University of Alberta

Landscape Position and Land Use Effects on Nitrogen and Phosphorus Cycling within a Riparian-Agricultural System in Central Alberta

by

Leslie Ropa Yasul ©

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Landscape Position and Land Use Effects on Nitrogen and Phosphorus Cycling within a Riparian-Agricultural System in Central Alberta

Abstract

The objective of this study was to examine the effects of landscape position (forage upland vs. forage riparian) or land use (native vegetation riparian vs. forage riparian) on rates of a) phosphorus mineralization, b) nitrogen mineralization/nitrification and c) denitrification within an agricultural system in central Alberta. Phosphorus and nitrogen mineralization followed a seasonal pattern of net immobilization during the winter to net mineralization throughout the growing season ranging from an average of -0.06 kg P ha^{-1} d^{-1} in the winter to 2.54 kg P ha^{-1} d^{-1} in August 2006 for P and 0.06 kg N ha^{-1} d^{-1} in the winter to 0.88 kg N ha^{-1} d^{-1} in June 2006 for N. The denitrification rates were higher during spring snowmelt especially in the forage riparian treatment (485 μg N_2O-N m^{-2} d^{-1}) compared with either the forage upland (222 μg N_2O-N m^{-2} d^{-1}) or the native vegetation riparian (129 μg N_2O-N m^{-2} d^{-1}) treatments.

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Chapter 1: Introduction

Riparian ecosystems are transitional areas between streams or wetlands and uplands, and support plants that need high moisture supply (Gregory et al. 1991). These ecosystems have a unique structure and function due to strong interactions between hydrologic, soil and plant processes (Groffman et al. 1998). The upland is usually the agricultural area that is at a higher elevation than the riparian area. Water from the upland generally flows towards the riparian area. It is difficult to determine the exact riparian area, however, when an agricultural crop has replaced the native vegetation without further investigation into the soils and topography.

There are concerns from the public that certain agricultural practices that degrade the riparian area can negatively affect the environment especially water quality. The use of nitrogen (N) and phosphorus (P) fertilizers, legumes and manures on the land has increased to intensify agricultural production. Agricultural practices have also changed the land use in riparian areas, where the native riparian vegetation has been replaced by agricultural production right up to the stream bank. Not all of the N and P applied by the producer are taken up by plants, they may also be incorporated into the soil, lost to the atmosphere, runoff into surface water or leached into the groundwater. Nitrate (NO_3^-) and soluble phosphate ($H_2PO_4^-$) are the dominant forms of N and P that are leached from the soil and can cause water pollution, leading to eutrophication and human health problems (Di and Cameron 2002; Gächter et al. 2004). The province of Alberta set the following surface water quality guidelines for the protection of freshwater aquatic life as 1.0 mg L^{-1} for total inorganic and organic N and 0.05 mg L^{-1} for total inorganic and organic P under chronic conditions (Alberta Environment 1999).

Soluble phosphate released from organic residues that enters into the soil solution has four possible fates: uptake by plants or microbes; precipitation with calcium, iron or aluminum ions to form insoluble salts; adsorption onto mineral surfaces or leaching from the rooting zone (Smith et al. 1999; Addiscott and Thomas 2000). Inorganic P fertilizers also provide readily soluble phosphate for plants and together with the mineralization of organic P, form the soluble phosphate pool. Soluble phosphate entering surface waters can also cause eutrophication of lakes and streams.

Studies of P mineralization along topographic gradients within an agricultural-riparian system have been few but soluble phosphate, hereafter referred to as available P, was found to be highest in the mid- to lower-slopes, where soil moisture content affects the distribution of P across the landscape, and encourages greater productivity on the lower slopes (Roberts et al. 1985; Schoenau et al. 1989). Comparisons between land uses within a riparian area by Schoenau et al. (1989) showed that the cultivated Gleysolic soils had higher available P than the native vegetation Gleysolic soils, attributing differences to the tillage and fertilization that increases the amount of available P in the soil. Flooding can also affect P mineralization because Reddy (1985) found that the alternate wetting and drying of wetland soils may enhance P mineralization because of changes in soil pH that could increase microbial activity, and thus, P availability.

Two important processes of the N cycle, nitrification and denitrification, affect the riparian area because they are two of the main regulators of N retention in soils and can control the amount of N available to plants (Robertson 1989; Abbasi and Adams 1998). Through the process of nitrification, NH_4^+ is converted to NO_3^-, and NO_3^- can be denitrified to atmospheric nitrogen.

Net N mineralization is the process by which organic N is converted to plant-available inorganic forms and has been studied on topographical gradients including riparian-agricultural systems. Soon and Malhi (2005) and Burke et al. (2005) showed that N mineralization rates were higher in the lower slope than in the upper slope position because of higher soil moisture content and organic matter. Also, in the Aspen Parkland Ecoregion of Alberta, Zhang et al. (2004) showed that potential mineralized N was higher in the lower slopes than in the higher slope positions. In contrast, within a wet growing season, Manning et al. (2001) found that N mineralization was lowest in the lower slopes compared to the upper landscape position because N was lost via denitrification. Forest and grassland sites within a riparian area in Oregon, U.S.A., were compared by Entry and Emmingham (1996), who discovered that the forest site had more extractable N than the grassland site because the forest woody debris slowly decomposed to create a litter layer that held nutrients in the vegetation and organic matter.

Riparian ecosystems are dominated mostly by wet surface soils that have a high capacity to lose NO_3^- via denitrification because of the anaerobic conditions needed for denitrification to occur (Groffman et al. 1998). These conditions give rise to a unique role riparian ecosystems play in removing excess NO_3^- originating from the upland before it reaches the surface waters. Along with denitrification, plant uptake is also an important process of NO_3^- removal in riparian ecosystems because plant uptake allows N to cycle within the ecosystem (Willems et al. 1997) and acts as a buffer to reduce pollution. In comparison to the upland landscape position, riparian soils have been found to have higher denitrification rates because of the increased occurrence of saturated condition and greater quantities of microbially available C (Lowrance et al. 1995; Ettema et al. 1999; Machefert and Dise 2004). On the Canadian prairies, studies have been conducted along topographic gradients (e.g. Pennock et al. 1992; Nyborg et al. 1997; Lemke et al. 1998; Izaurralde et al. 2004) but few of these include a riparian component. The studies found that denitrification was highest in the level-concave, depressional and footslope areas and lowest on the shoulder position and was found to have a seasonal pattern of increased rates during snowmelt and early summer (Pennock et al. 1992; Nyborg et al. 1997; Lemke et al. 1998; Izaurralde et al. 2004).

We have a poor understanding of nutrient cycling, especially N and P, in riparian ecosystems. This study aims to improve our understanding of N and P cycling processes in a riparian area within an agricultural landscape in Central Alberta. Improving our understanding of N and P cycling, and how those processes interact with groundwater, vegetation and soil properties, is critical in the determination, recommendation and implementation of appropriate Beneficial Management Practices (BMPs) on agricultural landscapes with a riparian component.

The objective of this study was to examine the effects of landscape position (forage upland vs. forage riparian) and land use (native vegetation riparian vs. forage riparian) on rates of a) phosphorus mineralization rate, b) nitrogen mineralization/nitrification rate and c) denitrification within an agricultural system.

The following four hypotheses were tested in this study:

1. Soil nitrogen and phosphorus mineralization rates in the 0-10 cm and 10-20 cm soil depth increments are higher in the forage upland areas than in the forage riparian areas throughout the growing season because of distance from the creek and elevation, aerobic conditions would be higher in the forage upland than the forage riparian areas.
2. Soil nitrogen and phosphorus mineralization rates in the 0-10 cm and 10-20 cm soil depth increments are higher in the forage riparian than in the native vegetation riparian areas throughout the growing season because of higher soil temperatures due to no canopy cover and external inputs of inorganic N and P fertilizers applied over many years on the forage riparian than in the native riparian areas.
3. Denitrification rates in the 0-10 cm and 10-20 cm soil depth increments are higher in the forage riparian than in the forage upland in the growing season because anaerobic conditions would be higher in the forage riparian than the forage upland due to closer proximity to the creek.
4. Denitrification rates in the 0-10 cm and 10-20 cm soil depth increments are greater in the native vegetation riparian than in the forage riparian areas since there is no removal of litter and vegetation in the native riparian than the forage riparian, providing more organic C for denitrifying organisms.

