THE FATE OF NITRATE IN SOIL TREATED WITH HOG MANURE

BY

COLLEEN P. FLYNN

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Soil Science University of Manitoba Winnipeg, Manitoba

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ABSTRACT

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The Fate of Nitrate in Soil Treated with Hog Manure. Major Professor; C. M. Cho. Hog production is becoming an increasingly important component of agriculture in Manitoba. The investigation of the fate of manure nitrogen after the application of hog manure was composed of three main components; a field study, a laboratory study and a mathematical model. The field study examined NO₃ distributions in the soil profile to a depth of 3 m on an Emerson silty clay loam and a Poppleton loamy sand. The effects of precipitation and irrigation were considered in the analysis and interpretation of NO₃ distribution.

Nitrate levels were highest at the surface and decreased with depth. The addition of water, through irrigation or precipitation, resulted in leaching or disappearance of NO₃ through denitrification. Nitrate levels that exceeded the Canadian drinking water guidelines were found in the groundwater at the Poppleton site, suggesting that caution should be exercised in the application of N containing fertilizers and hog manure on sandy soils. Manitoba guidelines for manure applications need to be refined and caution should be exercised, particularly on coarse textured soils.

In the laboratory study, nitrate disappearance rates in the Emerson and Poppleton soils were examined as denitrification is one of the most significant ways that NO₃ is lost

from the soil system. Denitrification intensities of the two soils in saturated anaerobic environments were examined with respect to depth, temperature and treatment.

Results from the laboratory study indicated that the disappearance rates of NO₃⁻ were a function of temperature and soil depth. The rate was shown to be highest at the higher temperature. However, under constant temperature, the NO₃⁻ disappearance rate was highest at the surface and decreased with soil depth. The magnitudes of the rates for N disappearance of surface samples were similar between the Emerson and the Poppleton soils, with slightly higher values for the Emerson soil. However, as the soil depth increased, the NO₃⁻ disappearance rate decreased with a much greater rate in the Poppleton sand than with the Emerson silty clay loam.

The model incorporated field values such as moisture contents and bulk densities and laboratory determined NO₃ disappearance rates, to estimate the aerobic-anaerobic boundary and hence NO₃ stability in the profile under various conditions. Transient state oxygen concentration distributions were also calculated in order to determine the effect that a rainfall event would have on the stability of NO₃.

The depth of the aerobic boundary and the oxygen consumption rates of microorganisms at the boundary were found to be important in controlling the stability of NO₃. In general, oxygen penetrated to a greater depth in the sand profile than the silty clay loam profile, except when the moisture content of the sand was extremely high. Irrigated profiles, which were higher in moisture contents had shallower aerobic boundaries as opposed to non-irrigated profiles.

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CHAPTER 1

INTRODUCTION

Farmers in Manitoba currently apply manure to fields as both a means of disposal and as a fertilizer. Intensified hog operations that are increasing in number throughout Manitoba will increase the amount of manure that will be produced in the province and therefore more information on how to deal with increased quantities of manure will have to be considered. Land application of animal manure is generally the most economical and environmentally acceptable means of disposal while allowing the reuse of nutrients present in the manure. Hog manure is an excellent fertilizer which poses environmental risks only when mismanaged. In fact when manure is properly used, it not only provides nutrients to the crop, but improves soil tilth and increases soil organic matter. However, if manure is applied in excess, some of its components such as N, P, soluble salts and micro-nutrients can pollute soil and water lowering crop performance and in severe cases lowering soil productivity. Health of infant children and livestock may be adversely impacted by consuming groundwater high in nitrate. Thus, one of the problems that agriculture in Manitoba currently faces, is the disposal of an increasing amount of animal manure while maintaining crop yields as well as soil and water quality.

The main objective of this study was to examine the fate of nitrate in the soil and groundwater after the application of hog manure. To achieve both agricultural and environmental sustainability, studies such as this can help refine manure management guidelines ensuring that manure loading rates optimize nutrient use and minimize

potential groundwater contamination. In order to determine appropriate application rates, it is necessary to examine the potential fates of the manure nitrogen including: crop uptake, immobilization, mobilization, ammonia volatilization, nitrification, nitrate leaching and denitrification.

In order to carry out the objective, the study consisted of three main components; a field study, a laboratory study, and the use of a mathematical model. The field portion of the experiment examined the distribution of NO₃ in the soil profile after the application of hog manure on an Emerson silty clay loam and a Poppleton loamy sand. Two irrigation events which simulated 4 cm of precipitation were also initiated at two different times in the summer in order to see how NO₃ distribution in the profile was affected. The laboratory portion of the study examined the denitrification intensity of both the sand and the clay with respect to depth, treatment and temperature. Four different depths, to a depth of 120 cm and temperatures of 7.5°C and 15°C were examined in the laboratory. The final component of the study involved utilizing a mathematical model which incorporated values from both the field study and the laboratory study in order to determine the steady state oxygen distribution profile based on a mass balance equation at various soil temperatures and moisture contents. The steady state oxygen distribution profile would indicate the stability of NO, in both the Emerson silty clay loam and the Poppleton sand profile. Transient state oxygen concentration distributions from one moisture content to another were also calculated in the model in order to determine the effect that a rainfall event would have on the stability of NO₃ in the soil profile.

CHAPTER 2

LITERATURE REVIEW

2.1 Manitoba Pork Production

Since the mid-1980's there has been a restructuring of the livestock industry in Manitoba and the most remarkable change in the livestock industry has occurred in the swine industry. The basic sow herd has doubled and the number of finished animals has more than doubled (Dickson 1996). Canada ranks 13th in the world for hog production and it is the fourth largest exporter of pork products. In fact in 1993, Manitoba accounted for 25 % of Canada's hog production. The farm value of the hog livestock production was 50 million in 1971 and in 1993 it was close to 300 million (Manitoba Pork 1994).

Data in Table 2.1 illustrates that from 1988-1994 the number of hogs in Manitoba have increased from 1.07 x 10⁶ hogs to 1.61 x 10⁶ hogs (Manitoba Agriculture 1994).

Manitoba's hog production has doubled over the past 12 years and it is expected to double again by the year 2000 (Manitoba Pork 1994), resulting in larger hog operations on smaller landbases.

Continued increases in hog production will need to address the problems of increased quantities of manure so that producers may maintain a healthy and sustainable agricultural system. In particular, land application of manure as a fertilizer, the composition of manure, NO₃ distributions in the soil profile and the various fates of

manure nitrogen as a result of the application of hog manure will have to be examined in detail.

Table 2.1 Trends in Livestock Population².

Livestock		Numbers ¹				··
Туре						
_	1986	1990	1991	1992	1993	1994
Total Cattle	1115	1075	1109	1167	1238	1340
Total Hogs	1071	1221	1287	1434	1440	1618

¹ Numbers of animals are in thousands

2.2 Land Application of Manure as a Fertilizer

Agricultural specialization has resulted in larger livestock operations on smaller landbases leading to the production of excessive quantities of manure nitrogen which exceed the needs of the associated landbase. Therefore, many livestock producers have considered manure a liability rather than a resource (Sommerfeldt et al. 1988; Smith and Chambers 1993) as storage and transportation of manure is very expensive (Wilkinson 1979; Freeze and Sommerfeldt 1985). The "break-even hauling distance" or the costs associated with transportation versus the reduction in costs for inorganic fertilizers was determined to be 15 km (Freeze and Sommerfeldt 1985). However, Wilkinson (1979) concluded that in many situations replacement fertilizer value of manure can exceed waste management costs which can in turn change manure from a waste to a resource.

The main merits of utilizing manure on agricultural land as a fertilizer include: the plant nutrient value of the manure (Bernal and Roig 1993a; Campbell et al. 1986;

² Modified from, (Manitoba Agriculture 1994)

Kirchmann and Witter 1992) which could supplement and thus cut the cost of inorganic fertilizer (Haynes 1984; Sutton 1994), the improvement soil physical properties (Sommerfeldt and Chang 1985, 1987), increased soil organic matter (Dubetz et al. 1975; Khaleel et al. 1981; Sweeten and Mathers 1985; Dormaar et al. 1988; Sommerfeldt et al. 1988) and improvement of crop yield (Dubetz et al. 1975; Campbell et al. 1986; Freeze and Sommerfeldt 1985; Jokela 1992). Manure has also proven invaluable in restoration of severely eroded soils (Dormaar and Sommerfeldt 1986; Dormaar et al. 1988). In fact the improved physico-chemical properties that occur on some manure treated soils may be as important if not more important than the actual nutrient composition of the manure.

However, when using hog manure as a fertilizer, negative influences on soil characteristics or contamination of groundwater must also be considered. It has been shown that excessive application rates result in the contamination of soil and groundwater (Power and Shepers 1989; Reneau et al. 1990; Racz 1993; Eghball and Power 1994; Chang et al. 1991; Chang and Entz 1996). Determining application rates which match crop nutrient requirements are difficult to predict due to the heterogeneous nature of the manure and the contribution of available N from the organic fraction of the manure. Thus the fate of manure N is even less predictable than inorganic fertilizers. Some studies have shown that manure treated soils can yield lower (Hoyt and Rice 1977; Beauchamp 1983) or about the same as soils treated with commercial fertilizer (Mathers and Stewart 1974; Dormaar et al. 1988; Mackay et al. 1989; Motavalli et al. 1989).

The specific nutrient content and therefore fertilizer value of manure is difficult to predict. Burton (1996) estimated that approximately 18 million tons of manure are produced annually by Manitoba's livestock population. The fertilizer value of the

manure for all types of animals produced annually in Manitoba for nitrogen, phosphorous and potassium was then estimated at 126×10^6 , 20×10^6 and 45×10^6 kg yr⁻¹. respectively (Burton 1996). However if only hogs were considered the nitrogen, phosphorus and potassium values would be estimated at 18×10^6 , 2.9×10^6 and 5.7×10^7 kg yr⁻¹ respectively (Burton 1996). These estimates are based upon 1993 census data reported in the Manitoba Agriculture Yearbook (Manitoba Agriculture 1993). The numbers of animals reported in this census were used to calculate total manure output. organic nitrogen output, total phosphorus output and total potassium output using "typical" daily production values cited by the American Society of Agricultural Engineers (ASAE 1993). From the estimated fertilizer values based on all of the animal manure types, Ewanek (1996) estimated that, using 1995 fall fertilizer prices, the annual value of manure produced in Manitoba was in the order of 131 million dollars. The estimated annual value of fertilizer applied to Manitoba's fields is about 286 million dollars (Ewanek 1996). Therefore it is obvious that, manure is a potentially valuable resource which could supplement Manitoba farmer's inorganic fertilizer and improve soil qualities when used properly.

2.3 Nutrient Content of Manure

The composition of the manure can vary depending on the animals age, the feed type and the manure management system (including animal housing, handling, storage and method and timing of application) (Haynes 1984; Burton and Beauchamp 1986; Bernal et al. 1993; Smith and Chambers 1993). On average 70-75 % of the ingested N is excreted in animal manure (Baldwin 1982). When considering the fertilizer value of hog manure the most important nutrient characteristics include nitrogen and phosphorous,

however hog manure also contains minerals such as potassium, sulfur and various other micronutrients. The ultimate fate of these nutrients depends to a large degree on the quantities of nutrients in manure and how these nutrients react within the soil environment.

2.3.1 Nitrogen

Nitrogen is of major importance as a nutrient because it influences crop yield and protein content. The nutrient analysis of manure N is normally in the range of 2-8 % nitrogen on a dry matter basis (Haynes 1984) and exists in one of two forms; organic N and inorganic N. The form determines how readily the nitrogen is available for crop uptake. The inorganic form of nitrogen in manure consists predominantly of ammonium nitrogen as well as very small quantities of nitrate nitrogen depending on whether the manure has been stored under aerobic or anaerobic conditions prior to land application. The portion of N present as ammoniacal N in manure varies from 10 % in solid "farmyard" manure to 50-75 % in liquid cattle manure and liquid poultry manure (Beauchamp 1983) and 50-70 % in hog manure (Kirchmann and Witter 1992). The remainder of the N in manure occurs as organic N which is composed of proteins and other organic compounds and is not available to the crop until it is mineralized. The rate at which this occurs varies depending on soil conditions and not all of the organic N will become available in the first year of application.

Nitrogen in manure is also of great importance due to the potential environmental impacts which it can cause. Nitrogen in the ammoniacal form is subject to volatilization (Beauchamp 1983; O'Halloran 1993) and hence air pollution whereas nitrogen in the NO₃ form is subject to leaching to groundwater (Chang and Entz 1996). Another

consideration is that under reducing conditions NO₃ can be denitrified. One of the products, N₂O, contributes to possible global warming and depletion of ozone in the stratosphere (Crutzen and Enhalt 1977; Kinzig and Socolow 1994).

2.3.2 Phosphorus

Phosphorus in hog manure exists in both a readily available (inorganic) form and a non readily available (organic) form (Bernal et al. 1993). The organic phosphorus can undergo mineralization via soil bacteria to convert the fraction to an inorganic form. The amount of P in manures normally range from 0.2-0.9 % on a dry matter basis (Haynes 1984). Inorganic phosphorus is generally not mobile in the soil. In Manitoba where agricultural soils are predominantly calcareous, the calcium and magnesium in the soil react with phosphorus rendering it immobile. However, phosphorus may be one of the more important elements limiting long-term manure application (McCalla 1974; Miller 1992) because after phosphorus saturates the fixing capacity of the soil, it can become mobile and contaminate ground and surface waters. Although applications of manure are usually based on rates that meet crop N requirements, studies have shown that this practice can result in the overapplication of P and K causing nutrient imbalances in the soil (Sharpley et al. 1994, Sutton 1994).

2.3.3 Potassium

Potassium in manure is water soluble and immediately available for crop production (Bernal et al. 1993). Manure analysis normally shows that the amount of K on a dry matter basis ranges from 1-4 % (Haynes 1984). Although in the majority of cases potassium levels in manure do not pose a major problem, Bernal et al. (1993) stated that potassium leaching is possible in sandy soils with low cation exchange capacities.

2.3.4 Micronutrients and Salts

Manure contains micronutrients such as iron (Fe), copper (Cu), manganese (Mn), zinc (Zn), boron (B), and chloride (Cl). Overapplication or long term application of manure may result in elevated levels of micronutrients in the soil and this could have a negative impact on the environment. Bernal et al. (1993) determined that copper toxicity could occur after repeated applications of hog manure. However, Bernal et al. (1993) also determined that micronutrients such as Fe, Mn, Cu and Zn from pig slurries were usually immobilized in calcareous soils and this was attributed to the high pH and the small amount of organic matter in both the slurries and the soils tested. Micronutrients in manure have also been shown to improve soil quality upon application by correcting soil zinc deficiencies (McCalla 1974; Haynes 1984).

Salts such as sodium and potassium are present in manures and these can cause a problem when high application rates of manure are used (McCalla 1974; Sweeten and Mathers 1985; Power and Shepers, 1989; Chang et al. 1990).

2.4 Nitrate Distributions in the Soil Profile

Although problems of NO₃ accumulation and leaching from animal manures should not occur in Manitoba due to the large landbase available for utilization of manures (Dickson 1996), some studies (Ewanek 1995) have illustrated that potential problems due to overapplication do exist. In 1992, 1993, and 1994, Manitoba Agriculture surveyed 84 fields which received manure on a regular basis. Forty six of the fields had NO₃ levels in excess of 160 kg ha⁻¹ in the top 1.2 m of the profile and this was considered too high. In 26 of the fields, NO₃ had moved below 1.2 m. Thus, these results indicated

that nitrates had built up in the soil and moved down the profile raising concern about the potential threat for groundwater contamination from current management practices.

Chang et al. (1990; 1991) also found that manure applications greatly affected the NO₃ content of the soils and groundwater on both irrigated and non-irrigated land that were continuously cropped to barley in Southern Alberta. Manure was applied to irrigated land at 0, 60, 120 and 180 Mg ha⁻¹ and to non-irrigated land at 0, 30, 60, and 90 Mg ha⁻¹. Nitrate concentrations increased in the soil profile with increases being the greatest at the 30-60 cm and 60-90 cm depths for non-irrigated and irrigated land respectively. Monitoring of shallow groundwater during 1991 under irrigated-manured plots showed excessively high NO₃ concentrations. Under non-irrigated plots, there was no accumulation of NO₃ in the groundwater. However, it was concluded that because the soil above the groundwater had high levels of NO₃, a season of high precipitation could cause contamination of the groundwater from the downward movement of NO₃.

In 1996, Chang and Entz illustrated again that long term annual application of cattle manure at the maximum recommended level of 60 Mg ha⁻¹ was not advised because of potential soil and water contamination problems. Under non-irrigated conditions, a significant accumulation of NO₃⁻ occurred in the root zone which posed as a potential threat to groundwater during years of high precipitation. Under irrigated conditions NO₃⁻ moved deeper in the soil profile and this was an even greater potential hazard because if excess precipitation occurred it could cause leaching beyond the 150 cm depth.

Cooper et al. (1984) conducted a study to investigate the concentration and distribution of the various nitrogenous components present in the soil profile amended with elevated rates of cattle and poultry manure. It was determined that the primary

inorganic N component in the soil profile was NO₃ and its zone of maximum accumulation was between 2 and 2.5 m. In most cases the nitrate levels in the upper soil profile were high and then decreased to low or nil amounts in the lower layers (Meek et al. 1974; Mills and Zwarich 1982). Soil nitrate profiles, however, are dependent on a variety of complex factors which affect the fate of nitrogen in the soil.

Meek et al. (1974) showed that NO₃⁻ concentration in the soil solution of manured soils increased in the profile at the 20-40 cm depth, but the concentrations of NO₃⁻ in manured and non-amended soils at the 140 cm depth were similar. They concluded that the lack of NO₃⁻ at the lower depths was the result of a suitable environment for denitrification due to the presence of significant amounts of soluble organic carbon at the 80 cm depth along with the restricted oxygen movement to these depths. They also found that frequent irrigation's on fields that received high manure application rates resulted in reducing conditions and hence a loss of nitrates from the soil profile during the season.

Xie and MacKenzie (1986) studied the effect of applying fresh cow manure, composted cow manure, liquid hog manure and urea to soils at rates of 0-240 kg N ha⁻¹ and found soil NO₃⁻ levels were significantly increased whereas soil NH₄⁺ levels were only temporarily increased. Highest NO₃⁻ levels were noted 30 and 60 days after N application due to delayed nitrification and hog manure applications resulted in the greatest NO₃⁻ concentrations in the soil. Evans et al. (1977) found that soils that had received applications of liquid beef manure were consistently higher in NO₃⁻ concentrations than soil with solid beef manure, liquid hog manure or inorganic fertilizer.

The depths to which NO₃ penetrates depends on the rate of application and environmental conditions. Mathers and Stewart (1974) reported that applying beef

manure at 112 and 224 tons ha⁻¹ for 3 successive years resulted in an accumulation of NO₃⁻ to a depth of 360 cm and increased electrical conductivity in the top 30 cm of soil. Murphy and Smith (1967) also found that the application of beef feedlot manure at about 300 tons ha⁻¹ (dry weight) for 2 successive years resulted in increased NO₃⁻ concentrations which extended down to 200 cm. In contrast, Sutton et al. (1974) found no accumulation of NH₄⁺ and NO₃⁻ on a silty clay loam after 2 years of applying liquid hog manure at rates of 134 tons ha⁻¹. However, Sutton et al. (1974) did find NO₃⁻ to a depth of 122 cm after the first year of application to a sandy loam soil. Thus it is evident that soil texture greatly influences the movement of NO₃⁻ in the soil profile. Gillam et al. (1978) also demonstrated that there is a general relationship between soil texture and denitrification which influences the stability of NO₃⁻ in the profile. It was shown that soils with heavy textured subsoils reduced NO₃⁻.

Sommerfeldt et al. (1972) concluded that manure application for 40 years at a rate of 70 tons ha⁻¹ did not cause an undesirable build up of N, P or soluble salts however this was attributed to a unique combination of soil and climatic conditions in southern Alberta which limited soil and water pollution. In summary, the distribution of NO₃ in the soil profile after the application of manure N is variable and is a result of one or more of the various fates manure N undergoes.

2.5 Fate of Nitrogen After the Application of Hog Manure.

If used efficiently, there are many benefits to land application of hog manure.

However, before it can be determined how much manure can be safely applied to the soil, it is necessary to understand the fate of manure nitrogen in the soil and groundwater.

There are many possible fates of manure nitrogen including: crop uptake, immobilization,

mineralization, ammonia volatilization, nitrification, surface runoff, NO₃ leaching and denitrification. After nutrients leave the rooting depth the two main processes in which nitrogen is lost from the system include denitrification and leaching.

2.5.1 Crop Uptake

Most of the nitrogen requirements of plants are taken up by the roots in the form of mineral nitrogen as ammonium and nitrate. Plant uptake of nitrogen can account for 100 kg ha⁻¹ yr⁻¹ or approximately 5 % of the total soil N for high-yield arable crops (Killham 1994). Nutrient uptake values will vary with soil and climatic conditions as well as crop type. Plant nutrients removed by crops in kg ha⁻¹ (in both seed and straw) can range from values as low as 73 and 75 kg ha⁻¹ for flax and wheat to values as high as 319 and 325 kg ha⁻¹ for fababeans and forages respectively (Western Canada Fertilizer Association 1992). When nitrogen is applied in excess, plants can accumulate excessive amounts of NO₃, which can be toxic to humans and animals if ingested (Stewart et al. 1963; Murphy and Smith 1967; Beegle and Lanyon 1994).

The effect of manures on crop production has been found to be dependent not only on type of crops cultivated, but also on properties of soils on which manures were applied. Bernal et al. (1993) determined maximum crop nutrient uptakes of 41%, 40% and 91% for N, P, and K, respectively, with a small addition of pig slurry in the first year after application. Motavalli et al. (1989) estimated that the N, P, K utilization by corn from injected dairy manure in the first year after application ranged from 12-63, 12-89, and 24-153 % of the manure applied, respectively.

Due to the high concentrations of NO₃ accumulating deep in some soil profiles, studies have been conducted to determine the effectiveness of alfalfa in removing NO₃

from the soil and groundwater (Mathers et al. 1975; Muir et al. 1976; McGill 1991;

Peterson et al. 1991; Entz et al. 1993a). It was generally concluded that alfalfa was

effective in removing NO₃ due to it's deep rooting system but the depth and magnitude to

which this occurred varied. Alfalfa roots can penetrate to depths of more than 6 m in

well-drained soils and the zone of water extraction is roughly proportional to root

distribution (Mathers et al. 1975). Entz et al. (1993b) found that alfalfa effectively

extracted deep-leached soil nitrogen, to a depth of 1.2 m in the year of establishment and

1.8 m in year two. Brunger (1993) reported that some alfalfa varieties can remove up to

392 kg N ha⁻¹.

2.5.2 Mineralization and Immobilization

An understanding of the mineralization and immobilization processes aids in understanding the fate of manure N in soils and this is essential to sustainable utilization of manure in crop production. Mineralization refers to the soil processes by which organic nitrogen is converted to mineral nitrogen. Immobilization is the opposite of mineralization, being the conversion of soil mineral nitrogen into organic forms. The two processes are mutually dependent and operate simultaneously in the soil. The amount of available mineral nitrogen (usually as ammonium and nitrate) found in soil will largely depend on the difference between rates of immobilization and mineralization (Killham 1994).

The availability of the organic N fraction of manure in the first year after application could range from 0-64 % depending on the source, N content, stage of decomposition and various factors involved in the management of the manure. Shepers and Mosier (1991) listed decay constants for various manures (Table 2.2). It is evident

that the majority of N in hog manure is released in the first year with much smaller amounts of N mineralized in subsequent years.

