with disturbed soil by hand-packing or with relatively undisturbed soil by pounding the tubes into the soil and then extracting intact cores. When filled by hand-packing, the IER/SC soil can be homogenized to reduce the high variability inherent in the spatial distribution of soil N. Also, the addition of manure N to IER/SC can be more highly controlled when IER/SC are hand-packed.

If used to study *RON* mineralization, it is desirable to fill IER/SC with soil that has little *LON* in order to decouple *RON* and *LON* mineralization processes. Figure 3.7 illustrates the short lifespan of labile organic compounds using the farm record continuous corn scenario. *RON* is not shown in Figure 3.7 because it fluctuates between 700 to 740 kg N ha^{-1} in this scenario and including it in the chart would require a scale making *LON* difficult to see. In this scenario, *LON* peaked at 27 kg ha^{-1} on 24 September when the corn was harvested and again on 10 October when manure was applied. Twenty four days after corn harvest, on 6 October, *LON* decreased to 19 kg ha^{-1}.

Assuming a soil bulk density of 1.4 g cm^{-3} and assuming that all *LON* is in the top 17 cm of soil used to construct an IER/SC tube, a *LON* mass of 19 to 27 kg ha^{-1} equals a concentration of only about 8 to 11 mg N kg^{-1} soil. This labile organic N influence on an IER/SC experiment begun in the fall could be further minimized by ensuring that the soil is collected from between the corn rows and that any visible leaf or stalk detritus is removed from the soil surface before collecting soil.

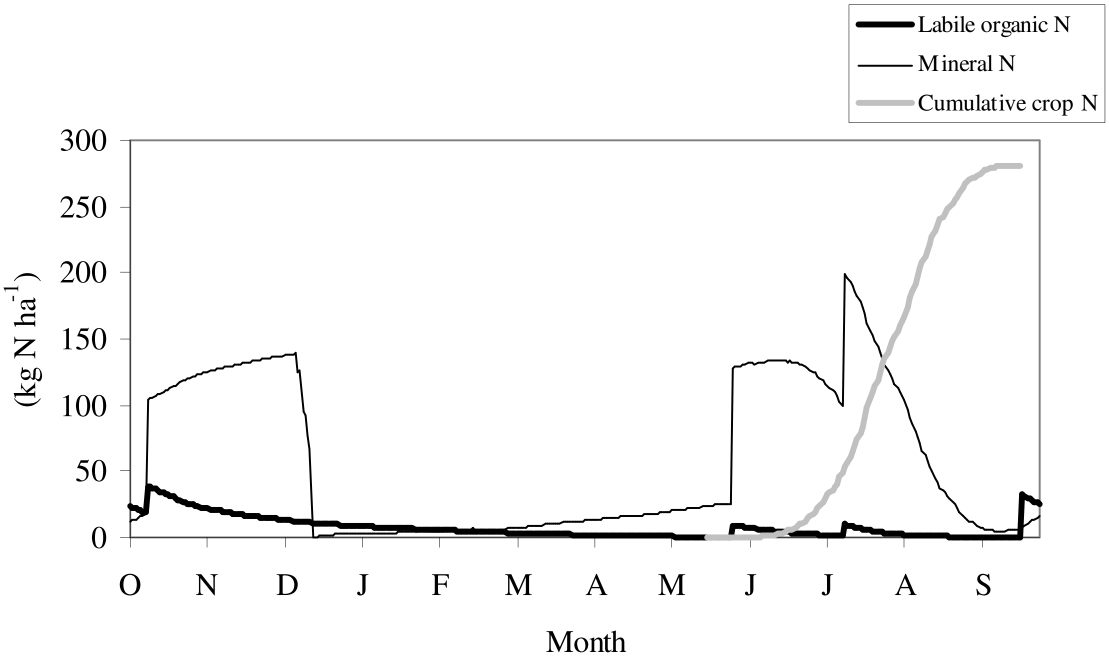

Figure 3.7. Labile organic, mineral and cumulative crop N pools in the farm record continuous corn RONDIMS simulation. Manure was applied to the soil in October, June and July. Crops residues were added to the soil following harvest in September. Labile organic N increased after each of these organic N additions and then decreased slowly as the labile organic N mineralized. Mineral N increased dramatically with each manure addition due to NH_4^+ in the manure. Mineral N increased slowly after each organic matter addition due to organic N mineralization. Mineral N decreased rapidly in December due to leaching and decreased slowly through the summer due to crop N uptake.

3.4.7 RONDIMS limitations

RONDIMS achieves the objective of a simple, easily parameterized model to investigate *RON* dynamics in manured soils. The results, as described above, are consistent with field study results in the literature. RONDIMS, however, has numerous limitations.

First, and most importantly, RONDIMS has not been validated with field studies. The RONDIMS simulations were used as an initial step in examining the dynamics of cool season *RON* mineralization. These simulations indicated cool season *RON* mineralization could be important and, consequently, IER/SC experiments were devised to measure actual cool season *RON* mineralization. These IER/SC studies (described in Chapters 4 and 5 of this project) were not designed to validate RONDIMS, however. The IER/SC experiments were conducted on real farms with complex cropping systems and manure applications that were both temporally and spatially variable. As described previously, the farm records used for the simulations on these fields were from only one or two year's data (depending on the field). These farm records were approximate, imprecise and not verifiable and thus did not lend themselves to RONDIMS validation.

Functional limitations to RONDIMS include the lack of a nitrification routine, the lack of a carbon : nitrogen ratio routine, no consideration of denitrification, the lack of an old stable organic matter (humus) pool and the use of an immediately mature root system. Finally, the simulations described here assumed one cropping system and consistent annual manure applications. This was a useful simplification to examine the dynamics of *RON* in this study. Actual cropping systems are more complex and, while RONDIMS is capable of simulating more complex cropping systems, this was not done in this study.

3.5 Conclusions

The simulations described in this study included four cropping systems based on optimized manure and irrigation applications and three cropping systems based on farm records. The simulations used 10 years of weather data (1995 to 2005) at Corvallis, Oregon. The beginning *RON* pool was manipulated until there was no net change in *RON* from the beginning to the end of each simulation. This assumes that constant annual systems of manure, irrigation and crops were employed until RON reached a steady-state in each simulation. This assumption was a significant deviation from the farm fields upon which the farm record simulations were roughly based. The simulated cropping systems were continuous corn, corn-annual ryegrass and perennial grass. Six liquid and one solid manure scenario were used. The objectives were to use this model to simulate the contribution of manure to soil *RON* and the subsequent mineralization of *RON* during the cool season.

The model predicted differences in hydrology for the simulations, with the continuous corn system having the most percolation and the longest cool season. Cool season was defined as the period during which the rolling 10-day average precipitation exceeded the rolling 10-day average evapotranspiration. Perennial grass had the shortest cool season and the least percolation of water below the root zone. RONDIMS predictions indicated that irrigation amount affected the amount and timing of percolation. For example, percolation below root zone 5 (the lowest root zone) began in October for the optimal scenarios. For the farm record scenarios, which received less irrigation water during the summer, percolation below root zone 5 did not begin until November.

RONDIMS predicted that steady-state *RON* pools would be approached within 20 to 25 years (assuming an annual mineralization of a mass equivalent to 90% of the annual *RON* additions) or 40 to 50 years (assuming an annual mineralization of a mass equivalent to 99% of the annual *RON* additions). The solid manure system had a substantially larger *RON* pool at steady-state than the other simulations, although the simulations based on farm records with very high liquid manure applications also resulted in large *RON* pools. As has been documented in numerous other studies (for example, Deans et al., 1986), RONDIMS predicted the *RON* pool to be considerably larger than the *LON* pool.

The model predicted that manure was a more important source of *RON* than crop residue, especially for the annual crop and solid manure systems. The model predicted that N harvested in crops was the most important sink, with N efficiencies (harvested N / applied N) varying from 38 to 78%. RONDIMS predicted that the *LON* pool originated from both manure and crop residue additions to the soil.

RONDIMS predicted that *RON* and *LON* mineralizing during the cool season were important contributors to leached N. Proportionally, cool season *RON* mineralization contributed more to N leaching in the optimized scenarios than in the simulations based on farm records. This was because the farm record simulations tended to have manure N applications that, compared to crop N uptake, were either too large or occurred at the wrong time, or both. RONDIMS predicted that four of the seven scenarios would have average annual leachate equal to or greater than the 10 mg N L^{-1} drinking water standard.

Overall, RONDIMS predicted that residual soil mineral N could be reduced by applying manure at rates and timing that corresponded to crop N uptake. However, due to cool season *RON* and *LON* mineralization, applying manure at optimal rates and times to supply N for the summer crop was not sufficient to prevent leachate concentrations from exceeding the drinking water standard of 10 mg N L^{-1} at some time during the year. In addition to optimal manure application, the use of grass crops (either annual or perennial) to utilize cool season mineral N from *RON* and *LON* mineralization was required to keep leachate N concentrations below the drinking water standard during all months of the year.

RONDIMS predicted that cool season *RON* mineralization was greatest with repeated solid manure applications. The build-up of excessive *RON* could be avoided by rotating solid manure applications to different fields over time.

RONDIMS predicted that, with appropriate timing and methodology of fall soil collection, the *LON* concentration in IER/SC could be minimized, thus allowing studies that decouple the dynamics of labile versus *RON* mineralization.

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CHAPTER 4. COOL SEASON MINERALIZATION OF RECALCITRANT ORGANIC N IN UNDISTURBED CORES OF MANURED SOILS

4.1 Abstract

Nitrogen (N) is the most important mineral nutrient for most agricultural crops and nitrate (NO_3^-) is the predominant form of N used by crops. NO_3^-, however, can also contaminate ground and surface water or denitrify into the greenhouse gas nitrous oxide, especially during the cool season of fall, winter and early spring when precipitation tends to exceed evapotranspiration and crop uptake of N is low. The aim of N management in agriculture is simple: supply enough NO_3^- to produce acceptable yields, but minimize the mass of NO_3^- available for environmental degradation. Although simple, this goal is not easily achieved, especially on fields fertilized with manure. Trends toward the concentration of livestock onto fewer farms with greater numbers of animals and new legislation regulating the use of fertilizer and manure in the United States and Europe have made N management goals increasingly important.

The objectives of this study were to (1) quantify cool season N mineralization from recalcitrant organic N in soils with a history of manure application, (2) compare the magnitude of cool season N mineralization to the residual soil mineral N concentration in the fall and (3) examine the relationship between cool season recalcitrant organic N mineralization and a fall mineralizable N index. *In situ* trials, using ion exchange resin / soil cores (IER/SC), were conducted with undisturbed soil cores in Oregon's Willamette Valley during the cool seasons of 2003-2004 and 2004-2005.

On all soils tested, organic N mineralized during November to February, when crops would either not be present or would not be able to utilize the mineral N. The mean net mineralization exceeded 20 mg N kg^{-1} during this time period for both years of the study. Additional N mineralized between February and May. In the fall, most mineral N was present as NO_3^- in the soil mass. During the winter, most of the mineral N in each soil core leached to the resin below the soil. During the spring, NO_3^- levels increased in the soil and less NO_3^- leached to the resin. The mean cool season N mineralization by February (22.9 mg kg^{-1}) was significantly less ($p < 0.01$) than the residual soil mineral N concentration in October (59.7 mg kg^{-1}). Estimated NO_3^- leachate concentrations of N mineralized during November to February regularly exceeded the drinking water standard of 10 mg N L^{-1}.

Recalcitrant organic N mineralization in the cool season was not correlated to the fall mineralizable N index or the residual fall soil mineral N. The size of the recalcitrant organic N pool did not necessarily determine the amount of cool season N mineralization, although in six of the seven soils tested it appeared that recalcitrant organic N was the source of most of the mineralized N.

4.2 Introduction

The application of animal manure to cropland was once considered a necessary and simple part of animal agriculture. With the concentration of greater numbers of animals on farms, importation of feed from distant farms, growing concerns about the environmental impacts of manure and enactment of new regulations, animal manure application has remained necessary, but is no longer simple. One of the challenges associated with applying manures to cropland is to achieve an adequate, but not excessive, concentration of mineral N (NO_3^- plus NH_4^+) in the soil.

Mineral N is essential to agriculture because it is the limiting nutrient for non-leguminous crops and yields suffer if an adequate supply is not present during the growing season (Tisdale and Nelson, 1975). Animal manure can be a good source of mineral N for crops (Gollehon et al., 2001). However, animal manure applications to cropland can also increase the likelihood of NO_3^- runoff to surface water (Cameron, 1986; Bushee et al., 1998), which impacts reservoirs used for drinking water, contributes to the eutrophication of some surface water bodies and can lead to hypoxic zones in marine systems (EPA, 2002). Manure applications can also increase the rate of denitrification and result in emissions of the greenhouse gas N_2O (Lowrance et al., 1998). Manure applications can increase leaching of NO_3^- to groundwater (Holloway et al., 1996), which can impact aquifers used for drinking water.

Local, state and federal levels of government in the United States have developed regulatory and incentive programs to address the environmental and human health concerns of manure[1] (USDA and EPA, 1999). One aim of these programs is to encourage farmers to manage manure applications to produce an adequate supply of mineral N in the soil during the growing season, but to have low concentrations of residual mineral N in the soil at the end of the growing season. Residual mineral N is subject to leaching, runoff and denitrification, (Grant, 1991; Hofman et al., 1994; Hack-ten Broeke et al., 1996; Brandi-Dohrn et al., 1997).