The first part of the experiment measured N and P mineralization rates in field plots comparing landscape positions and different land uses. The second part of the experiment measured denitrification rates in field plots to determine if there were differences between landscape positions and land uses.

This thesis consists of five chapters. This chapter is an introduction to the entire thesis and comprises the rationale, the background which highlights the importance of riparian areas in agricultural landscapes, and the objectives of the study. The next chapter (Chapter 2) reviews the literature related to P mineralization, N mineralization and denitrification with upland - riparian landscapes that have multiple land uses in agricultural systems. Hypotheses 1 and 2 are discussed in Chapter 3 with respect to P mineralization and Chapter 4 with respect to N mineralization. In Chapter 5, hypotheses 3 and 4 are discussed with respect to denitrification. The last chapter (Chapter 6) provides a synthesis of the 2 experiments and relates to the determination, recommendation and implementation of appropriate BMPs on agricultural landscapes with a riparian component, and suggests future research.

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Chapter 2: Literature Review

Riparian areas are important and unique areas on the landscape supporting high productivity and high biodiversity, and are an essential component of the land-water interface (Groffman et al. 1998; Fitch et al. 2003). Their function has been previously studied within agricultural landscapes, in particular the movement of nitrogen (N) and phosphorus (P) from the agricultural upland through the riparian areas and into water bodies such as rivers, lakes and streams (e.g., Peterjohn and Correll 1984; Haycock and Pinay 1993; Jordan et al. 1993). Hill (1996) described riparian areas as "complex environments that are spatially heterogeneous in both a horizontal and vertical dimension with respect to hydrology, sediment characteristics and biological processes."

The objective of this review is to synthesize the literature on N and P cycling in riparian areas within agricultural landscapes and relate them to the current study. In particular, I will review the N and P cycles, discuss the role of landscape positions and land uses on the N and P cycle, and describe the factors that affect P mineralization, N mineralization, and denitrification. Comparisons between various methods for measuring P mineralization, N mineralization and denitrification will also be made. Additionally, I will relate current Beneficial Management Practices (BMPs) that are being promoted by Environmental Farm Planning organizations and both provincial and federal governments in relation to riparian management on the Canadian Prairies.

2.1. The Phosphorus Cycle

The soil P cycle is a dynamic system that includes soil, plants and microorganisms (Smil

2000). Phosphorus is an important macronutrient for the growth and health of plants and animals. In plants, P is important for many vital plant growth processes and is essential in energy storage and transfer (Havlin et al. 2005). Phosphorus, however, can also cause eutrophication when present in surface waters, leading to problems in water supplies because of overgrowth of algae and cyanobacteria (Smith et al. 1999; Bowman and Vigil 2002). Recycled very slowly, P cannot be accessed by plants when it is in an insoluble state (Holford 1997). There are four main biospheric reservoirs of P: 1) oceans and fresh waters (9.3×10^{16} g P), 2) soil (inorganic and organic) ($4.0\text{-}5.0 \times 10^{13}$ g P), 3) flora and fauna (6.0×10^{14} g P) and 4) anthropogenic (people, animals, wastes, fertilizers) (3.0×10^{12} g P) (Smil 2000). The main focus of this discussion will be on P cycling in the soil.

The three main pools of P in the soil are 1) inorganic P (labile and nonlabile P), 2) organic forms of P (labile and nonlabile P) and 3) soil solution P where soluble P forms ($H_2PO_4^-$ and HPO_4^-) are found (Figure 2.1; Addiscott and Thomas 2000). All three P pools are in equilibrium with each other. The soil solution P pool when depleted by plant uptake, for example, is constantly being replenished by P from the other two pools (Figure 2.1; Dorioz et al. 2006). Proportionally to the rest of the P present in the soil, the solution P pool is very small but very chemically and biologically active (Dorioz et al. 2006). The solution P pool is where most plant uptake of soluble forms of P occurs.

Organic forms of soil P can be supplied from plant and animal residues that are mineralized by microorganisms, producing other organic compounds and releasing soluble inorganic phosphate ($H_2PO_4^-$). Soil available phosphate that is released from organic residues and humus mineralization into soil solution has several possible fates:

uptake by plants or microbes from the soil solution P pool; precipitation as barely soluble salts with calcium, iron or aluminum primary and secondary minerals (non-labile inorganic forms of P); adsorption by anion exchange or sesquioxides (labile inorganic P); formation of labile and non-labile organic P compounds such as esters that are adsorbed onto Al, Fe and Ca surfaces; and leaching from the rooting zone into surface waters which increase the potential of environmental pollution such as eutrophication of lakes and streams (Addiscott and Thomas 2000; Smith et al. 1999).

The inorganic nonlabile forms of P, through time, can be released into the soil solution P pool by weathering. Labile inorganic P is readily soluble and can enter the soil solution P pool quickly in comparison to non-labile P. Where the soil solution P pool is depleted by absorption by plant roots, $H_2PO_4^-$ and HPO_4^- in the soil solution P pool will be resupplied by dissolution of mineral P or release of adsorbed P to re-establish the P equilibrium.

P mineralization and immobilization occur simultaneously in soils where organically held P can be mineralized into inorganic phosphate ions, which are part of the soil solution P pool. Inorganic phosphate ions can also be immobilized by microbes back into organic P (Dalal 1977):

$$\text{Organic P} \quad \underset{\textit{Immobilization}}{\overset{\textit{Mineralization}}{\rightleftarrows}} \quad \text{Inorganic P } (H_2PO_4^-/HPO_4^{-2})$$

Should organic residues that are low in P but high in C in combination with other nutrients be added to a soil, microbes would increase their activity and immobilize the P in their biomass. The available P would temporarily disappear, just like NH_4^+ and NO_3^- in the N mineralization process. Net immobilization of soluble P is most likely to occur if residues added to the soil have a C/P ratio > 300/1 while net mineralization has C/P ratio < 200/1 (Stevenson and Cole 1999). As plant residues decay, net P mineralization can occur as the C:P ratio of the residue decreases because of decreased CO_2 respiration from organisms and increased P via immobilization.

2.1.1 Factors That Affect P Mineralization

Similar to the environmental factors that affect N mineralization/immobilization, the main factors affecting P mineralization/immobilization are: soil temperature, soil moisture, P fertilization and soil pH (Dalal 1977).

2.1.1.1 Soil Temperature

Optimum P mineralization occurs where the temperature is between 30-35°C (Dalal 1977). Soil temperatures do not remain at this level throughout the growing season on the Canadian Prairies but P mineralization still occurs (Dalal 1977). For this research site, soil temperature was classified as moderately cold cryoboreal with mean summer soil temperature of 8°C to <15°C (Juma and Martin 1997; Agriculture and Agri-Food Canada 2006). When soil temperatures are low, such as in the fall and winter, both plant growth and P availability are low.

2.1.1.2 Soil Moisture

Soil moisture content at field capacity is optimal for P mineralization (Wild 1988). The field capacity of a soil is the amount of water held in the soil when percolation of water down through the soil has stopped. Soil moisture is important for microbial activity and diffusion of nutrients from the soil solution to plant roots (Johnson et al. 2005).

2.1.1.3 Soil pH

The fate of mineralized forms of P is dependent on soil pH. At pH 6.0 to 6.5, P availability is highest and P adsorption onto mineral surfaces is lowest (Barrow 1984). Outside this range, P adsorption onto mineral surfaces increases and P availability decreases. Calcareous soils in Central Alberta are Ca-saturated and have low plant available P (Bowser et al. 1973). Most inorganic P would likely precipitate onto highly reactive calcium carbonate surfaces, therefore, these calcareous soils would be low in plant available P but high in total P (Havlin et al. 2005).