However, even though the data of Shepers and Moisier (1991) indicated that most of the N in hog manure was available in the first year, the addition of pig slurry may increase the immobilization of N. Flowers and Arnold (1983) and Bernal and Kirchmann (1992) found that addition of pig slurries to soil in the laboratory resulted in a temporary immobilization of N followed by a slow linear mineralization. Kirchmann and Lundvall (1993) concluded that fatty acids in slurry act as an easily decomposable C source for microorganisms and this in turn caused immobilization of N. Bernal and Roig (1993b) reported that some researchers found that the mineralization of the organic nitrogen in pig slurry is very slow and that much of it is not available to the crop in the short term although it contributes overall to the nutritional pool in the soil. Lindeman and Cardenas (1984) and Paul and Beauchamp (1996) concluded that the net mineralization rates on sludge or manure amended soils did not increase due to the fact that mineralization was offset by the increased denitrification potential of manured soils.

Table 2.2 Nitrogen content and annual decay constants for various animal manures¹

Manure Source	N in manure	Decay constants			
		1	2	3	4
	%		·[
Poultry	•		•		
Hens, fresh	4.5	0.90	0.10	0.05	0.05
Broilers and		0.75	0.05	0.05	0.05
turkeys, fresh	3.8				
Broilers and		0.60	0.05	0.05	0.04
turkeys, aged					
covered	< 3.0				
Swine	2.8	0.90	0.04	0.02	0.02
Dairy					
Fresh	3.5	0.50	0.15	0.05	0.05
Liquid manure	< 3.0	0.42	0.12	0.06	0.04
tank					
Anaerobic lagoon	2.0	0.30	0.08	0.07	0.05
Beef feeders					
Fresh	3.5	0.75	0.15	0.10	0.05
Stockpiled or dry	2.5	0.40	0.25	0.06	0.03

¹ From Schepers and Mosier (1991)

2.5.3 Volatilization

More than half of the total N in hog manure is ammonium N and thus, a large portion of the N is at risk of being lost by volatilization (O'Halloran 1993; Sommer and Ersboll 1994). Ammonia volatilization from animal manures is a major mechanism for N loss from soil-plant-animal systems (Adriano et al. 1974; Lauer et al. 1976; Alkanani et al. 1992; O'Halloran 1993; Sutton 1994). Consequently, losses of NH₃ by volatilization may significantly reduce the value of the manure for crop production. Volatilization of ammonia is usually highest under hot, dry, windy conditions in alkaline soils (Killham 1994). Pain and Thompson (1989) estimated that the amount of ammonium N lost

Bernal et al. (1993) reported losses in the range of 24-74%. Hoff et al. (1981) found 82.5 % of the applied NH₄⁺-N was lost during an 8 day sampling period when fresh swine manure was surface applied. Lauer et al. (1976) found that the 85 % of the total NH₄⁺-N was volatilized during spreading of dairy manure.

In order to maximize the utilization of N in manure applied to cropland, management techniques to minimize NH₃ volatilization in the field and in storage have been used. Losses of NH₃ were greatly reduced if the manure is injected or incorporated into the soil (Thompson et al. 1987; Smith and Chambers 1993). Jarvis and Pain (1990) reported that slurry dry matter content and soil moisture conditions were the most important factors affecting ammonia volatilization following field applications, although management factors (application rate, method of storage and crop cover) and environmental conditions (wind speed, temperature and rainfall) also influenced losses.

2.5.4 Nitrification

Nitrification is an agronomically important process because it is the microbial formation of NO₃⁻ which is the major means whereby plants assimilate nitrogen (Schmidt 1982). If NO₃⁻ is not used by crops or immobilized by microflora, it is susceptible to loss from the soil by leaching. Nitrification has often been defined as a series of reactions resulting in the production of NO₃⁻ or NO₂⁻ (Groffman 1989). However, more recently, the definition of nitrification has been extended to include the "biological oxidation of any reduced form of nitrogen to a more oxidized form" (Killham 1994). It is important to realize that nitrification is a necessary prelude to denitrification which leads to N disappearance from the soil. Biological denitrification can not occur unless there is an initial oxidation of reduced nitrogen. However, once nitrite, nitrate, or other

intermediates appear, the denitrifying bacteria have suitable substrates to serve as electron acceptors in respiration (Killam 1994).

Nitrification is performed by autotrophic and heterotrophic microorganisms, however it is generally accepted that the dominant form of nitrification in most soils is autotrophic with the two main autotrophic genera including *Nitrosomonas* and *Nitrobacter* (Schmidt 1982; Killham 1994). *Nitrosomonous* are ammonium oxidizers while nitrobacter are nitrite oxidizers (Killham 1994). Populations of *Nitrosomonas* and *Nitrobacter* in most soils are quite small. Populations in excess of 10⁵ g⁻¹ of soil are rare in unfertilized soils, however when the soil is treated with manure or ammonium fertilizer, the nitrifier populations may reach values in excess of 10⁶ and 10⁷ g⁻¹ (Schmidt 1982).

Nitrification takes place in virtually all soils where NH₄⁺ is present and conditions are favorable with respect to temperature, moisture, pH and aeration (Schmidt 1982; Williams et al. 1992). At the field scale nitrification is strongly controlled by NH₄⁺ supply either from fertilizer or from mineralization of organic compounds (Groffman 1989). In a review paper, Schmidt (1982) summarized the work of Mahendrappa et al. (1966) which stated that the optimum temperature for nitrification varies widely among soils with optimum values as low as 20-25°C to values as high as 40°C. Cold wet soils are essentially inactive with respect to nitrification until the soil warms to approximately 4 or 5°C (Anderson and Boswell 1964; Schmidt 1982). The majority of observations on pH indicate that nitrification can occur at a pH as low as 4 but it has also been reported in the ranges of 4 to 6 and 6 to 8 (Schmidt 1982). Decreased oxygen levels can also be

limiting to nitrification and factors which contribute to decreased oxygen include high soil temperatures, high soil moisture and increased oxidizable organic matter (Schmidt 1982).

Moisture content effects the soil nitrifying population (Goodroad and Keeny 1984; Groffman 1989) and the greatest nitrifying activity has been noted at about half to two-thirds of the soil's moisture-holding capacity (Alexander 1965; Williams et al. 1992). It was also determined that nitrate was not formed in air dry soil nor is it produced at very low moisture levels. However, nitrate has been noticed to be produced rapidly in the wet period following a prolonged drought or in the rainy season following a long dry spell (Birch 1958; Alexander 1965). The effect of moderately high moisture levels (pF 1.0-2.0) enhances nitrification in most soils so long as aeration is adequate (Schmidt 1982).

2.5.5 Nitrate Leaching

Nitrate leaching is yet another potential fate of manure nitrogen. Although agriculture is not the only source of NO₃⁻ contamination of groundwater, NO₃⁻ at levels above 10 mg N L⁻¹ have often been associated with agricultural activities (Kimble et al. 1972; Westerman et al. 1987; Knox and Moody 1991; Jones and Schwab 1993). Nitrate leaching is of great environmental concern as elevated concentrations of NO₃⁻ in drinking water can have adverse effects on human and animal health. Nitrate-nitrogen concentrations in drinking water that exceeded 10 mg N L⁻¹ have been linked to the incidence of methemoglobinemia (blue baby syndrome) (Hedlin 1971; Strebel et al. 1989) and increased carcinogenic effects from nitrosamine compounds (Selenka 1985). High concentrations of NO₃⁻ in surface waters, such as estuaries, streams, and lakes, may increase the rate of eutrophication (Sadeghi and Kunishi 1991).

Nitrate leaching tends to increase significantly with increased application rates of available N, either as manure or commercial fertilizer, to levels exceeding that required by the crop. It should be noted that although NO₃⁻ leaching is usually the main concern when manure is applied in excess of crop requirements, nitrogen in pig slurry can also be leached through soil in the form of ammonium (Pandey et al. 1992). Hog and poultry manures have a large proportion of nitrogen in readily available forms, increasing the risk of NO₃⁻ leaching as compared to other manures which have most of the nitrogen tied up in organic forms (Shepherd 1991).

Some studies have shown that manured soils have higher amounts of NO₃ in their profiles (Murphey and Smith 1967; Mathers and Stewart 1974; Evans et al. 1977), and thus there is a greater risk of NO₃ leaching on manured soils. Miller and Mackenzie (1978) applied 150 kg N ha⁻¹ as ammonium nitrate, hog manure and cattle manure and they found NO₃ levels were higher on the manured soils the year after application.

Other studies found that manured soils result in less NO₃⁻ leaching to the groundwater than soils fertilized with inorganic fertilizers when applied at recommended rates (Kimble et al. 1972; Burton 1994b; Xie and MacKenzie 1986; Jokela 1992). It was found that some manured soils had less NO₃⁻ in their profiles and thus less leaching because of the increased denitrification potential of these soils (Kimble et al. 1972; Paul and Beauchamp 1996). Straw and other organic material in manure has the potential to immobilize inorganic nitrogen and/or enhance denitrification (Burton 1994b). Meek et al. (1974) concluded that frequent irrigations with high manure rates on a fine textured soil resulted in reducing conditions and the movement of soluble organic carbon to the lower profile, resulting in the loss of NO₃⁻ from the soil profile as a result of increased

denitrification. Discrepancies in the effect of manure application on the amount of NO₃ in the profile relate, in part, to extent of surface and subsurface denitrification. The magnitude of denitrification depends on many factors including manure type, soil type, time of application, depth to groundwater and denitrification potential for different soil types. It is also important to realize that while many studies have reported increased NO₃ near the soil surface, conditions favorable to denitrification lower in the profile may result in disappearance of this NO₃.

Soils differ in their NO₃⁻ leaching potentials and soil properties related to water movement play a major role in influencing this (Khakural and Robert 1993). Coarse textured soils experience comparatively more NO₃⁻ leaching than fine textured soils (Hedlin 1971; Strebel et al. 1989; Manitoba Agriculture 1995). NO₃⁻, an anion, is readily transported through the soil with water and thus, leaching losses occur when there is both a high soil NO₃⁻ content and water movement. Increased water through rainfall or precipitation results in a greater potential of groundwater contamination (Chang and Entz 1996) by increased NO₃⁻ leaching. Campbell et al. (1983) reported that on the Canadian prairies considerable amounts of NO₃⁻ leached beyond the rooting zone of cereal crops in years of above average precipitation and also in some relatively dry years with heavy spring rains. Muir et al. (1976) also reported that leaching of NO₃⁻ to the water table was apparent in most irrigated soils located in low lying positions and in sandy soils.

Soil nitrate data from a study done by King et al. (1985) suggested that the application of medium to high rates of swine manure would result in pollution of groundwater with NO₃. Evans et al. (1977) concluded that applying hog manure for two successive years at a rate of 636 tons ha⁻¹ (wet weight) resulted in the rapid movement of

NO₃ below the rooting depth and thus these rates were considered too high for continued annual application. In fact NO₃ leaching was determined to be high even when recommended manure application rates of 60 Mg ha⁻¹ were applied to a clay loam soil in Alberta (Chang and Entz 1996).

Nitrate leaching can lead to the contamination of ground water and many have examined the fate and persistence of NO₃⁻ in groundwater (Power and Schepers 1989; Gillham 1991; Knox and Moody 1991; Burkart and Kolpin 1993; Spalding and Exner 1993; Chapelle et al. 1995). Partridge and Racz (1972) suggested that NO₃⁻ in groundwater could undergo denitrification. Strebel et al. (1989) confirmed that denitrification can play an important role in the loss of NO₃⁻ from groundwater. Similarly an investigation of vertical nitrate gradients in a shallow unconfined aquifer in North Dakota also showed that denitrification was occurring in an aquifer (Patch and Padmanabhan 1994).

2.5.6 Denitrification

Denitrification plays an important role in determining the fate of manure nitrogen. Aulakh et al. (1992) summarized that denitrification losses were usually in the range of 12 to 20 % of the available N added, however values in excess of 30 % had also been reported. Firestone (1982) reported N losses due to denitrification ranging from 0 to 70 % of the added N. Annual emissions of 1 to 16 kg N₂O ha⁻¹ in dry regions with low rainfall were reported by McKeeney et al. (1980). Moiser et al. (1982) observed that N₂O emissions accounted for 0.4 to 1.5 % of the 150 kg of fertilizer N applied per hectare. Thus it is evident that large variations in the amounts of denitrification can occur (Firestone 1982) and this variation can occur even within small areas in the same field

(Burton and Beauchamp 1985). Variations of denitrification in a field have been largely attributed to spatial variability in soil water (Biggar 1978).

Both biological (enzymatic) and chemical (non-biological or non-enzymatic) denitrification occurs in soils. In chemodenitrification the generation of N gas is catalyzed by abiotic agents, but this process may only be of importance in acidic or frozen soils (Christianson and Cho 1983). In contrast to biological denitrification, chemodenitrification involves decomposition of NO₂⁻, which can occur in an aerobic environment in the absence of microbes and it can also occur in well-drained acid soils (Broadbent and Clark 1965). There have been many detailed reviews on denitrification (Wijler and Delwiche 1954; Nommik 1956; Bremner and Shaw 1958; Broadbent and Clark 1965; Knowles 1982; Payne 1981; Beauchamp et al. 1989; Aulakh et al. 1992).

Biological denitrification was defined by the Soil Science Society of America as the dissimilatory reduction of NO₃⁻ or NO₂⁻ to gaseous N either as N₂ or N₂O (Reneau et al. 1990). Denitrification has also been defined as a form of anaerobic bacterial respiration during which nitrogen oxides, principally nitrate and nitrite are reduced sequentially through NO and N₂O to N₂ (Aulakh et al. 1992). The commonly accepted reductive pathway for denitrification is as follows:

The bacteria responsible for denitrification are facultative anaerobes and these bacteria have the ability to use both oxygen and oxides of nitrogen as electron acceptors provided sufficient energy sources are available. In the absence of molecular oxygen,

nitrogen oxides serve as terminal electron acceptors (Firestone 1982). Table 2.3 summarizes a list of the known denitrifying bacteria (Beauchamp et al. 1989). Some denitrifying bacterial strains possess the complete pathway for denitrification whereas others may only be capable of catalyzing one or several steps of the pathway. Bollag et al. (1973) observed that some bacteria are not capable of reducing NO₃⁻ and NO₂⁻ to N₂O without the production of N₂.

There has been much discussion and disagreement on the definite sequence of products that occur in the denitrification pathway. Although it is generally accepted that N_2O and N_2 are the major products with their proportions differing depending on the environmental factors, there are still some questions about N_2O being a precursor to N_2 and the role of NO as an intermediate (Firestone 1982). Almost all denitrifying organisms are capable of completely reducing N oxides to N_2 but a variety of environmental parameters, such as acidity, nitrate availability, and C availability can result in the accumulation of NO_2 , NO or N_2O as end products (Firestone 1982).

There are many factors that influence the denitrification process such as temperature, pH, water content, oxygen and redox potential, concentration of nitrogen oxide, and the organic carbon supply. Thus, these factors will be examined in detail along with the specific effects of manure on the denitrifying process.

Table 2.3 Known denitrifying bacteria¹.

Reference
Payne, 1981
Pfitzner and Schlegel, 1973
Payne, 1981
Payne, 1981
Payne, 1981
Adkins and Knowles, 1984
Payne, 1981
Payne, 1981
Payne, 1981
Verhoeven et al. 1954; Bovell, 1967;
Cader et al. 1980
Payne, 1981
Nishimura et al. 1980
Balderston et al. 1976
Aida et al. 1986
Ishaque et al. 1973; Garcia et al. 1977;
Auling et al. 1978
Payne, 1981
Payne, 1981
Payne, 1981
Ishaque and Aleem, 1973; Aiminuddin
and Nicholas, 1974a, 1974b
Timmer-Ten Hoor 1975, 1976, 1977
Trevors and Beauchamp, 1985
Payne, 1981

¹ Data from (Beauchamp et al. 1989).

2.5.6.1 Temperature. Much research has been performed on the rate of denitrification under a wide range of temperatures (Nommik 1956; Bremner and Shaw 1958; Bailey and Beauchamp 1973a; Stanford et al. 1975b; Cho and Mills 1979; Knowles 1982).

Denitrification rates, like many other biological processes, increase with increasing temperature until an optimum is reached above which it decreases (Aulakh et al. 1992).

The effect of temperature on biochemical rate processes is exponential and adheres within limits to the classical Arrhenius equation,

 $K = Ae^{-Ea/RT}$ [2.1]

where K is the rate constant, A is a constant, Ea is the activation energy per mole, R is the universal gas constant (8.31 J K⁻¹mole⁻¹) and T is the temperature in Kelvin.

Denitrification was found to be temperature-dependent in the range of 10-35°C (Nommik 1956; Bailey and Beauchamp 1973; Knowles 1982). Nommik (1956), Bremner and Shaw (1958) and Keeney et al. (1979) found that the rate of denitrification increased rapidly with a rise in temperature from 2°C to 25°C however, the optimum temperature for biological nitrate reduction in soil was 60-75°C and that above this temperature, the rate decreased rapidly (Knowles 1982; Aulakh et al. 1992). It has been speculated that the high optimum temperature for denitrification could be caused by the activity of thermophilic organisms such as the species *Bacillus* (Focht and Chang 1975), biological reactions (Knowles 1982) or the combination of the two (Keeney et al. 1979).

Denitrification rates at 2°C have been reported as zero in some but not all soils (Bremner and Shaw 1958; Knowles 1982). Stanford et al. (1975b) found denitrification rates minimal between 0 and 5°C, increasing ten fold between 5 and 10°C. Cho and Mills (1979) and Bailey and Beauchamp (1973a) reported that denitrification ceased below 2.8°C and 5°C, respectively. Even though denitrification is limited at lower temperatures, some speculate that the denitrification processes can occur at 0°C (Smid and Beauchamp 1976; Aulakh et al. 1992). Temperatures below zero are reported to increase chemical denitrification of nitrite as a result of increased NO₂⁻ concentration (Christianson and Cho 1983).

The Q_{10} value (ratio of the rates observed at 10°C difference (e.g. K_T/K_{T-10})), is commonly used to describe the effect of temperature on biological processes. Focht and Chang (1975) reported that the Q_{10} value for denitrification in soil was in the range of 5 to 16 for temperatures below 12 to 15°C. However others have stated a Q_{10} value of about 2 in the range of 10-35°C (Stanford et al 1975b; Aulakh et al. 1992). Bremner and Shaw (1958) found that the change in the rate constant was proportionally greater between 2 and 10°C than with an equal increment at higher temperatures.

The relative proportions of products that result from denitrification are also affected by temperature. It has been reported that relatively more N₂O is produced at lower temperatures but more molecular nitrogen is produced at higher temperatures (Bremner and Shaw 1958; Sahrawat and Keeny 1986; Aulakh et al. 1992).

2.5.6.2 pH. The rate of denitrification is affected by the pH of the soil, with the optimum pH for denitrification being near neutrality and this declines with acidic or alkaline pH's (Firestone 1982). Optimal, pH ranges of 6.0 to 8.0 have been reported by Bremner and Shaw (1958) and Aulakh et al. (1992), while ranges between 7.0 to 8.0 were reported by Nommik (1956) and Knowles (1982). Wijler and Delwiche (1954), and Bremner and Shaw (1958) found that the rate of denitrification increased linearly from pH 4, plateaued between pH 7 and 8 and then declined. However, denitrification occurred even at a pH of 9.5. It was also found that neutral to alkaline pH ranges not only affected faster rates of denitrification, but also resulted in the complete reduction of N to N,.

Bremner and Shaw (1958) determined that significant amounts of denitrification will not occur if the pH of the soil is less than 5. However Wijler and Delwiche (1954) reported that denitrification was retarded below a pH of 6, but even at a pH of 4.9 more than 70 % of the nitrate was lost within 2 weeks. Despite the fact that denitrification is favored at slightly alkaline pH, denitrification was reported to occur at pH's as low as 3.5 and was found to account for significant N losses in naturally acid soils (Aulakh et al. 1992). Davidson et al. (1989) also found that denitrifying organisms were not highly sensitive to acidity.

The proportion of N₂O and N₂ produced were found to be pH dependent (Wijler

and Delwiche 1954; Firestone 1982; Aulakh et al. 1992). Above neutral, nitrous oxide was readily reduced to nitrogen whereas below pH 7, the reduction of N₂O was strongly inhibited. Below pH 6, the formation of nitric oxide became more prominent and the rate of denitrification decreased (Wijler and Delwiche 1954; Aulakh et al. 1992).

2.5.6.3 Soil Aeration and Water Many studies illustrate that aeration as influenced by soil water content is a major factor which drives denitrification (Linn and Doran 1984; Aulakh et al. 1992; Davidson, 1992; Hutchinson et al. 1993). The rate of denitrification is inversely related to the oxygen concentration (Allison et al. 1960; Knowles 1982), as denitrification occurs only when the supply of oxygen required by the soil microorganisms is restricted. The level of oxygen is controlled by the relative rates of supply and consumption. Oxygen flow in soil is hindered primarily by slow diffusion through water (Groffman and Tiedje 1989; Cho et al. 1996). Thus at high moisture contents, the supply of oxygen is dramatically reduced and this leads to a greater degree of anaerobisis for a given biological demand. Fluctuations in soil moisture content have a

dramatic effect on the stability of nitrate because of the controlling effect of soil moisture on the supply of oxygen diffusing through the soil (Pilot and Patrick 1972).

Microbial activity depends on soil water content and microbial activity is maximum at a water content where the limiting effects of substrate diffusion and oxygen supply are equal (Skopp et al. 1990). Knowles (1982), Linn and Doran (1984) and Doran et al. (1990) reported that the critical moisture level for denitrification in the soil was about 60 % of the water holding capacity of the soil. Above this critical moisture level, denitrification was found to increase rapidly with increases in moisture content, however below this moisture content practically no denitrification occurred. Bailey and Beauchamp (1973b) similarly found that increased soil moisture content increased NO₃⁻¹ reduction and that below the permanent wilting point, the lack of moisture was directly responsible for decreased amounts of denitrification. However, denitrification has also been reported under aerobic conditions and it was speculated that NO₃⁻¹ loss that was occurring under aerobic conditions was due to denitrification that was occurring in small anaerobic pockets within soil aggregates (Smith 1980; Myrold and Tiedje 1985; Hojberg et al. 1994).

Several studies (Macrae et al. 1968; Aulakh et al. 1982; Sexstone et al. 1985) reported that nitrate disappeared rapidly in all soils after flooding and this was due to the depletion of soil oxygen and the retarded diffusion of oxygen into the soil. Under flooded soils, NO₃⁻ will be the preferred electron acceptor and N₂O will not be reduced until NO₃⁻ is removed from the system (Cho and Sakdinan 1978). Gillam et al. (1978) concluded that any soil characteristic that impeded water flow through the soil will be positively linked to denitrification.

2.5.6.4 Concentration of Nitrate or Nitrite. There have been various opinions on the role of nitrate and how it affects denitrification. Although the presence of an oxidized form of nitrogen such as nitrate is obviously necessary for denitrification to occur, the kinetics of the relationship between nitrate concentration and denitrification are largely unresolved. Broadbent and Clark (1965) reported that several researchers found that denitrification rate is independent of nitrate concentration over a wide range. Wijler and Delwiche (1958) stated that nitrate concentration had little effect on the rate of denitrification indicating that kinetically it was a zero order process.