Achieving low residual soil NO_3^- concentrations in fields fertilized with manure is challenging. Essentially none of the N in manure is in the form of NO_3^- and much of the N is contained in organic compounds that must mineralize before becoming available to plants (USDA-NRCS, 1992). To plan manure applications that meet, but do not greatly exceed, the N needs of a crop, farmers or their advisors must accurately predict the rate of N mineralization. This biological process is largely affected by organic matter composition, temperature and moisture.

A first order mineralization model with two organic N pools is commonly used to describe mineralization rates in soils (Molina et al., 1980; Deans et al., 1986; Bonde and Rosswall, 1987; Gilmour et al., 1996):

$$N_{min} = N_O S(1 - \exp(-ht)) + N_O(1 - S)(1 - \exp(-kt)) \qquad [4.1]$$

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[1] Programs generally address environmental concerns of phosphorus, bacteria and biological oxygen demand, in addition to NO_3^-.

where N_{min} is the organic N (mg N kg^{-1} soil) mineralized over time t (d), N_O is the potentially mineralizable organic N (mg N kg^{-1} soil) when mineralization begins, S is the fraction of potentially mineralizable organic N that is labile (quickly mineralized), 1-S is the recalcitrant (slowly mineralized) fraction, h and k (d^{-1}) are the mineralization rate constants for the labile and recalcitrant organic N respectively and "exp" is the exponential function[2].

In research settings, N_O is determined by *in vitro* incubation of soil samples and measurement of N_{min} over time. These incubations can last over 200 days. The results are modeled with a non-linear curve fitting program, with initial values for N_O, S, h and k estimated. If the iterative curve fitting process does not converge, then new initial values for the variables are selected. As a simplification, only one organic N pool may be considered, in which case S is set to zero in Eq. [4.1] (Deans et al., 1986).

To estimate N_O for agronomic purposes, 200 day incubations are not desirable because farmers need to make decisions on a much shorter time frame. Accordingly, quicker methods have been developed to estimate indices of N mineralization potential. These indices may be correlated to N_O and can sometimes be used to adjust N fertilizer rates to account for expected N mineralization. For example, the N mineralization index recommended by Oregon State University for winter wheat employs a two week anaerobic incubation of soil samples, followed by NH_4^+ analysis (Hart et al., 2006).

Rate constants can be adjusted to actual soil temperatures, assuming a Q_{10} (temperature coefficient) of 2 (Vanotti et al., 1995):

$$k = k_{Tr}(0.933^{(Tr-T)}) \qquad [4.2]$$

where k is the temperature-adjusted rate constant (units of inverse time), k_{Tr} is the rate constant at temperature T_r (the experimental reference temperature in °C at which a mineralization experiment was conducted), 0.933 is a constant that applies when the reaction rate halves with every 10°C decrease in temperature and T is the actual mean soil temperature (°C).

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[2] Throughout this paper, "exp" is used to denote the natural exponential function in which the base of the natural logarithm (*e*) is raised to the power of the parenthetical value immediately following "exp."

Deans et al. (1986) calculated N mineralization rates from data originally published by Stanford and Smith (1972) and found labile organic N rate constants to range between 0.041 and 0.500 d^{-1} (mean = 0.157 d^{-1}) and recalcitrant organic N rate constants to range between 0.00057 and 0.00986 d^{-1} (mean = 0.00454 d^{-1}) for eight Maryland soils incubated for 210 days at 35°C. Other rates reported in the literature vary. Gilmour et al. (1996) found labile rates of approximately 0.17 d^{-1} and recalcitrant rates of 0.003 d^{-1} with bio-solid amended soil in Arkansas. Quemada et al. (1997) estimated N mineralization rates for carbohydrate and protein (the labile portion of crop residue) to range from 0.14 to 0.67 d^{-1} and for lignin and cellulose (the recalcitrant portion of crop residue) to range from 0.00095 d^{-1} to 0.021 d^{-1}. In the work cited above, labile organic N rate constants ranged from 0.041 to 0.67 d^{-1} and recalcitrant organic N rate constants ranged from 0.00057 to 0.021 d^{-1}. A simple approximation would be to use $h_{Tr} = 0.100$ d^{-1} and $k_{Tr} = 0.001$ d^{-1} for labile and recalcitrant rate constants, respectively, at $T_r = 35$°C.

Recalcitrant organic N includes compounds associated with lignin from plant residues and animal waste, organic compounds and microbial matter protected from mineralization by adsorption onto clay or by containment inside soil aggregates. Part of the old organic matter (humus) can be considered recalcitrant, but much of the humus fraction of soil is so stable that it is generally considered to be not potentially mineralizable (Van Veen et al., 1984). Most of the organic N in agricultural soils that *is* potentially mineralizable is recalcitrant. For example, Deans et al. (1986) determined that recalcitrant organic N accounted for 75 to 97% of the potentially mineralizable N in 20 soils from Connecticut, Maryland and Minnesota.

Using an approximate labile mineralization rate of $h_{Tr} = 0.100$ d^{-1}, Eq. [4.1] and [4.2] predict that 65% of labile organic N will mineralize within the first 30 d and 99% of the labile N will mineralize within 120 d with a soil temperature of 20°C. In contrast, using an approximate recalcitrant rate constant of $k_{Tr} = 0.001$ d^{-1}, only 1% and 4% of the recalcitrant organic N would mineralize within the first 30 and 120 d, respectively, at a soil temperature of 20°C. Because of this slow mineralization rate, repeated applications of recalcitrant organic N can enlarge the soil recalcitrant organic N pool (Fried et al., 1976). This combination of a large pool plus slow mineralization rates makes recalcitrant organic N difficult to manage. It could take years to manipulate the size of the recalcitrant organic N pool, and thus the amount of N that mineralizes from it. The time of year that recalcitrant organic N mineralizes is also difficult to manage because it is weather-dependent.

Italian ryegrass (*Lolium multiflorum* L.) is often seeded as a fall cover crop to scavenge N after silage corn (Gangwer, 1999). However, Italian ryegrass does not accumulate significant N during the coldest months of November through January (Griffith et al., 1997). Because of this, in Oregon's Willamette Valley, farmers are advised to begin applying N fertilizer to grass crops at T-Sum 200, just before Phase II accelerated N uptake by the crop begins (Pirelli et al., 2004). T-Sum 200 is based on Growing Degree Days (*GDD*) calculated by:

$$GDD_i = Ta - Tb \quad , \text{if } Ta >= Tb \tag{4.3}$$

$$GDD_i = 0 \quad , \text{if } Ta < Tb \tag{4.4}$$

$$GDD = \sum_{i=\Phi}^{\Omega} GDD_i \tag{4.5}$$

where GDD_i is a single day's contribution to *GDD*, *Ta* is the mean air temperature for that day (°C), *Tb* is the base temperature, Φ is the date calculations begin and Ω is the date calculations end. For T-Sum 200 calculations, $Tb = 0$°C, $\Phi = 1$ January. T-Sum 200 is reached when $GDD = 200$. At T-Sum 200, Ω is usually between 30 January and 14 February in Oregon's Willamette Valley.

Based on the Recalcitrant Organic Nitrogen Dynamics in Manured Soils (RONDIMS) spreadsheet model, using precipitation and evapotranspiration data from Corvallis Oregon (see Chapter 3), "cool season" was defined as late September to mid-May. During this period, RONDIMS predicted that the rolling 10-day average precipitation would exceed the rolling 10-day average evapotranspiration for typical cropping systems including silage corn (*Zea mays* L.) and annual ryegrass (*Lolium multiflorum* Lam.) in Oregon's Willamette Valley. Nitrate is likely to be lost to leaching, runoff and denitrification throughout the cool season, and the period from November to T-Sum 200 is especially critical due to the low N uptake by cool season grasses before T-Sum 200.

Because of this potential for NO_3^- loss during the cool season, soil is often tested for residual NO_3^- remaining after the warm season crop is harvested in late summer or early fall. In western Oregon, if residual soil NO_3^- concentrations exceed 15 mg N kg^{-1} soil for perennial grass (various species) or 20 mg N kg^{-1} soil for silage corn (*Zea mays* L.), farmers are advised that manure applications during the growing season were excessive and should be reduced in future years (Sullivan and Cogger, 2003). Assuming a soil sampling depth of 30 cm and soil bulk density of 1.4 g cm^{-3}, 15 to 20 mg N kg^{-1} equals approximately 63 to 84 kg N ha^{-1}.

These western Oregon recommendations are consistent with those from other agricultural regions. For example, some states in Germany and the Netherlands have set goals for residual soil NO_3^- on cropland to be below 45 to 70 kg N ha^{-1} to reduce the potential for NO_3^- losses to the environment (Hofman et al., 1994; Ilsemann et al., 2001). Zebarth et al. (1995) estimated an acceptable upper limit of residual soil NO_3^- at 100 kg N ha^{-1} in south-coastal British Columbia to safeguard groundwater in this region where annual water flow through the soil profile is approximately 1,000 mm.

The literature reports no recommendations for maximum levels of cool season N mineralization in Europe, Canada or the United States. Because N mineralized *during* the cool season is subject to the same loss pathways as NO_3^- present at the *beginning* of the cool season, this project used the western Oregon residual soil NO_3^- benchmark of 20 mg N kg^{-1} soil as an approximate standard for cool season N mineralization. That is, in this study, cool season mineralization of 20 mg N kg^{-1} soil or greater was considered excessive.

The objectives of this study were to (1) quantify cool season N mineralization from recalcitrant organic N in soils with a long history of manure application, (2) compare the magnitude of this cool season N mineralization to residual soil mineral N concentration in the fall and (3) to examine the relationship between cool season recalcitrant organic N mineralization, a fall mineralizable N index, the % total soil N and the residual fall soil mineral N.

To accomplish these objectives, soil was incubated *in situ* using ion exchange resin/soil cores (IER/SC). Incubations began in late October or early November and ended in February or May. Although most of the soil cores were obtained from fields with long histories of manure application, none of these fields had received manure or other organic matter additions within two months of core collection. Thus, little labile organic N should have been present in the cores. Cores were tested for a mineralizable N index and % total N before the incubations. Mineral N (NH_4^+-N plus NO_3^--N) was measured before and after the incubations.

4.3 Materials and methods

4.3.1 Soil core construction

Mineralization experiments were conducted on soil samples from six fields in Oregon's Willamette Valley using ion exchange resin/soil cores (IER/SC) similar to those first documented by DiStefano and Gholz (1986). Soils, cropping systems and manure histories are summarized in Table 4.1. All but Field F had a long history of dairy manure applications, but none of the fields had received manure, other organic amendments or fertilizer within two months of core collection. This ensured that little labile organic N remained from previous manure applications. Soils were collected from 4 to 5 sites in each field, with each site located approximately 25 m apart. Soil samples from recently harvested corn fields were collected at the midpoint between rows to avoid fertilizer bands.

Cores were constructed as shown in Figure 4.1. Aluminum pipes, 10 cm diameter, were placed in a straight line, with each pipe spaced 10 cm from the adjacent pipe, and driven to a depth of 20 cm with a rubber mallet. Weeds and detritus larger than 1 cm in length were removed from the soil surface before driving the pipes. The pipes were carefully removed by inserting a steel rod through two holes drilled in the upper 5 cm of the pipe and then lifting up on the steel rod. Using this technique, excess soil remained attached to the core bottom and was trimmed off in the field. The cores were sealed with foil, placed in polyethylene bags and refrigerated at 4 ° C within five hours of collection.

After removing the cores, soil between the resulting holes was excavated to a depth of 17 cm with a metal scraper. This loose soil was sealed in clean plastic pails, transported back to the lab and refrigerated at 4℃ within five hours of collection. The loose soil was used for baseline (pre-incubation) analysis of soil moisture and chemistry. For each experiment, one core from each field was fitted with a Hobo® recording thermometer (Onset Computer Corporation, 2006) and one core from each field was fitted with a Watermark® granular matrix moisture sensor (Irrometer Company, 2006). Cores were kept at 4 ° C until placement in the field for incubation.

Just before incubation, the bottom 3 cm of soil was scraped from each core and two ion exchange resin (IER) bags were fitted into the bottom. The IER bags were nylon mesh and contained equal volumes of Sybron Ionac C-249 and ASB-1P. The "below soil IER bags" contained a net mass of 104 g moist IER and the "bottom IER bags" contained 80 g moist IER. Eghball (2000) reported that IER can be destroyed by freezing temperatures. As illustrated in Table 4.5, minimum temperatures in the cores were only minimally below freezing in the experiments described here. Myrold et al. (1992) successfully used the IER/SC method during winter in western Oregon. Inspection of the IER after incubation revealed no physical damage to the IER in these experiments.

Although the soil core construction process was similar to that described in the literature (DiStefano and Gholz, 1986; Raison, 1987; Kolberg et al., 1997; Sullivan et al., 1999), the modifications used in this study included the use of larger diameter pipe and two IER bags in the bottom of each core. The larger diameter pipe reduced compaction when the pipe was hammered into the ground to collect samples. Another benefit to the larger cores was probably reduced variability of results due to the larger mass of soil being incubated. Large diameter cores necessitate significantly more IER to be used, which was an additional cost. The below soil IER captured NO_3^- and NH_4^+ leaching out of the soil core. The bottom IER prevented contamination from below in case a seasonally high water table saturated the soil surrounding the core. High water tables were a concern because the incubations were conducted during the winter rainy season. Any leaching of organic N from the cores was assumed to be insignificant.

Table 4.1. Field characteristics. Fields D and G are on the same farm. Field A soil was collected for incubations in both years.