2.1.1.4 Fertilizer

Phosphorus is an essential nutrient for plants. Where P in the soil cannot fulfill plant requirements, inorganic and organic P fertilizers and manures provide readily soluble phosphate ions for plants. These fertilizers initially increase the solution P pool but P is transformed into labile and non-labile forms that are not easily available for plant uptake. As a result, producers tend to add more fertilizer than is actually needed. Producers and agronomists know that when applying inorganic P fertilizer to a low P soil, the majority of this P is adsorbed or precipitated into insoluble forms that plants cannot acquire. Usually, producers would then apply more P to their soil than that which is actually needed and thus, alter the P equilibrium in the soil. When applying manure in Alberta, the rate is based on N recommendations and not P, so often the amount manure applied provides more than required P for optimal crop growth (Olson and Paterson 2005).

If these practices are continued year after year, there can be a buildup of P to a level that P can be easily removed from the soil because the capacity for the vegetation to take up more P is limited and the sorption sites where P would precipitate onto minerals or be adsorbed by anion exchange sites on clays become saturated (Dorioz et al. 2006). The excess P in the soil can lead to particulate and dissolved P forms leaving the agricultural land via runoff towards water bodies such as streams and lakes (McDowell et al. 2001). Eutrophication can occur when too much P ends up in a water body. Eutrophication is the increase in the nutrient status of natural waters that causes accelerated growth of algae or aquatic plants, depletion of dissolved O_2, increased probability of fish kills, increased turbidity and a general degradation of water quality (Smith et al. 1999; Pierzynski et al. 2005).

In the case of Alberta, the lakes, streams and rivers differ from water bodies elsewhere in Canada and the United States because they are naturally highly productive (eutrophic) and experience prolific algae and weed growth (Howard et al. 1999). Thus, the surface waters in Alberta are extremely sensitive to further P enrichment because P is the limiting nutrient controlling the level of algae growth. In Alberta, the surface water quality guideline for the protection of freshwater aquatic life for P (total inorganic and organic) is 0.05 mg L^{-1} under chronic conditions (Alberta Environment 1999).

2.1.1.5 P Mineralization and Availability within a Riparian-Agricultural System

On the Canadian Prairies, there have been few toposequence studies within a riparian-agricultural transect. Schoenau et al. (1989) did research in Saskatchewan between landscape positions and land uses where there was cultivated and native vegetation on a Brown Chernozemic soil zone located in the upland and cultivation and native vegetation of the lower slopes in the Gleysolic soil zone which periodically flooded after spring melt. Lower concentrations of labile forms of P were found in the cultivated upland than in the Gleysolic soils when comparing landscape positions. Schoenau et al. (1989) suggested that the continuous cereal-fallow cultivation in the upland for 70 years may have contributed to the lower amount of labile P in comparison to the Gleysolic soils in the lower slope. The Gleysolic soils with native vegetation had higher labile forms of P than the cultivated Gleysolic soils when comparing land uses within the same lower slope landscape position. Schoenau et al. (1989) also found that both native and cultivated Gleysolic soils had a higher proportion of P in labile inorganic and organic forms than the upland Chernozemic soils. This higher proportion of P may be attributed to a large quantity of organic P in the soils which replenishes the labile inorganic P pool through mineralization.

Flooding within riparian areas is a common occurrence in comparison to the upland because of its close proximity to surface waters and therefore, has an effect on P mineralization. In a study by Reddy (1985), wetland soils that were subject to alternate wetting and drying had enhanced P mineralization due to changes in soil pH that increased P availability and increased microbial activity than in dryland soils creating the potential for P movement by runoff.

2.2 The Nitrogen Cycle

Nitrogen is an essential nutrient for plants and yet is frequently deficient. Nitrogen is found in the atmosphere (3.9×10^{21} g), oceans (2.4×10^{19} g), soil (1.5×10^{17} g), plants (1.5×10^{17} g), microbes in the soil (6.0×10^{16} g), animals (2.0×10^{15} g) and in people (1.0×10^{14} g) (Havlin et al. 2005). The N cycle is a series of oxidation and reduction transformations that will be summarized with an emphasis on the soil component.

Atmospheric N (dinitrogen, N_2) is reduced into organic N through biological N fixation. Biological N fixation is carried out by a limited number of groups of microorganisms where many are in symbiotic relationships with higher plants such as legumes (Vitousek et al. 1997). The soil organic N pool, which contains 95–99 % of the N in the soil, also receives N by decomposition of plant and animal residues, dry and wet deposition (lightning and precipitation such as rain and snow) and fertilization (organic and inorganic N applications).

Nitrogen mineralization is the only soil-based microbiological means of generating the N forms usable by green plants from organic N into ammonium (NH_4^+) and nitrate (NO_3^-) (Abril et al. 2001). The N mineralization process consists of aminization, ammonification and nitrification (Fig. 2.2). Aminization is the conversion of proteins into organic N compounds such as amino acids, amines and urea (Havlin et al. 2005). Ammonification is the process of converting organic N into NH_4^+ by bacteria, fungi and actinomycetes. Nitrification is the rapid oxidation process of NH_4^+ into nitrite (NO_2^-) and then NO_3^- which provides energy to the nitrifiers such as *Nitrosomonas* spp. and *Nitrobacter* spp. Nitrate is the preferred form of N that plants take up but plants take up both NH_4^+ and NO_3^-.

Nitrogen immobilization is the microbial assimilation of mineral N compounds when the environmental conditions favor microbial growth such as low N in decreasing organic matter.

⟶ Mineralization ⟶

$$\mathit{Proteins} \xrightarrow[\substack{\mathit{Bacteria}\\ \mathit{Fungi}}]{} R-NH_2 + 2H_2O \longrightarrow OH^- + R-OH + NH_4^+ + O_2 \xrightarrow[\mathit{Nitrosomonas}]{}$$

Aminization **Ammonification**

$$4H^+ + energy + NO_2^- + 1/2O_2 \xrightarrow[\mathit{Nitrobacter}]{} energy + NO_3^-$$

Nitrification

⟵ Immobilization⟵

2.2.1 Factors That Affect N Mineralization in Upland and Riparian Areas

About 1.5 to 3.5% of organic N is mineralized each year, but <0.1% is in available N compounds, NH_4^+ and NO_3^-, at any one time (Brady and Weil 1996). The amount of NH_4^+ and NO_3^- present in the soil is dependent on many factors such as temperature, moisture, aeration of the soil, carbon supply, N concentration and pH (White and Reddy 1996). Optimal conditions for mineralization include a warm climate (25-35°C), well-aerated soils, neutral to slightly basic pH, with an ample energy supply of organic C for mineralizing microorganisms and a fluctuating moisture content hovering around field capacity (Brady and Weil 1996; Tate 2000; Havlin et al. 2005). Fine-textured soils were also favorable for N mineralization (Pastor et al. 1984). Not all these optimal conditions, however, can be found within temperate climates or riparian ecosystems in the Canadian Prairies.

A trend was observed that A horizon thickness, solum thickness, organic matter content, soil moisture and NO_3^- concentrations were greatest in the lower slopes and lowest in the higher slopes, thus, N mineralization would also be greatest at the lower slope position (Manning et al. 2001a; Manning et al. 2001b; Burke et al. 1995). Inorganic N availability was also greatest during relatively wet periods in the spring when the lowland was enriched in silt, clay, C and N, in comparison to the upland (Hook and Burke 2000). Riparian areas receiving sediment deposition from a water body and from the upland could, over time, have finer texture soils and an increase in available nutrients to plants (Soon and Malhi 2005). According to Gale and Gilmour (1988), N mineralization occurs differently between aerobic and anaerobic conditions. Under aerobic conditions, there is an initial flush of N mineralization in the soil but then a lag occurs throughout the intermediate phase of plant decomposition which coincides with microbes immobilizing N due to a high C:N ratio. Net N mineralization began again during the slow decomposition phase. In contrast, under anaerobic conditions, N mineralization happens more rapidly because of higher metabolic efficiencies of the anaerobic microbial populations and ceases after decomposition is completed. Riparian areas have been studied extensively but much is unknown about their soil chemical and physical properties (Mikha et al. 2005).