Others (Reddy et al. 1978; Stanford et al. 1975) described NO₃ disappearance as a first-order reaction indicating that the reaction was linearly dependent on NO₃ concentration. However, it should also be noted that Reddy et al. (1978) found that the NO₃ disappearance rate followed a zero-order reaction when the soil water content was lowered. Further studies concluded that the use of Michaelis-Menten type kinetics to describe the rate of nitrate disappearance (Kohl et al. 1976; Focht and Chang 1975) was the most appropriate. Patrick and Reddy (1976) illustrated that where oxygen was absent or limiting, nitrification either did not occur or occurred at a lower rate resulting in a reduced amount of nitrate available for the denitrification process.

Cho and Sakdinan (1978) reported that high concentrations of NO₃ and NO₂ have been known to inhibit the reduction of N₂O to N₂ due to the competition between NO₃ and N₂O as electron acceptors (Cho and Mills 1979).

2.5.6.5 Organic Carbon Supply Various forms of organic carbon are used by denitrifying organisms as electron donors for energy and for synthesis of cellular constituents (Davidson et al. 1989). Carbon availability appears to limit denitrification in

many agricultural soils (Beauchamp et al. 1989). Thus denitrification is strongly dependent on the availability of organic compounds such as root exudates, green and animal manures, crop residues and soil organic matter (Aulakh et al. 1992). The rate of denitrification increases with organic matter content (Wijler and Delwiche 1954; Beauchamp et al. 1989) and organic substrate supply in soils is one of the most important factors limiting the denitrification process in soils (Knowles 1982; Beauchamp et al. 1989). Bremner and Shaw (1958) illustrated that the rate of denitrification in soil depends largely on the type of organic material present. However, most denitrifiers can use a wide array of organic compounds (Knowles 1982).

Beauchamp et al. (1989) summarized the work of Bremner and Shaw (1958) which illustrated that several readily decomposable organic materials such as sodium citrate, sucrose, mannitol and glucose induced rapid denitrification. Other carbon sources that have been reported to increase the denitrification process include cellulose and lignin (Bowman et al. 1974) or plant residues such as straw and alfalfa (deCantanzaro and Beauchamp 1985), root debris and exudates (Woldendorp 1962; Bailey et al. 1976; Wheatly et al. 1991) and animal manures (Beauchamp et al. 1989).

There have been many studies which showed significant amounts of denitrification in manured soils (Olsen et al. 1970; Kimble et al. 1972; Guenzi et al. 1978; Cooper et al. 1984; Parkin 1987; Beauchamp et al. 1989). Researchers attributed the increased denitrification potential in manured soils to an increased supply of water-soluble carbon (Burford and Bremner 1975; Stanford et al. 1975a). Paul and Beauchamp (1989) found that denitrification rates in manure amended soils were closely related to the presence of volatile fatty acids (including acetate, propionate, and butyrate) and water-

soluble C in manures. Manure increases denitrification by providing an energy source for the denitrifying bacteria (Sherwood 1980; Beauchamp et al. 1989; Thompson 1989). Addition of manure to soil may also promote denitrification by creating an anaerobic environment (Beauchamp et al. 1989). Denitrification in manure-amended soil depends on the source of manure and extent of decomposition of the manure (Paul and Beauchamp 1989). Sherwood (1980) concluded that the carbon in pig slurry is readily available to the denitrifying bacteria in the soil.

Guenzi et al. (1978) illustrated that gaseous loss of N by denitrification could occur after large amounts of manure are applied to fields and this denitrification process could be enhanced further by periods of wet weather and warm temperatures. Guenzi et al. (1978) also pointed out that the addition of cattle manure to the soil increased microsites which had sufficient reducing conditions for denitrification while other sites were conducive to the oxidative process of nitrification. Thus it is evident that the fate of manure N in the soil can vary greatly within the landscape due to heterogeneity. Parkin (1987) introduced the concept of organic 'hot-spots', in which the intensity of microbial respiration creates an oxygen demand that exceeds the diffusive supply for a limited time. In agricultural ecosystems where livestock manure is used there is a tendency for 'hot spots' to form. 'Hot spots' from manures were shown to sustain denitrification (Thompson et al. 1987, Thompson 1989), since manure provides a high concentration of available carbon (Beauchamp et al. 1989) and NO₃ from the nitrification of the NH₄ in the manure (Terry et al. 1981).

CHAPTER 3

MATERIALS AND METHODS

3.1 Effect of Hog Manure on the Distribution of NO₃-N in Soil and Groundwater

Large livestock operations are replacing traditional small farms resulting in very large quantities of manure on a small landbase. Manure and fertilizer guidelines state that nitrogen should not be applied at rates greater than which the crop can utilize (Manitoba Agriculture 1995). Due to the high nitrogen and phosphorus contents of hog manure, and due to the fact that the amount of manure that is being handled on individual farms is increasing, it is extremely important that studies be conducted to examine the effects of manure upon nutrient distribution in the soil.

The main objective of this study was to determine the fate of nitrogen from hog manure on a sand and a clay textured soil. A field study using farm application techniques was conducted and NO₃ distributions in the soil profile to a depth of three meters were determined on an Emerson silty clay loam and a Poppleton sand. Nitrate content of the groundwater at the Poppleton sand site was also examined to determine if NO₃ entered the groundwater. The effects of precipitation and irrigation on NO₃ distribution were also studied.

3.1.1 Site Descriptions and Site Histories

Two field sites were selected in September 1994. The first site was located east of Niverville, Manitoba (E25-7-4E), on a Gleyed Rego Black Emerson Series (silty clay loam), and the other site was located south of Steinbach, Manitoba (SW3-6-6E), on a Gleyed Dark Grey Poppleton Series (loamy sand).

Hog manure had been applied to the Niverville site every fourth year for a number of years, the last application being in 1990. Inorganic fertilizer was also used along with the manure in the cropping history however no inorganic fertilizer was applied to field plot in 1995. The landscape was flat to undulating. The crop rotation from 1990 to 1994 included sugarbeets, wheat, wheat, barley, sugarbeets and in 1995 it was cropped to wheat.

Application of manure to the Steinbach site occurred every two years, and the last application was in 1992. Again inorganic fertilizer was also being used in conjunction with manure as a nutrient source although no inorganic fertilizer was applied to the field plot in 1995. The landscape of the site was flat to undulating. The crop rotation from 1993-1994 included corn and canola, and in 1995 corn was grown on the site.

3.1.2 Soil Description - Chemical and Physical Properties

Emerson Silty Clay Loam

Several physical and chemical characteristics for the Emerson soil are summarized in Table 3.1. Soil organic matter content was determined by wet oxidation in a potassium dichromate conc. H₂SO₄ solution as described by Yeomans and Bremner (1988). Field capacity was determined for the 0-15, 15-30, 30-60 and 100-120 cm depths as described by Cassel and Nielsen (1986). The average bulk densities for the Emerson

15 cm intervals to a depth of 100 cm. Soil pH was measured on a soil water (1:1) slurry using a Fisher model 520 digital pH/ion meter equipped with a combination glass/calomel electrode. Conductivity was also measured on a soil water slurry (1:1) with an Orion conductivity meter. The pipette method of particle size analysis was performed for the 0-15, 30-60 and 100-120 cm depths as described by Gee et al. (1986).

The organic matter content of the Emerson soil was highest at the 0-15 cm depth (6.33%) and decreased with depth to a value of 0.75% at the 100-120 cm depth. Field capacity was also highest at the surface (37%) and decreased to 31 % at the 100-120 cm depth. Bulk densities increased with depth and values ranged from 1.00 at the surface to 1.32 at the 100-120 cm depth. Values for pH varied from 7.5 to 7.7 and conductivity values ranged from 1.26 dS m⁻¹ on the surface to 1.02 dS m⁻¹ at 100-120 cm. The Emerson soil exhibited soil textural qualities of a silty clay loam in the 0-15 and 100-120 cm depths. However, at intermediate depths, particle size analysis revealed soil textural qualities of a silt.

Table 3.1 Characteristics of the Emerson Soil (Gleyed Rego Black Series)*.

Soil Depth	Organic Matter	Field Capacity	Bulk Density	рĦ	Conductivity	Sand	Silt	Clay	Soil Texture
em		- %	g cm·3		dSm ⁻¹		%		
0-15	6.33	37	00.1	7.5	1.26	4.8	64.9	31.8	SiCI
15-30	2.71	37 ·	1.27	7.6	1.17	-	-	-	•
30-45	2.52	37	1.03	7.6	1.28	2.8	87.3	10.0	Si
45-60	2.52	37	1.20	7.4	1.29	2.8	87.3	10.0	Si
60-75	-	-	1.23	7.5	2.12	-	-	-	-
75-90	-	-	1.31	7.6	1.61	-	-	-	-
100-120	0.75	31	1.32	7.7	1.01	0.7	66.8	32.6	SiCl

^{*} All measured values represent the average of at least three replicates.

Poppleton Sand

Physical and chemical characteristics of the Poppleton soil are summarized in Table 3.2. The Poppleton series consists of imperfectly drained soils developed on moderately to strongly calcareous, coarse textured deltaic deposits. These coarse textured deposits overlay fine textured lacustrine deposits. (Manitoba Soil Survey 1953). Thin pebbly to gravely lenses occurred at 50 and 100 cm.

The organic matter content of the Poppleton sand decreased markedly with depth and overall values were much lower than those for the Emerson silty clay loam. The 0-15 cm depth had an organic matter content of 2.72 %, the 30-60 cm depth had only 0.08 % and no organic matter was detected at the 100-120 cm depth. Field capacities (% by weight) ranged from 19 % for the surface soil to 10 % at the 100-120 cm depth. Bulk densities ranged from 1.06 for surface soils to 1.88 at the 100-120 cm depth. Dramatic changes in soil texture occurred due to the presence of gravel and small stones at both the 50 cm and 100 cm depths. Thus some of the high bulk density values were due to the presence of gravel lenses in the soil profile. Bulk density values that measured above 1.69 (marked with an asterisk in Table 3.2) were considered too high for use in the model and values above this were assigned bulk densities of 1.69. Values for pH ranged from 7.2 at the 0-15 cm depth to 8.1 at the 100 cm depth. Conductivity values ranged from 0.16 dS m⁻¹ at the 0-15 cm depth to 0.21 dS m⁻¹ at the 100 cm depth. Particle size analysis revealed that the soil was a sand.

Table 3.2 Characteristics of the Poppleton Soil (Gleyed Dark Grey Series)*.

Soil Depth	Organic Matter	Field Capacity	Bulk Density	рH	Conductivity	Sand	Silt	Clay	Soil Texture
cm		- %	g cm ⁻³		dSm ⁻¹		%	**********	
0-15	2.72	19 %	1.06	7.2	0.16	87.0	7.0	1.6	LS
15-30	1.25	14 %	1.52	7.7	0.18				
30-45	0.08	8 %	1.88*	7.9	0.28	87.2	5.9	7.0	S
45-60	0.08	8%	1.96*	7.9	0.26	87.2	5.9	7.0	S
60-75	-	-	1.69	8.1	0.30	-	-	-	•
75-90	-	-	1.67	8. I	0.19	-	-	•	-
100-120	0	10 %	1.89*	8. I	0.22	94.1	4.6	1.4	S

^{*} All measured values represent the average of at least three replicates.

3.1.3 Plot Design

Plot design was identical for the two sites and consisted of a randomized complete block design with 3 treatments, replicated three times. The treatments were randomized within the blocks. Each experimental site was 20 by 65.7 m and each plot was 20 m by 7.3 m (Figure 3.1). The treatments included: a control (no manure), and two rates of application identified as rate 1 and rate 2. The amount of manure added for the rate 1 and rate 2 treatments for each site is given in Table 3.3.

An irrigation treatment was conducted at both sites to study the effects of large rainfall events on the distribution of NO₃⁻ in the soil profile and how this would differ at different times of year. Two separate applications of 4 cm of water were added to a 2 m x 2 m area of replicate three (rate 2 treatment) on July 7 and September 14. The water was added with a garden hose from a plastic tank in the back of a half ton truck. The area that was irrigated was enclosed with a wooden frame to prevent water runoff during the application of water. Soil samples were taken 5 days after the 4 cm of water was applied and then every 2 to 3 weeks for the duration of the summer on the regular sampling days.

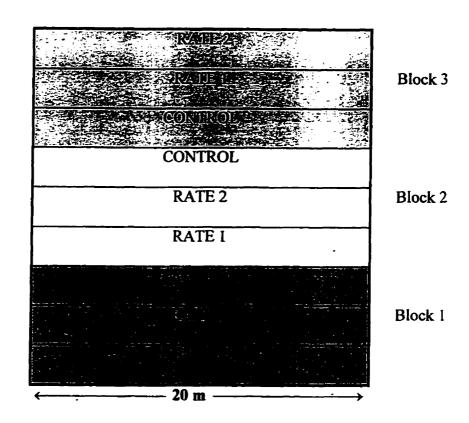


Figure 3.1 Plot Design for the Emerson and Poppleton Sites.

3.1.4 Manure application

Manure was surface applied to the Poppleton and Emerson soils on October 19th, 1994 and November 23rd, 1994, respectively. Wet field conditions did not permit an earlier application on the Emerson soil.

The volume and solid content of the manure added to each plot was measured.

Inorganic N (NO₃⁻ and NH₄⁺) in the manure was extracted using 2 M KCl and the concentration of NO₃⁻ and NH₄⁺ measured (Bremner and Hauck 1982). Total N content of manure was determined by the Kjeldahl method (McGill and Figeiredo 1993). Both of these determinations were based on three replicates and the manure source was taken from the one tank load that it took to spread the manure on the field at the time of

application. Nutrient contents are shown in Table 3.3 and were used along with the values of volume applied and solid content of the manure to calculate rates of total N applied.

Table 3.3 Characteristics and amount of manure applied.

Manure Characteristics	Emerson Soil	Poppleton Soil		
Source	Feeder Hogs	Sows and weanlings		
Storage Facility	Enclosed underground cement pit	Open outdoor lagoon		
Solid Content	10 %	1 %		
Volume added	$15 \times 10^3 L$	$20 \times 10^{3} L$		
Rate of application	37 x 10 ³ L ha ⁻¹	$34 \times 10^3 \text{L ha}^{-1}$		
NO ₃ -N content	0.1 μg NO ₃ - g ⁻¹	non-detectable		
NH ₄ ⁺ -N content	$3.86 \times 10^3 \mu g NH_4^+ - N g^{-1}$	1.00 x 10 ³ μg NH ₄ +-N g-1		
Total N	$4.0 \times 10^3 \mu g g^{-1}$	$1.1 \times 10^3 \mu g g^{-1}$		
Rate 1	143 kg N ha ⁻¹	37 kg N ha ⁻¹		
Rate 2	286 kg N ha ⁻¹	75 kg N ha ⁻¹ .		

3.1.5 Soil and Groundwater Sampling

Soil Sampling

Soil samples from each replicate were taken in the fields before manure application and analyzed for NO₃. Soil samples which examined soil moisture and soil NO₃ values were taken every two to three weeks from May to September in 1995. Both soil moisture and NO₃ values were analyzed for each replicate and the average of the three replicates was illustrated in the results, except for the irrigated treatment which was comprised of a single replicate. May soil samples were taken by hand using a Dutch auger to a depth of 120 cm at 15 cm intervals. Samples were taken to a depth of 300 cm during June to September with a Giddings drill at 15 cm intervals to a depth of 120 cm and then samples were taken from the following increments 120 to 150 cm, 150 to 200 cm, 200 to 250 cm and 250 to 300 cm. Sampling dates in 1995 for the Emerson site

were: May 15, May 30, June 13, July 11, August 2, August 23, and September 18.

Sampling dates for the Poppleton site were: May 11, May 25, June 13, July 11, August 3, August 24, and September 18. Soil samples were placed in plastic bags to prevent water loss and frozen immediately until analysis could be completed. Storage time ranged from 2 weeks to 4 months.

Groundwater Sampling

Two wells made of PVC pipe were installed in May 1995 on the first replicate of the control plot of the Poppleton sand to a depth of 1.5 meters. A hole in the soil profile was made with the Giddings drill and then the pipe was inserted into the hole. The PVC pipe was 10 cm in diameter, had 6 small holes drilled in the side of the tube near the bottom, and a cap was placed on the bottom of the pipe. Due to the deeper depth to the aquifer in the Emerson silty clay loam, a well was not installed.

3.1.6 Precipitation Data

Daily precipitation values for the period May to September were obtained from Environment Canada weather stations located close to the field sites. The weather station near the Poppleton sand site (#5022780) was located at 49 32' 96 47' or (2-7-5E). The weather station near the Emerson silty clay loam site (#5022043) was located at 49 39' 97 07' or (17-8-4E). The rainfall events were plotted and examined with respect to NO₃. distributions in the soil profile. It should be noted that although the weather stations were very close to the plots, some precipitation events may not be as accurately represented as they would have been if rain gauges were located at the field sites and checked daily as precipitation values can vary with distance.

3.1.7 Analysis of Soil and Water Samples

Water content of the soils was determined gravimetrically after drying at 103°C. Extraction of the soil samples were done by adding 15 mL of 2 M KCl to field moist soil in a 50 mL centrifuge tube and then this was shaken for 45 minutes on a shaker (Maynard and Kalra 1993). Following this, suspensions were filtered, the extracts were stored in a refrigerator at 1°C, and then samples were analyzed for NO₃-N on an autoanalyzer as described in Bremner and Hauck (1982). Every twelfth soil sample was analyzed twice and two standard soils were analyzed every 25th sample with each batch of extractions as a measure of quality control-quality assurance.

Amounts of nitrate were expressed both on a soil (dry wt) and solution basis. The main difference in nitrate expressed on a soil or solution basis is that soil moisture content is taken into account when expressing NO₃ on a solution basis. Expression of NO₃ on a soil solution basis gives a more accurate picture of the NO₃ distribution when transport is the main focus of the study.

Water samples taken from each well were analyzed for NO₃ using the procedures outlined above. Groundwater results presented represent the average NO₃ content of the two site wells.

3.1.8 Statistical Analysis

Wilcoxon's Signed Rank Test, a non-parametric test, was used to determine significant differences in NO₃⁻ distribution among treatments at each depth throughout the soil profile. The Wilcoxon's method was chosen because it assumes that the soil system is a continuous system. In other words each soil increment sampled can not be assumed

to be independent of the other increments above or below it when examining NO₃. distribution. The interactions that were compared using Wilcoxon's non-parametric test included the following pairs: control vs. rate 1, control vs. rate 2, rate 1 vs. rate 2 and rate 2 vs. rate 2 irrigation. Statistically significant findings according to Wilcoxon's test were stated at the 5 % level in the results and discussion section and a summary table of the findings are shown in the appendices

After close examination of the field data using Wilcoxon's statistics, an analysis of variance, ANOVA was also conducted on the first two profile depths to examine if the application of manure significantly affected the NO₃ levels in the surface soils. The effect of treatment and depth were examined. The difference between the control, rate 1 and rate 2 were examined for 0-15 cm depth and the 15-30 cm depth. The irrigated treatment could not be statistically compared with other treatments using an ANOVA as the irrigated treatment consisted of only one replicate. Significant anova tables are illustrated in the appendices. ANOVA's were also performed on the total amount of NO₃ in the profile to a depth of three meters. Coefficients of variation for the NO₃ field distributions are also shown in the appendices.

3.2 Rate of Denitrification of Soil With and Without Manure

Denitrification is one of the most important ways in which NO₃ is lost from the soil system (Firestone 1982). In order to obtain information regarding the denitrification potential within the soil profile, a laboratory study on nitrate disappearance rates was conducted.

Soil profile samples were taken from the non-manured plots at depths of 0-15, 15-30, 30-60 and 100-120 cm. Samples were air-dried, and ground to pass through a 2-mm sieve. Samples of 12.5 g of soil were placed into incubation vessels (Figure 3.2) designed by Cho and Sakdinan (1978). The incubation containers were approximately 42 ml in capacity, had a tapered standard 24/40 joint, a high vacuum stopcock and a tapered standard 10/18 cone joint. Soil samples were incubated with 25 ml of 25 mg NO₃⁻ L⁻¹ as KNO₃. The 25 ml solution was sufficient to ensure that water covered the entire soil surface. Oxygen was evacuated from the container and argon gas was added to achieve an internal pressure of 88 kPa as described by Cho and Sakdinan (1978).

The incubation vessels were then placed horizontally on a shaker and incubated with shaking at temperatures of 7.5 or 15°C. Sixteen samples were incubated for each depth and temperature for various time periods up to 15 days. After incubation the samples were removed from the shaker and extracted with 15 ml of 2 M KCl in a 50 ml centrifuge bottle with shaking for 45 minutes. Samples were centrifuged for 10 minutes and the liquid was stored in the refrigerator at 1°C prior to analysis

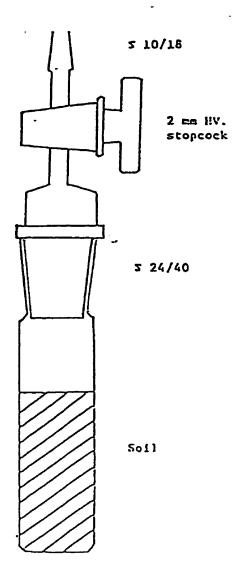


Figure 3.2 Laboratory incubation vessel

Samples stored for periods longer than three weeks were frozen. Samples were analyzed for NO₃-N content on the auto-analyzer using flow injection analysis (Bremner and Hauck 1982).

To determine if manure application affected the denitrification rate of the surface soil, soil samples from the 0-15 cm depth of the rate 1 and rate 2 treatments were taken in June 1995. Denitrification potential was assessed as described for the non-manured soils except that samples were incubated on a shaker at 15°C for 1, 2, 3, 4, 5, 6, 7, and 7.5 days for the Poppleton sand and 1, 1.5, 2, 2.5, 3, 3.5, 4, and 4.5 days for the Emerson clay loam soil. Decreases in the concentration of NO₃⁻ were plotted against time in order to obtain the specific rate of nitrate disappearance for both manured and non-manured soils.

3.3 Simulation of the Steady State Oxygen Distribution and Aerobic-Anaerobic Boundaries in the Soil Profile to Predict the Stability of NO₃

The stability of NO₃ in the soil profile under various conditions has received considerable attention (Christensen et al. 1990; Cho et al. 1996). In order to determine the fate and transport of NO₃ in the soil environment, it is essential to determine it's stability. If NO₃ is stable in the soil profile, the potential for NO₃ to move to lower soil depths and groundwater is high. In contrast, if NO₃ is unstable in the profile and undergoes denitrification, the risk for leaching is reduced but the emission of N₂O gas from the soil poses another environmental problem as N₂O is a green house gas which contributes to the depletion of the ozone layer and an increase in the potential for global warming (Crutzen and Enhalt 1977; Kinzig and Socolow 1994).

Stability of NO₃⁻ and the presence of O₂ in the soil atmosphere are inversely related. Under aerobic conditions, NO₃⁻ is produced from the NH₄⁺-N form and is generally stable. Under anaerobic conditions, NO₃⁻ becomes a terminal electron acceptor and is reduced to NO₂⁻, N₂0 and N₂. It has been reported that denitrification can occur even under aerobic conditions (Allison et al. 1960; Broadbent and Clark 1965; Knowles 1982). Some workers (Smith 1980; Myrold and Tiedje 1985; Hojberg et al. 1994) stated that the reason denitrification was being reported under aerobic conditions was because denitrification was occurring in anaerobic pockets within soil aggregates. It had been speculated that the macro-pore space between the macro aggregates may be aerobic while the micropores within a soil aggregate may be anaerobic. Consequently, the NO₃⁻ in the interior of the soil aggregate could be denitrified. There is, however, no known

"threshold" concentration of O_2 for initiation of denitrification in soil. Even though the "threshold" concentration of O_2 for the denitrification is not known, the distribution pattern of O_2 in soil, if it can be either predicted or observed would be a very valuable means to predict the stability of NO_3 within a soil. The oxygen concentration of the soil decreases with increasing soil depth and it depends on the soil conditions to determine when and if an anaerobic boundary is formed.