Field	Soil series	Soil class	Drainage class	% Clay	pH	%C	%N	C:N	Previous crop
A	Newberg fine sandy loam	coarse-loamy, mixed, mesic fluventic haploxerolls	well to somewhat excessive	11.9	6.5 (0.08)	1.20 (0.07)	0.11 (0.01)	11.3 (0.06)	silage corn §
B	McBee silty clay loam	fine-silty, mixed, mesic cumulic ultic haploxerolls	moderately well	23.8	6.6 (0.12)	3.42 (0.25)	0.32 (0.02)	10.6 (0.11)	Perennial grass (meadow foxtail) §
D	Woodburn silt loam	fine-silty, mixed, mesic aquultic argixerolls	moderately well	13.1	6.8 (0.06)	3.94 (0.40)	0.32 (0.03)	12.3 (0.43)	silage corn §
E	Wapato silty clay loam	fine-silty, mixed, mesic fluvaquentic haplaquolls	poor	19.7	5.4 (0.06)	1.68 (0.07)	0.16 (0.01)	10.3 (0.08)	silage corn §
F	McBee silty clay loam	fine-silty, mixed, mesic cumulic ultic haploxerolls	moderately well	35.0	6.4 (0.19)	2.08 (0.14)	0.21 (0.02)	9.9 (0.18)	silage corn ‡
G	Woodburn silt loam	fine-silty, mixed, mesic aquultic argixerolls	moderately well	16.6	6.2 (0.11)	3.02 (0.21)	0.24 (0.02)	12.4 (0.18)	silage corn §

Clay % determined by pipette method, %C and %N determined by Leco CNS-2000 macro-analyzer, pH determined by 1:2 soil to water. All analyses in this table were by the Oregon State University Central Analytical Lab (Horneck et al., 1989). Parenthetical values are S.E.

§ Indicates fields with a history of annual dairy manure applications for greater than 10 years.

‡ Indicates field with no recent manure applications.

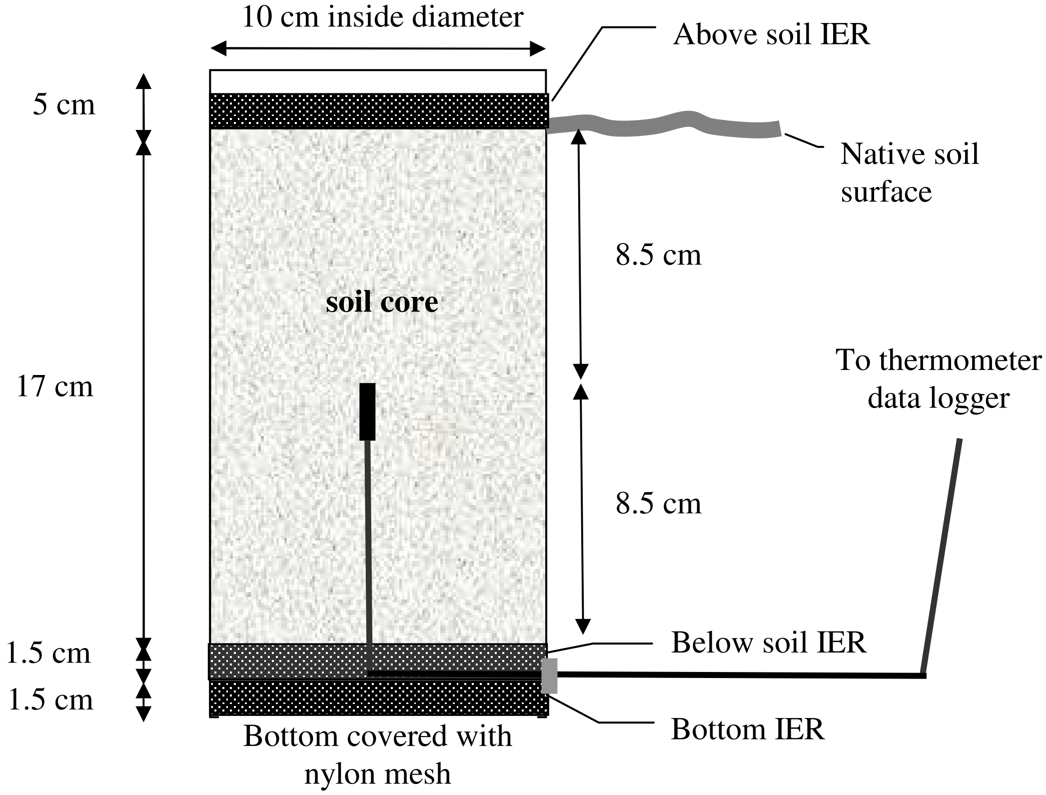

Figure 4.1. Diagram (not to scale) of IER/SC construction, using 10 cm inside diameter aluminum irrigation pipe. One core from each field was fitted with a recording thermometer with a cable lead entering the lower side through a rubber septum as shown. The recording point of the cable was in the center of the core. Another core from each field was fitted with a Watermark© moisture sensor and the remaining cores did not contain sensors. In the 2003 to 2004 incubation, the above soil IER bags captured little mineral N and, in the 2004 to 2005 incubation, the cores were constructed without the above soil IER bags.

4.3.2 Incubations

Cores were constructed in the lab and then installed with a completely randomized design (Mendenhall and Sincich, 1995) in a field seeded to soft white winter wheat (*Triticum aestivum* L.). The cores were incubated in this field under conditions that simulated natural soil temperatures and, to some extent, natural soil moisture. All cores were incubated in the same field in order to eliminate spatial weather variability between the farms where soils were collected.

The incubation field was near Forest Grove Oregon (45.59°N, 123.14°W), approximately 43 kilometers west of Portland. This farm is in the Willamette Valley ecoregion (EPA, 2003) and has 30 year (1971 to 2000) mean annual precipitation of 117 cm and mean annual air temperature of 11.7℃. The coldest and wettest month is December (4.1℃ mean temperature and 19.9 cm mean precipitation). The warmest month is August (mean temperature 20.4℃) and the driest month is July (mean precipitation 1.3 cm) (Oregon Climate Service, 2005).

A Hobo® recording thermometer and a Watermark® granular matrix soil moisture sensor were installed in the in-field soil adjacent to the cores and at the same depth (8.5 cm) as the sensors inside the cores. Temperatures were automatically recorded every 1 to 2 hours and soil moisture was recorded manually throughout the incubation. The fields, dates of soil collection, beginning incubation dates, harvest dates and replication numbers are summarized in Table 4.2. Early in the 2003 to 2004 incubation, the Field E cores began to overflow with water as precipitation rate exceeded infiltration rate in this silty clay loam soil. IER bags (100 g mixed resin) were placed above the soil as shown in Figure 4.1. However, when these above-soil IER bags were analyzed after the incubations, they accounted for only 8% of the total mineral N. Because the above-soil IER bags tended to rip and because the IER was expensive to analyze, above soil IER bags were not employed in the 2004 to 2005 incubation. Not employing IER bags above the soil cores allowed some contamination of the cores by atmospheric N deposited via rain. Atmospheric N deposition via rain and snow is estimated at 0.5 to 2 kg N ha^{-1} per year in the Pacific Northwest (Thompson et al., 2000), which is less than 1 mg N kg^{-1} soil, an insignificant amount compared to the mineral N concentrations measured in the cores.

In both years, the February core harvest was done at T-Sum 200, as calculated in Eq. [4.3] through Eq. [4.5]. Air temperature was as reported by the Forest Grove Agrimet weather station (Bureau of Reclamation, 2005), located approximately 13 km south of the incubation sites. Oregon State University recommends fertilizing pasture grasses with N at T-Sum 200 because at that time cool season grasses begin to utilize increasing amounts of N (Pirelli et al., 2004).

Table 4.2. Incubation trials. Numbers in parentheses indicate the number of cores per field harvested on that date.

	2003-2004	**2004-2005**
Fields	A,D,E	A,B,F,G
Soil collection	3-10 Oct. 2003	12-15 Oct. 2004
Incubation begun	1 Nov. 2003	27 Oct. 2004
First harvest (n)	15 Feb. 2004 (12)	15 Dec. 2004 (5)
Second harvest (n)	18 May 2004 (12)	4 Feb. 2005 (5)
Manure applied	none	22 Dec. 2004
Manured core harvest (n)	none	4 Feb. 2005 (5)

On 22 December 2004, liquid dairy manure at 0.081 g total N per core was surface applied to five cores from Fields B and five cores from field G. This rate equaled 42 kg NH_4^+-N plus 58 kg organic N per ha (total manure N applied = 100 kg ha^{-1}) and averaged 51 mg N kg^{-1} soil in the cores. Manure analysis was conducted by a commercial lab, AgriCheck Inc., in Umatilla Oregon.

For all incubations, the cores were shielded with foil caps when the fields were fertilized but were otherwise left open. If weeds grew in the cores, they were either pinched off before reaching 2 cm in height or were killed with a small amount of glyphosate herbicide. At the end of incubation, the cores were removed from the ground, sealed with foil, placed in plastic bags and then refrigerated at 4 ° C within four hours.

4.3.3 Analysis

The loose soil collected for baseline analysis was mixed thoroughly, sifted through a 1 cm screen to remove stones and larger pieces of detritus and then sub-sampled as follows. A 100 g sub-sample was used to determine initial moisture content (Gardner, 1965). A separate, air-dried, sub-sample was sent to the Oregon State University Central Analytical Laboratory for mineralizable N index analysis (Keeney, 1982; Horneck et al., 1989). A separate 20 g moist sub-sample was extracted with 100 ml 2M KCl (one hour on a reciprocating shaker) and then filtered with a Whatman 934-AH glass microfibre filter or a Whatman Puradisc 25AS 0.45 um syringe filter. The filtered extracts were colorimetrically analyzed for NO_3^--N by cadmium reduction and diazotization and for NH_4^+-N by the alkaline phenol/hypochlorite method (Astoria-Pacific, 1998).

After incubation, the soil from each core was removed, weighed, mixed thoroughly and sub-sampled for moisture, NO_3^--N and NH_4^+-N analyses using the same methods used for baseline analyses. The bottom IER bag was discarded and the below-soil IER was weighed and emptied into a polyethylene bag. This IER was mixed thoroughly and then a 10 g moist IER sub-sample was removed and placed in a fresh nylon bag. The IER sub-samples were extracted with four sequential 50 ml aliquots of 2M KCl with 15 minutes of shaking. Following each sequential extraction, the extract was decanted from the bag by pouring the contents through a funnel. After the extract drained from the IER bag, the bag was rinsed with a separate 10 ml aliquot of 2M KCl. All rinses and extracts were combined for each bag and analyzed for NO_3^--N and NH_4^+-N with the same colorimetric analyses used for the soils. This method of IER extraction yielded 95% of the NO_3^--N and 106% of the NH_4^+-N in a trial with standard solutions adsorbed onto IER.

The experimental design did not include measurement of NH_3 volatilization or NO_3^--N denitrification losses. These measurements were beyond the scope of this project as standard methods for measuring the gaseous losses are expensive and time consuming (Aulach et al., 1991; Lara Cabezas et al., 1999). Simple mass-balance techniques are not rewarding in estimating denitrification and NH_3 volatilization because the mass of total N in soil is so high compared to these gaseous losses. For example, Table 4.1 gives the total N in the incubated soils as ranging from 0.11% to 0.32% (1,100 to 3,200 mg N kg^{-1} soil) with S.E. values of 0.01% to 0.03% (100 to 300 mg N kg^{-1} soil). Denitrification and NH_3 volatilization are generally less than N mineralization (Myrold et al., 1992; USDA-NRCS, 1992) and the highest N mineralization measured in this study was less than 100 mg N kg^{-1}. Thus, the gaseous losses of N from the IER/SC were most likely less than one S.E. of the total soil N, which made estimates of gaseous losses by mass balance of total N infeasible.

Also, the soils were refrigerated for 2 to 3 weeks in October before the cores were ready for incubation. During the refrigeration period, N mineralization was essentially halted in the cores, but would certainly have continued under normal field conditions. Due to probably gaseous losses and the 2 to 3 week preparation time, net N mineralization results presented here are conservative and actual net N mineralization in field soils during these time periods is somewhat greater.

4.3.4 Calculations

The IER analyses for NO_3^--N and NH_4^+-N were normalized to the mass of dry soil in each core and added to the post-harvest soil NO_3^--N and NH_4^+-N analyses to determine the total mineral N present after incubation. The baseline NO_3^--N and NH_4^+-N concentrations were subtracted from the post-incubation analyses to determine net mineralization. Student's t-tests were calculated in Microsoft Excel 2003.

4.4 Results and discussion

4.4.1 Mineral N over time

Mean mineral N concentrations[3] before, during and after the incubations were calculated for 2003 to 2004 and 2004 to 2005 and are compared in Tables 4.3 and 4.4. In all of the fields and in both years, the residual mineral N concentrations in October were greater than the 20 mg N kg^{-1} benchmark discussed in Section 4.2 above. This was true even for field F, which had not received manure applications for at least 10 years. In four of the seven soils tested, there was a significant ($p < 0.10$) increase in mineral N by T-Sum 200.

Mean net N mineralization is displayed in Table 4.6. The mean net mineralization (all fields combined), from the beginning of incubation to T-Sum 200, was greater than 20 mg N kg^{-1} in both years. Mineralization in individual fields ranged from 2.2 to 37.2 mg N kg^{-1} by T-Sum 200. Additional N mineralized between T-Sum 200 and May 2004, resulting in net mineralization (1 November 2003 to 18 May 2004) of from 23.8 to 98.2 mg N kg^{-1} soil.