2.2.2 Available NH_4^+ and NO_3^-

Ammonium can be transformed into NO_3^- via nitrification and transformed back into soil organic N via immobilization. Ammonium can also be taken up by plants; fixed as biologically unavailable N in the lattice of certain clay minerals such as vermiculite and mica; and a small amount can be volatilized into NH_3 that is slowly released back into the atmosphere.

Nitrate can also be transformed in different ways: 1) immobilization back to soil organic N; 2) uptake by plants; 3) return to the atmosphere as N_xO or N_2 through denitrification; and 4) leaching into the groundwater and taken to surface waters as NO_3^- and is highly mobile and very soluble in water.

Studies have been conducted to understand how to prevent the flow of excess NO_3^- from the uplands into the streams and lakes from groundwater sources because of its potential to deteriorate surface water quality which can cause eutrophication, algal blooms, fish poisoning and risks to human health (Gillam 1994; Di and Cameron 2002; Schultz et al. 2004). In Alberta, the surface water quality guideline for the protection of freshwater aquatic life is 1.0 mg L^{-1} for N (total inorganic and organic) under chronic conditions (Alberta Environment 1999). Riparian ecosystems are dominated mostly by wet soils that have a high capacity to consume NO_3^- via denitrification because of the anaerobic conditions needed for denitrification to occur (Groffman et al. 1998). These conditions give riparian ecosystems a valuable role in removing excess NO_3^- from the upland before it reaches the surface waters. Along with denitrification, plant uptake is also an important process of NO_3^- removal in riparian ecosystems because plant uptake allows N to cycle within the ecosystem and acts as a buffer to reduce pollution (Willems et al. 1997) however, NO_3^- is not completely removed from the ecosystem since it can be returned via decomposition of plant material and N mineralization. Nitrate can also be removed by microbial immobilization and this process has not been thoroughly studied in riparian ecosystems (Hill 1996).

Leaching of NO_3^- from the soil profile is a legitimate concern because of the loss of productivity by plants and serious environmental problems. Leaching occurs as a function of climate (especially precipitation), amount of surplus NO_3^- and soil properties (Janzen et al. 2003). Just like phosphorus, as excess fertilizers and manures are applied over time, plants and microbial pools become enriched or saturated with N and their N absorption capacity decreases. This increases the possibility of N leaching from the soils into surface and groundwaters (Aber et al. 1989). When excess water occurs, often during spring melt in Central Alberta, NO_3^- can reach the surface water through overland flow or can percolate down the soil profile into the groundwater and discharge into the surface water. Timing of fertilizer N application is very important not only for when the plant will utilize it but also to prevent NO_3^- leaching from occurring. On the Canadian prairies, Fairchild et al. (2000) suggests that leaching may be minimal because potential evapotranspiration greatly exceeds precipitation when fertilizer is applied.

2.3 Denitrification

The denitrification process can be both microbial and chemical, but the microbial process dominates in most soils through the dissimilatory reduction of nitrate and nitrite to produce gaseous N forms by a diverse group of bacteria in a stepwise reduction to atmospheric nitrogen (N_2):

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO(g) \rightarrow N_2O(g) \rightarrow N_2(g)$$

Nitrate *Nitrite* *Nitric oxide* *Nitrous oxide* *Dinitrogen*

Nearly all denitrifying organisms prefer to use O_2 as their electron acceptor and will reduce N-oxides only when O_2 is not available (Tiedje et al. 1989). Chemical denitrifrication is a non-biological reaction that occurs at low pH and is the chemical decomposition of NH_4^+ to NO_2^- or NO_3^- with organic or inorganic compounds to form NO or N_2O (van Cleemput and Baert 1984). Chemical denitrification is when nitrifying or denitrifying microorganisms react chemically to form gaseous N compounds. Since the significance of this process has yet to be established in the field (Sigunga 2003), the focus will be on biological denitrification.

The denitrifying microorganisms that make biological denitrification occur are bacteria such as *Pseudomonas* and *Bacillus* and autotrophs like *Thiobacillus denitrificans* and *Thiobacillus thioparus*. The dominant denitrification product is N_2 which can account for 90% of the total N gas products, however, N_2O loss can be greater under less reduced conditions (Havlin et al. 2005).

2.3.1 Factors That Affect Denitrification in Riparian Ecosystems

When studying denitrification in riparian areas, one of the objectives is to understand the interaction of the soils with the subsurface water or groundwater as riparian ecosystems play an important role in removing NO_3^- from the subsurface water before it enters surface water bodies (Cosandey et al. 2003). There is also a need to understand the land use activities that are occurring in the upland that may affect the denitrification rate in the riparian ecosystems, specifically in terms of high input agriculture where the vast majority of inorganic fertilizers promotes denitrification (Mulvaney et al. 1997).

Denitrification can also occur within many ecosystems including well-drained soils in forests, grasslands and agricultural lands but at much lower rates caused by anaerobic micro-sites that are found in unsaturated soils (Seitzinger et al. 2006). According to Parkin et al. (1985), rapid diffusion of oxygen through gas-filled pore spaces confine denitrification to anaerobic micro-sites such as detritus and aggregates of soil particles where oxygen levels might be low, allowing denitrification to happen.

The riparian ecosystem has favourable environmental conditions for denitrification because of the high amount of organic carbon for denitrifying bacteria's energy needs. There is potentially an ample supply of NO_3^- from the upland that may come from sources such as inorganic fertilizers or animal wastes and the saturated soils can create an anaerobic environment for the denitrifying microbes to use NO_3^- instead of O_2 as the terminal electron accepter for their energy requirement (Watts and Seitzinger 2000; Dhondt et al. 2002). When the riparian ecosystem is altered with agronomic practices such as cropping, changes to the soil through fertilizer N addition and tillage of soils can make N losses are made possible through denitrification (Horwath et al.1998).

Denitrification has the largest spatial and temporal variability of all the processes in the N cycle and is one of the major processes removing NO_3^- in riparian ecosystems (Tiedje et al. 1989). The amount of NO_3^- that is removed by denitrification instead of plant uptake is dependent upon several factors, including hydrology, vegetation and soil properties such as the amount of organic matter, NO_3^- concentration, soil aeration, soil moisture content, soil pH, soil temperature and their interactions (Hanson et al. 1994; Tate 2000).

2.3.1.1 Amount of Organic Matter Available

Organic matter is the primary energy source for the denitrifying microbes. Generally, there is a correlation of denitrification rates with available organic carbon (Burford and Bremner 1975). The amount of carbon that is available to the denitrifiers can be a limiting factor for denitrification. There is 20 - 200 times more organic carbon in the surface soils than the subsurface soils and with greater soil depths, denitrification activity decreases, often due to the lack of decomposable organic matter that is available to the microbes (Willems et al. 1997). Although there is evidence that there is not enough organic carbon available at subsoil depths, there is a heterogeneous pattern of organic matter distribution throughout the entire soil profile. An example of the variability in the soil is the discovery of carbon-enriched patches of organic matter for microbial activity called 'hotspots' (Flite et al. 2001; Dhondt et al. 2002; Mosier et al. 2002). These hotspots are where the majority of the denitrification is occurring in the soils and these hotspots have a denitrification rate up to 10 times higher than the average denitrification rate for a typical field (Brady and Weil 1996).