A mathematical model, based on a mass balance equation, which incorporated values for soil temperatures, moisture contents and nitrate disappearance rates was used to determine the distribution of oxygen in the profile at steady state (Cho et al. 1996). The distribution of oxygen in the soil profile, after a change in water content, was also calculated in order to determine the effect of a rainfall event on the stability of NO₃⁻ in the soil profile.

Cho et al. (1996), described the transport of O_2 in the soil as:

$$\frac{\partial c}{\partial t} = \frac{1}{\phi_a} \frac{\partial}{\partial x} \left(\phi_a D^o \frac{\partial C}{\partial x} \right) - \frac{\phi}{\phi_a}$$
 [3.1]

where c is the concentration of O_2 in air-filled porosity, ϕ_a is the fractional value of air-filled porosity, D^o is the diffusion coefficient of O_2 in the air-filled porosity, and x and t are distance and time, respectively. The oxygen consumption rate, ϕ , was defined on a unit volume of soil. In order to solve equation [3.1], ϕ_a , D^o , and ϕ as functions of independent variables, x and t have to be known. The moisture content and bulk density are needed to obtain ϕ_a (air filled porosity) and D (diffusional coefficient of oxygen) distribution information. ϕ is known to be a function of soil depth and temperature.

Since the transport of oxygen occurs through the air filled porosity, the total porosity and soil moisture content have to be known in order to estimate the air-filled porosity.

The model required the distribution patterns of microbial activity expressed in terms of oxygen consumption rate per unit volume of soil. Since the rate is a function of soil depth and soil temperature, the dependency of the rate upon these two independent values had to be obtained. Cho et al. (1979) illustrated that the microbial respiratory activity distribution, measured as CO₂ production rate, was not constant throughout various soil profiles. The magnitude was generally high at the soil surface and then decreased with depth. Burford and Bremner (1975) and Beauchamp et al. (1989) reported that the denitrification capacity in soils under anaerobic conditions was controlled largely by the supply of readily decomposable organic matter. Temperature also greatly affects microbial activity in a soil profile. Since soil temperature distributions were not measured in the field, an average seasonal temperature distribution model was used to estimate the temperature distribution at various times of the year. The seasonal soil temperature profile was estimated by the relation (Carslaw and Jaeger 1959; and Cho et al. 1979):

$$T = T^* + A^* \exp(-x/d) \sin(Tt - x/d + \varphi)$$
 [3.2]

where $T^* = 5.5$ °C, $A^* = 12.5$ °C, d = 140 cm, T = 0.5236 month⁻¹ $\phi = -1.964$ and t is time expressed in numerical month and x is depth in cm. However, since temperatures were slightly above average in the summer of 1995 the magnitude of A^* was slightly modified to $A^* = 15.5$ °C as opposed to 12.5°C. The temperature distribution of the soil profile was a function of time and depth (x). Only the angular frequency (T) and shift in

phase(φ) were adjusted using time of the year, t=0 at January 1. The effects of temperature distribution were examined between the months of May and September for both sites.

Soil moisture and bulk density distribution data from the Emerson silty clay loam and the Poppleton sand field studies were utilized in the model. Soil moisture contents were measured as previously described. Average bulk density values were taken in four replicates in the fall. Measuring soil moisture contents and bulk densities enabled an estimation of the air filled porosity of the soil at field conditions.

Oxygen consumption rates, ϕ , of soil at various depths were not determined.

Instead, the distribution was derived from experimentally observable nitrate disappearance rates at 15°C that were determined in the laboratory under saturated conditions. The measured NO₃ disappearance rates of soil profile samples (as described in laboratory studies) were plotted against the soil depth in a semi-log manner. For the Emerson silty clay loam the following equation was obtained:

$$R_{15} = 7.438 \exp(-0.0258x)$$
 [3.3]

where R₁₅ is the nitrate disappearance rate for a unit weight of soil at 15°C, and the coefficient, 7.438, is the nitrate disappearance rate expressed in μg g⁻¹ day⁻¹ at the soil surface at 15°C. The magnitude corresponds to 3.7 x 10⁻⁴ μmol g⁻¹ min⁻¹.

Since the standard temperature chosen to describe the temperature effect was based on 20°C, the experimentally obtained values at 15°C were corrected to 20°C, using a Q_{10} =2.68, which was obtained in the laboratory. The maximum NO_3^- disappearance rate of the surface soil at 20°C became 4.9 x 10^{-4} µmol g^{-1} min⁻¹

In order to obtain the oxygen consumption rate, the nitrate disappearance rate was multiplied by the value of 2.1, the ratio of OCR to nitrate disappearance rate (Cho 1982). The maximum (surface) value of OCR became 1 x 10^{-3} µmol O_2 g⁻¹ min⁻¹ at 20° C for the Emerson profile.

The oxygen consumption rate at 20°C for the Poppleton sand was derived similarly using the laboratory data. It was:

$$R_{15} = 1.4 \times 10^{-3} \exp(-0.13x)$$
 [3.4]

$$\phi_{15} = 2.1 \times R_{15}$$
 [3.5]

where R_{15} is the nitrate disappearance rate for a unit weight of soil at 15°C, the coefficient 1.4 x 10⁻³ is the nitrate disappearance rate expressed in $\mu g g^{-1} min^{-1}$ at the soil surface at 15°C, ϕ_{15} is the OCR at 15°C, and 2.1 is the ratio of OCR to nitrate disappearance rate.

Appropriate temperature and OCR to nitrate disappearance rate corrections were made in order to obtain the OCR at 20°C. The O₂ consumption rate for the Poppleton series could be expressed as:

$$\phi_{20} = 3 \times 10^{-3} \exp(-0.13x)$$
 [3.6]

where ϕ_{20} is the OCR at 20°C. The oxygen consumption rate of a particular soil depth with temperature, T, will be:

$$\phi = A\phi_{20}(T-B)\exp(-kx)$$
 [3.7]

where A is the temperature dependent rate of OCR and B is the threshold temperature of respiration. In this model calculation, B was chosen to be 1°C, and A was 0.0526 C⁻¹. The coefficient k is hereafter called the depth coefficient.

Since the seasonal temperature distribution within the soil was also a function of soil depth, Eq [3.2], was substituted into Eq [3.7], and the resulting equation was then substituted into Eq [3.1].

The equations used were:

$$\frac{\partial c}{\partial t} = \frac{1}{\phi_a} \frac{\partial c}{\partial x} \begin{pmatrix} \phi_a D^o & 0 \\ 0 & 0 \end{pmatrix} - \frac{\phi}{\phi_a}$$
 [3.8]

$$\phi = A\phi_{20}[T^* + A^*\exp(-x/d)\sin(Tt - x/d - \varphi) - B]\exp(-kx)$$
 [3.9]

The oxygen consumption values for the Emerson and Poppleton profiles along with the exponential k value were used in the model to determine the steady state distribution of oxygen. Negative values of \$\phi\$ were discarded and the transient equation was numerically solved until steady state values of c were obtained. Thus, the measured field values which described the physical condition of the two profiles and the laboratory values which illustrated the optimum amount of nitrate disappearance in a saturated condition can be used to predict the steady state oxygen concentration profile.

An additional factor that was considered in the model was the examination of what would happen to the stability of NO₃⁻ in the soil profiles after a rainfall event. A water balance model for pre- and post-rainfall profiles was calculated using a similar pattern reported by Salvucci and Entekhabi (1994). Moisture redistribution after the rainfall event was carried out for both sites. At the Emerson silty clay loam site large rainfall events of 6 cm occurred at the end of August and in the beginning of September. Thus, the rainfall distribution calculation for the Emerson silty clay loam used an initial

moisture content of the irrigated plots in the field in August and September and the final rainfall distribution was determined to have had 6 cm of rain added to the initial concentration. Bulk density of the soil profile in the field was also considered. Moisture distribution after 6 cm of rain was calculated assuming the 6 cm rainfall had penetrated to a certain depth with a fixed surface moisture content. The new moisture distribution was assumed to follow an exponentially decreasing pattern from the surface to a certain depth where the moisture content was unaffected by the rainfall event. The total amount of increases in the moisture from surface to depth was equivalent to the amount of rainfall. The newly calculated moisture distribution was then used in the model, to determine the oxygen profile and to observe how the addition of water changed the O₂ distribution from the previous steady state. This was then related back to the stability of NO₃ in the profile.

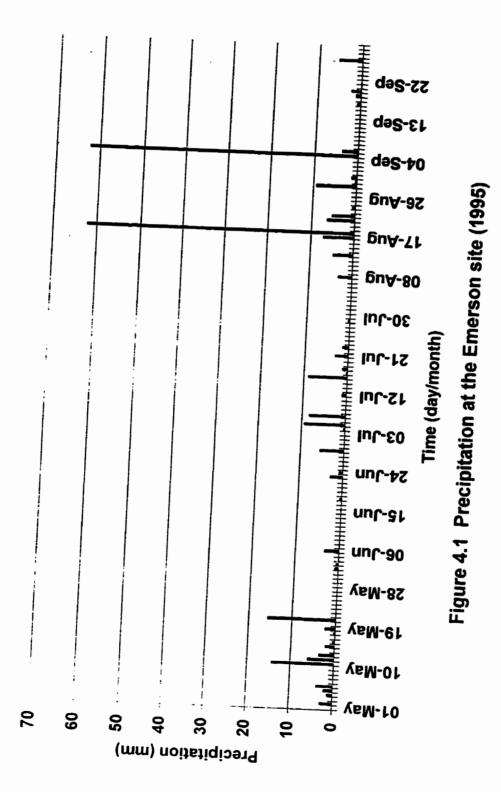
Moisture redistribution in the Poppleton sand after a rainfall event was also calculated using the same method as described above. The majority of rain at the Poppleton site occurred in the end of August and the largest rainfall event measured close to 8 cm of rain. Therefore 8 cm of rain and the August soil conditions of soil moisture were used in the model. Thus, soil moisture and bulk density values from the field along with the calculated final moisture contents were used to determine the change in oxygen concentration with time. Time zero corresponded to the soil moisture content before the rainfall event and the change in oxygen concentration was examined up until day 5.

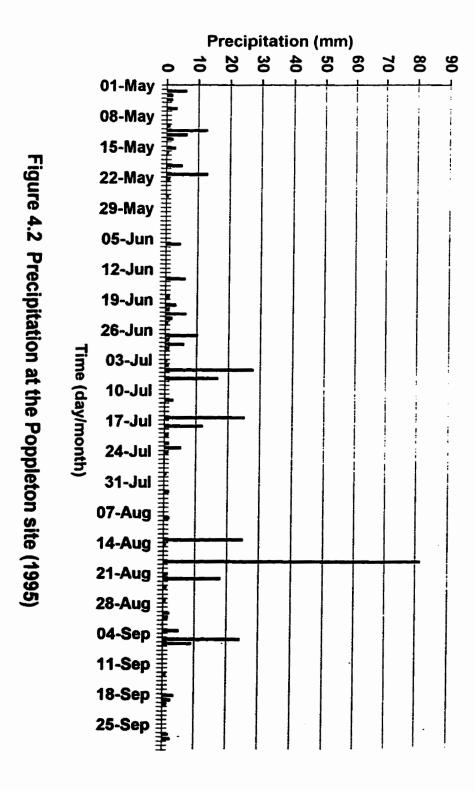
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Hog Manure on the Distribution of NO₃ in Soil and Groundwater 4.1.1 Precipitation

Precipitation values from May to September for the Emerson and Poppleton sites in 1995 are illustrated in Figures 4.1 and 4.2, respectively. Precipitation events at the Emerson site (Figure 4.1) during May, June, July and the early part of August were infrequent, small and below average (Environment Canada 1995). Precipitation in May, June and July was 54 mm, 14 mm and 34 mm respectively as compared to the average precipitation values of 61 mm, 93 mm and 74 mm, respectively. After mid August, precipitation values were higher than average and were 100 and 75 for August and September as compared to averages of 62 and 52 mm, respectively. Rainfall events of 62 and 52 mm were recorded for Sept 5 and Sept 18, respectively. There was also an appreciable amount of precipitation before the last sampling date (September 18, 1995) that occurred in a relatively short period of time.





Precipitation rates in May, June, July and August were 55 mm, 42 mm, 94 mm, and 134 mm, respectively, at the Poppleton site (Figure 4.2). Precipitation at the Poppleton site was below average for May and June but above average in July, August and September (Environment Canada 1995). Rainfall events of 28, 25, and 12 mm occurred on July 5, 7, and 18 respectively. The biggest rainfall event occurred on August 18th and totaled 82 mm. The majority of precipitation for the month of September occurred before September 5. The precipitation events were graphed daily so that the effect of precipitation on the movement or leaching of NO₃⁻ could be compared with the NO₃⁻ distributions in the soil profiles.

4.1.2 Soil Moisture

Soil moisture distributions between the irrigated and non-irrigated soil profiles were compared and expressed on a volumetric basis. Soil moisture profiles for both the irrigated and non-irrigated treatments of the Emerson site from the months of July to September illustrated a similar pattern. Soil moisture was approximately 30 % at the surface, decreased to about 20 % at 40 cm, and then gradually increased with depth to values of about 40 % at the 300 cm depth (Figures 4.3-4.5). The addition of 4 cm of water to the irrigated profile did not produce measurable or consistent differences in soil moisture content when measured 5 days after irrigation. The lack of detectable differences between treatments could be due to the sampling time or the inherent spatial variability in soil moisture.

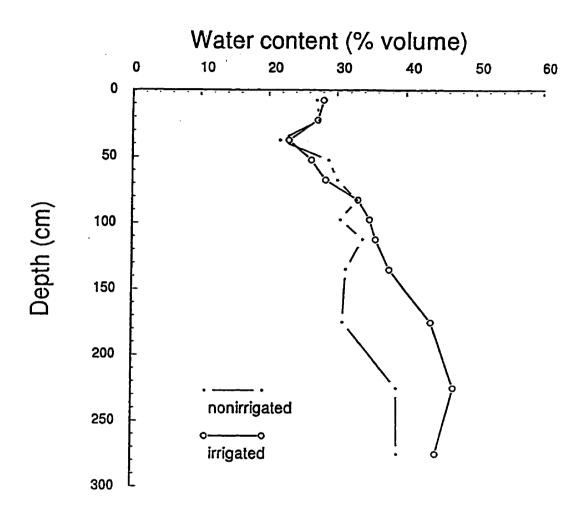


Figure 4.3 Volumetric water content of the Emerson profile on July 11, 1995

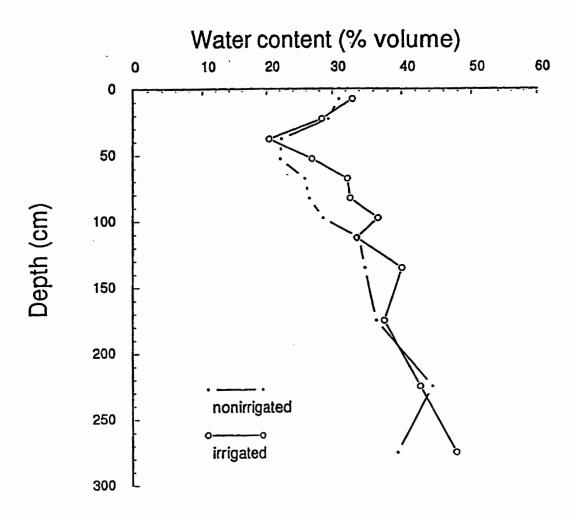


Figure 4.4 Volumetric water content of the Emerson profile on August 23, 1995

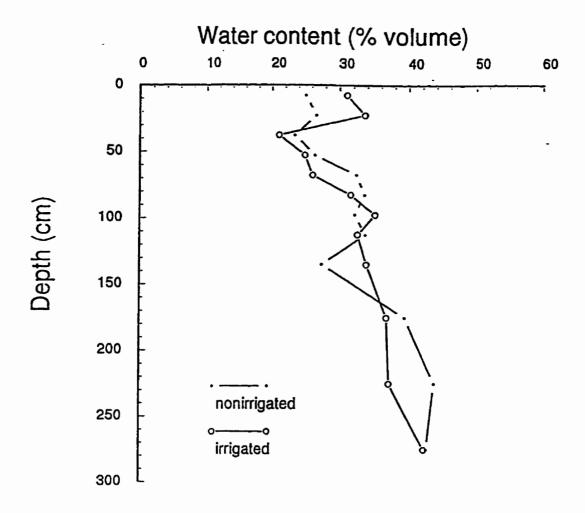


Figure 4.5 Volumetric water content of the Emerson profile on September 18, 1995

The distribution of soil moisture in the Poppleton sand was similar in pattern to that of the Emerson soil during July to September, except that the moisture contents in the surface layers were lower in magnitude (Figure 4.6-4.8). The soil moisture content was relatively low at the surface (approximately 10-20 %) and then it gradually increased with depth to values of 38 to 48 % at the 300 cm depth. Again the lack of detectable differences between the irrigated and the non-irrigated treatments was likely due to the time of sampling and soil variability.

4.1.3 Soil Temperature

Soil temperatures were not measured at the two field sites. The average temperature distribution of Manitoba soils was used to help explain and discuss the trends seen in the NO₃ distribution throughout the profile. Typical temperature distributions with depth from May to September are shown in Figure 4.9. The data indicates that the surface soil was near 10°C and was about 3°C at 150 cm in May. As the season progressed, the surface temperature increased to a high of 18°C on August 24. However, the rise in temperature of the subsurface soil was rather slow. During September, the temperature of the surface soil started to decrease while subsoil temperatures continued to increase. The subsoil temperatures in September were warmer than those in July or August.

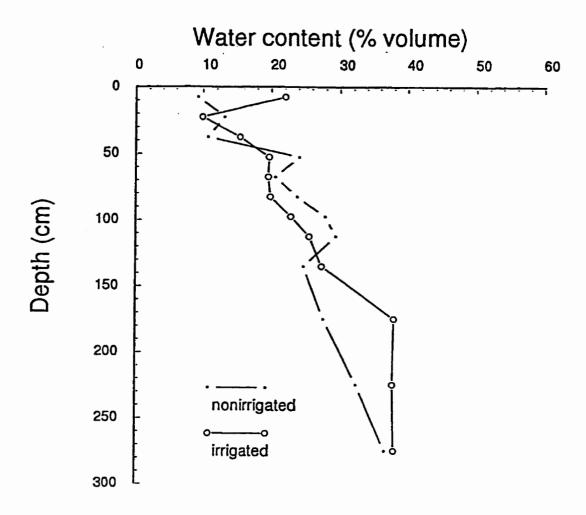


Figure 4.6 Volumetric water content of the Poppleton profile on July 11, 1995

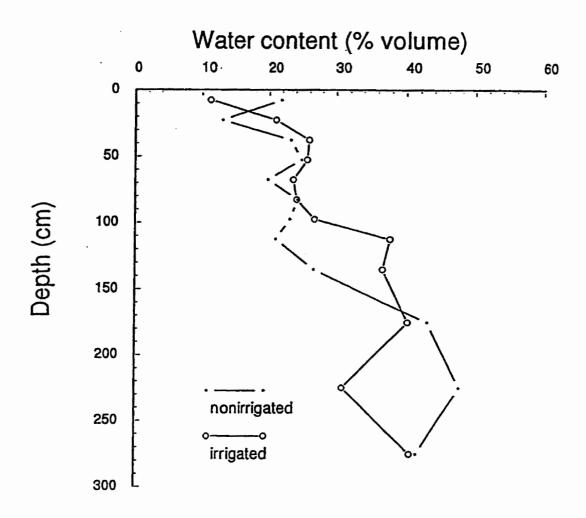


Figure 4.7 Volumetric water content of the Poppleton profile on August 24, 1995

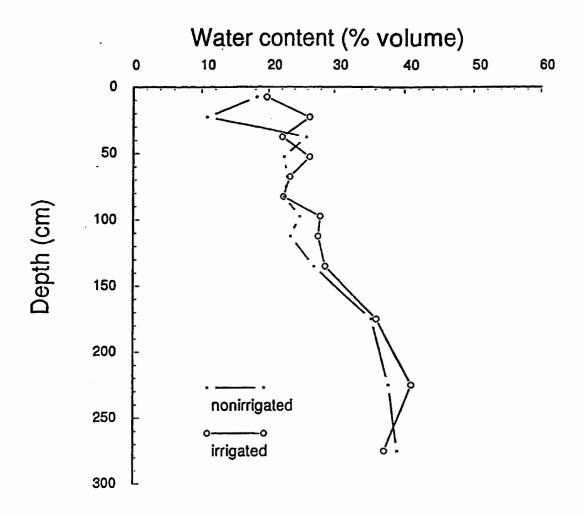


Figure 4.8 Volumetric water content of the Poppleton profile on September 18, 1995

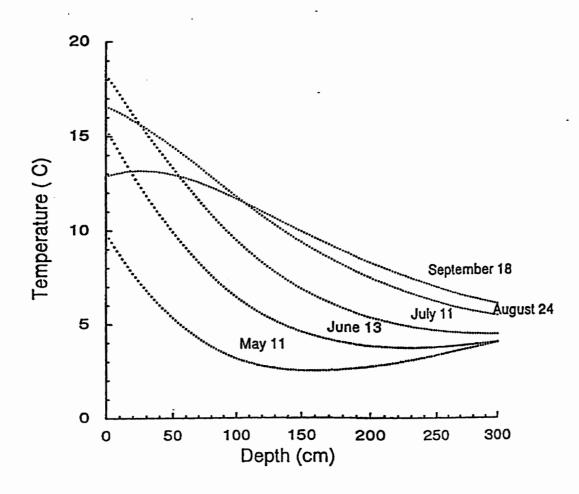
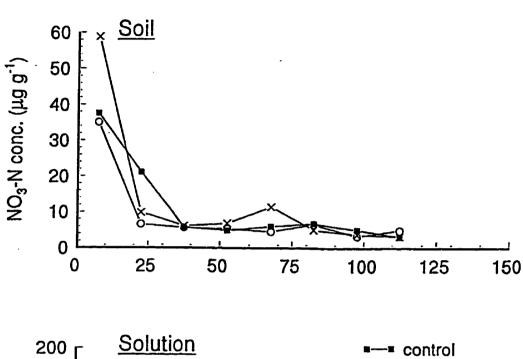


Figure 4.9 Average soil temperature profiles of Manitoba soil at several times of the year (as estimated by Carslaw and Jaeger 1959; Cho et al. 1979)

4.1.4 Nitrate Distribution of the Emerson Silty Clay Loam

The patterns of NO₃ distribution in the soil profiles, based on the average of three replicates, were similar when expressed on either a soil basis or a solution basis with the exception that the values expressed on a solution basis were always higher (Figures 4.10-4.14). The concentration of NO₃ at the Emerson site in May and June was high in the surface soils, decreased rapidly with depth to a depth of about 35 cm, then remained relatively constant with depth (Figures 4.10 and 4.11). Treatment had little or no effect on the distribution pattern of NO₃ in the soil except in the months of August and September. The concentration of NO₃ was high at the surface and then decreased rapidly with depth to about 50 cm in July, August and September. However, in contrast to the distribution pattern for NO₃ observed in May and June, an accumulation or bulge of NO₃ at a depth of 50 to 200 cm was observed for July and August. The NO₃ concentration at the bulge was found to be significantly higher for the rate 2 irrigated treatment than for the non-irrigated treatments. Statistically significant reductions in NO₃ concentrations were noticed in the end of the summer. A significant disappearance of NO₃ in the 50 cm region in August for the rate 2 treatment and a reduction at the 50-100 cm region for the rate 2 irrigated treatment in September were observed.