The residual mineral N concentrations were highly variable within fields, with coefficients of variation ranging from 23 to 81%. High variability in fall mineral N concentration was expected. For example, Ilsemann et al. (2001) reported coefficients of variation for fall NO_3^- ranging from 31 to 36% for agricultural sites in Germany.

Interestingly, the Field B and G plots receiving 51 mg N kg^{-1} soil on 22 December 2004 had less mineral N on February 4, 2005 than the non-manured plots from Fields B and G. For Field G, the manured plot mineral N content was not significantly different ($p < 0.10$) on February 4, 2004 than on October 27, 2003. This may have been due to immobilization of mineral N or increased denitrification due to the recently applied manure (Myrold et al., 1992).

Table 4.3. 2003 to 2004 mineral N concentrations. November data are the sum of NO_3^--N plus NH_4^+-N in the soil before beginning incubation. February and May data are the sum of NO_3^--N plus NH_4^+-N in the soil and IER after incubation. February data are at T-Sum 200.

			Mineral N	
Field		**1-Nov**	**15-Feb**	**18-May**
		-----------------------	**mg N kg^{-1}**	**-----------------------**
A	mean	27.3	47.1*	54.5**
	S.E. (n)	8.3 (4)	5.2 (12)	4.1 (12)
D	mean	137.6	172.9	235.7**
	S.E. (n)	28.1 (4)	15.9 (12)	18.2 (12)
E	mean	45.6	52.3	69.4*
	S.E. (n)	21.4 (3)	5.6 (9)	6.9 (9)

* significantly greater than 1 Nov. value at $p < 0.10$
** significantly greater than 1 Nov. value at $p < 0.01$

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[3] The baseline mineral N analyses for one of the Field E sites in the 2003 to 2004 incubation was very high (207.5 mg N kg^{-1}) compared to the mean value for the other Field E sites (45.6 mg N kg^{-1}). Cores constructed from that site were eliminated from the study.

Table 4.4. 2004 to 2005 mineral N concentrations. October data are the sum of NO_3^--N plus NH_4^+-N in the soil before beginning incubation. December and February data are the sum of NO_3^--N plus NH_4^+-N in the soil and IER after incubation. February data are at T-Sum 200.

Field		Mineral N 27-Oct	 15-Dec	 4-Feb
		----------------------	mg N kg^{-1}	----------------------
A	mean	52.5	57.7	57.2
	S.E. (n)	5.8 (5)	9.0 (5)	7.7 (5)
B	mean	48.5	59.3	82.3*
	S.E. (n)	9.5 (5)	9.4 (5)	13.1 (5)
B + manure §	mean	48.5	N/A	75.5*
	S.E. (n)	9.5 (5)	N/A	6.5 (5)
F	mean	37.4	41.8	74.6**
	S.E. (n)	6.8 (5)	2.9 (5)	8.8 (5)
G	mean	72.5	69.6	94.6*
	S.E. (n)	7.5 (5)	14.7 (5)	11.4 (5)
G + manure §	mean	72.5	N/A	82.0
	S.E. (n)	7.5 (5)	N/A	6.4 (5)

* significantly greater than 27 Oct. value at $p < 0.10$

** significantly greater than 27 Oct. value at $p < 0.01$

§ received liquid manure at 21 mg NH_4^+-N kg^{-1} + 30 mg organic-N kg^{-1} on 22 Dec.

4.4.2 Soil moisture

Soil core moisture, as measured with Watermark© granular matrix sensors, is charted in Figure 4.2. The cores began at various moisture contents because the soil used to construct the cores was collected from different fields on different days. By the end of

November, however, all of the cores reached moisture levels near saturation. From late November to late February, moisture levels inside the cores were similar to soil moisture levels outside the cores. In March, April and May, the soil outside the cores began to dry out between storms due to evapotranspiration of the soft white winter wheat (*Triticum aestivum* L.) planted in the field where the cores were incubated. Because no roots penetrated the cores, the core soil remained very moist until the incubation ended on May 18, 2004.

This tendency of cores to remain more moist than natural field soils has been noted by others (Myrold et al., 1992). N mineralization is most rapid at soil moisture potential of approximately -30 kPa (Myers et al., 1982). Based on Figure 4.2, elevated moisture levels may have affected mineralization rates inside the cores, relative to what would occur naturally in the fields from which the soil samples were collected, during March through May. However, moisture levels inside the cores were essentially the same as those outside the cores during November through February.

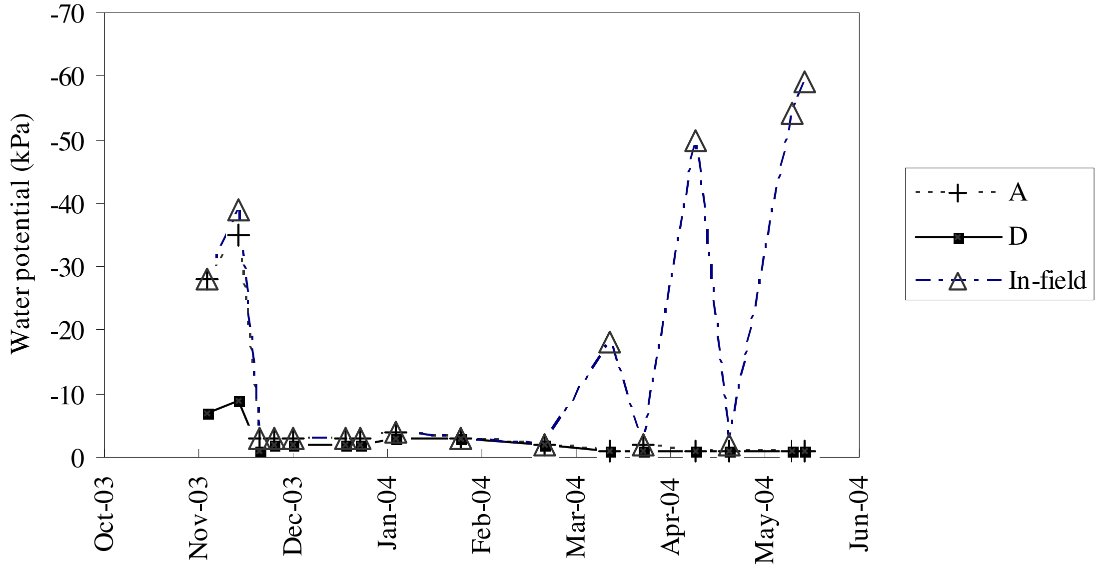

Figure 4.2. Comparison of water potential in IER/SC cores and in-field site (outside but adjacent to cores) for the winter 2003 to 2004 incubation. Moisture contents varied early in the incubation, but all of the cores and the in-field site quickly exceeded

field capacity and remained in that very moist state until March. In March, the in-field soil began to get dryer than the IER/SC soils between rain storms.

4.4.3 Soil temperature and degree days

Soil core temperatures are summarized in Table 4.5. Mean soil core temperatures for all fields differed by less than 0.2℃ from each other and from the field soil outside the cores over the incubation periods. Some cores were harvested in both years at T-Sum 200 (February), calculated with ambient air temperatures beginning on January 1 as per Eq. [4.3] through Eq. [4.5]. Although ambient air temperature is a convenient method for predicting growth of plants, mineralization rates are influenced by soil temperatures. Eq. [4.1] and [4.2] can be combined:

$$N_{min} = N_O S(1 - \exp(-h_{Tr}(0.933^{(Tr-T)}t))) + N_O(1 - S)(1 - \exp(-k_{Tr}(0.933^{(Tr-T)}t))) \quad [4.6]$$

Rather than calculating N_{min} on a daily basis, where T is the mean daily temperature and $t = 1$ day, the time and temperature components of Eq. [4.6] can be written as:

$$MDD = \frac{\left(\sum_{i=1}^{\Pi} 0.933^{(Tr-Ti)}\right)}{w} \quad [4.7]$$

where MDD is the mineralization degree days, Tr is the reference temperature, Ti is soil temperature (℃) recorded at every time interval (i), Π is the number of time intervals over the entire mineralization period and w is the number of time intervals per day. For time intervals when Ti is less than 0℃, no MDD are generated. Eq. [4.7] is similar to Eq. [4.5] except that Eq. [4.7] captures the exponential effect of temperature changes and is calculated over a finer time scale. Eq. [4.6] and [4.7] can be combined:

$$N_{min} = N_O S(1 - \exp(-h_{Tr}MDD)) + N_O(1 - S)(1 - \exp(-k_{Tr}MDD)) \quad [4.8]$$

MDD, beginning on the day after installing cores in the field plots, were calculated with Eq. [4.7] for soil core temperatures (Ti) taken every two hours ($w = 12$) and a reference temperature (T_r) equal to 35℃. The concept of MDD is similar to "temperature adjusted time" described by Crohn (2006).

MDD are given in Table 4.5, along with minimum, maximum and mean core temperatures. The *MDD* from the beginning of incubation until the February harvest of cores were 13.5 and 13.0 d for 2003 to 2004 and 2004 to 2005, respectively. Thus, the incubations up to the February harvest of cores were theoretically equivalent to a mineralization period of approximately 13 days at a soil temperature of 35°C.

Table 4.5 also displays *GDD*, calculated as in Eq. [4.3] through Eq. [4.5], with the base temperature (*Tb*) equal to 0°C and the beginning date (Φ) and ending date (Ω) of calculation as shown in the Time Period column. Soil Degree Days (*SDD*) are also given in Table 4.5. Soil Degree Days are calculated as in Eq. [4.3] through Eq. [4.5] except using soil core temperature rather than air temperature. Throughout the fall and spring incubation periods, *GDD* values were similar to *SDD*.

Net mineralization per *MDD*, summarized in Table 4.6, varied between fields from a low of -0.41 mg N kg^{-1} MDD^{-1} (net immobilization) to a high of 5.56 mg N kg^{-1} MDD^{-1}. This is not surprising, given that recalcitrant organic N pools would be expected to vary in size between fields.

If the organic N that mineralized during the experiments was mostly recalcitrant (S in Eq. [4.8] is small), and if the mineralization was adequately described by Eq. [4.8], then the N mineralization per *MDD* would be expected to decrease slowly over time as the recalcitrant organic N pool ($N_O(1 - S)$ in Eq. [4.8]) mineralized. This, however, was not the case. For Field A, N mineralization per *MDD* was substantially less in the second incubation (both years). This suggests that labile organic N was a significant factor in this soil and that the labile organic N pool was depleted in the first incubation periods. For all other fields, mineralization per *MDD* was greater in the second incubation. This result is not explained by the simple model presented in Eq. [4.8]. It is possible that some mineral N immobilized in the early stages of incubation but later mobilized as organic matter decomposed and soil C:N ratios decreased (Whitmore and Handayanto, 1997).

It was also surprising that the greatest mineralization rate (5.56 mg N kg^{-1} MDD^{-1}) occurred in Field F between 16 December 2004 and 4 February 2005. Field F was the only field in the study without a history of manure application. For the overall time period of October 2004 to February 2005, however, the Field F net mineralization rate was much less at 2.86 mg N kg^{-1} MDD^{-1}. Possibly there was some microbial immobilization of mineral N initially, followed by a relatively rapid release of mineral N in this field. The low net mineralization rate for Field E from 1 November 2003 to 15 February 2004 may have been due to denitrification. Water quickly ponded in these cores and the soil appeared gleyed and mottled when removed for analysis (Figure 4.3), indicating oxidation-reduction potentials suitable for denitrification (Atlas and Bartha, 1993).

Table 4.5. Soil core temperatures. Mean soil core temperatures for all fields varied by less than 0.2° C. This table provides the minimum, maximum and mean soil core temperatures, averaged for all soils.

	Soil Core Temperature			**Mineralization Degree Days §**	**Soil Degree Days †**	**Growing Degree Days ‡**
Time period	**Minimum**	**Maximum**	**Mean**			
	--------------------- °C	-----------------------				
2 Nov 2003 - 15 Feb 2004	-0.6	12.6	5.1	13.5	541	565
16 Feb 2004 - 18 May 2004	3.3	19.4	11.4	17.8	1013	1004
28 Oct 2004 - 15 Dec 2004	1.4	14.3	7.0	7.1	338	334
16 Dec 2004 - 4 Feb 2005	-0.3	11.9	4.3	5.9	218	277

§ Mineralization degree days (MDD) calculated as in Eq. [4.7].

† Soil Degree Days calculated as in Eq. [4.3] through Eq. [4.5] using soil core temperatures rather than air temperature.

‡ Growing Degree Days (GDD) calculated as in Eq. [4.3] through Eq. [4.5] using mean air temperature.

Table 4.6. N mineralization. Rates are expressed as net N mineralization over the incubation period and as net N mineralization normalized per mineralization degree day (*MDD*).

Field	1 Nov 2003 - 15 Feb 2004	16 Feb 2004 - 18 May 2004	1 Nov 2003 - 18 May 2004	27 Oct 2004 - 15 Dec 2004	16 Dec 2004 - 4 Feb 2005	27 Oct 2004 - 4 Feb 2005
A	19.9 (1.47) §	7.3 (0.41)	27.2 (0.87)	5.1 (0.72)	-0.5 (-0.08)	4.7 (0.36)
D	35.4 (2.62)	62.8 (3.53)	98.2 (3.14)			
E	6.7 (0.50)	17.1 (0.96)	23.8 (0.76)			
B				10.8 (1.52)	23.0 (3.90)	33.8 (2.60)
F				4.4 (0.62)	32.8 (5.56)	37.2 (2.86)
G				-2.9 (-0.41)	25.0 (4.24)	22.1 (1.70)
Mean	20.7 (1.53)	29.1 (1.63)	49.7 (1.59)	4.4 (0.62)	20.1 (3.40)	24.5 (1.88)

§ Values outside parentheses are net mineralization (mg N kg^{-1}).