2.3.1.2 Nitrate Concentration

Between land uses within a riparian area, Horwath et al. (1998) and Schnabel et al. (1997) showed that the cultivated riparian area had higher denitrification rates, because of N fertilizer addition, than in the non-cultivated native riparian area. Soils must first produce, or have been amended with NO_3^-, and then enter an anaerobic period so that denitrifying organisms will respond to the increase in available NO_3^- in order for denitrification to occur (Hanson et al. 1994; Pierzynski et al. 2005). The opposite occurs where denitrification is inhibited by a decrease in nitrification and/or an increase of NO_3^- removal through plant uptake, leaching and/or aerobic conditions.

2.3.1.3 Soil Aeration and Soil Moisture Content

Soil moisture content varies over time and in space and is dependent on soil texture, precipitation and groundwater table fluxuations (Pinay et al. 1993). The denitrification process is usually found in anaerobic conditions where high soil moisture content lowers oxygen concentration in the soil. In anaerobic conditions, denitrifying organisms must use NO_3^- to obtain O_2, thus NO_3^- is reduced to nitrous oxide and dinitrogen. Low denitrification rates, for example, are found in well-drained soils but as moisture content increases in the soil, loss of NO_3^- by denitrification increases. Riparian ecosystems are ideal areas for denitrification to occur because flooding and inundation of soils can happen more frequently than in the upland. Along toposequences in Alberta and Saskatchewan, the depressional areas had a higher denitrification rate than the shoulder positions due to the higher moisture regime found in the lower landscape position (Izaurralde et al. 2004). Schnabel et al. (1997), Ettema et al. (1999) and Machefert and Dise (2004) all discovered that denitrification decreased as the distance increased from the stream. Groffman and Tiedje (1989) reported that poorly-drained soils consistently had higher concentrations of soil NO_3^-, higher rates of denitrification, higher organic carbon and nitrogen concentrations as compared with well-drained soils. Denitrification can occur at high rates for brief periods of time when there are anaerobic conditions and available C and NO_3^-.

2.3.1.4 Soil pH

Denitrification can occur within a pH range of approximately 3.9 to 9.0 (Koskinen and Keeny 1982). The overall rate of denitrification is lower in acidic soils than neutral or slightly alkaline soils because there are lower amounts of organic carbon and NO_3^- available for denitrifying organisms (Šimek and Cooper 2002). Where the soil is acidic, more N_2O is produced than N_2. Above pH 7.0 N_2 was the dominant product (e.g., Nägele and Conrad 1990; Thomsen et al. 1994; Šimek and Cooper 2002). The optimal rate of denitrification has been suggested to be in the range of pH 7.0 to 8.0 (Koskinen and Keeny 1982). Šimek et al. (2002) suggested that the term "optimal pH for denitrification" should not be used because different denitrification characteristics are obtained using different methodologies and if it is, it should be clarified with the type of denitrification measurement used (e.g., denitrification flux, potential denitrification rates, activity of denitrifying enzymes in soil). Šimek et al. (2002) also suggested that regardless of pH, the largest amount of soil denitrifiers and thus, highest denitrification rates occurred when soil pH was at near natural conditions.

2.3.1.5 Temperature

The optimal temperature range for denitrification is between 15–35 °C (Stanford et al. 1975) with a Q_{10} value of 2, meaning that this process is reasonably sensitive to fluctuations in soil temperature (Tate 2000). Generally, the minimum temperature for denitrification is around the freezing point and with increasing temperatures comes increases in the denitrification rate. Seasonal and daily variation in the denitrification process is expected; so time of day when sampling for a field study should be taken into consideration. Just the daily heating and cooling of the soil surface will affect the quantity of N_2O and N_2 lost through denitrification (Groffman and Tiedje 1989; Pinay et al. 1993; Hanson et al. 1994; Dhondt et al. 2002).

Although the optimal temperature range for denitrification is between 15 and 35°C, studies on the Canadian prairies have found denitrification to be lowest in the summer and highest in the spring during spring snowmelt (e.g. Nyborg et al. 1997; Lemke et al. 1998; Izaurralde et al. 2004). Soil temperatures would be higher in the summer compared to the rest of the year, however, low soil moisture content would be the limiting factor for denitrification. In the spring, soil temperatures are lower compared to during the summer season, but increased soil moisture content after spring melt would allow for anoxic conditions and low gas diffusion through the soil (Pinay et al. 1993). Plant uptake of both water and NO_3^- would also be low during early spring (Groffman and Tiedje 1989; Hanson et al. 1994).

2.3.1.6 Hydrology

Groundwater flow and overall hydrology of the riparian area and associated uplands are important factors that affect the denitrification rate. Often it is the groundwater flow from the upland that brings excess N in the form of NO_3^- into the riparian area (Peterjohn and Correll 1984). Willems et al. (1997) found that the amount of NO_3^- removed from the groundwater passing through the soil horizons was positively correlated with the amount of N_2O released via denitrification in the water flow regardless of temperature and flow rate.

2.3.1.7 Vegetation

Vegetation is a source of energy for denitrifying microbes in the form of organic carbon from litter and root decay (Tate 2000). Vegetative riparian buffers are often effective in preventing pollutants such as excess NO_3^- from entering surface water bodies. Although riparian buffers have many functions, ranging from creating shade for improved aquatic habitats to providing a source of woody debris and habitat for organisms, their function as filters between the upland and aquatic ecosystems is the focus of denitrification studies (Schultz et al. 2004). With the buffer slowing water flow, plant uptake and denitrification can remove NO_3^- out of the system. The slow flow of water creates anaerobic conditions for the denitrification process to occur. Groffman et al. (1992) suggested that denitrification should be considered the preferred mechanism of removing NO_3^- because there is the probability that plant uptake of N in a NO_3^- enriched area will lose its effectiveness over time. Yet, one of the products produced by denitrification is N_2O, a known greenhouse gas that contributes to global warming (Machefert and Dise 2004).

Factors that affect the denitrification process are interdependent of each other. To analyze just one factor is nearly impossible because in order to understand how a particular factor is affecting the denitrification process, analysis of the other factors is needed to put the whole process into context.

2.3.2 Role of Denitrification in Nitrogen Cycling in Riparian-Agricultural Systems

In riparian ecosystems denitrification removes the excess NO_3^- that comes from the upland and returns it to the atmosphere to prevent pollution of surface water. The alternating anaerobic and aerobic conditions that occur in riparian areas from flooding and drying will determine the final products released (NO, N_2O, and N_2). The alternating anaerobic and aerobic conditions are problematic because N_2O is one of the greenhouse gases that contribute to the destruction of the earth's ozone layer. With a better understanding of factors controlling denitrification in riparian areas, we can optimize N_2 production which would help improve water quality and decrease atmospheric pollutants like N_2O (Jordan et al. 1998). Controlling the type of N gas released in a riparian area via denitrification is difficult when riparian ecosystems are very heterogeneous in terms of hydrology, soils and vegetation. There are still many unknowns in the riparian ecosystem regarding vegetation and hydrological interactions with nutrient dynamics. Quantifying and understanding the roles and relationships of plants and water with respect to NO_3^- removal are an important aspect of nutrient dynamics that should continue to be investigated.

2.4 Measurement of N and P Mineralization

There is a paradigm shift in acknowledging that plants can take up both inorganic and organic N (Schimel and Bennett 2004). Yet, net N mineralization is still the widely accepted index for available N for plants. There is no standard method that accurately measures mineralization rates in the field; nor is there a standard method to measure available N and P. Two methods of interest are the buried-bag method and ion-exchange membranes to measure nutrient availability in the soil.