A statistically significant difference in NO₃⁻ distribution was also observed between the control and rate 1 in August with the NO₃- N concentration in the control being lower than that of rate 1 especially at the soil surface. In September a large statistical difference was noted in the distribution of NO₃⁻ between rate 1 and rate 2 as the concentration of NO₃⁻ in rate 2 was generally lower than that of rate 1. This difference could be attributed to increases in the amount of available carbon associated with the rate



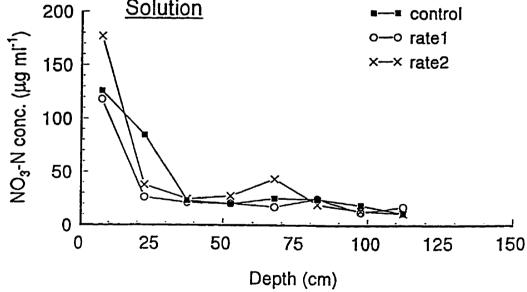
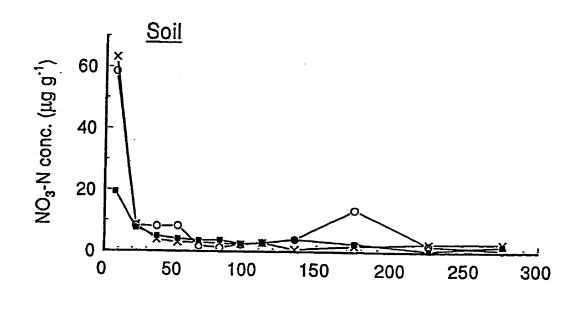


Figure 4.10 Distribution of NO₃-N in the Emerson profile on May 30, 1995 as affected by different treatments



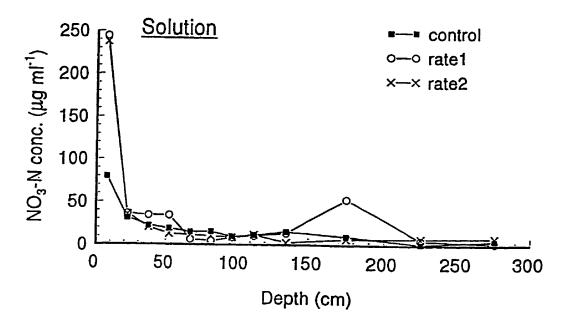


Figure 4.11 Distribution of NO₃-N in the Emerson profile on June 13, 1995 as affected by different treatments

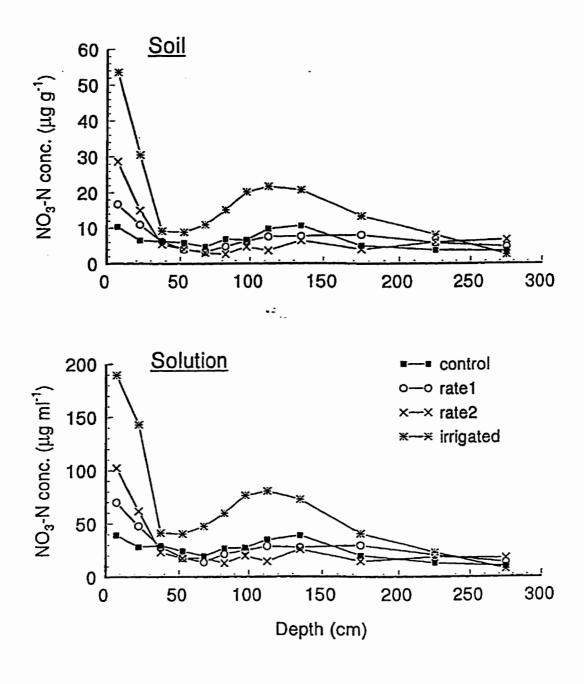


Figure 4.12 Distribution of NO₃-N in the Emerson profile on July 11, 1995 as affected by different treatments

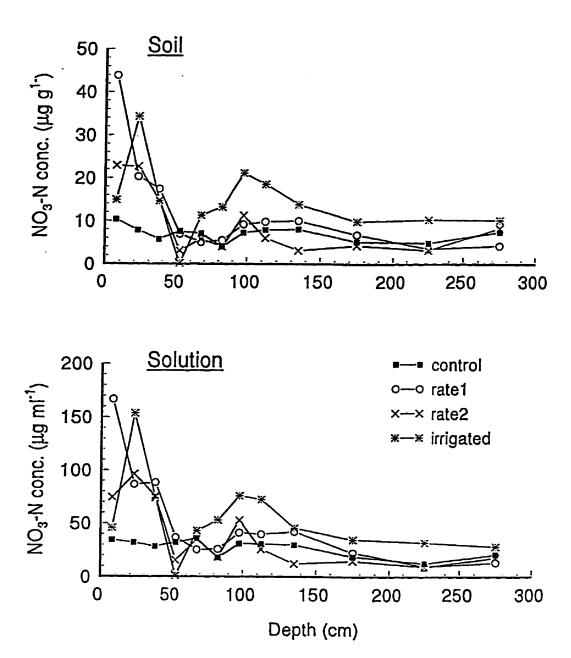


Figure 4.13 Distribution of NO₃-N in the Emerson profile on August 23, 1995 as affected by different treatments

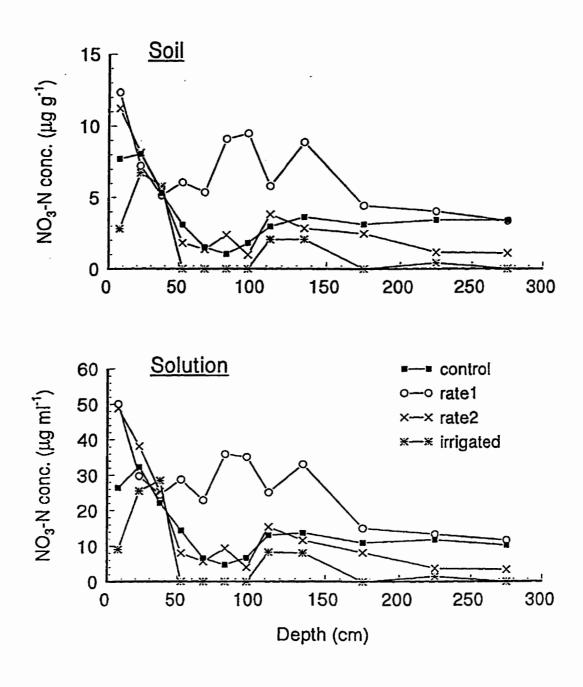


Figure 4.14 Distribution of NO₃-N in the Emerson profile on September 18, 1995 as affected by different treatments

2 treated soil and the highly favorable denitrifying conditions that occurred in the fall. In a review on the effects of carbon on denitrification, Beauchamp et al. (1989) stressed the importance of carbon on denitrification.

The general NO₃ distribution patterns of the Emerson clay (high at the soil surface and lower with depth) also showed accumulation and disappearance patterns in the profile depending on the conditions. In July the irrigation of 4 cm of water had an effect on the NO₃ distribution. It showed high nitrate levels at the surface followed by a decrease in the concentration around 50 cm and then it increased with depth, showing a maximum near the 100-150 cm depth. The presence of a bulge of NO₃ near 100-150 cm could be due to leaching of NO₃-N from the surface layers or due to the possibility that the addition of water to a previously dry profile would have increased the potential for nitrification (Birch 1958; Aulakh et al. 1983). Increasing soil temperature and moisture that occurred during July and August probably enhanced microbial activity and nitrification in the surface soil resulting in the production of NO₃ which then moved to depths of 100-150 cm with the irrigation water and various rainfall events. Soil temperatures in July at the 50 and 200 cm depths would be about 15 and 6°C. respectively and the soil moisture for the irrigated plot in July at the same depth was about 38-40 % as opposed to 30 % in the non-irrigated profile. Alexander (1965) and Williams et al. (1992) suggested that for nitrification to proceed at an optimum rate, moisture content of the soil should be between half and two thirds of it's moisture holding capacity. Nitrification rates have also been reported to increase over the range of 2 to 40°C (Kowalenko and Cameron 1978). The possibility of increased NO₃-N concentrations in the soil profile from the irrigation water was ruled out as the total N and NO_3 -N levels in the irrigation water were very small measuring 0.56 and < 0.04 mg L⁻¹ respectively (City of Winnipeg 1995).

The reduction in NO₃ concentration at the 50 cm depth (Figure 4.13) observed for the rate 2 and the rate 2 irrigated treatment may have been due to denitrification. When precipitation values for the August 23 sampling date were examined, it was found that there was a large amount of rain which occurred prior to this sampling date. It was speculated that the rainfall event prior to the sampling date may have caused the low NO₃ content at the 50 cm depth as precipitation resulted in a higher moisture content and temporarily decreased oxygen content in the first 50 cm of the Emerson profile making an anaerobic zone which intensified the denitrification process at this intermediate depth. Under similar moisture conditions, the same intensity of denitrification did not occur bellow the 50 cm depth, and this was probably due to lower soil temperatures which limited microbial activity, and hence limited the rate of denitrification.

According to van Kessel et al. (1993), soil water content is the most dominant factor controlling denitrification activity, followed by the concentration of NH₄⁺ and NO₃⁻ and total soil respiration. There have been many studies (Smith and Tiedje 1979a; Mosier et al. 1982; Sexstone et al. 1985; Aulakh et al. 1992) that illustrated that an increase in soil moisture due to rainfall or irrigation resulted in a dramatic increase in gaseous nitrogen fluxes within hours which suggested that levels of denitrifying organisms present in agricultural soils are sufficient to respond quickly to changes in aeration. Smith and Tiedje (1979a) also reported that most nitrogen is lost from soils during brief periods beginning a few hours after rainfall or irrigation. The NO₃⁻ concentration in the Emerson soil profile in September was significantly different for the

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irrigated treatment and non-irrigated rate 2 treatment. Thus, it is possible that increased moisture in the irrigated soil, increased denitrification.

In September, the rate 2 irrigated treatment seemed to promote the disappearance of NO₃⁻ from the 50-100 cm region through denitrification. In contrast, the same manure treatment with the addition of 4 cm of water in did not promote denitrification in July; instead the NO₃⁻ moved down the profile and accumulated at the 50 to 200 cm depth. Conditions that occurred in September, including warmer subsurface temperatures and increased soil moisture were probably the reason for the different fates of NO₃⁻.

The high levels of NO₃⁻ in the surface soils during May to July could be partially due to increased nitrification. In July, the rate 2 irrigated treatment had a noticeably higher NO₃⁻ concentration in the surface soils (60 μg g⁻¹) than other treatments (10-30 μg g⁻¹). Increased nitrification and mineralization in July for the irrigated treatment, was probably due to the increased water content coupled with warmer temperatures. It is also possible that during June and July when the soil conditions were very dry that some NO₃⁻ may have moved up the profile via capillary rise with evaporating water. The upward movement of NO₃⁻, which is usually confined to the upper 30 to 45 cm of a soil in dry periods, was observed by Wetselaar (1961). A decrease in NO₃⁻ concentration in the 30 to 45 cm region was seen at the Emerson site.

The amounts of nitrate-nitrogen per hectare to a depth of 300 cm were calculated on the Emerson silty clay loam for all treatments (Table 4.1).

Table 4.1 Nitrate-nitrogen for the Emerson silty clay loam at various times of 1995 (Kg ha⁻¹ to 300cm).

Treatment	June 13	July 11	August 23	September 18						
	NO ₃ -N (Kg ha ⁻¹ to 300cm)									
Control	146	238	264	143						
Rate 1	306	276	363	228						
Rate 2	229	262	298	112						
Irrigated -	-	582	513	45						
Rate 2										

Plots treated with manure usually contained higher amounts of NO₃ than plots without manure. Plots treated with the high rates of manure contained less nitrate than plots treated with the low rate of manure. The lower amounts of NO₃ in the plots treated with the high rate of manure may have been due to a greater rate of denitrification associated with an increased organic C content of the rate 2 treatment. Denitrifiying organisms use organic C compounds as electron doners for energy and for synthesis of cellular constituents and thus denitrification is strongly dependent on the availability of organic compounds such as manures (Beauchamp et al. 1989; Aulakh et al. 1992).

Burford and Bremner (1975) concluded that denitrification in soils under anaerobic conditions is controlled largely by the supply of readily decomposable organic mater. In fact the production of nitrous oxide which is an intermediate in the denitrifying process was also shown to increase in manured soils which would also indicate the importance of

manure enhancing the denitrification process (Burford and Bremner 1975; Christensen 1985). Many researchers (Olsen et al. 1970; Guenzi et al. 1979; and Cooper et al. 1984; Beauchamp et al. 1989) have speculated that increased denitrification can occur on manured soils.

Irrigation when the soil was relatively dry to begin with increased the amounts of nitrate in the soil profile during July and August (Table 4.1) and this was most likely a result of greater nitrification and mineralization rates. Nitrification rates were probably increased by the higher moisture contents of surface soils on the irrigated plots.

However, decreases in the total amount of NO₃ observed in the soil profiles in September were probably a result of denitrification. Subsurface soil temperatures were warmer and soil moisture was higher due to increased precipitation in September as opposed to previous months. Increased temperature and water content can facilitate greater rates of denitrification (Knowles 1982).

Differences in the total amounts of NO₃-N in the 0-3 m depths among treatments were not statistically significant at the 0.05 P level. Significant differences were probably not observed due to a great deal of field variability among replicates. Variability in replicates could have been due to the heterogeneity of the manure, the unevenness of the manure application, the nature of the soil and differing microbial activity as a result of varying moisture. Also, manure has been applied once every four years for the last 20 years to this site and the control had high background levels of NO₃ which masked the effects of the manure applied to this study. Coefficients of variation for NO₃ distributions with depth also exhibited high variability due to heterogeneity of the manure and soil system.

A two way ANOVA was carried out on the data for the Emerson silty clay loam to see if there was any effect of the application of the manure on the concentration of NO₃ in the surface soil (0-15 and 15-30 cm). The main effects of depth (0-15 cm vs 15-30 cm) were examined as well as treatments (control, rate 1 and rate 2) and their interaction. Significant differences in NO₃ content between the top two layers occurred only on May 30, June 13 and July 11. In most cases, NO₃ content of the top two depths were not significantly different. The lack of significance was probably due to rainfall events which readily moved nitrate from surface layers (0-15 cm) to lower depths (15-30) negating any differences which may be expected due to mineralization and denitrification. The treatment effect on the surface soil of the Emerson clay loam proved to be significant only in the month of July.

4.1.5 Nitrate Distribution of the Poppleton Sand

The patterns of NO₃⁻ distribution in the soil profile of the Poppleton sand were similar to those of the Emerson clay loam, however, the nitrate concentrations of the sand were slightly lower on average (Figure 4.15-4.19). The change in NO₃⁻ concentration from the surface soil to the lower soil depths was less dramatic for the Popppleton site than for the Emerson site.

The concentration of NO₃ in the Poppleton sand in May was high in the surface soil, decreased rapidly with depth to a depth of about 25 cm and then remained relatively constant with depth. In June, July, and September, NO₃ concentration expressed on a soil basis was high at the surface, decreased rapidly within the first 50 cm, and then increased from 100 to 300 cm. However, with NO₃ concentrations expressed on a

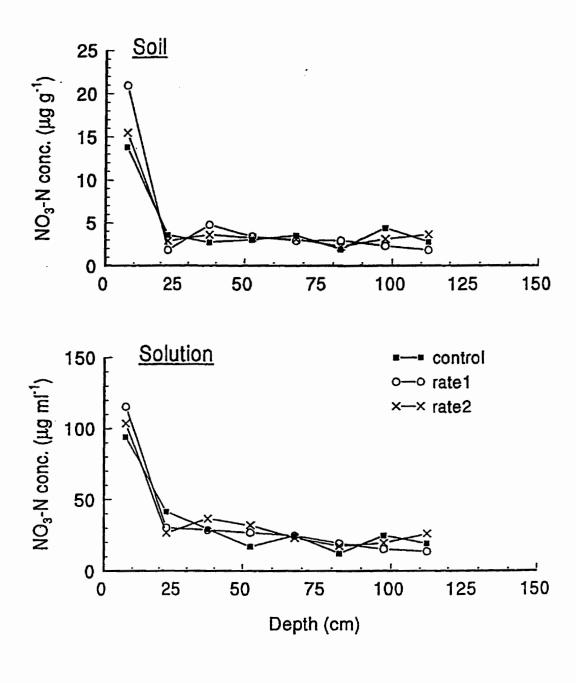


Figure 4.15 Distribution of NO₃-N in the Poppleton profile on May 25, 1995 as affected by different treatments

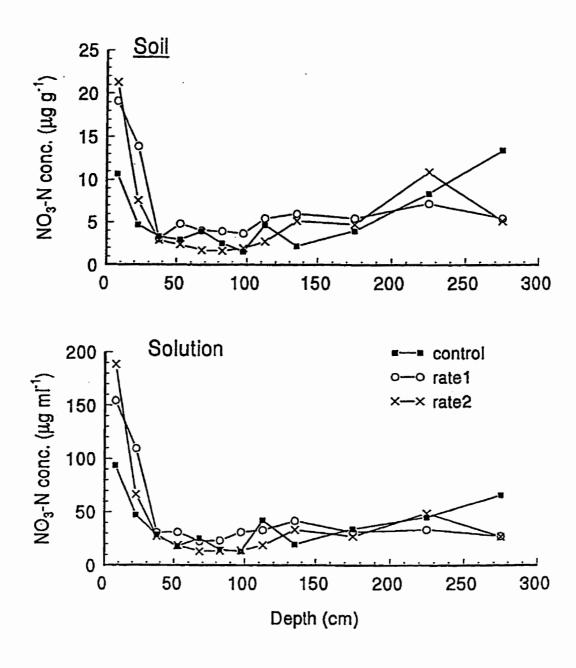


Figure 4.16 Distribution of NO₃-N in the Poppleton profile on June 13, 1995 as affected by different treatments.

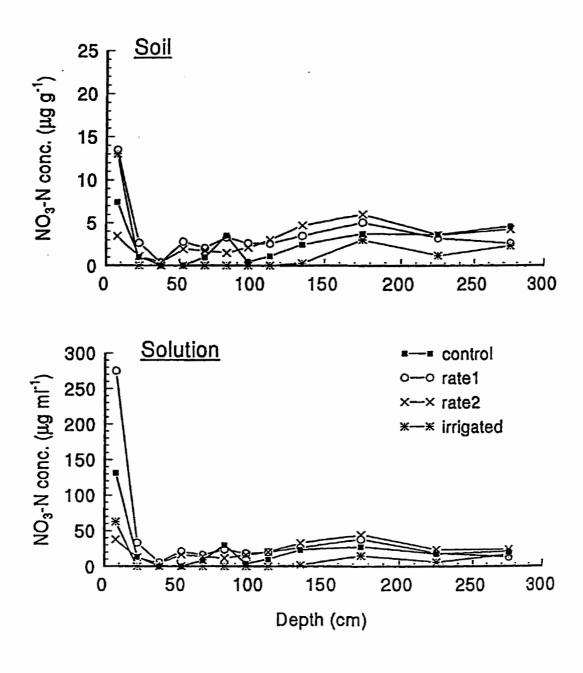


Figure 4.17 Distribution of NO₃-N in the Poppleton profile on July 11, 1995 as affected by different treatments.

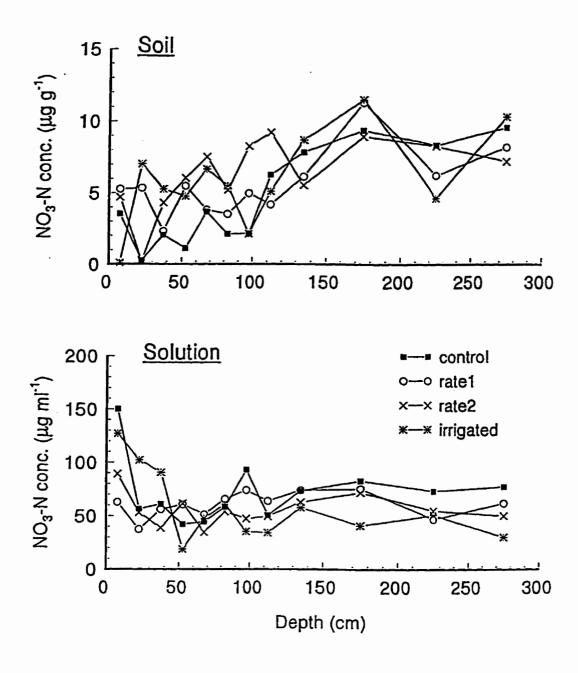


Figure 4.18 Distribution of NO₃-N in the Poppleton profile on August 24, 1995 as affected by different treatments.

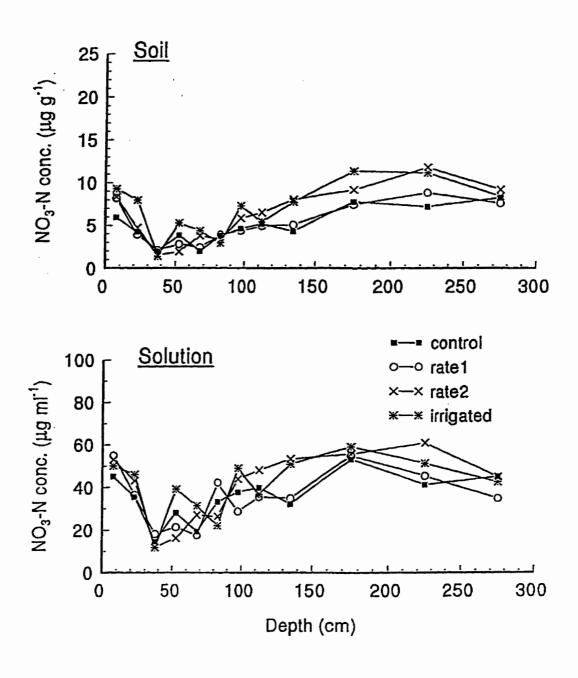


Figure 4.19 Distribution of NO₃-N in the Poppleton profile on September 18, 1995 as affected by different treatments.

solution basis, NO₃ concentrations at depths of 100 and 300 cm were similar to those at 50 to 100 cm. Thus, since no concentration gradient existed in solution, there would be no net movement of NO₃ to lower depths in the Poppleton sand via diffusion.

The rise in NO₃⁻ concentration with depth seen when expressed on a soil basis, which was not seen when expressed on a solution basis is an important observation and is particularly evident for data presented in Figure 4.17. The concentration of NO₃⁻ expressed on a soil basis in the control plot from 150 cm to 300 cm increased with depth. In contrast, NO₃⁻ concentration remained around 30 μg NO₃⁻ g⁻¹ for all depths when expressed on a solution basis. This discrepancy is solely due to changes in moisture content which increased with soil depth. This example illustrates the importance of expressing the NO₃⁻ on a solution basis to test if transport via diffusion is possible. Even though there was no concentration gradient of NO₃⁻ in soil solution, the leaching of nitrate must have occurred previously since the NO₃⁻ levels were about 45 μg NO₃-N g⁻¹ at depths of 100 to 300 cm.

The NO₃⁻ distribution pattern in August was similar for all treatments.