§ Values inside parentheses are net mineralization per MDD (mg N kg^{-1} MDD^{-1}).

Figure 4.3. Representative sample from Field E core. This core was harvested from the incubation plots on 4 February 2004. Gleying and mottling indicates anaerobic conditions occurred within the core. Scale is in cm.

4.4.4 Estimates of potentially mineralizable organic N

N_O and S can be approximated by solving Eq. [4.8] iteratively using the values of N_{min} and *MDD* that were measured for the two incubation periods in each experiment and the assumed rate constants of $h_{T2} = 0.100$ d^{-1}, and $k_{T2} = 0.001$ d^{-1} discussed previously. This calculation, applied to *MDD* (Table 4.5) and N mineralization (Table 4.6), predicted that five of the seven soils had negative labile organic N pools and the other two soils had labile organic N pools less than 25 mg kg^{-1}.

Negative values for labile organic N pools are physically impossible, but the calculation described above could predict negative values if N immobilization or denitrification occurred. The calculation was made again assuming no labile organic N was present ($S = 0$) and using only the total mineralization from fall to the end of the second incubation period in both years. With these assumptions, the recalcitrant organic pools were estimated at 882, 3183 and 771 mg N kg^{-1} for fields A, D and E, respectively, in 2003 to 2004. These values convert to 2302, 6102 and 1666 kg N ha^{-1}, respectively, using the mean core soil mass and surface area. For fields A, B, F and G in 2004 to 2005, the estimated recalcitrant organic N pools were 364, 2619, 2882 and 1712 mg N kg^{-1} (800, 5070, 5410 and 3260 kg N ha^{-1}), respectively.

4.4.5 Estimates of NO_3^- leachate concentrations

Table 4.7 displays estimates of NO_3^- leachate concentrations that could result from cool season N mineralization before T-Sum 200. In this table, N mineralization results have been converted to units of kg N ha^{-1} using each soil core's dry bulk density, which ranged from 1.05 to 1.33 g cm^{-3}. RONDIMS[4] predictions of N uptake by an annual ryegrass cover crop (*Lolium multiflorum* Lam.) and deep percolation of water are also provided in Table 4.7. RONDIMS predictions were for the incubation periods in the IER/SC experiments.

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[4] See Chapter 3 for a description of the RONDIMS model.

Table 4.7. Estimates of NO_3^- leachate concentrations. These estimates are based on IER/SC mineralization results combined with RONDIMS predictions of potential cover crop N uptake and percolation.

Field	Year	N mineralization (kg ha^{-1})	Cover crop potential N uptake § (kg ha^{-1})	Percolation with cover crop § (cm)	Percolation without cover crop § (cm)	Leachate with cover crop † (mg N L^{-1})	Leachate without cover crop † (mg N L^{-1})
A	2003-2004	19.9	14.4	49.5	49.9	6.2	9.0
D	2003-2004	35.4	14.4	49.5	49.9	9.9	12.7
E	2003-2004	6.7	14.4	49.5	49.9	0.0	2.7
mean	2003-2004	20.7	14.4	49.5	49.9	5.3	8.1
A	2004-2005	4.7	19.2	14.8	19.5	0.0	5.0
B	2004-2005	33.8	19.2	14.8	19.5	29.0	31.8
F	2004-2005	37.2	19.2	14.8	19.5	31.9	34.1
G	2004-2005	22.1	19.2	14.8	19.5	13.9	20.4
mean	2004-2005	24.5	19.2	14.8	19.5	18.7	22.8

§ Values predicted by RONDIMS model.
† Estimated as in Zebarth (1995).

Leachate concentrations were estimated with Eq. [4.9] (Zebarth, 1995):

$$N_L = N_F \times (10 / P) \qquad [4.9]$$

N_L is the NO_3^- concentration of leachate (mg N L^{-1}), N_F is the NO_3^- free to leach (cool season N mineralization minus cover crop N uptake, kg N ha^{-1}), P is percolation (cm) of water below the root zone and 10 is a constant to convert leachate units to mg N L^{-1}. Note that N_F does not include residual soil NO_3^-. For the cases without a cover crop, N_F equals the N mineralization.

Table 4.7 illustrates that RONDIMS predicts somewhat lower percolation of water below the root zone when a cover crop is grown, due to increased evapotranspiration. The 2003-2004 precipitation (69.7 cm) was close to the 1995-2005 mean precipitation (67.5 cm) for the incubation period. The 2004-2005 incubation period was considerably drier, though, with only 24.9 cm of precipitation. This difference in precipitation accounts for the difference in predicted percolation between the two years. The 2003-2004 incubation period was slightly cooler (mean air temperature of 5.6º C), compared to the 2004-2005 incubation (6.1 º C) or the 1995-2005 mean (6.2º C). The higher 2004-2005 air temperatures resulted in the higher RONDIMS potential N uptake by the cover crop during that winter.

As described previously, the period from November to T-Sum 200 in February is characterized by a low N uptake by cool season grasses (Griffith et al., 1997; Pirelli et al., 2004). Thus, the predicted leachate concentrations in Table 4.7 are only somewhat lower for the cases with cover crops than for those without. The estimates in Table 4.7 indicate that NO_3^- leachate concentrations from cool season mineralization alone can regularly exceed the drinking water standard of 10 mg N L^{-1} whether or not a cover crop is grown.

4.4.6 Cool season N mineralization versus residual soil mineral N

Table 4.8 compares cool season N mineralization (beginning of incubation to T-Sum 200) to residual soil mineral N concentrations in the fall. Mean cool season N mineralization to T-Sum 200 for all fields (22.9 mg N kg^{-1}) was significantly less ($p < 0.01$) than mean residual soil mineral N concentration (59.7 mg N kg^{-1}). The cool season N mineralization to T-Sum 200 was less than the mean residual soil mineral N concentration in each field tested and in both years, however the difference was not significant in all cases. High concentrations of residual soil mineral N in the fall is caused by manure applications made at excessive rates or incorrect times (Sullivan and Cogger, 2003). Cool season N mineralization, however, occurs regardless of manure application rates or timing (see Chapter 3).

Table 4.8. Comparing cool season N mineralization to residual fall soil mineral N concentration.

Field	Year		Residual soil mineral N §	Cool season N mineralization †
			--------------------- mg N kg^{-1}	---------------------
A	2003-2004	mean	27.3	19.9
		S.E. (n)	8.3 (4)	2.7 (12)
D	2003-2004	mean	137.6	35.4*
		S.E. (n)	28.1 (4)	9.7 (12)
E	2003-2004	mean	45.6	6.9
		S.E. (n)	21.4 (3)	9.6 (9)
A	2004-2005	mean	52.5	4.7**
		S.E. (n)	5.8 (5)	6.6 (5)
B	2004-2005	mean	48.5	33.8
		S.E. (n)	9.5 (5)	5.8 (5)
F	2004-2005	mean	37.4	37.2
		S.E. (n)	6.8 (5)	13.4 (5)
G	2004-2005	mean	72.5	22.1*
		S.E. (n)	7.5 (5)	14.2 (5)
All	all	mean	59.7	22.9**
		S.E. (n)	7.4 (31)	3.6 (53)

§ Residual fall soil mineral N before incubation began in the fall.

† Net N mineralized from beginning of incubation in the fall to T-Sum 200.

* significantly less than residual N at $p < 0.05$

** significantly less than residual N at $p < 0.01$

4.4.7 Mineral N distribution in soil cores

Distribution of mineral N for Field D cores in 2003 to 2004 is displayed in Figure 4.4. In the fall, almost all mineral N was present as NO_3^-. By T-Sum 200 (15 February 2004), most of the mineral N was NO_3^- that had leached into the IER, although some NH_4^+ also leached to the IER. By 18 May 2004, the soil NO_3^- concentration had begun to increase again as temperatures warmed and precipitation decreased. These results are consistent with field observations of the loss of NO_3^- from the soil profile quickly in the fall (Zebarth and Paul, 1997). The results also suggest that N mineralized between 15 February and 18 May 2004 was less likely to leach.

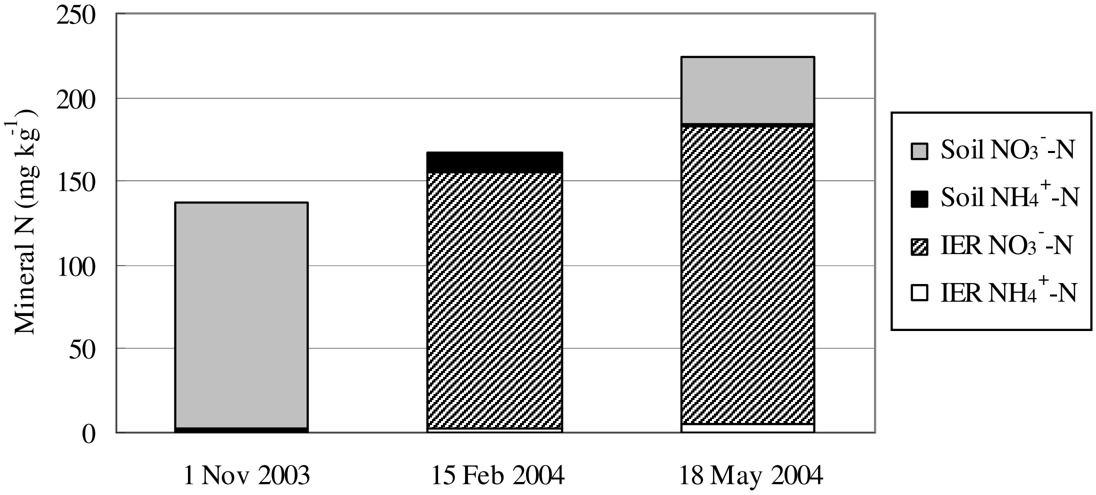

Figure 4.4. Distribution of mineral N in Field D cores. Although the total amount of mineral N was higher for this field than others in the study, the partitioning of mineral N was typical of all fields.

4.4.8 Predicting cool season N mineralization

Figures 4.5, 4.6 and 4.7 compare net cool season N mineralization (beginning incubation to T-Sum 200 in February) to, respectively, a mineralizable N index before incubation began, % total N in the soil and residual fall soil mineral N. The mineralizable N index was determined by the Oregon State University Central Analytical Lab in Corvallis Oregon using anaerobic 7 day incubation at 40℃ (Horneck et al., 1989), a modification of a method described by Keeney (1982). The mineralizable N index has been useful in predicting N mineralization to aid fertilizer decisions for winter wheat. However, the mineralizable N index had no value in predicting N mineralization from the beginning of core incubations in late October or early November through T-Sum 200 in February in either year of this study. Also, neither the % total soil N nor the residual fall soil mineral N was useful in predicting cool season mineralization.

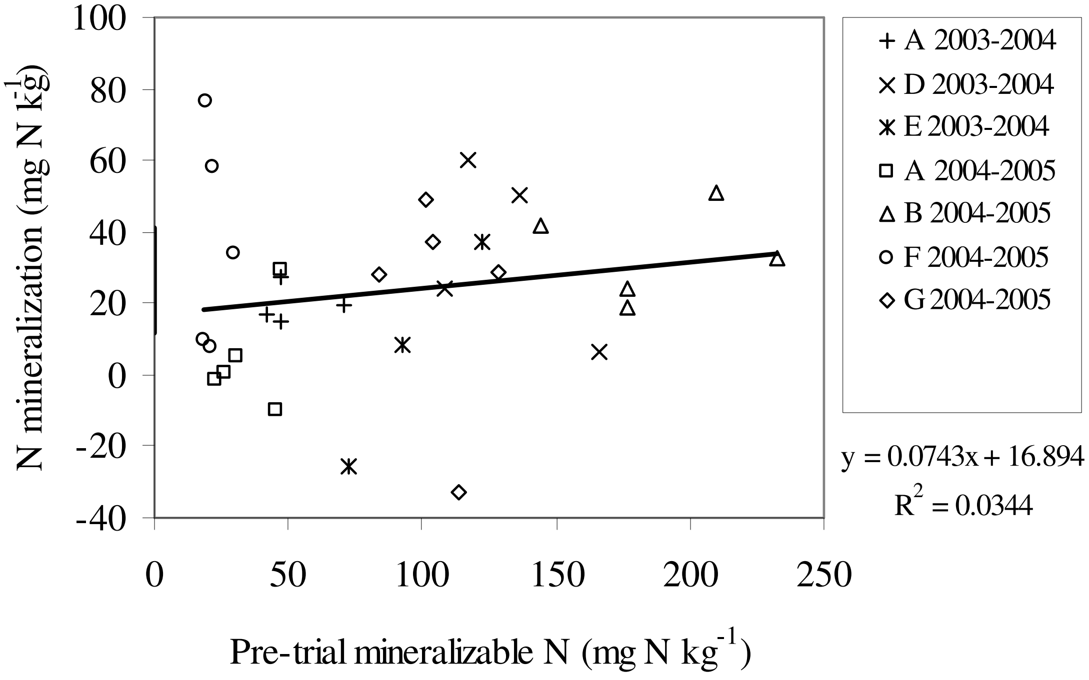

Figure 4.5. Predicting cool season N mineralization from a mineralizable N index. N mineralization is from beginning of incubations to T-Sum 200 in February. Mineralizable N is the Oregon State University Central Analytical Lab mineralizable N index (Horneck et al., 1989) before incubations began. Letters in the key denote fields from which the soil samples were taken (see Table 4.2). N mineralization was not correlated to pre-trial mineralizable N ($p < 0.10$).