The buried-bag incubation is a standard method for measuring N availability *in situ* and has been used for measuring P availability as well (e.g., Binkley and Hart 1989; Jonasson et al. 1993; Bridgham et al. 1998; Schmidt et al. 1999). Soil samples are incubated in polyethylene bags in the field and net mineralization can be measured. Gross N and P mineralization cannot be measured using the buried-bag method because microbial immobilization of ammonium, nitrate, and phosphate over the incubation period is not determined. The buried-bag method takes into account the effects of daily and seasonal temperature fluctuations (Pastor et al. 1984). The bags are permeable to gases but not ammonium, nitrate, phosphate nor water. One drawback of this method is that moisture conditions in the soil surrounding the bag may fluctuate while it does not inside the bag. These differences may cause an overestimation or underestimation of mineralization of N or P in the bag. Nitrification could also be enhanced because there is no N uptake by plant roots in the bags so there is less competition for ammonium with the nitrifying organisms (van Schreven 1968; Pastor et al. 1984).

Ion-exchange membranes are an increasingly popular method for measuring soil nutrient availability including N and P (Hangs et al. 2004). At longer residence times in the soil, the ion exchange membranes give a measure that includes ion diffusion from greater distances and nutrient release from mineralization or dissolution (Qian and Schoenau 2002). They are generally easy to work with, cause minimal disturbance of the soil and allow remeasurement in the soil over time in comparison to traditional soil sampling techniques (Johnson et al. 2005). Ion-exchange membranes are sensitive to soil water status, temperature and root competition for nutrients and microbes (Huang and Schoenau 1997; Hangs et al. 2004). Johnson et al. (2005) found that in a comparison between soil extractions, ion exchange resins (IERs) and ion exchange membrane measures, that both ion exchange methods (resin and membrane) do not relate well to N mineralization or the patterns of extractable N over time because of spatial variation within the incubated soils and the importance of solution contact for the IERs. Johnson et al. (2005) also suggested that the ion exchange methods may not be good in dry conditions because the soil solution is the major contact between the soil and the resin surface. Comparisons of results between the buried-bag and ion exchange membrane methods are difficult as the ion-exchange membranes are related to nutrient adsorbed per unit of adsorbing surface area per unit time of burial in the soil instead of relating nutrient per specific amount of soil.

When determining which method to use for measuring soil P availability, there are more than 100 different chemical extractions that have been developed depending on the soil type (Kuo 1996). Alberta Agriculture and Food did a review of agronomic thresholds for soil available P in Alberta and found that the two versions of the Modified Kelowna method were commonly used to determine soil P availability and recommended that one of these versions should be chosen as the standard test for Alberta (Alberta Agriculture, Food and Rural Development 2005).

2.5 Methods of Measuring Denitrification

Denitrification is difficult to measure because measurement techniques are limited and denitrification rates are highly variable in space and time (Hill 1996). Tiedje et al. (1989) outlined three reasons explaining the difficulties of the current methodology for measuring denitrification: (1) the inability to measure the product, N_2, because it is found in high concentrations in the Earth's atmosphere and can only be measured in sealed microbial or biochemical laboratory studies which means N_2 cannot be directly measured in field experiments. The alternative is to measure the substrate disappearance, NO_3^-, but again, that is very difficult to measure because of the different sources and outcomes that NO_3^- may take; (2) using a radioactive isotope to follow the denitrification process. Isotopes like ^{13}N are not convenient at a field scale level because of the very short half-life; and (3) the denitrification process is very dynamic with several regulators and interactions that make measuring the denitrification process very difficult.

There is not one ideal method for measuring denitrification but there are a few methods that are currently used for measuring denitrification both *in situ* and in the lab. One method currently used in surface measurement studies within riparian is the acetylene inhibition method.

2.5.1 Acetylene (C_2H_2) Inhibition Method

The acetylene (C_2H_2) inhibition or acetylene block method is one of the most common of all direct measurements of denitrification and is most frequently used in riparian zones because it represents a sensitive and reliable technique that allows a large number of samples to be assayed under natural substrate conditions (Tiedje et al. 1989; Mengis et al. 1999). This method gives a value for total N evolved via denitrification from either fertilizer-amended or untreated soils (Hauck 1986). According to Tiedje et al. (1989), the best way to sample for natural rates of denitrification is by maintaining the soil structure because disturbance can provide a fresh supply of carbon to the denitrifiers and stimulate denitrification that would not necessarily occur. Since it is difficult to separate an elemental gas like N_2 that is in high concentration, roughly 80% of the Earth's atmosphere, from what is being released from soil through denitrification because of a lack of sensitivity of analysis, C_2H_2 at a concentration of 0.01 atm inhibits the reduction of N_2O to N_2 by micro flora during denitrification to allow easier measurement of the accumulated N_2O (Yoshinari et al. 1977).

The C_2H_2 inhibition method, however, has a few limitations when applied as a field measurement for denitrification:

1. Uneven penetration of acetylene into soil microsites. Hauck (1986) states that it is difficult to maintain an acetylene concentration of 5–10 % total volume throughout the soil atmosphere in the field so there will be instances of decreasing acetylene and therefore an increase of N_2O production rate.
2. Failure of C_2H_2 to effectively inhibit N_2O reduction to N_2 can lead to an underestimation of denitrification rates. Incomplete inhibition can occur during a low soil nitrate concentration (< 10 µmol L^{-1}), addition of organic carbon, and the presence of sulfides. The solution is to keep incubation time for samples at a minimum exposure to C_2H_2 (Tiedje et al. 1989).
3. Commercial acetylene may contain impurities, including carbon and/or acetone that can act as a source of carbon enrichment for denitrifying bacteria. The solution is to "scrub" the commercial acetylene by passing it through a sulfuric acid/distilled water wash or a solution of cupric chloride in concentrated hydrochloric acid (Martin et al. 1999).
4. The major limitation of the C_2H_2 inhibition method is that nitrification can be inhibited preventing NO_3^- that is being formed from NH_4^+ (Rolston 1986). This causes an underestimation of denitrification when nitrate supply is limited and where NH_4^+ or urea are the primary initial fertilizer sources (Mosier 1980).

The acetylene method, when used correctly, is acceptable to measure denitrification *in situ* (Parkin et al. 1985; Tiedje et al. 1989).

2.6 Beneficial Management Practices (BMPs) for Riparian-Agricultural Systems

Beneficial Management Practices (BMPs) are defined as any agricultural management practice which ensures the long-term health and sustainability of land-related resources used for agricultural production; positively impacts the long-term economic and environmental viability of the agricultural industry; and minimizes negative impacts and risk to the environment (Agriculture and Agri-Food Canada 2007a). BMPs that are promoted by Environmental Farm Planning organizations and provincial and federal governments in relation to riparian management on the Canadian Prairies include riparian health assessments; erosion control structures such as grassed waterways, bank stabilization, drop inlet and in-channel control structures; and buffer strips including the planting of herbaceous buffer strips and the seeding and planting of native riparian plants. All these practices can protect and enhance the riparian area and also affect the movement of N and P in these areas. Producers who voluntarily complete Environmental Farm Plans are eligible to receive financial and technical assistance for BMPs under the National Farm Stewardship Program (NFSP) (Agriculture and Agri-Food Canada 2007a).

The current attention on riparian BMPs is primarily on buffer strips and their effectiveness in removing excess nutrients such as nitrate or phosphate from the soil before it reaches the surface waters. Buffer strips can be defined as: "any strip of vegetation between a river, stream or creek and an adjacent upland land use activity" and "may be composed of native vegetation that is intentionally left intact…as well as re-established" (Hickey and Doran 2004). There have been encouraging results from site-specific studies that show that buffer strips have many functions, including reducing and filtering sediments, chemicals and nitrates while increasing total organic carbon, soil microbial biomass and denitrification in buffer strips (Schultz et al. 2004; Stone et al. 2004; Lovell and Sullivan 2006). Vought et al. (1995) and Syversen and Borch (2005) also found that particle-bound nutrients like P can also be effectively filtered by vegetation buffer strips. Two limitations that Sheppard et al. (2006) discovered in a study on agricultural fields in Manitoba, Canada is: 1) buffer strips are usually found in the lower topographical position rather than the adjacent agricultural field, which is prone to ponding of precipitation runoff or flooding that increases the chances of available P to be lost to the surface waters and 2) runoff tends to flow through localized portions of the buffer strip which may not have sufficient capacity to retain runoff that contains P in the long term. Management through the removal of vegetation in the buffer zone such as mowing, hay cropping or coppice harvesting for fuel was recommended as the only effective practice to ensure that retained P in the buffer strip vegetation is removed prior to entering the surface waters and also allows land owners to gain income to a portion of the land that would otherwise not be generating any monetary return. Removal of material from the buffer zone would only be done when the risk of removal of nutrients into a water body is low and that the vegetation that is closest to the water body is not removed.