Concentration of nitrate, expressed on a soil basis was low at the surface and increased with depth. This could be attributed to the heavy rainfall event that occurred on August 19th 1995 which probably leached a considerable portion of NO₃⁻ from the surface to deeper depths. The probability of leaching occurring is supported by the distribution pattern of NO₃⁻ in the soil solution. The concentration of NO₃⁻ in soil solution below 100 cm was almost uniform and were higher than those observed in July (Figure 4.17). The presence of high concentrations of NO₃⁻ in surface soils (solution basis), not observed

when expressed on a soil basis, may be due to evaporation of soil moisture at the surface after the rainfall event or due to increased mineralization at the surface.

Statistical analysis of the data obtained for June, July, and September, revealed a statistically significant difference in NO, distribution between the irrigated and nonirrigated profile. There was a marked reduction in NO₃ content at the 20 to 140 cm region for the rate 2 irrigated treatment in July (Figure 4.17). The decrease in NO₃ content was either due to leaching or denitrification. However, since an accumulation of NO₃ below 1.5 meters, was not observed, denitrification was most likely responsible for the loss. Normally it would be assumed that denitrification would occur less frequently on a sand as compared to a fine textured clay. However, this depends largely on the soil conditions. Prior to sampling of the Poppleton sand on July 11, there was an appreciable amount of precipitation and the surface soil had a high moisture content. The increased moisture content decreased the oxygen content of the sand which created an anaerobic zone in the profile favorable for denitrification. It has also been shown that rather shallow groundwater tables may induce or enhance the denitrification processes in soil resulting in a loss of nitrate (Strebel et al. 1989). Another statistically significant difference for data obtained in July was between the control and rate 1 treatment. The control had very low concentrations of NO, at the beginning of the year whereas the rate 1 treatment consistently had higher concentrations throughout the profile. Nitrate concentrations of the soil solution for the surface soil was about 130 µg NO₃-N g⁻¹ for the control and 280 µg NO₃-N g⁻¹ for treatment 1 (Figure 4.17) Irrigation on the Poppleton sand had no measurable effect on NO₃ distribution in September (Figure 4.19). Rainfall

events probably masked expected differences. It is also possible that the sampling interval after the application of water was too long to illustrate effects of irrigation on the sand. A significant difference between the rate 1 and rate 2 treatments was determined for the Poppleton sand in September. Concentrations of NO₃⁻ for the rate 2 treatments were higher than for the rate 1 at the lower profile depths. In general there were fewer statistical differences among treatments for the Poppleton sand than for the Emerson silty clay loam.

The total quantities of nitrogen per hectare to a depth of 3 meters were calculated for the Poppleton sand (Table 4.2).

Table 4.2 Nitrate-nitrogen in the Poppleton sandy loam at various times of 1995 (Kg ha⁻¹ to 300 cm).

Treatment	June 13	July 11	August 24	September 18						
	NO ₃ -N in 1 ha-300cm									
Control	248	117	254	228						
Rate 1	259	145	264	243						
Rate 2	242	136	274	303						
Irrigated -	-	70	282	323						
Rate 2										

Plots treated with the high rates of manure showed lower quantities of nitrate than plots without or with low rates of manure in June and July. Again, increased organic carbon may have increased losses via denitrification. Irrigation greatly decreased the amount of NO₃ present in the profile in July most likely due to denitrification. However,

irrigation did not seem to have an effect on the amount of nitrate in the profile in September. Statistical analysis of the data for the entire profile showed no significant differences among amounts of nitrate in the control, rate 1 and rate 2 treatments at the 0.05 P level. Coefficients of variation for NO₃ distributions with depth also exhibited high variability due to heterogeneity of the soil profile which had two gravel lenses.

A two way ANOVA was performed on the data for the Poppleton sand to test if the amounts of NO₃ in the surface soil was affected by the manure treatments. The main effects of depth (0-15 cm vs 15-30 cm) were examined as well as treatments (control, rate 1 and rate 2) and their interaction. Except for August, depth was found to be significant for all of the sampling days as nitrate content on surface layers was significantly greater than the lower depths. Treatment in the surface two layers had no significant effect at any time.

The NO₃⁻ concentration in the well water throughout the growing season is illustrated in Figure 4.20. The concentration of NO₃⁻ in the groundwater was about 45 μg NO₃ -N L⁻¹ during May to early August and about 20 μg NO₃-N L⁻¹ at the end of August. The NO₃-N concentration in the groundwater was very high and it exceeded the maximum allowable concentration of 10 μg NO₃-N L⁻¹(CCREM 1987). The high NO₃-N levels seen from the well water samples were further supported and emphasized when the NO₃-N concentrations on a soil solution basis were examined as they were also around 45 μg NO₃ -N L⁻¹ until August. The decrease of NO₃⁻ concentration in August was probably due to denitrification. Sub-soil temperatures and soil moisture contents were higher in August than in the spring and thus conditions were more favorable for denitrification in

August than earlier in the growing season. The high levels of NO₃⁻ in the groundwater indicate that NO₃⁻ has leached to the groundwater from previous manure and fertilizer applications. It is generally known that NO₃⁻ leaching is of greater concern in coarse textured soils as opposed to fine textured soils (Hedlin 1971; Burton 1994a;). Chang et al. (1996) and Ewanek (1996) have also showed that NO₃⁻ leached to groundwater from manure applications.

4.1.6 Review of Data in Relation to Current Guidelines

One of the goals of this study was to help devise guidelines to assist farmers in determining sustainable rates for manure application. The current 1995 guidelines for hog producers states that the producer should not apply more nitrogen than the crop can utilize (Manitoba Agriculture 1995). Uptake of N by crops generally vary from about 78 to 112 kg N ha⁻¹ (Manitoba Agriculture 1995). Manitoba agriculture currently recommends the following in the manure management guidelines: If NO₃-N levels in the top 120 cm are 160 kg ha⁻¹, the values are considered too high, and no manure should be applied. If the nitrogen concentration below 120 cm are greater than 22.3 kg ha⁻¹ per 30 cm depth, nitrates have moved or leached down the soil profile (Manitoba Agriculture 1995). The data obtained for the Emerson silty clay loam and the Poppleton sand were examined with respect to the current Manitoba guidelines. Quantities of NO₃-N per hectare in the top 120 cm were calculated (Table 4.3). Nitrate content of the Emerson clay loam, irrespective of treatment was higher than the Poppleton sand with some values being higher than the recommended maximum level of 160 kg N ha⁻¹ in the top 120 cm. It should be noted that although levels of nitrate in the top 120 cm were high, nitrate concentration (on a soil basis) at depths below 120 cm were

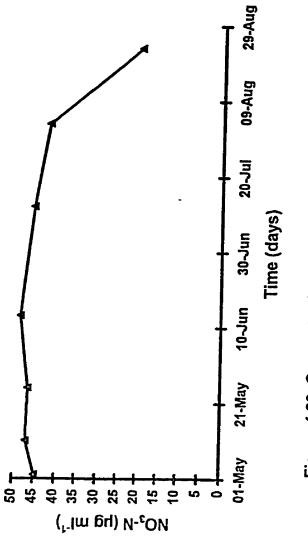


Figure 4.20 Concentration of NO₃-N in the groundwater during the year at the Poppleton site

relatively low (about 5 μ g g⁻¹). This is close to the guideline limit proposed by Manitoba Agriculture. In contrast, some nitrate concentrations of the soil solution at depths greater than 120 cm exceeded 10 μ g ml⁻¹ N. Thus if this solution moved to the groundwater, the groundwater would exceed the safe limit for water for domestic use (10 μ g ml⁻¹ N). Whether or not contamination of groundwater would occur would depend on whether or not sufficient denitrification would occur below depths of 120 cm to reduce nitrate concentrations to less than 10 μ g ml⁻¹ N. In September however, none of the Emerson clay loam treatments exceeded the maximum recommended level on a soil or solution basis. Increased fall denitrification was probably responsible for the decrease in NO₃.

Table 4.3 Amounts of NO₃-N in the soil profile (Kg N ha⁻¹ to 120 cm).

		Emerson clay loam			Poppleton sand				
Date	Control	Rate 1	Rate 2	Irrigated	Control	Rate 1	Rate 2	Irrigated	
	NO ₃ -N (kg ha ⁻¹ 120 cm)								
May 11/10	274.9	288.1	271.3	NI*	88.4	108.6	80.8	NI*	
May 30/25	181.0	144.5	210.7	NI*	99.9	81.9	74.6	NI*	
June 13	97.5	183.0	178.7	NI*	68.9	115.9	84.2	NI*	
July 11	114.2	122.6	126.6	340.3	29.1	59.6	30.5	26.1	
August 3/2	227.8	76.8	101.8	195.2	92.8	104.3	83.0	90.2	
August 24/23	116.1	236.5	181.3	256.5	42.4	69.8	91.0	73.1	
September 18	63.0	121.2	70.4	34.8	63.3	65.1	71.9	87.6	

^{*} NI: not irrigated

The levels of NO₃ in the Poppleton sand were not above Manitoba's recommended maximum of 160 kg ha⁻¹ (Table 4.3). This would lead one to believe that on the Poppleton sand there was no problem with respect to NO₃ levels in the soil and that more nitrogen could safely be applied to the site. However, the NO₃-N concentration in the groundwater was about 45 μg NO₃-N L⁻¹ and greatly exceeded the Canadian drinking water guidelines. Nitrate-nitrogen expressed on a soil solution basis (Figures 4.10-4.19) also illustrated the concentration of NO₃ was about 45 μg NO₃-N L⁻¹ in the soil solution. Drainage of soil water from the 0 to 120 cm depth to the groundwater would thus result in concentrations well above the 10 μg NO₃-N L⁻¹ limit. The nitrate concentrations were especially high at the lower depths. It is obvious from the groundwater and soil solution analysis that addition of more nitrogen (in commercial or organic form) to this site should be done with extreme caution as leaching is occurring and NO₃ is accumulating in the groundwater.

It is important to realize that soil moisture is a very important factor to consider when determining the NO₃⁻ distribution in soil profiles. Soil moisture varies with soil texture and thus the concentration of NO₃⁻ expressed on a soil basis will also vary with moisture, however the NO₃⁻ concentration expressed on a soil solution basis will not vary and it will be a more constant measure. It should also be noted that the interpretive guidelines for Manitoba used to determine acceptable NO₃⁻ levels have to be viewed and used with caution and common sense. When determining acceptable NO₃⁻ levels in soil profiles it is strongly advisable to sample to depths greater than 120 cm to get a more complete picture of the NO₃⁻ distribution and to determine if NO₃⁻ is leaching in the system. In order to determine if there is a potential long term problem, sampling should

be taken to at least 300 cm in order to obtain information on NO₃ distribution within and below the root zone. Soil texture should also be included in the guidelines as the fate, distribution and movement of NO₃ on a sand and a clay will vary dramatically.

Field studies to determine the fate of nitrogen from hog manure is important and essential to sustainable agriculture. The study reported herein did not quantify the losses of NO₃⁻ from the system. The study was also of short duration and thus long-term trends could not be examined. The data, however, showed the distribution patterns of NO₃⁻ in a sand and a clay profile and illustrated some of the potential fates of the NO₃⁻ such as leaching and denitrification. It also illustrated that manure application rates should be different for a sand or a clay textured soil. In general, at both sites, the application of hog manure resulted in NO₃⁻ levels that were highest at the surface and decreased with depth. It became evident that the addition of water through irrigation or precipitation, resulted in the movement or disappearance of NO₃⁻. It was also observed that caution should be exercised when applying hog manure or other N containing fertilizers on a sand as the groundwater at the Poppleton sandy site was contaminated with NO₃⁻.

4.2 Rates of Denitrification of Soil with and Without Manure

4.2.1 Emerson Silty Clay Loam

Nitrate concentrations remaining in soil suspensions incubated at 15°C under anaerobic conditions were examined as a function of time and depth. It was determined that the concentration of NO₃⁻ was a function of both time and soil depth (Figure 4.21). Nitrate concentrations decreased rapidly with time for surface soils. Conversely, under the same anaerobic conditions, NO₃⁻ content decreased very gradually with time for soils at the 100 to 120 cm depth. Nitrate concentrations in samples taken at the 15 to 30 cm and 30 to 60 cm depth decreased at rates between those observed for the surface depth and depths of 100 to 120 cm.

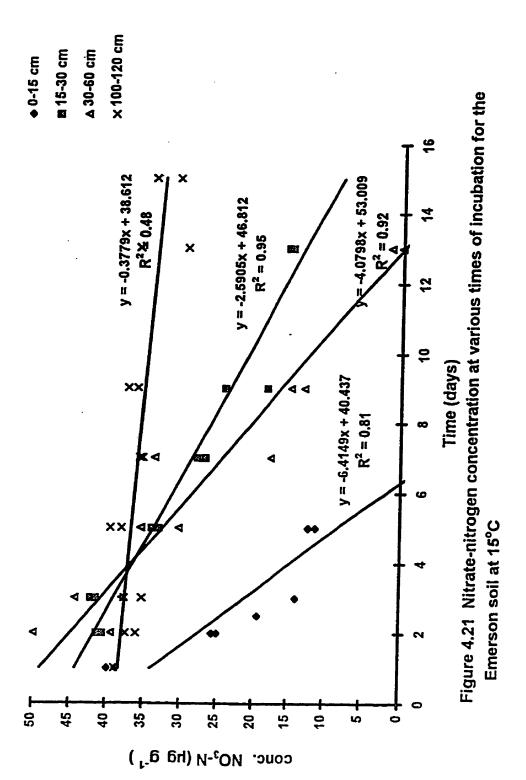
Linear regression, of concentration of nitrate vs time was calculated to determine the rate NO₃ disappearance (b), expressed in μg NO₃-N g⁻¹d⁻¹ (Figure 4.21). The nitrate disappearance rate was highest for the surface soil, (6.41 μg NO₃-N g⁻¹d⁻¹) and lowest for the 100 to 120 cm depth (0.38 μg NO₃-N g⁻¹d⁻¹). Normally, it is expected that microbial activity will be highest at the surface and decrease with depth in an exponential manner. However, in the Emerson silty clay loam profile, even though activity was the highest at the surface and lowest at the lower depth, it was noticed that the measured NO₃-disappearance rate was greater in the 30 to 60 cm sample than in the 15 to 30 cm sample. The reasons for this discrepancy are unknown. The coefficient of variation, r², ranged from 0.95 to 0.48. The lowest value of 0.48 was obtained for the 100 to 120 cm depth

sample. The extremely low value of r^2 for the 100 to 120 cm depth sample, was partly due to the very low rate of nitrate disappearance and short duration of incubation.

4.2.2 Poppleton Sand

Nitrate disappearance rates for the Poppleton sand showed a similar pattern to that observed with the Emerson silty clay loam (Figure 4.22). The rate of disappearance was fastest for the 0-15 cm sample and decreased with increasing soil depth. The nitrate disappearance rate for the surface sample was about 5.75 µg NO₃-N g⁻¹d⁻¹ and then decreased very rapidly with soil depth to a low of 0.21 µg NO₃-N g⁻¹d⁻¹ for the 100-120 cm depth. Cho and Sakdinan (1978) also found that the denitrification intensity decreased with soil depth. McCarty and Bremner (1993) indicated that a slow rate of denitrification in Iowa subsoils was not due to a lack of denitrifying microorganisms, but rather to a lack of organic C that can be utilized by these microorganisms for reduction of NO₃. As was observed with the Emerson clay loam, whenever the rate was large, the coefficient of variation, r², was large. As soil depth increased, the rate decreased and the magnitude of r² decreased as well. The nitrate disappearance rates, were also determined at 7.5°C and are shown along with those at 15°C at all depths in Table 4.4.

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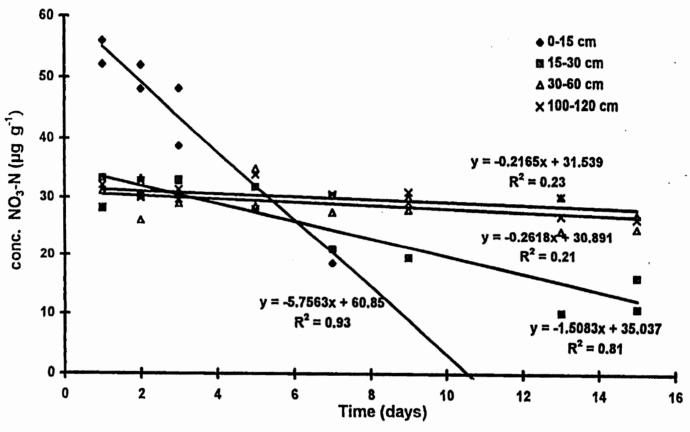


Figure 4.22 Nitrate-nitrogen concentration at various times of incubation for the Poppleton soil at 15°C

Table 4.4 Nitrate-Nitrogen disappearance rates of the Emerson clay loam and Poppleton sand profiles at 7.5°C and 15°C.

Soil Depth	Emerson Clay Loam		Poppleton Sand	
	7.5°C	15°C	7.5°C	15°C
cm	———μg NO ₃ -N g ⁻¹ d ⁻¹			
0-15	2.84	6.41	2.56	5.76
15-30	1.49	2.59	0.99	1.51
30-60	1.77	4.08	0.19	0.26
100-120	0.16	0.38	0.09	0.22

Nitrate disappearance rates at 7.5°C were about one-half of those at 15°C. The Emerson clay loam exhibited slightly higher rates of NO₃ disappearance in the 0-15 cm depth than the Poppleton sand at both temperatures; the difference was probably due to the greater organic matter content of the Emerson soil (6.33% vs 2.72 %). However, as soil depth increased, the nitrate disappearance rate decreased at a much faster rate in the Poppleton sand than in the Emerson clay loam. The magnitude of the rate at the 30-60 cm depth of the Poppleton sand was nearly one tenth of that observed with the Emerson clay loam.

In order to obtain the NO₃ disappearance rate as a function of soil depth, a semilog plot of the rate against soil depth was used. The results obtained with the Emerson clay loam at 7.5°C (Fig. 4.23) and 15°C (Fig. 4.24) showed that the rate could be reasonably expressed as a semi-log linear function of soil depth.

The regression equations were:

$$y = 1.3055 - 0.0273x$$
 $r^2 = 0.93$ at 7.5°C [4.2.1]

$$y = 2.0066 - 0.0258x$$
 $r^2 = 0.88$ at 15°C [4.2.2]

and these can be expressed as:

$$R_{7.5} = 3.69 \exp(-0.0273x)$$
 [4.2.3]

$$R_{15} = 7.44 \exp(-0.0258x)$$
 [4.2.4]

In the above equations, $R_{7.5}$ and R_{15} represent nitrate disappearance rates at 7.5°C and 15°C, respectively, whereas x is soil depth in cm.

The intercepts, 3.69 and 7.44, correspond to the nitrate disappearance rate for the soil surface at 7.5°C and 15°C, respectively. The depth dependent coefficients, -0.0273 and -0.0258 for 7.5°C and 15°C, respectively, are virtually the same, indicating that depth dependency of a soil profile was independent of temperature. The inverse of the depth dependent coefficients, 36.6 cm and 38.7 cm for 7.5°C and 15°C, respectively, correspond to the decrease in nitrate disappearance rate by 1/e for the Emerson clay loam.

The ratio between the two nitrate disappearance rates for 7.5 and 15°C was 2.01. Under ambient temperatures, Q_{10} , the ratio of rates at a temperature difference of 10°C, is generally 2 for many biological processes. In this observation, Q_{10} was 2.68, slightly higher than the value normally observed.

Coefficients of variation, for the Poppleton sand were less than those of the Emerson soil and were 0.82 and 0.67 for 7.5 and 15°C, respectively (Fig 4.25 and Fig. 4.26).

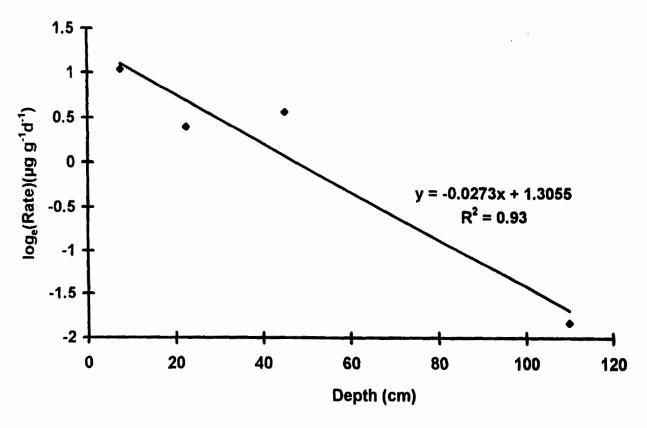
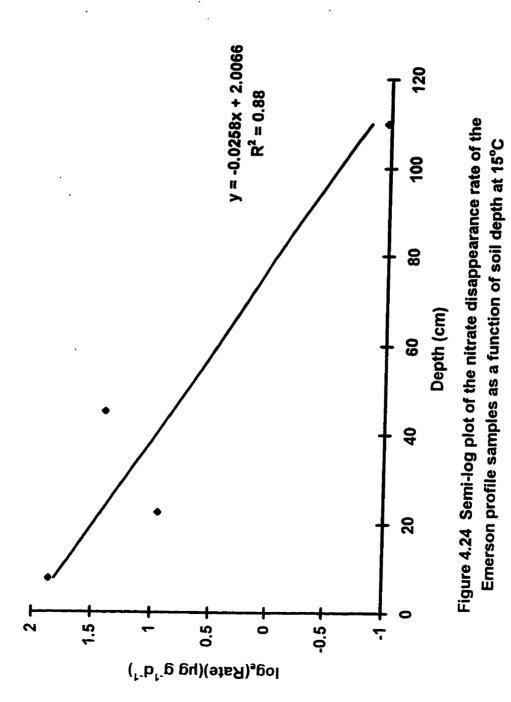


Figure 4.23 Semi-log plot of the nitrate disappearance rate of the Emerson profile samples as a function of soil depth at 7.5°C



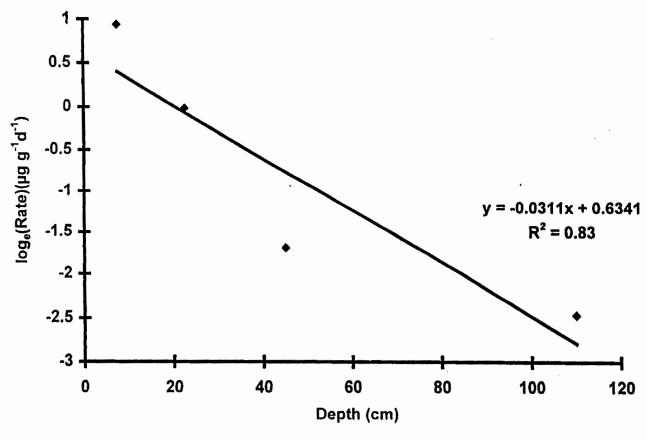


Figure 4.25 Semi-log plot of the nitrate disappearance rate of the Poppleton profile samples as a function of soil depth at 7.5°C

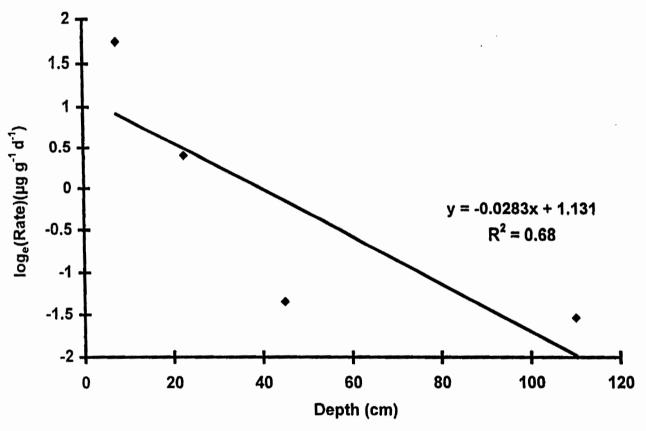


Figure 4.26 Semi-log plot of the nitrate disappearance rate of the Poppleton profile samples as a function of soil depth at 15°C

The semi-log linear model did not describe the Poppleton relationship well.