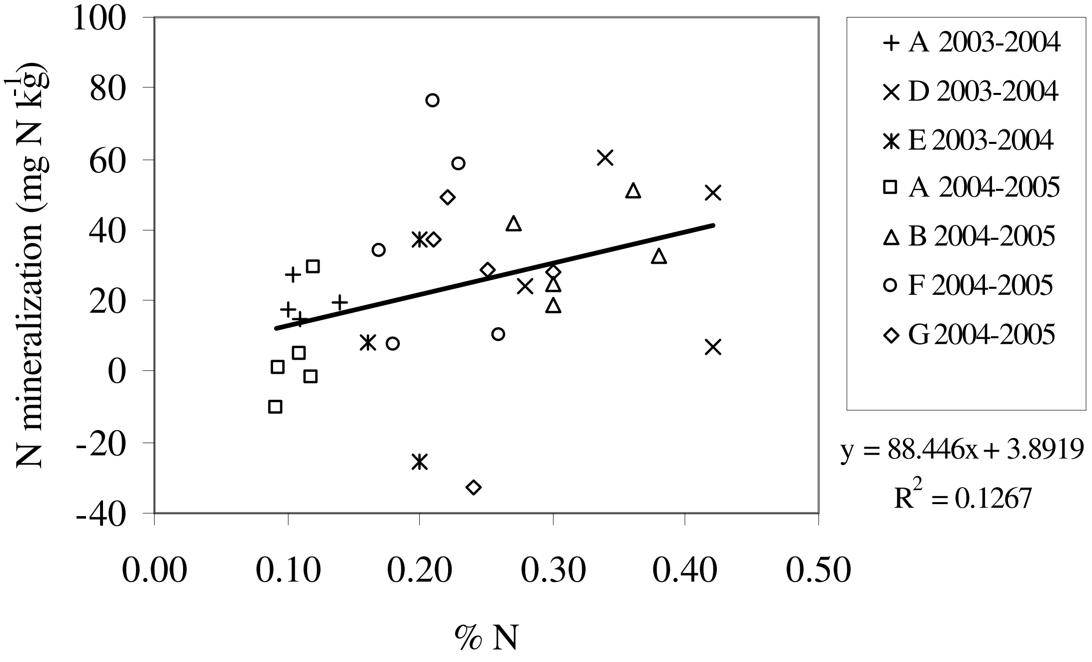

Figure 4.6. Predicting cool season N mineralization from % total soil N. N mineralization is from beginning of incubations to T-Sum 200 in February. The % total soil N was measured by a Leco CNS-2000 macro-analyzer (Horneck et al., 1989) before incubations began. Letters in the key denote fields from which the soil samples were taken (see Table 4.2). N mineralization was not correlated to % total soil N ($p < 0.10$).

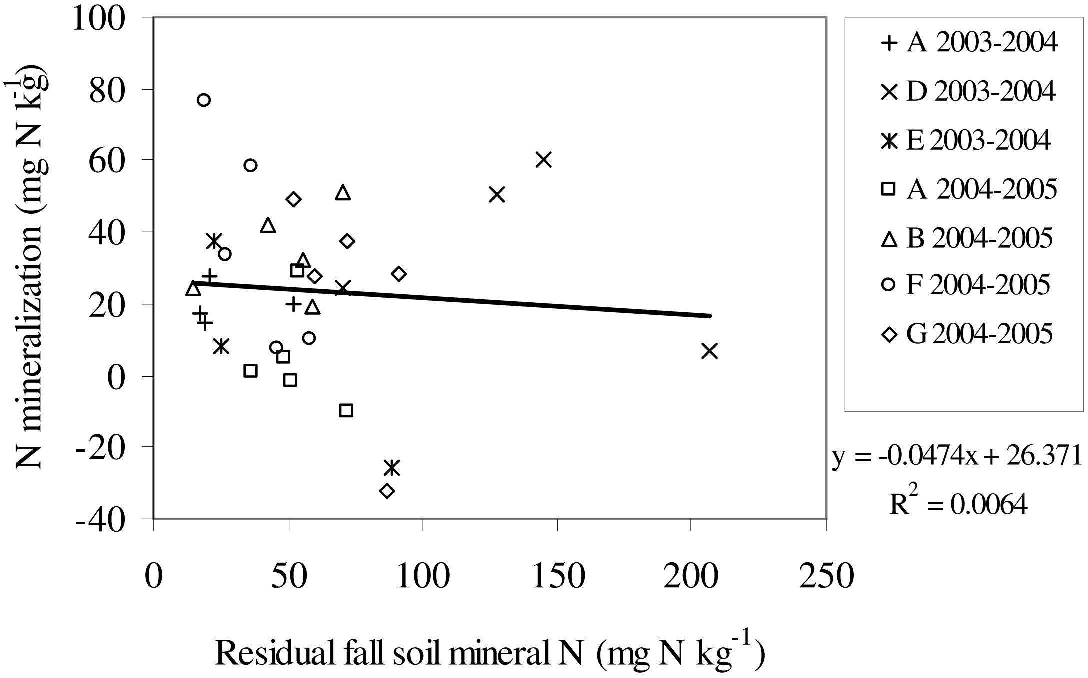

Figure 4.7. Predicting cool season N mineralization from residual soil mineral N. N mineralization is from beginning of incubations to T-Sum 200 in February. Residual soil mineral N is NH_4^+-N plus NO_3^--N before incubations began. Letters in the key denote fields from which the soil samples were taken (see Table 4.2). N mineralization was not correlated to residual fall soil mineral N ($p < 0.10$).

4.5 Conclusions

A useful standard for determining if residual fall soil NO_3^- in western Oregon is excessive, consistent with recommendations from Europe and Canada, is 20 mg N kg^{-1} soil (Hofman et al., 1994; Zebarth et al., 1995; USDA-NRCS, 2002; Sullivan and Cogger, 2003). This study used 20 mg N kg^{-1} as a benchmark to gauge whether cool season N mineralization was excessive.

The study defined "cool season" in Western Oregon as late September to mid-May. Because there is little uptake of mineral N by plants during the cool season, N mineralized during this period has the potential to be lost to the environment. The period from November to T-Sum 200 is especially critical due to the low N uptake by cool season grasses before T-Sum 200. There was net mineralization of organic N from November to T-Sum 200 on all soils tested in this study and the mean net mineralization exceeded 20 mg N kg^{-1} during this time period for both years of the study. Additional N mineralization occurred between T-Sum 200 and May.

The N mineralization measured in this study was a conservative estimate of total N mineralization under field conditions because denitrification and NH_3 volatilization were not measured and the incubations were started in late October or early November. Thus, this study demonstrates that cool season N mineralization can contribute a significant mass of NO_3^- to the soil at a time when that NO_3^- is vulnerable to loss via leaching, runoff and denitrification.

In the fall, most of the mineral N in each soil core was present as NO_3^- in the soil. By T-Sum 200, most of this NO_3^- as well as most of the newly mineralized N had leached to the IER below the soil. Between T-Sum 200 and May, much of the additional N that mineralized remained in the soil rather than leaching to the IER. This suggests that mineralization from T-Sum 200 to May in these soils is less likely to contaminate groundwater than mineralization from November to T-Sum 200.

The addition of liquid manure (100 kg N ha^{-1}) on 22 December 2004 did not affect the mineral N concentrations present at T-Sum 200 in 2005 in either the soil core or the resin below the core. This may have been due to microbial immobilization of the mineral N, but suggests that further studies into late season manure applications may be warranted.

All fields tested exceeded the 20 mg N kg^{-1} benchmark for residual fall soil NO_3^-. The mean cool season N mineralization (22.9 mg N kg^{-1}) from the beginning of incubation in the fall to T-Sum 200 in February was less than the mean residual soil mineral N concentration (59.7 mg N kg^{-1}) in the fall. Furthermore, cool season N mineralization was less than residual fall soil mineral N concentration in every field studied and in both years, although not significantly so in all cases. Thus, although cool season mineralization contributed a significant mass of NO_3^- prone to loss in the fields studied, residual soil mineral N was even greater. These results are consistent with the predictions of RONDIMS in Chapter 3 of this project.

On manured fields, residual soil mineral N is best reduced by applying manure at the correct rate and time (Sullivan and Cogger, 2003). Annual grass cover crops have also been suggested to scavenge residual soil mineral N before it leaches (Gangwer, 1999). RONDIMS simulations (Chapter 3) predicted that perennial grass crops or cool season annual grass cover crops can also help reduce losses of N mineralized *during* the cool season, however the effectiveness of this practice is limited from November through January when N uptake by grasses is low. The results of this study suggest that, in some fields and some years, cool season mineralization of recalcitrant organic N may result in NO_3^- leachate concentrations that would exceed the 10 mg N L^{-1} drinking water standard whether or not manure was applied at the correct rate and time and whether or not a winter cover crop was grown.

This study used soil mineralization degree days (*MDD*) to simplify calculations using first order mineralization models with temperature-corrected rate constants. As expected, net N mineralization per *MDD* varied considerably between fields. Net N mineralization per *MDD* also varied considerably over time within fields. Except for the coarse-textured Field A, net N mineralization per *MDD* was greater in the second incubation periods than the first, suggesting that factors (possibly C:N ratio or denitrification) other than simply the size of the organic N pools affected the net N mineralization rates. Except for Field A, labile organic N contribution to cool season N mineralization appeared to be insignificant in the soil cores examined in this study. Cool season N mineralization was not well correlated to the fall mineralizable N index, the % total soil N or the residual fall soil mineral N.

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CHAPTER 5. COMPARING DISTURBED AND UNDISTURBED SOIL CORE METHODS

5.1 Abstract

Nitrogen (N) mineralization in soils has been studied extensively, both in the lab and in the field. *In vitro* studies allow greater control of variables such as temperature and moisture. *In situ* studies provide temperature and moisture conditions that more closely mimic the natural conditions under which N mineralization occurs. One widely-used technique of *in situ* N mineralization research is the use of ion exchange resin - soil cores (IER/SC), in which soil cores incubate inside tubes set in a field. The cores are open on the top and bottom to allow for exchange of water and gases with the soil and atmosphere. Nitrate (NO_3^-) and ammonium (NH_4^+) that leach out of the cores is captured by a bag of ion exchange resin installed below the soil core. In some studies, “undisturbed” cores are prepared by driving tubes into the soil and then extracting the cores before inserting the IER bag. In other studies, “disturbed” cores are prepared by excavating soil, homogenizing it and then filling the tubes. Theoretically, undisturbed cores more closely mimic soil conditions in nature, while disturbed cores should have reduced variability. The undisturbed and disturbed techniques, however, have never been compared in a controlled experiment in the field. The objectives of this study were to compare mean N mineralization, N mineralization variability, soil temperature and soil moisture levels in disturbed and undisturbed IER/SC.

Soils from 6 agricultural fields (5 of which had histories of dairy manure application) were incubated in IER/SC. Four trial periods were used, including both summer and winter incubations. A total of 13 field/time period combinations were tested.

Of these, 9 exhibited greater N mineralization in the disturbed cores; 3 of these were statistically significant ($p < 0.10$). In all four trial periods, the disturbed plots exhibited less N mineralization variability; two of these were statistically significant ($p < 0.10$). There was little difference in mean temperatures or soil moisture conditions in disturbed versus undisturbed cores. There was a small but significant ($p < 0.05$) tendency for the undisturbed cores to have a greater daily temperature range (maximum daily temperature minus minimum daily temperature).

5.2 Introduction

The use of ion exchange resin / soil cores (IER/SC) is an *in situ* approach to measuring N mineralization rates and, in some situations, NO_3^- losses from soils. IER/SC use tubes made of PVC, aluminum or galvanized pipe and typically measure 5 cm inner diameter by 15 to 50 cm long (Myrold et al., 1992; Kolberg et al., 1997; Sullivan et al., 1999; Eghball, 2000). IER/SC are open at both the top and the bottom to allow exchange of gases and water, however the bottom of each core is fitted with ion exchange resins that capture NO_3^- and NH_4^+ leaching from the soil column.

The cores exclude living plant roots and thus there is no plant uptake of mineral N. This allows a fairly direct measurement of net N mineralization. However, the lack of living plants can cause core soil moisture levels to be higher than soil in cropped fields (Myrold et al., 1992). Because of this, core mineralization rates may differ somewhat from true mineralization rates in the field.

Cores can either be constructed with relatively undisturbed soil by pounding the tubes into the soil or with disturbed soil by hand-packing. When filled by hand-packing, the soil can be homogenized, which may reduce the high variability inherent in the spatial distribution of soil N. Also, the addition of animal waste to cores can be more highly controlled when they are hand-packed. Undisturbed cores, however, more closely mimic natural soil conditions and thus may provide more accurate measurements of soil N mineralization.

Soil disturbance in hand-packed core preparation may alter N mineralization rates (Raison, 1987). Theoretically, this is because disturbing the soil destroys some of the protective capacity of soil aggregates, thereby allowing formerly protected organic N compounds to be mineralized and/or mineral N compounds to be released into the soil solution (Paul and Clark, 1989). However, Sullivan et al. (1999a) collected data from hand-packed cores and adjacent field soils and concluded that the effect of soil disturbance in hand-packed cores appeared to be insignificant.

The effect of soil disturbance on nitrogen mineralization has been studied (Franzluebbers, 1999), but no published studies have compared disturbed and undisturbed IER/SC. The objective of this study was to make that comparison, using cores from fields in Oregon's Willamette Valley. N mineralization, temperature and moisture content in disturbed and undisturbed cores were compared during four trial periods.