The implementation of buffer strips requires some planning and financing by the landowner in terms of the design, width and length, species composition of the buffer, cost to move currently productive into non-productive land and costs to establish and maintain the buffer (Lovell and Sullivan 2006). It is important to not only understand nutrient cycling at a landscape or land use level but also when combined into a farming system where both landscape and land use levels interact and create management issues for the producer. A bigger question is how the overall implementation by all landowners across a bigger spatial scale affects the ecological health of entire watersheds. One study that is currently underway to examine multi-watershed health using BMPs in Canada is called the Watershed Evaluation of BMPs (WEBs). WEBs is a multi-year multi-partnered project that has all levels of government, non-governmental organizations, research organizations and universities quantifying the environmental and economic performances on selected BMPs that are recommended within the NFSP on 7 watersheds across Canada (Agriculture and Agri-Food Canada 2007b).

There is a lot of promotion for more buffer strips and other BMPs to be implemented in the riparian area, yet BMPs being implemented in the upland such as no till farming were shown to also alleviate some of the environmental impacts of intensive agriculture that would have an effect on riparian and surface water quality (Moore and Palmer 2005).

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Figure 2.1 The phosphorus cycle in the soil. Adapted from Brady and Weil (1996) and Havlin (2005).

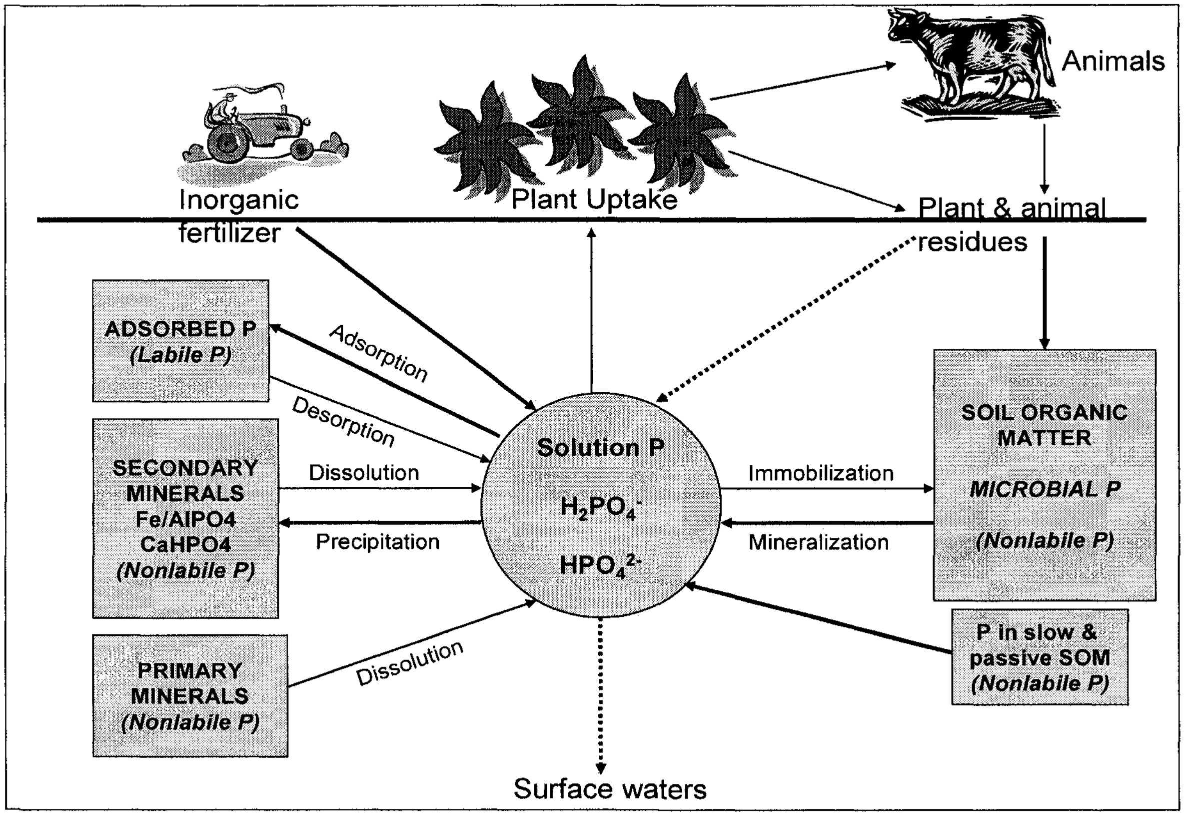
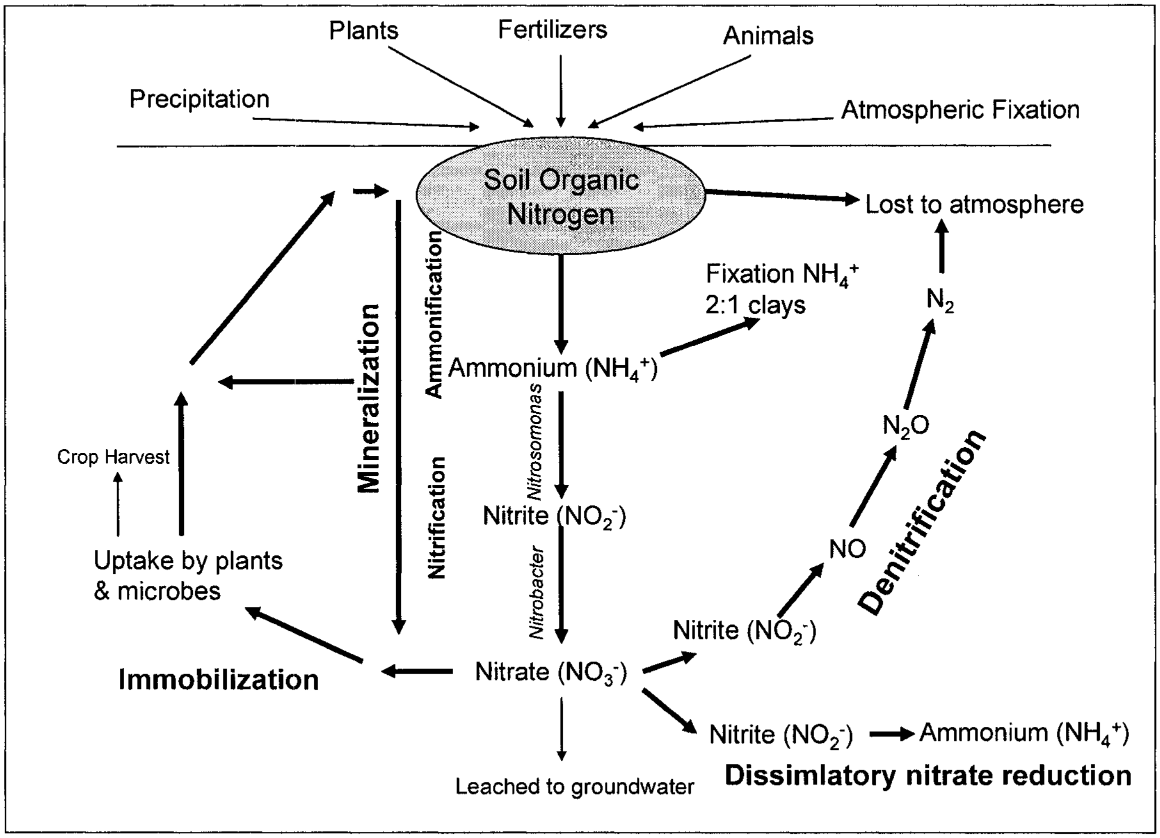


Figure 2.2 The nitrogen cycle in the soil. Adapted from Martin et al. (1999).