Thus, a different mathematical manipulation was used to more accurately describe the biological activity distribution of the Poppleton profile (Figures 4.27-4.28).

It was assumed that the Poppleton distribution could be expressed as R = A + Bexp(-kx), where R is the rate, A, B, k are coefficients and x is soil depth. The data point at the 100 to 120 cm depth, represented by A in the equation, was assumed to be constant because there was very little reduction in NO_3 at this depth. Thus, the value for A was subtracted from the other data points and the resulting values were plotted in a semi-log manner. The regression equations obtained were:

$$y = 1.6667 - 0.0868x$$
 $r^2 = 0.99$ at 7.5°C [4.2.5]

$$y = 2.8735 - 0.130x$$
 $r^2 = 0.99$ at 15°C [4.2.6]

Consequently the rate of NO₃ disappearance could be expressed as a function of soil depth as:

$$R_{7.5} = 0.082 + 5.296 \exp(-0.0868x)$$
 [4.2.7]

$$R_{15} = 0.202 + 17.70 \exp(-0.13x)$$
 [4.2.8]

In the above equations R_{7.5} and R₁₅ represent nitrate disappearance rate at 7.5 and 15°C, respectively. The r² obtained for these equations (Figure 4.27 and Figure 4.28) at 7.5°C and 15°C were much higher than those obtained for when the data was initially examined. The depth dependent coefficients for the modified Poppleton profile, 0.0868 and 0.13 varied more than those observed for the Emerson profile.

The nitrate disappearance rates extrapolated to the soil surface were 5.30 and 17.70 for 7.5°C and 15°C, respectively.

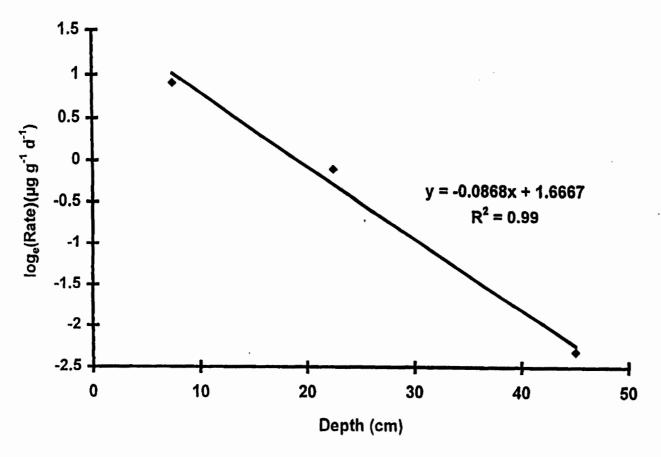


Figure 4.27 Modified Semi-log plot of the nitrate disappearance rate of the Poppleton profile samples as a function of soil depth at 7.5°C

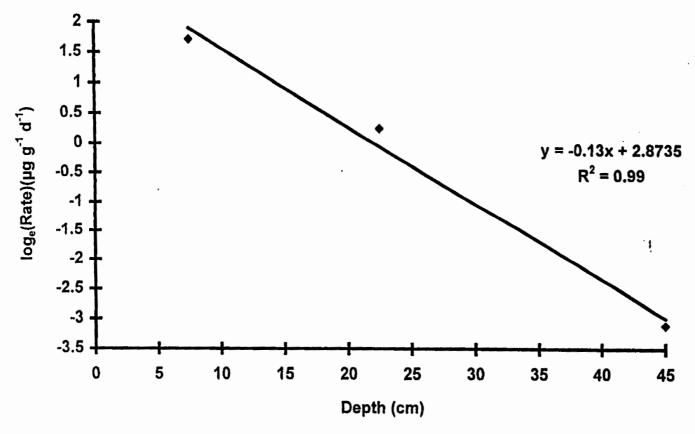


Figure 4.28 Modified Semi-log plot of the nitrate disappearance rate of the Poppleton profile samples as a function of soil depth at 15°C

The ratio of the rates was 3.34. Under ambient temperatures, the Q_{10} which is the rate between a temperature difference of 10° C ($Q_{10} = k_{T+10} / k_{T}$), is generally 2. However, since ordinary temperatures are near 300 K (27°C), many biological reactions will vary in rate by a factor of 2 or 3 over a temperature range of 10° C (Bray et al. 1957). In the Poppleton soil, the ratio based on the Q_{10} expression would be 4.45, which is slightly higher than normal, but within the range reported for denitrification (Focht and Chang 1975).

Just as the Poppleton semi-log linear was modified, Mills and Zwarich (1982) also resolved their denitrification intensity into two semi-log linear equations when they found it could not be described by one semi-log linear for sewage treated soil.

4.2.3 Nitrate Disappearance Rates of Manured Surface Soil

The NO₃ concentration remaining in the suspension of surface soils from the rate 1 and rate 2 manured treatments for both sites were plotted as a function of time at 15°C.

Again the concentration of NO₃ decreased with time (Figures 4.29, 4.30, 4.31 and 4.32).

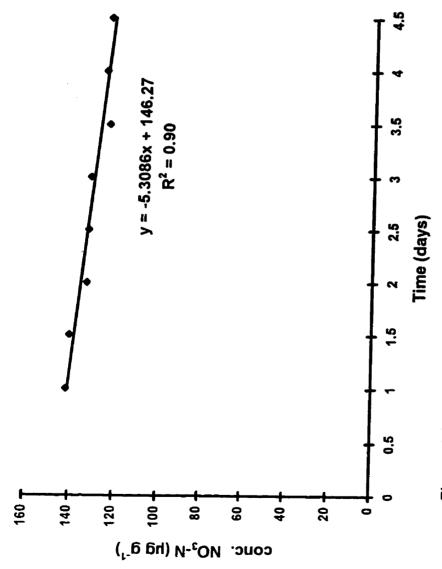


Figure 4.29 Concentration of NO₃-N in the surface samples of the rate 1 manured Emerson soil incubated at 15°C

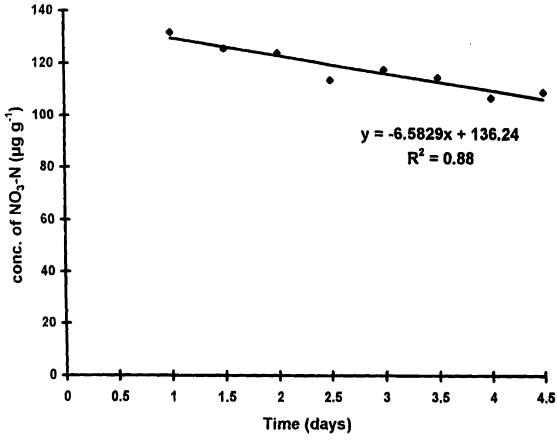


Figure 4.30 Concentration of NO₃-N in the surface samples of the rate 2 manured Emerson soil incubated at 15°C

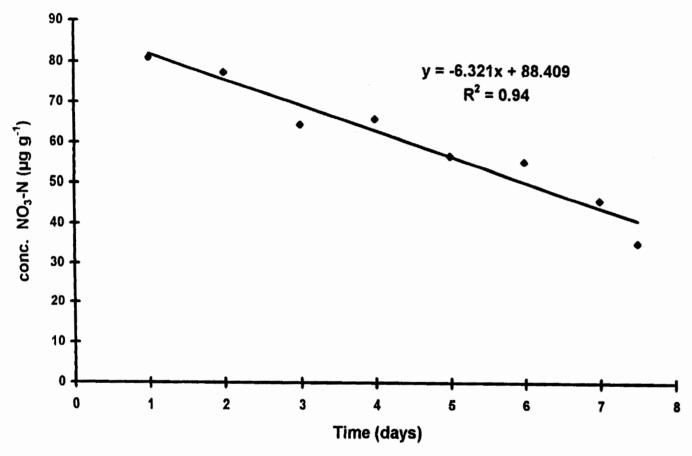
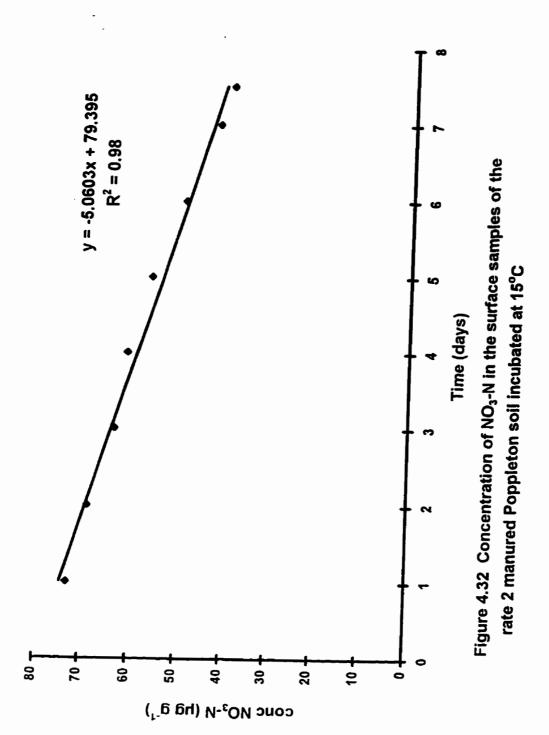


Figure 4.31 Concentration of NO₃-N in the surface samples of the rate 1 manured Poppleton soil incubated at 15°C



Denitrification rates in soils are usually increased when soils are manured if C or N is limiting denitrification (Olsen et al. 1970; Kimble et al. 1972; Guenzi et al. 1978; Cooper et al. 1984; Parkin 1987; Beauchamp et al 1989). However, in this study the NO_3 -disappearance rates, in Table 4.5 and 4.6, for both the Emerson site and the Poppleton site, were similar regardless of manure treatment. Coefficients for a and b and r^2 for linear equations (y = a + bx) related NO_3 -disappearance with time.

Table 4.5 Linear correlation equation, y = a + bx, to express the decrease in NO₃-N concentration when incubated under anaerobic conditions for control and manured surface samples of the Emerson clay loam at 15°C.

Treatment	Initial NO ₃ -N content	NO ₃ -N Disappearance Rate	r²
	μg g ⁻¹	μg g ⁻¹ d ⁻¹	
Control	40.4	-6.41	0.81
Rate 1	146.27	-5.31	0.90
Rate 2	136.24	-6.58	0.88

Table 4.6 Linear correlation equation, y = a + bx, to express the decrease in NO₃-N concentration when incubated under anaerobic conditions for manured surface samples of the Poppleton sand at 15°C.

Treatment	Initial NO ₃ -N content	NO ₃ -N Disappearance Rate	r²
	µg g ^{·l}	µg g ⁻¹ d ⁻¹	
Control	60.8	-5.75	0.93
Rate I	79.40	-5.06	0.98
Rate 2	88.41	-6.32	0.94

Denitrification rates may not have increased due to manure treatments in our study because of previous manure applications masking effects of the single application studied. The Emerson soil had been manured every 4 years during the past 24 years and thus organic carbon may not have limited denitrification even in the untreated soil. Similarly the Poppleton sand had received manure every two years over the last 10 years. The chemical and physical properties of the soils which have received many applications of manures are greatly altered (Sommerfeldt and Chang 1985, 1987) and this in turn may have affected the rate of NO₃ disappearance. It is also possible that there may not have been enough soluble C available to increase the denitrification rates on the manured soils.

4.3 Simulation of the Steady State Oxygen Distribution and Aerobic-Anaerobic Boundaries in the Soil Profile to Predict the Stability of NO₃

4.3.1 Seasonal steady-state oxygen distribution

Steady state distributions of oxygen in the two soil profiles under different moisture contents and temperatures were determined. The effect of temperature upon the aerobic-anaerobic boundary within the soil profile and the stability of NO₃ were examined using the distribution patterns of temperature for the months of May to September with and without irrigation. Typical temperature distributions of Manitoba soils were shown previously in Figure 4.9. Surface soil was near 10°C in May and then decreased with depth to 3°C at 150 cm. As the season progressed, the surface temperature rose to a maximum of 18°C. However, the rise in temperature of the sub-soil was rather slow. During September, the surface soil temperature started to decrease rather quickly whereas subsoil temperatures continued to increase.

The depth of the aerobic zone was estimated using the calculated seasonal temperature profile, the moisture and bulk density values from the field and estimated oxygen consumption rates using laboratory measured nitrate disappearance rates. The silty clay soil had a maximum surface oxygen consumption rate of 0.001 µmol ml⁻¹min⁻¹ at 20°C and a depth coefficient, k, of 0.0258 cm⁻¹. The Poppleton sand had a maximum surface oxygen consumption rate of 0.003 µmol ml⁻¹min⁻¹ and a depth coefficient, k, of 0.13 cm⁻¹. Oxygen consumption rates in the field could not be measured with depth thus, interpretation of NO₃ stability was based on the calculation of the oxygen profile.

4.3.1.1 Emerson Silty Clay Loam The oxygen content in the soil decreased with increasing soil depth and an anaerobic zone was usually encountered. The degree of anaerobiosis within the soil profile is one of the most important factors that determines the stability of NO₃⁻ and hence it's fate. Nitrate within the aerobic layer of the profile would be relatively stable, however, just below the aerobic-anaerobic interface, NO₃⁻ would be subject to denitrification. The model used in this study determines where the aerobic-anaerobic interface occurs from parameters measured in the field and laboratory and hence predicts the stability of NO₃⁻. The biological activity of the soil, expressed as the oxygen consumption rate, at the aerobic-anaerobic boundary, was also calculated (Table 4.7).

Table 4.7 Depth of Aerobic-Anaerobic boundaries and the Oxygen Consumption Rate (OCR) at the Boundaries.

Date	Emerson Clay Loam		Poppleton Sand	
	Boundary	OCR	Boundary	OCR
	cm	μ mol mi^{-ι}min^{-ι}	cm	μ mol ml⁻¹min -1
May 15/11	102	7.99 x 10 ⁻⁶	> 300	-
June 13	194	9.27 x 10 ⁻⁷	286	3.04×10^{-20}
July 11	272	1.59×10^{-7}	184	3.09×10^{-14}
July 11	148	7.15 x 10 ⁻⁶	208	1.19×10^{-15}
(irrigated)				
August	180	3.76×10^{-6}	200	5.48×10^{-15}
23/24				
August	166	6.22×10^{-6}	140	1.86×10^{-11}
23/24				
(irrigated)				
September	226	1.06×10^{-6}	170	3.51×10^{-13}
18				
September	194	2.8 x 10 ⁻⁶	154	3.01×10^{-12}
18				
(irrigated)				

The shallowest boundary for the Emerson soil was at 102 cm and occurred in May. The boundaries varied from as shallow as 102 cm in May to as deep as 272 cm in July. The very deep aerobic boundary on July 11 was likely due to low soil moisture contents due to lack of precipitation (Figure 4.1). Low soil water content would result in more soil pores filled with air as opposed to water and this in turn would allow oxygen to penetrate deeper in the profile and the NO₃ would be more stable in the profile. For nonirrigated treatments on the Emerson soil the depth to the aerobic zone was 272 cm by July and then decreased to 166 cm in August. Precipitation in August was 99.5 mm and this undoubtedly caused a decrease in the depth to the anaerobic boundary. The decrease in depth to the anaerobic boundary would favor more denitrification higher up in the soil profile. Increases in soil moisture are known to decrease NO₃ stability and increase denitrification (Wijler and Dlewiche 1954; MaCrae et al. 1968; Bailey and Beauchamp 1973b; Aulakh et al. 1982; Doran et al. 1990). Apart from the increased moisture content, there was also an increase in the subsurface soil temperatures at the aerobicanaerobic boundary from May (3.1°C) to August (8.4°C) (Figure 4.9). Cho et al. (1996) found that the magnitude of denitrification was smallest in the spring and largest in September because of the fact that in September subsurface temperatures were warmer. In this study the calculated aerobic boundary was slightly deeper in September than August. This was probably attributable to the higher amounts precipitation that occurred in August as opposed to September.

Irrigation of the Emerson soil increased the soil moisture content enough to reduce the depth to the aerobic-anaerobic boundary. Irrigation reduced boundaries from 272 to 148 cm and from 226 to 194 cm in July and September respectively. Thus, the

addition of water, made the soil more anaerobic and enhanced the disappearance of NO₃. It was also noticed that although there was no irrigation in August, the irrigated plot still had slightly higher moisture contents than the non-irrigated plot. The aerobic boundary for the irrigated and non-irrigated plots were 168 cm and 226 cm respectively. The addition of water was a dominant and controlling factor that affected the stability of NO₃ in the profile.

The rate of oxygen consumption by microorganisms also affects the stability of NO₃ in the profile. Oxygen consumption rates (OCR) and nitrate disappearance rates (NDR) normally decrease with depth from the aerobic boundary due to decreases in soil temperatures and decreases in microbial activity. Cho et al. (1996) illustrated that the depth of the aerobic zone was important in controlling the magnitude of denitrification since the microbial activity generally decreased with depth. It was concluded that when the depth to the aerobic-anaerobic boundary was deep and the microbial activity was low, denitrification was also slow. For example, the oxygen consumption rate in May at the 102 cm depth was very low (7.99 x 10⁻⁶ μmol ml⁻¹min⁻¹). The corresponding NDR was about one half the OCR. It was noted, however, that both the OCR and the NDR were still quite small below the 102 cm boundary and thus denitrification would be very small. Low oxygen consumption rates at the aerobic boundary are one of the main reasons that quantities of NO₃ still remain below the boundary level. For example, there was some NO₃ at the 194 cm boundary in the soil on June 13 (Figure 4.11). It is possible that the concentration of NO₃ in this region may have been due to continued influx of NO₃ from upper depths and/or the relatively slow rate of denitrification as indicated by the low

oxygen consumption rate (9.27 x 10⁻⁷ μmol ml⁻¹min⁻¹) at the boundary. This was seen again in July when the field study indicated that there was still some NO₃⁻ present at the calculated aerobic-anaerobic boundary of 272 cm. This could be due to the low rainfall or the low OCR and NDR as a result of low temperatures, low levels of substrate and low microbial activities (Figure 4.12).

4.3.1.2 Poppleton Sand The Poppleton sand was very heterogeneous in nature mainly due to the presence of two gravel lenses in the profile. These gravel lenses gave rise to discrepancies between bulk densities and measured soil moisture values which posed problems when using the model to predict NO₃ stability and aerobic-anaerobic boundaries. Thus in order to obtain continuous moisture distributions, bulk densities determined to be greater than 1.69 were disregarded and assigned a value of 1.69.

The aerobic-anaerobic boundary was below the 300 cm depth in May. The shallowest boundary, excluding irrigation treatments, occurred in September and was at a depth of 170 cm. The decreased boundary in September was due to warmer subsoil temperatures coupled with increased soil moisture. Increases in water content and temperature favor instability of NO₃ (Knowles 1982; Aulakh et al. 1992; Cho et al. 1996). Depth to the boundary was greatest in the spring and generally decreased during the growing season and early fall.

Irrigation in July at the Poppleton site did not affect the depth to the aerobicanaerobic boundary. However, in September, depth to the boundary was less for the irrigated plots than for the non-irrigated plots. Moisture contents of the irrigated and nonirrigated profiles in July were similar thus differences in depths to the boundary were not observed. Again, similar to the Emerson soil, the decreased aerobic boundary seen in September was due to greater soil temperatures and increased soil moisture. It is also possible that more rain in the end of the summer moved the NO₃ further down the profile.

The oxygen consumption rates at the aerobic boundary of the Poppleton sand were very small and even slower than those observed at the Emerson clay loam. Oxygen consumption rates for the Emerson clay loam were usually in the magnitude of 10⁻⁶-10⁻⁷ μmol ml⁻¹min⁻¹ whereas the oxygen consumption rates in the Poppleton sand were 10⁻¹¹-10⁻²⁰ µmol ml⁻¹min⁻¹. These findings were not surprising because it was expected that the oxygen consumption rates on the sand would be smaller since the sand had a low organic matter content (Table 3.1 and Table 3.2). Oxygen consumption rates on the sand were smallest in the spring and increased in the fall when the subsurface temperatures increased. As previously seen in the clay, the presence of nitrate below the aerobic boundary in the sand was also predicted by the model and illustrated in the field. Again, the presence of nitrate at depth was probably attributed to low microbial activity due to lower temperatures and less substrate causing low OCR's and hence lower nitrate disappearance rates. Low oxygen consumption rates would result in a very slow decrease in NO₃ concentrations whereas high oxygen consumption rates would result in greater NO₃ disappearance rates.

In summary, the boundaries determined by the model were similar to those seen in the field and it explained the field distributions of NO₃⁻ well. The examination of oxygen consumption rates at the aerobic boundary also explained some of the NO₃⁻

distribution patterns seen in the field. The non-irrigated Poppleton profiles in May, June, and August had deeper aerobic boundaries than the Emerson silty clay loam. The deeper boundaries obtained for the Poppleton sand were expected as sands have large and continuous pores which facilitate rapid air and water movement. In contrast, clays have very small pore spaces which result in slower transport of air and water. However, it was noticed that the Poppleton sand had a shallower boundary than the Emerson clay on July 11 and September 18 because the soil moisture content in the sand was very high (29-35 %). The increased moisture content could be attributed to the water table moving up in the soil profile.

4.3.2 Soil Moisture Redistribution

4.3.2.1 Emerson Silty Clay Loam In order to more specifically determine the effect of additional water or rainfall on the aerobic-anaerobic boundary and thus the stability of NO₃ in the soil profile with time, a redistribution of O₂ from one moisture content to another was modeled. Initial moisture values were based on the soil moisture contents of the irrigated plots as measured in the field. Final moisture values were calculated assuming 6 cm of precipitation occurred (an amount chosen to closely simulate a 6 cm rainfall event that occurred in the summer of 1995) on the Emerson silty clay loam. Moisture redistribution within the profile to a depth of three meters was determined assuming the fresh rainfall was redistributed in the surface zone, with the surface moisture starting at 42 % which then decreased exponentially with depth, similar to the data shown by Salvucci and Entekhabi (1994). Oxygen redistribution events were calculated for the months of September and August as this was when most of the rain occurred in the summer of 1995. In this model, the post-rainfall event is wetter than the

pre-rainfall event. However the major differences in the moisture distribution occurred in the top part of the soil profile. According to the model, the greatest change in moisture distribution occurred above the 135 cm depth in August and above the 105 cm depth in September for the Emerson clay loam. Below the 135 and 105 cm depths the moisture distribution for the post rainfall event was assumed to be the same as for the pre-rainfall event. The non-steady state oxygen concentration profiles for August and September were plotted against soil depth and are shown in Figure 4.33 and Figure 4.34. The top line on the graph represents the steady-state oxygen distribution before the 6 cm rainfall event and each corresponding line represents days 1-5 after the rainfall event. The concentration of oxygen decreased at about the 50-60 cm region after the initial rainfall event. This pattern was observed in both August and September, however, oxygen concentrations decreased to a greater extent in August than in September. If the model had been run for 10 days as opposed to 5 days it is likely that the oxygen concentration would have reached zero at the 50-60 cm region. The 50-60 cm region not only had an increased amount of soil moisture and decreased oxygen contents, but it also had a relatively high amount of microbial activity due to warm temperatures and the presence of sufficient substrate for denitrification.