5.3 Materials and methods

5.3.1 Site descriptions, soil core construction, incubation and analysis

The sites were the same as described in Chapter 4 except that a 2003 summer incubation was added. The undisturbed core construction described in this trial were the same as described in Chapter 4.

Disturbed cores were constructed for this trial with the soils excavated from between the holes left after the undisturbed cores were removed from the ground during the initial soil collection. These disturbed soils were the same as used for determining baseline chemical analyses. The soils were placed in clean plastic pails, the lids were sealed and the soils were refrigerated at 4ºC until the disturbed cores were constructed. For disturbed core construction, the soil was mixed thoroughly and sieved through a 10 mm mesh. Detritus and gravel larger than 10 mm diameter were removed and discarded. Two IER bags were inserted into the bottom of each 10 cm diameter aluminum tube in the same configuration used for the disturbed cores. Disturbed soil was then added through the top of the tube and compacted to a density of 1 g cm^{-3} dry soil.

One undisturbed core and one disturbed core from each field was fitted with a Hobo® recording thermometer (Onset, 2005). One undisturbed core and one disturbed core from each field was fitted with a Watermark® moisture sensor (Irrometer Company, 2005). Cores were kept at 4°C until placement in the field for incubation. The placement of cores in the field, the incubations, the collection of cores at the end of incubation, the processing of the cores and the analysis of soils was as described in Chapter 4 except that, for the summer 2003 trial, the cores were installed midway between rows of silage corn (*Zea mays* L.). The incubation trials for this study are summarized in Table 5.1. Field characteristics are summarized in Table 5.2.

Table 5.1. Incubation trial summary.

Trial	**1**	**2**	**3**	**4**
Incubation begins	28-29 June 2003	1 Nov. 2003	27 Oct. 2004	27 Oct. 2004
Incubation ends	22 Sept. 2003	18 May 2004	15 Dec. 2004	4 Feb. 2005 ‡
Undisturbed cores (n)	10	36	20	20
Disturbed cores (n)	20	12	20	20
Fields	D,E,F †	A,D,E	A,B,F,G	A,B,F,G

† Field F cores in summer 2003 were monitored for soil temperature and moisture but not for N mineralization.

‡ Although N mineralization incubations ended on 4 Feb. 2005 for Trial 4, cores with recording thermometers and moisture sensors were left in the field until 17 May 2005.

Table 5.2. Field characteristics. Fields D and G are on the same farm. Manure history "yes" indicates annual dairy manure applications for greater than 10 years; "no" indicates no manure applications in past 10 years.

Field	Soil series	Soil class	Drainage class	% Clay	pH	%C	%N	C:N	Previous crop
A	Newberg fine sandy loam	coarse-loamy, mixed, mesic fluventic haploxerolls	well to somewhat excessive	11.9	6.5	1.20	0.11	11.3	silage corn §
B	McBee silty clay loam	fine-silty, mixed, mesic cumulic ultic haploxerolls	moderately well	23.8	6.6	3.42	0.32	10.6	Perennial grass (meadow foxtail) §
D	Woodburn silt loam	fine-silty, mixed, mesic aquultic argixerolls	moderately well	13.1	6.8	3.94	0.32	12.3	silage corn §
E	Wapato silty clay loam	fine-silty, mixed, mesic fluvaquentic haplaquolls	poor	19.7	5.4	1.68	0.16	10.3	silage corn §
F	McBee silty clay loam	fine-silty, mixed, mesic cumulic ultic haploxerolls	moderately well	35.0	6.4	2.08	0.21	9.9	silage corn ‡
G	Woodburn silt loam	fine-silty, mixed, mesic aquultic argixerolls	moderately well	16.6	6.2	3.02	0.24	12.4	silage corn §

Clay % determined by pipette method, %C and %N determined by Leco CNS-2000 macro-analyzer, pH determined by 1:2 soil to water. All analyses in this table were by the Oregon State University Central Analytical Lab (Horneck et al., 1989).

§ Indicates fields with a history of annual dairy manure applications for greater than 10 years.

‡ Indicates field with no recent manure applications.

5.3.2 Calculations

As described in Chapter 4, the IER analyses for NO_3^--N and NH_4^+-N were normalized to the mass of dry soil in each core and added to the soil NO_3^--N and NH_4^+-N analyses to determine the total mineral N present after incubation. The baseline NO_3^--N and NH_4^+-N concentrations were subtracted from the post-incubation concentrations to determine net N mineralization. Student's t-tests were calculated to compare mean net N mineralization in each field's disturbed and undisturbed cores. The Levene statistic was used to compare variance of N mineralization. Tukey box-and-whisker plots were used to illustrate the variability of the two IER/SC methods. Core temperature and moisture were analyzed with ANOVA. All statistical analyses were done with SPSS (1999).

5.4 Results and discussion

5.4.1 Mean N mineralization

Table 5.3 summarizes mean N mineralization for all soils and trial periods. Field A disturbed cores had significantly higher N mineralization than Field A undisturbed cores during Trials 2 and 4. All fields in Trial 3 (October – December 2004) had greater mean N mineralization in the disturbed cores; Field G disturbed core mineralization was significantly greater in Trial 3. For other fields and trial periods, there was little difference between mean N mineralization in disturbed versus undisturbed cores. Figure 5.1 is a graphical illustration of net N mineralization in the disturbed and undisturbed cores.

Field A soil had the lowest clay content (11.9%) and carbon content (1.20%) of all fields tested (Table 5.2). Clay protects soil organic matter from mineralization and a low clay content soil would be expected to have less protected organic matter, and less organic matter overall, than a high clay content soil (Van Veen et al., 1984; Paul and Clark, 1989). The protection process may involve both isolation of organic matter and soil microbial biomass inside of aggregates and adhesion of organic molecules to clay particles (Hassink et al., 1993; Six et al., 2002). When a soil is physically disturbed by mixing or drying and wetting, the protective capacity of aggregates can be reduced and a short-term flush of mineralization may occur. Because of this, it might be expected that disturbing clay soils would increase mineralization more than disturbing sandy soils. However, Franzluebbers and Arshad (1997) found comparatively greater organic carbon mineralization in lower clay-content soils after crushing aggregates and hypothesized that the low clay soils may have had a greater percentage of their protected organic N sequestered inside aggregates as compared to adsorbed onto clay minerals. This process could explain the increased N mineralization in Field A disturbed versus undisturbed cores.

Table 5.3. Comparison of mean N mineralization in undisturbed and disturbed IER/SC.

Trial	Field ‡	Incubation Dates	Net Mineralization Undisturbed Cores	 Disturbed Cores	t-test †
			------------------------ mg N kg^{-1}	------------------------	
1	D	Jul 03 - Sep 03	91.9 (10.3, 5)§	88.1 (3.1, 10)	n.s.
1	E	Jul 03 - Sep 03	49.3 (7.0, 5)	47.5 (1.7, 10)	n.s.
2	A	Nov 03 - May 04	27.2 (2.4, 12)	48.4 (2.7, 4)	**
2	D	Nov 03 - May 04	98.2 (12.5, 12)	104.2 (11.5, 4)	n.s.
2	E	Nov 03 - May 04	-6.1 (17.1, 12)	-0.9 (34.5, 4)	n.s.
3	A	Oct 04 - Dec 04	5.1 (7.0. 5)	15.8 (3.4, 5)	n.s.
3	B	Oct 04 - Dec 04	10.8 (10.8, 5)	22.2 (3.9, 5)	n.s.
3	F	Oct 04 - Dec 04	4.4 (8.1, 5)	12.2 (2.9, 5)	n.s.
3	G	Oct 04 - Dec 04	-2.9 (16.5, 5)	33.7 (4.8, 5)	*
4	A	Oct 04 - Feb 05	4.6 (6.6, 5)	19.7 (1.2, 5)	*
4	B	Oct 04 - Feb 05	33.8 (5.8, 5)	36.7 (5.1, 5)	n.s.
4	F	Oct 04 - Feb 05	37.2 (13.4, 5)	32.4 (9.0, 5)	n.s.
4	G	Oct 04 - Feb 05	22.1 (14.2, 5)	24.0 (9.6, 5)	n.s.
all	all	all	31.6 (5.1, 86)	40.9 (4.0, 72)	*

‡ Soils from some fields were tested in multiple trials.
† One-tailed Student's t-test of difference between means.
§ Values in parentheses: (SE, number of observations).
* ,** Difference between means significant at 0.10 and 0.01 probability levels, respectively.
n.s. Difference between means not significant at $p < 0.10$

Another possible explanation for the increased mineralization in Field A disturbed cores is the relative strength of aggregates. Field A soil was observed to have weak aggregates which thoroughly broke into pieces much smaller than the 10 mm screen through which they passed during IER/SC preparation. For all other fields, the soil aggregates were observed to break into pieces that were often only just smaller than the

10 mm screen. Measuring the size distribution of soil aggregates, however, was beyond the scope of this project.

Trial 3 had a very short incubation period of only 49 days under cool conditions and N mineralization in all cores in Trial 3 was low. A brief acceleration in N mineralization in disturbed cores is consistent with findings of lower C:N ratios for organic compounds within soil aggregates compared to organic compounds outside of soil aggregates (Hassink, 1992). By 4 February 2005, disturbed and undisturbed N mineralization rates in Trial 3 cores from Fields B, F and G were similar.

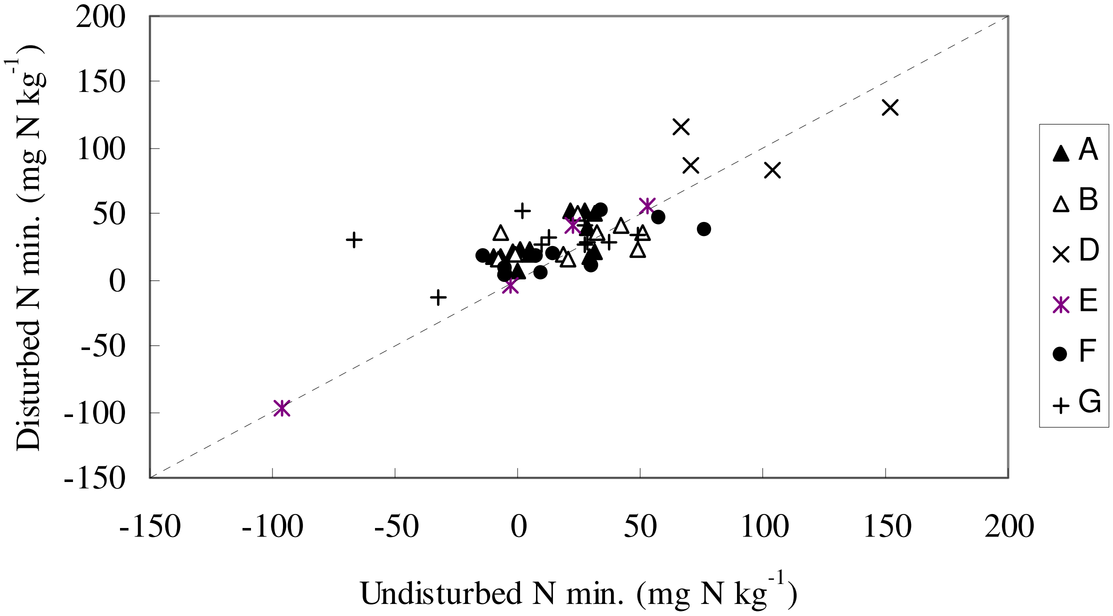

Figure 5.1. Comparison of net N mineralization in disturbed and undisturbed cores for winter incubations. Summer 2003 data are not charted. Each point is the average N mineralized in the cores from one site in a field during one incubation period. Dashed line is $y = x$ for comparison.

5.4.2 N mineralization variability

The standard error (SE) of N mineralization was greater in undisturbed cores compared to disturbed cores for 11 of the 13 field/trial period combinations (Table 5.3). The Levene statistic demonstrated a significant difference ($p < 0.10$) in variance between the disturbed and undisturbed cores for Trials 3 and 4. Tukey box-and-whisker plots in Figure 5.2 graphically illustrate the spread of N mineralization data for disturbed versus undisturbed plots in the 2004 to 2005 incubations.

Soil organic matter is highly spatially variable in agricultural fields (Cahn et al., 1994). Each disturbed core was constructed from a well-mixed sample of approximately 35,000 cm^3 of soil, whereas each undisturbed core only represented a 1,300 cm^3 soil sample. It is not surprising that the disturbed core method resulted in less variability of N mineralization compared to the undisturbed cores.

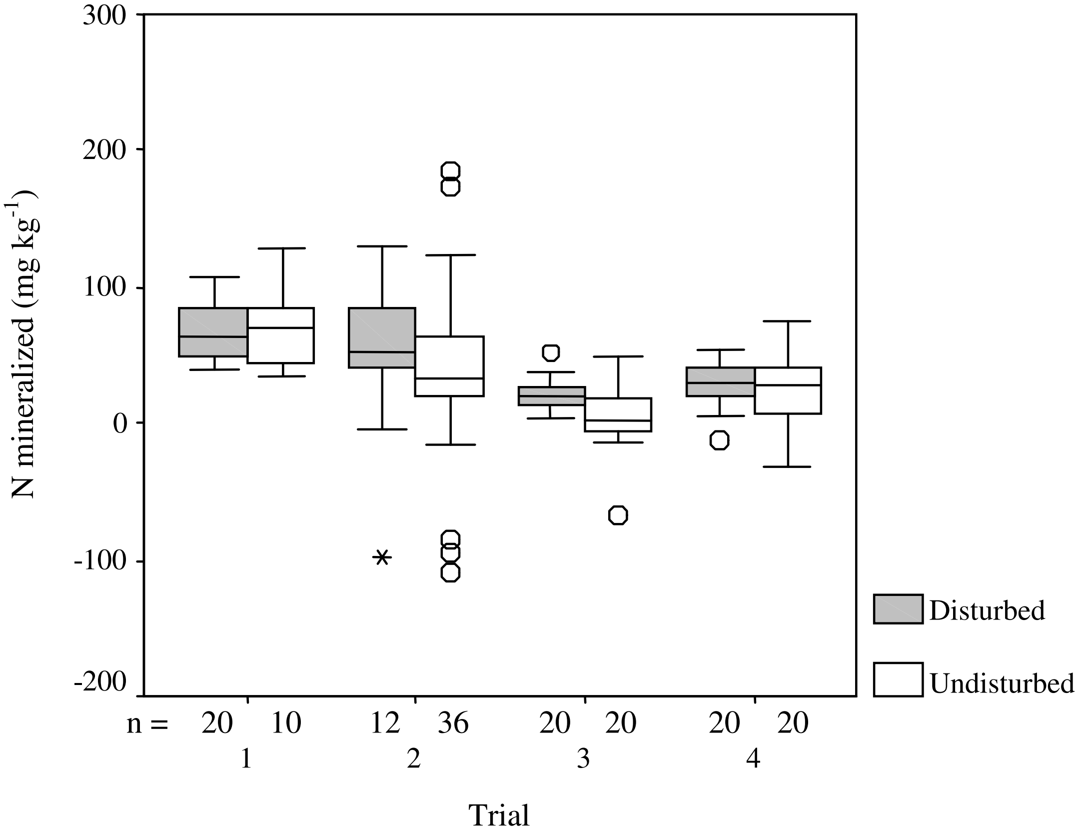

Figure 5.2. Tukey box-and-whisker plots of disturbed and undisturbed cores from all trials. The horizontal line in the middle of each box is the median, the bottom and top of each box are the 25th and 75th percentiles, respectively, and the whiskers show the range of data values that are within 1.5 box lengths of the bottom and top of each box. The “O” marks are data outliers (1.5 to 3 box lengths from the bottom or top of the box) and the “*” is an extreme value (more than 3 box lengths from the bottom of the box).

5.4.3 Soil temperature

Soil temperature is an important physical factor influencing N mineralization (Vigil and Kissel, 1995). Table 5.4 summarizes the mean core temperatures and the daily range of temperatures for the summer 2003 and the winter 2004 to 2005 incubations. Temperatures were not recorded for disturbed cores during the winter 2003 to 2004 incubation. Although the daily mean temperature varied slightly between some fields, there was no significant difference in daily mean temperature between disturbed and undisturbed cores. There was a small but significant ($p < 0.05$) tendency for the undisturbed cores to have a greater daily temperature range (maximum daily temperature minus minimum daily temperature). In the summer 2003 incubation, this difference in daily temperature range was 0.46°C and in the winter 2004 to 2005 incubation, this difference was 0.42°C.

In Trial 1 (summer 2003), cores were incubated at Field F. The mean daily soil temperature at 8.5 cm depth outside the cores in the incubation plot was 20.39°C, which was slightly but significantly ($p < 0.01$) less than either the disturbed (20.85°C) or undisturbed (20.70°C) mean temperatures inside the Field F cores. Also, the mean daily temperature range at 8.5 cm depth outside of the cores was 3.03°C, which was significantly ($p < 0.01$) less than either the disturbed (5.13°C) or undisturbed (6.21°C) mean daily temperature range in Trial 1. The greater daily temperature fluctuation inside the cores was likely due to the aluminum pipe, which extended 5 cm above the soil surface and so collected solar radiation during the day and radiated heat away from the cores at night.

During the winter of 2004 to 2005, the cores could not be incubated in any of the fields from which soil was collected to prepare the cores. Therefore, the winter 2004 to 2005 incubations were conducted in a field of Woodburn silt loam that was not sampled for core construction. Because the Field G cores were constructed with Woodburn silt loam, they are the logical cores to compare with the in-field temperature data. The mean daily soil temperature at 8.5 cm depth outside of the cores was 7.62°C, which was slightly but significantly ($p < 0.05$) less than either the disturbed (7.89°C) or undisturbed (7.92°C) mean temperatures inside the Field G cores. Also, the mean daily temperature range at

8.5 cm depth outside of the cores was 4.74℃. This was slightly but significantly ($p < 0.05$) greater than the disturbed (4.09℃) and insignificantly less than the undisturbed Field G core (4.94℃) mean daily temperature range in the winter of 2004 to 2005. As would be expected, the tendency of the aluminum pipe to collect and radiate heat appeared to be much less during the winter incubation when the weather was often cloudy.

Table 5.4. Comparison of temperatures in undisturbed and disturbed IER/SC.

	Core Temperatures ‡			
	daily mean †		**daily range §**	
Field	**undisturbed**	**disturbed**	**undisturbed**	**disturbed**
	------- °C -------			
July 1 - Sept 21, 2003				
D	20.52^{a}	20.50^{a}	5.34	5.09
E	20.79^{b}	20.76^{b}	6.56	6.47
F	20.70^{c}	20.85^{c}	6.21	5.13
mean	20.67^{d}	20.70^{d}	6.03	5.57
in field ¶	20.39		3.03	
Nov 6, 2004 - May 17, 2005				
G	7.92^{e}	7.89^{e}	4.94	4.09
A	7.64^{f}	7.75^{f}	4.19	4.28
F	7.67^{g}	7.56^{g}	4.36	3.86
mean	7.74^{h}	7.74^{h}	4.50	4.08
in field	7.62		4.74	

‡ IER/SCM core temperatures at 8.5 cm depth.

† Mean of core temperatures recorded hourly in 2003 and every other hour in 2004-2005.

§ Mean of 24-hour maximum minus minimum core temperatures.

¶ "In field" temperatures taken at 8.5 cm depth outside of the cores.

a-f Results followed by the same lower case letter are not significantly different at $p < 0.10$.

5.4.4 Soil moisture

After temperature, soil moisture is the second most important physical factor affecting soil N mineralization rates (Gilmour et al., 1977). Measurements of soil water potential in the cores for both the summer 2003 and the winter 2004 to 2005 incubations (Table 5.5) showed no significant difference between disturbed and undisturbed cores ($p < 0.10$). Cores from different fields varied in initial moisture content, but quickly assumed similar moisture contents after being placed in the field for incubation. For example, on October 29, 2004, cores varied from -1 to -80 kPa water potential, but from November 19, 2004 through January 18, 2005, all cores had moisture contents between -1 and -5 kPa (Figure 5.3). Soil moisture was not measured in disturbed cores in the winter 2003 to 2004 trials.

IER/SC have no plant growth and thus tend to have lower evapotranspiration rates and higher moisture contents than native field soils (Myrold et al., 1992). This tendency was apparent, although statistically insignificant ($p < 0.10$), in the summer 2003 incubation. The in-field soil outside of the cores had a mean water potential of -82 kPa, compared to the Field F disturbed (-61 kPa) and undisturbed (-68 kPa) cores. In the winter of 2004 to 2005, when there was much less evapotranspiration in the field, this moisture effect was not apparent. During that incubation, the in-field soil had a mean water potential of -3 kPa, compared to the Field G disturbed (-7 kPa) and undisturbed (-9 kPa). These differences were not significant ($p < 0.10$).

Another IER/SC moisture characteristic is that, because of the necessary discontinuity between the soil at the bottom of the cores and the field soil beneath the cores, water content must reach saturation before it can drain out of the cores. This could cause anaerobic conditions at the bottom of the IER/SC and affect N mineralization rates as well as cause denitrification. However, Dowdell and Webster (1980) addressed this effect by comparing lysimeters with gravity drainage to those fitted with a porous ceramic cup connected to 10 kPa suction. They found no significant difference between the lysimeters for mass of NO_3^- in drainage water nor for plant N uptake.

Table 5.5. Comparison of core water potential in disturbed and undisturbed IER/SC. Moisture differences between disturbed and undisturbed cores were not significant ($p < 0.10$) for either incubation period.

	Core Water Potential ‡	
Field	**undisturbed cores**	**disturbed cores**
	------------------------- kPa	**-----------------------**
July 8 - Sept 22, 2003 §		
D	-57	-33
E	-43	-52
F	-68	-61
mean	-56	-49
in field †	-82	
Oct 29, 2004 - Jan 18, 2005 ¶		
A	-3	-3
B	-16	-9
F	-10	-6
G	-9	-7
mean	-10	-6
in field †	-3	

‡ Mean IER/SCM water potentials at 8.5 cm depth.
† "In field" water potential at 8.5 cm depth outside of the cores.
§ 9 moisture measurements made during incubation.
¶ 6 moisture measurements made during incubation.

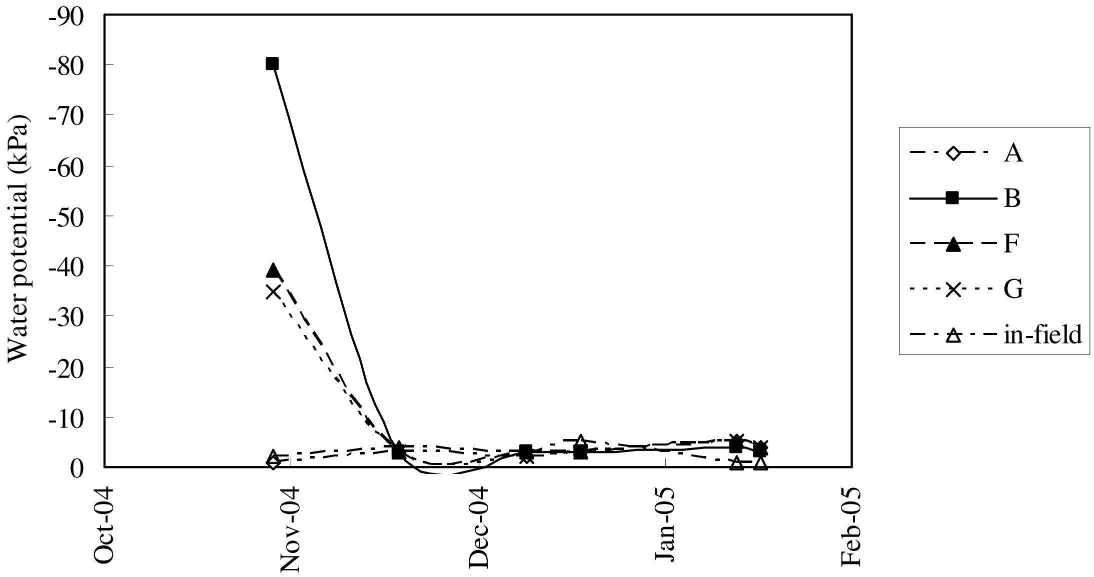

Figure 5.3. Comparison of water potential in cores and in-field site (outside but adjacent to cores) for the winter 2004 to 2005 incubation. The moisture contents varied early in the incubation, but all of the cores and the in-field site quickly approached saturation and remained in that very moist state throughout the incubation.

5.5 Conclusions

This study compared two methods of IER/SC preparation: disturbed and undisturbed. The disturbed method used soil samples that were thoroughly mixed before core preparation and the undisturbed method used soil samples that were captured by driving tubes into intact soil with little disturbance.

Of the 13 field/trial period combinations, 9 exhibited greater N mineralization in disturbed cores, as compared to undisturbed cores. Three of these were statistically significant ($p < 0.10$). The situations in which disturbed core mineralization exceeded undisturbed core mineralization were in Field A and in Trial period 3. Field A had a low (11.9%) clay content and low (1.20%) carbon content and thus may have had a greater percentage of its protected organic N inside aggregates as compared to adsorbed onto clay minerals. This organic N in Field A soil aggregates would be prone to mineralize when the aggregates were crushed in preparation of the disturbed cores. Trial period 3 was only 49 days long. Possibly, the greater N mineralization in disturbed cores during this period was due to a short-term decrease in C:N ratio following soil aggregate disruption. The disturbed cores had less variability in N mineralization than the undisturbed cores. Since reduced variability allows the use of fewer cores in mineralization studies and since the construction and analysis of cores is expensive, decreased variability is advantageous. Overall, this study indicates that there appears to be a trade-off in the use of disturbed versus undisturbed IER/SC incubations to study N mineralization: disturbed cores in this trial had lower variability, but had artificially increased N mineralization rates in some situations.

The mean core temperatures were not significantly different between disturbed and undisturbed cores and there was little difference between the mean core temperatures and the soil in the field outside of the cores. There was also little difference between disturbed and undisturbed core daily temperature ranges. During the winter 2004 to 2005 incubation, the difference between the daily temperature range of cores versus the soil in the field outside of the cores was less than 0.25°C. However, during the summer 2003 incubation, this difference was greater than 2.0°C. These results indicate that both disturbed and undisturbed cores tended to match natural soil temperature regimes well during the cloudy and cool Pacific Northwest winter, but not as well during the summer.

The mean core water potentials were similar for disturbed and undisturbed cores during both summer and winter incubations. In the summer incubation, the soil in the field outside of the cores was drier (the water potential was more negative) than either the disturbed or undisturbed core soil, although this difference was not statistically significant. This tendency of IER/SC to be artificially moist compared with natural field soils has been noted by others (Myrold et al., 1992). During the winter incubation, this effect was negligible, due no doubt to the low evapotranspiration rates at that time.

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