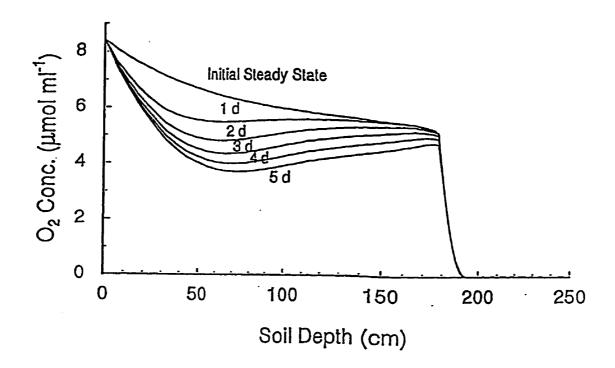


Figure 4.34 Calculated redistribution of O₂ after 6 cm of rainfall on the Emerson soil on September 18, 1995.

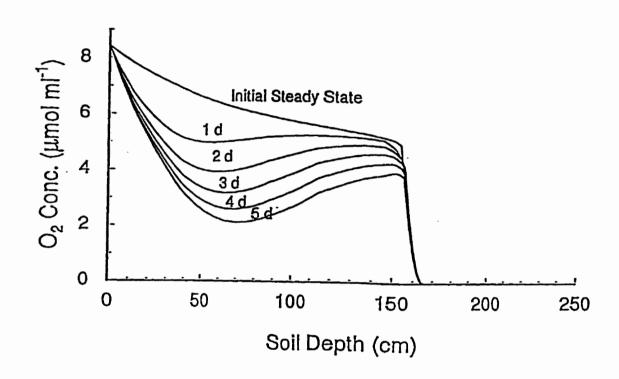


Figure 4.33 Calculated redistribution of O₂ after 6 cm of rainfall on the Emerson soil on August 23, 1995.

The model calculation of oxygen concentration after the rainfall event showed trends similar to those observed for NO₃ distribution in the field in August (Figure 4.13). Trends observed for NO₃ concentrations in the field in August decreased to zero in the irrigated plot at the 50 cm depth after a rainfall event. In September a similar pattern was demonstrated as NO₃ also decreased to non-detectable levels in the 50-100 cm region. Even though the model predicted a decrease in oxygen concentration at the 50-100 cm depth, the model did not predict zero values of O₂ concentration. Discrepancies in the amount of oxygen that disappeared at this depth was likely due to differences in moisture contents and the time period that was used in the model to calculate the oxygen concentrations. It is also possible that carbon availability may have altered the subsurface OCR rate. The important aspect to focus on is the pattern of oxygen depletion at various zones in the soil profile as oxygen concentration in the profile is the most important factor affecting NO₃ stability. Data from the field study showed that a rainfall event affected the distribution and stability of NO₃ in the soil profile. The rain created an intense area of denitrification at an intermediate depth. The predictions offered by this model, using similar conditions, confirmed that a rainfall event greatly affects the oxygen status of the soil profile, the stability of nitrate and thus nitrate distributions in soils. 4.3.2.2 Poppleton Sand In order to determine the effect of the addition of water or a rainfall event on the aerobic boundary and stability of NO₃ in the soil profile with time, a calculation of the distribution of O₂ after the rainfall event was also performed for the Poppleton sand. However, due to the heterogeneous mixture of the Poppleton profile which included two gravel lenses that occurred at 50 cm and at 100 cm a moisture redistribution calculation on this site could not be performed. The gravel lenses caused

problems when measuring bulk density and this in turn affected the moisture content values in the model. Since moisture contents affect oxygen distribution and NO₃⁻ stability, predicting the stability of NO₃⁻ after the moisture redistribution event on the sand proved unsuccessful.

CHAPTER 5

SUMMARY AND CONCLUSIONS

The basic objective of this project was to determine the fate of nitrate in clay (Emerson) and sandy (Poppleton) soils treated with hog manure. A field study, laboratory study and mathematical model were used to investigate the distribution of nitrate in the soil, and the fate of nitrate, particularly the losses via denitrification in the soil profile. Application of hog manure to field plots affected the distribution of NO₃ in the soil and groundwater. At both sites nitrate concentrations were highest in surface soils and decreased with depth. Water, added by irrigation or precipitation, resulted in the downward movement and/or disappearance of NO₃ (which was attributed to denitrification). High NO₃ levels in groundwater suggest caution should be exercised in the application of N containing fertilizers including hog manure on coarse textured soils. Denitrification was shown to occur in July on the sand. However, it was under conditions of high soil temperatures and extremely high moisture contents. These conditions would probably not occur frequently enough to denitrify all the NO₃ prior to leaching to the groundwater. The application of hog manure to the Emerson soil resulted in excessive levels of NO₃ in the 0-120 cm depth. However nitrate concentrations below this depth were small, particularly in the fall. The low concentration of nitrate at depths below 120

cm were attributed to losses via denitrification and this denitrification intensity increased in the fall due to warmer subsurface temperatures and increased soil moisture content.

Laboratory studies were conducted to determine the oxygen consumption rates and nitrate disappearance rates under anaerobic conditions at depths to 120 cm. This study was conducted to obtain information on the denitrification intensity of the soil profiles. The disappearance of NO₃ under anaerobic conditions was a function of soil temperature and depth. The NDR was higher at 15°C than at 7.5°C and decreased with soil depth. The Emerson silty clay loam had slightly higher NDR's than the Poppleton sand at the soil surface. The NDR of the Poppleton sand decreased very rapidly with depth and was much lower than the NDR for the Emerson profile at depths of 0 to 120 cm. Denitrification potential was not increased by the application of manures. Both sites had received manure on a regular basis for a number of years. Thus the control and treated soils were probably similar in physical properties, tilth, and amount of available carbon which may have accounted for the similar rates of denitrification among the treatments.

The nitrate disappearance rates determined in the laboratory study were used in the model to predict the stability of NO₃⁻ in the soil. The stability of nitrate, as predicted by the model, matched data observed in the field. Thus the model could be used to predict the stability of NO₃⁻ and hence the fate of NO₃⁻ under different situations. The depth to the aerobic-anaerobic boundary was found to be a controlling factor in the stability of NO₃⁻. Irrigated plots which had higher moisture contents than non-irrigated plots had shallower aerobic boundaries than non-irrigated values and hence NO₃⁻ was less stable in the irrigated plots. The model also illustrated that the oxygen consumption rates of the

microorganisms at the aerobic boundary affected the stability of NO₃. Low oxygen consumption rates, due to decreased temperatures and substrate at a deep aerobic boundary, resulted in slow decreases of NO₃ at that depth as NO₃ would be more stable. Oxygen consumption rates for the sand were lower than those for the clay. The oxygen consumption rates for the sand were lowest in the spring and increased in the fall whereas the oxygen consumption rates of the clay were more consistent over time.

The model was used to illustrate the effect of irrigation and/or a rainfall event on the moisture redistribution and thus oxygen concentrations with depth over time. Increased water content decreased NO₃ stability. The model showed that a rainfall event would affect moisture distribution and oxygen concentration in the soil, and an anaerobic zone formed at an intermediate depth where nitrate was not stable. Nitrate at this intermediate depth was subject to intense denitrification and this was not only due to increased moisture content but it was also enhanced due to the increased microbial activity as a result of warmer temperatures and higher levels of substrate at this intermediate depth as compared to a deeper depth. Thus it is evident that rainfall events can have a profound affect on denitrification. The ability to predict the stability of NO₃ with a model has important implications for determining the fate of manure N which would in turn help develop more accurate manure application rates in the future and prevent contamination problems.

It is evident from this study that the current Manitoba guidelines for manure and fertilizer applications need to be refined and that caution should be exercised particularly for manure application to coarse textured soils. When the concentration of NO₃-N was examined up to the 120 cm depth in the guidelines as suggested, the sandy soil appeared

to be within the regulation (<160 kg N ha⁻¹ to 120cm) even though both the groundwater and the soil solution measurements below this depth were in excess of the Canadian drinking water guidelines of 10 µg NO₃-N L⁻¹. From the excessively high levels found on the sand (45 µg NO₃-N L⁻¹), it is apparent that NO₃⁻ has been leaching and accumulating with depth. Therefore it is evident that manure application rates in the guidelines should take soil texture into account and manure rates should be less on a coarse textured soil as opposed to a fine textured soil. This point further stresses that the assessment of NO₃⁻ distribution in the soil profile and transport of NO₃⁻ to groundwater requires sampling to depths of at least 3 meters to see if NO₃⁻ is moving down past the rooting depth. It is also important to express concentrations of NO₃⁻ on a soil solution basis to obtain a more accurate picture of the transport of NO₃⁻ in the soil and groundwater.

The study reported herein did not obtain sufficient information on the fate of various rates of manure N in soils to make recommendations on sustainable rates of manure application on various soils. Specific application rates which result in increased crop yield while minimizing the potential for ground water contamination still need to be addressed. The study did determine some of the fates of manure N in soils. However, a complete understanding of the fate of manure nitrogen is still required. Data obtained in the field study were only of one year duration and residual effects of nitrogen from previous years could not be excluded totally from the interpretation of the results. Nitrate distribution is also greatly affected by climatic factors such as temperature and rainfall and studies over a period of several years are needed. Another factor that this investigation illustrated was that denitrification rates increased in the fall. Future work should be conducted to determine denitrification potentials of soils in the winter. In the future,

effects of other manure constituents particularly phosphorus, salts and micronutrients should also be examined

CHAPTER 6

CONTRIBUTION TO KNOWLEDGE

This project illustrated that a mathematical model developed using laboratory and field data could be used to predict the stability of NO₃⁻ in soil profiles reasonably well. Denitrification rates were determined to be a function of temperature, soil depth and moisture content. It was also found that the depth of the aerobic-anaerobic boundary along with oxygen consumption rates at these boundaries were important controlling factors in predicting the stability of NO₃⁻ in the soil profile. Determining the stability of NO₃⁻ is important to understand of the fate of manure N. A better knowledge of the fate of N is needed so that producers can maximize crop yields yet minimize soil and groundwater contamination.

Nitrate levels found in the Poppleton site which exceeded the Canadian drinking water guidelines illustrate that application rates and time of application of hog manure or other N containing fertilizers on coarse textured soils should be strictly controlled. In the clay soil, it was evident that below 120 cm the concentration of NO₃⁻ was quite small, especially in the fall, indicating that nitrate could be readily denitrified in the Emerson soil profile limiting the leaching of nitrate i.e. nitrate probably denitrified before it leached below rooting depth.

Large rainfall events or irrigation resulted in either an increased downward movement of NO₃ or a disappearance of NO₃ through denitrification. It was also observed that there was increased denitrification in the fall and studies on denitrification in late fall and winter in soils have to be conducted to more fully understand the fate of nitrate in manured soils.

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APPENDICES

I Significant differences found using Wilcoxon's test

Emerson Silty Clay Loam	Poppleton Sand		
Rate 2 vs Irrigation	Rate 2 vs Irrigation		
	Control vs Rate 1		
Rate 2 vs Irrigation			
Control vs Rate 1			
Rate 2 vs Irrigation			
Rate 2 vs Irrigation	Rate 1 vs Rate 2		
Rate 1 vs Rate 2			
	Rate 2 vs Irrigation Rate 2 vs Irrigation Control vs Rate 1 Rate 2 vs Irrigation Rate 2 vs Irrigation		

II a Emerson ANOVA of depth vs. treatment on May 30

Source	SS	df	MS	F	P	
Main Effects		***************************************	***************************************		***************************************	
Depth	4404.85	1	4404.85	10.87	.0064	**
	558.58	2	279.29	0.69	.5209	ns
Treatment						
Interaction						
Depth x Treatment	809.31	2	404.66	1.0	.3972	ns
Error	4864.35	12				
Total	10637.09	17				

II b Emerson ANOVA of depth vs. treatment on June 13

Source	SS	df	MS	F	P	
Main Effects		***************************************		***************************************	***************************************	***************************************
Depth	6801.67	1	6801.67	4.99	.0454	*
Treatment	1806.65	2	903.32	0.6622	.5335	ns
Interaction	1					
Depth x Treatment	1654.02	2	827.01	0.606	.5612	ns
Error Total	16367.10 26629.45	12 17	1363.93			

II c Emerson ANOVA of depth vs. treatment on July 11

Source	SS	df	MS	F	P	V
Main Effects					***************************************	
Depth	271.38	l	271.37	9.91	.0084	**
Treatment	542.51	2	271.26	9.90	.0029	**
Interaction						
Depth x Treatment	80.97	2	40.49	1.48	.2668	ns
Error Total	328.66 1223.51	12 17	27.39			

II d Poppleton ANOVA of depth vs. treatment on May 11

Source	SS	df	MS	F	P	*************************
Main Effects		1		***************************************	***************************************	***************************************
Depth	289.12	1	289.12	12.79	.0038	**
Treatment	64.87	2	32.44	1.44	.2761	ns
Interaction						
Depth x Treatment	47.18	2	23.59	1.04	.3820	ns
Error Total	271.16 672.33	12 17	22.60			

II e Poppleton ANOVA of depth vs. treatment on May 25

Source	SS	df	MS	F	P	·
Main Effects		***************************************		***************************************		***************************************
Depth	881.58	1	881.58	11.53	.0053	**
Treatment	24.92	2	12.46	0.16	.8514	ns
Interaction						
Depth x Treatment	63.39	2	31.70	.41	.6697	ns
Error Total	917.40 1887.30	12 17	76.45			

II f Poppleton ANOVA of depth vs. treatment on June 13

Source	SS	df	MS	F	P	
Main Effects						***************************************
Depth	310.25	I	310.25	5.026	.0446	*
Treatment	254.11	2	127.05	2.06	.1704	ns
Interaction						
Depth x Treatment	66.26	2	33.13	0.54	.5981	ns
Error Total	740.74 1371.37	12 17	61.73			

II g Poppleton ANOVA of depth vs. treatment on July 11

Source	SS	df	MS	F	P	
Main Effects	***************************************	***************************************		***************************************	***************************************	******************************
Depth	191.82	1	191.82	9.73	.0089	**
Treatment	103.26	2	51.63	2.62	.1139	ns
Interaction						
Depth x Treatment	53.54	2	26.77	1.36	.2941	ns
Error Total	236.64 585.26	12 17	19.72			

 Π h Poppleton ANOVA of depth vs. treatment on September 18

Source	SS	df	MS	F	P	
Main Effects	***************************************		***************************************		***************************************	
Depth	45.82	1	45.82	5.69	.0344	*
Treatment	6.35	2	3.18	0.39	.6824	ns
Interaction						
Depth x Treatment	5.34	2	2.67	0.33	.7239	ns
Error Total	96.57 154.08	12 17	8.05			

III a Emerson field coefficients of variation on May 30

	Control		Rate 1		Rate 2		
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution	
0-15	47.2	51.1	22.8	23.4	70.0	66.7	
15-30	83.0	87.4	32.7	37.5	68.7	67.9	
30-45	94.2	97.6	37.4	41.4	10.9	18.0	
45-60	64.4	69.8	41.5	37.8	76.3	76.9	
60-75	84.9	87.4	44.8	45.4	113.2	113.8	
75-90	90.7	85.6	60.2	59.3	52.9	53.8	
90-105	51.8	53.4	38.4	41.1	57.5	56.5	
105-120	49.3	44.5	36.7	35.6	32.6	36.2	

III b Emerson field coefficients of variation on June 13

	Control		Rate 1		Rate 2	······································
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	· 68.6	71.7	54.7	50.8	121.5	117.1
15-30	39.5	41.8	83.7	80.8	44.2	48.6
30-45	31.1	38.2	108.5	100.5	61.4	68 .1
45-60	49.1	55.5	127.2	129.7	42.2	40.1
60-75	52.6	54.3	92.7	95.3	173.2	173.2
75-90 .	82.9	79.6	84.3	84.8	86.8	86.1
90-105	46.8	46.4	59.4	62.5	54.4	54.8
105-120	113.0	115.2	112.0	104.4	42.7	40.6
120-150	87.4	90.6	23.1	19.6	105.5	100.6
150-200	59.1	66.4	120.3	123.0	152.2	154.6
200-250 ⁻	173.2	173.2	89.6	100.1	90.8	86.6
250-300	8.4	36.2	173.2	173.2	73.7	81.4

Ш с Emerson field coefficients of variation on July 11

	Control		Rate 1		Rate 2	
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	7.2	14.4	31.1	21.7	15.7	15.9
15-30	26.7	36.6	50.6	44.3	60.8	53.1
30-45	9.0	21.0	24.1	31.2	55.6	50.2
45-60	30.9	25.8	53.9	58 .1	76.9	76 .1
60-75	88.6	90.5	69.9	67.3	58.2	88.2
75-90	66.2	69.6	34.5	40.9	24.3	9.6
90-105	96.6	105.8	46.0	50.6	33.8	35.5
105-120	139.1	135.8	82.7	81.2	46.8	46.5
120-150	78 .6	74.9	73.7	65.7	62.0	62.2
150-200	113.2	115.9	66.5	70.3	34.4	44.9
200-250	70.1	70.2	10.2	9.2	23.7	43.3
250-300	64.2	63.1	9.3	17.0	32.0	27.5

III d Emerson field coefficients of variation on August 23

	Control		Rate 1		Rate 2	
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	· 16.0	7.8	96.6	88.2	89.7	91.1
15-30	68.1	65.2	117.9	114.4	59.5	61.6
30-45	123.0	123.0	124.5	121.1	38.3	44.6
45-60	116.2	107.9	95.7	90.4	29.8	32.2
60-75	129.1	134.9	39.2	47.9	56.4	79.2
75-90	109.3	116.1	116.4	122.0	71.3	57.9
90-105	107.3	112.2	48.0	53.4	113.9	107.8
105-120	108.9	110.8	94.7	80.4	46.4	36.9
120-150	86.5	81.7	85.5	95.7	35.3	30.7
150-200	53.5	49.7	60.1	57.9	40.1	45.9
200 -250	71.0	40.8	57.2	51.4	30.0	61.1
250-300	35.4	55.4	77.4	83.2	52.7	17.0

III e Emerson field coefficients of variation on September 18

	Control		Rate 1		Rate 2	
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	57.7	56.0	37.2	42.5	58.5	26.6
15-30	97.3	96.3	58.4	55.5	52.6	55.3
30-45	73.5	74.1	84.3	87.2	64 .1	60.3
45-60	117.6	122.4	63.9	66.8	173.2	173.2
60-75	99.1	96.3	86.7	81.5	70.7	67 .0
75-90	105.5	113.0	144.9	144.9	77.9	74.8
90-105	114.6	114.6	135.0	132.0	173.2	173.2
105-120	82.5	70.6	107.9	114.8	87.5	88.1
120-150	52.2	52.8	151.7	153.1	38.5	24.9
150-200	36.6	38.7	73.0	75.2	138.3	141.6
200-250	26.1	33.3	7 0.6	<i>7</i> 6.8	132.3	136.2
250-300	5.7	27.4	109.1	113.0	173.2	173.2

III f Poppleton field coefficients of variation on May 25

	Control		Rate 1	Rate 2			
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution	
0-15	51.7	33.5	92.2	72.1	32.3	30.3	
15-30	65.6	85.9	75.8	84.5	57.4	30.5	
30-45	64.5	88.1	91.1	99.4	62.1	55.6	
45-60	146.4	123.1	17.5	31.6	44.7	32.9	
60-75	57.2	76 .1	55.6	83.2	55.5	63.2	
75-90	89.7	91.2	11.8	42.7	26.9	41.9	
90-105	108.1	91.1	49.6	65.8	35.5	20.0	
105-120	90.1	87.0	79.3	0.08	59.1	74.5	

III g Poppleton field coefficients of variation on June 13

	Control		Rate 1		Rate 2	
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	72.3	78 .5	63.8	75.3	32.0	8.7
15-30	10.5	40.3	70.5	73.9	59.5	50.4
30-45	101.9	99.2	72.9	67.5	74.6	69.1
45-60	83.4	53.3	53.8	67.1	41.3	44.3
60-75	53.4	35.2	92.2	91.3	92.8	89.7
75-90	88.6	96.0	64.7	67.6	141.0	140.1
90-105	134.6	134.1	83.8	84.5	42.8	38.8
105-120	77.6	87.6	123.3	111.1	58.0	58.3
120-150	74.7	67.5	47.8	40.1	32.3	46.4
150-200	43.1	54.6	28.2	19.5	79.8	46.6
200-250	33.6	38.4	62.7	50.0	35.4	25.1
250-300	55.4	50.7	54.0	48.3	32.2	36.6

III h Poppleton field coefficients of variation on July 11

	Control		Rate 1		Rate 2	
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	. 79.0	93.5	61.7	101.5	58.6	60.1
15-30	117.6	131.5	89 .0	73 .7	173.2	173.2
30-45	0.0	0.0	173.2	173.2	100.4	96 .9
45-60	0.0	0.0	126.2	119.1	80.7	78.2
60-75	142.2	147.4	165.6	164.8	99.5	103.3
75-90	64.7	50.4	143.1	141.1	95.3	81.5
90-105	173.2	173.2	107.9	97.2	118.7	104.7
105-120	125.5	138.6	87.2	95.5	46.2	37.4
120-150	113.2	114.8	91.2	91.9	55.6	69.5
150-200	43.0	61.7	124.5	126.4	47.3	50.1
200-250	115.1	102.5	44.8	35.0	87.8	92.0
250-300	69.0	60.9	59.3	51.7	28.8	35.2

III i Poppleton field coefficients of variation on August 24

	Control		Rate 1		Rate 2	
Depth	cv soil	cv solution	cv soil	cv solution	cv soil	cv solution
0-15	47.0	50.1	30.2	17.6	35.9	67.5
15-30	173.2	173.2	106.5	106.3	146.6	133.1
30-45	95.6	89.1	108.9	114.2	54.7	54.6
45-60	99.3	104.7	30.7	17.7	27.3	24.9
60-75	52.0	57.5	73.9	72.6	32.0	46.8
75-90	55.6	53.4	9.7	12.5	27.4	37.1
90-105	138.4	145.3	64.1	62.7	22.4	28.4
105-120	43.9	46.5	43.1	41.6	51.1	43.9
120-150	24.9	10.6	33.7	25.4	45.0	68.0
150-200	34.2	55.0	21.4	25.5	37.4	23.2
200-250	26.8	12.8	19.6	22.1	59.8	53.5
250-300	30.0	29.2	58.3	62.6	87.1	88.5

III j Poppleton field coefficients of variation on September 18

***************************************	Control		Rate 1		Rate 2	
Depth	CY	CV	CV	CV	CV	CV
	soil	solution	soil	solution	soil	solution
0-15	- 70 .1	69.7	41.8	33.6	15.1	31.7
15-30	28.8	16.3	70.5	48.4	62.2	50.5
30-45	121.5	112.7	87.4	106.7	73.8	63.2
45-60	27.0	36.8	91.7	80.2	50.9	32.5
60-75	75.5	80.8	43.9	44.8	40.9	42.3
75-90	69.6	71.4	24.2	50.1	73.8	75.0
90-105	8.0	7.7	60.9	49.6	4.2	3.4
105-120	43.3	38.4	35.6	34.3	19.4	31.4
120-150	92.0	88.9	12.2	12.7	6.9	16.1
150-200	51.1	40.2	44.2	59.5	11.1	16.5
200-250·	18.9	17.3	10.6	24.8	28.2	13.2
250-300	32.7	38.8	53.3	44.5	19.6	20.9