Chapter 3: Landscape Position and Land Use Effects on Net Phosphorus Mineralization Rates within a Riparian-Agricultural System

3.1 Introduction

Although phosphorus (P) is an essential nutrient for plant growth, the intensive use of P fertilizers and manures in conventional agriculture systems has increased the environmental risk of the movement of P from the agricultural upland through the riparian areas into rivers, lakes and streams (Peterjohn and Correll 1984; McDowell et al. 2001). Current guidelines for manure application in Alberta are based on crop nitrogen requirement, which allow more P to be added to the soil than is actually needed by crops and therefore that poses a risk to water quality (Olson and Paterson 2005). Accumulated P in soils can be leached or run off from the soil and accelerate eutrophication especially in the P sensitive surface waters of Alberta (Howard et al. 1999; Smith et al. 1999). A shift from N-based to P-based manure application rates would in many cases require a larger land area to apply the manure to achieve an agronomically and environmentally sound management system (Eghball and Gilley 1999).

Within agricultural systems, many riparian areas have been converted for agricultural activities, leaving some patches of native riparian vegetation. These native riparian vegetation patches provide important habitat for wildlife, stabilize stream banks, reduce air pollution, reduce nutrient and pesticide runoff and protect water quality (Moffatt et al. 2004). Riparian areas, especially where there are vegetation buffer strips in place, are thought to act as filters to remove nutrients such as particle bound P from groundwater and runoff (Vought et al. 1995; Syversen and Borch 2005).

In the soil, P is found in its oxidized state as orthophosphates, which are mainly in insoluble complexes with Ca, Fe, Al and silicate minerals (Sharpley 1995). The principal water-soluble forms of P that are available for plant uptake are the interconvertible primary orthophosphate ($H_2PO_4^-$) and secondary orthophosphate (HPO_4^{-2}) ions (Figure 2.1; Addiscott and Thomas 2000). These primary and secondary orthophosphate ions are found in soil solution and are affected by many factors, including fertilizer application, soil moisture content, soil temperature and pH. Hereafter, phosphate will be abbreviated as available P.

Phosphorus fertilizer application is often required where there are low amounts of plant available P in the soil and these fertilizers, together with the mineralization of organic P, provide readily available P for plant uptake (Sharpley 1985). These fertilizers increase the solution P pool, but over time, the solution P pool decreases as the phosphate transforms into organic P or are weakly adsorbed to mineral surfaces. Phosphates are more available to plants (labile) than the bulk of the soil P. The majority of phosphates are strongly adsorbed by hydrous oxides of Fe and Al minerals and are part of the stable P pool that are less soluble (non-labile) and almost unavailable for plant uptake (Stevenson and Cole 1999; Havlin et al. 2005). To compensate for the loss of available P through those processes, producers tend to add P fertilizers on an annual basis. Over application of P fertilizers may have serious environmental implications such as P leaching and eutrophication of surface waters (McDowell et al. 2001).

Research on the Canadian Prairies has looked at the different forms of soil P along topographic sequences (e.g. Roberts et al. 1985; Schoenau et al. 1989). In the Black Chernozemic soils, Roberts et al. (1985) found that labile inorganic P concentrations were highest in the mid-slope position in the surface soils and highest in the lower slope position in the subsurface soils. They suggested that soil moisture is an important factor in the distribution of soil P across the landscape that encourages greater productivity in the lower slopes, resulting in more inorganic P removed from the subsoil and increased pedogenic weathering. Thus, more P is available for plant uptake and possible leaching from the profile. Schoenau et al. (1989) did a comparison between landscape positions and different land uses and found that when comparing landscape positions the upland cultivated Brown Chernozemic soils had lower labile inorganic P concentrations than the lower slope cultivated Gleysolic soils. They suggests that the 70 years of continuous cereal-fallow cultivation in the upland cultivated Chernozemic soils contributed to the lower amounts of P available in comparison to the Gleysolic soils. The cultivated Gleysolic soils had higher labile inorganic P (68.44 mg kg^{-1}) than the native Gleysolic soils (44.82 mg kg^{-1}) when comparing different land uses located in the same landscape position. An important characteristic that is particular to riparian areas that affects P mineralization are floods. Reddy (1985) found that in wetland soils where there was alternate soil wetting and drying, P mineralization was enhanced because of changes in soil pH that increase P availability and microbial activity. This may explain why the availability and mobility of P in these soils is greater under anaerobic conditions than in dryland soils, creating the potential for P movement from runoff. There have been few studies of P mineralization comparing between upland and riparian landscape positions or different riparian land use treatments in Central Alberta.

The objective of this study was to determine the effects of landscape position (upland vs. riparian) and land use (native vegetation vs. forage) on the net P mineralization rate in an agricultural landscape.

This chapter focuses on testing the following two hypotheses:

1) I hypothesized that soil net P mineralization rates were greater in the forage upland than in the forage riparian areas in Central Alberta. Greater net P mineralization rates could occur under aerobic conditions in the upland compared to anaerobic conditions that can be found in the riparian area.

2) I hypothesized that soil net P mineralization rates were greater in the forage riparian than the native vegetation riparian areas in Central Alberta. Greater net P mineralization rates could occur in forage riparian treatments because of higher available phosphorus concentrations due to inputs such as inorganic fertilizers placed on the forage riparian lands and warmer soil temperatures than in the native vegetation riparian area.

3.2 Materials and Methods

3.2.1 Study Site

The study site (53°18'57.2" N, 113°36'42.6" W) was located approximately 1.5 km west of the Edmonton International Airport in Alberta along Whitemud Creek, a tributary of the North Saskatchewan River. Situated on land owned by the Edmonton International Airport Authority, the study site is leased to a producer for agricultural production. The site is approximately 699 m above sea level in the riparian area and 702 m above sea level in the upland (S. Reedyk personal communication). Water levels in Whitemud Creek ranged from 698.5 m to 699.5 m (S. Reedyk personal communication). The study site belongs to the Aspen Parkland Ecoregion, which is part of the Prairies Ecozone (Ecological Stratification Working Group 1996). The Aspen Parkland Ecoregion is the transitional region between the boreal forest to the north and the grasslands to the south. The 30-year average annual precipitation from 1971 to 2000 recorded by the Environment Canada weather station at the Edmonton International Airport (53° 19' N, 113° 34' W) was 374.8 mm (343.6 mm occurred in the summer between May and September); the average snowfall was 121.4 cm; the mean annual temperature was 2.4 °C (13.1 °C in summer) (Environment Canada 2006a). The 30-year average frost-free period from 1971 to 2000 at the Edmonton International Airport, which is the number of days between the last date of 0 °C in the spring and the first date of 0 °C in the fall, is approximately 115 days from May 21 - September 13 (Alberta Agriculture and Food 2007). The 30-year average growing season from 1971 to 2000 at the Edmonton International Airport, which is the period when perennial crops can grow, is longer that the frost-free period and is approximately 185 days from April 16 to October 16 (Alberta Agriculture and Food 2007). The mean temperatures in summer 2005 and 2006, when this experiment was conducted, were 12.7 and 14.2 °C, respectively; the summer precipitation in 2005 and 2006 were 282 and 311 mm, respectively (Environment Canada 2006b).

The agricultural land was under a canola (*Brassica napus*) crop in 2004. Prior to the start of this project in 2005, the producer cultivated the land, sprayed with glyphosate at a rate of 1.0 L ha^{-1}, broadcast applied inorganic fertilizer and forage seed together and incorporated them into the soil to a 1.3 cm depth with a cultivator. The hay forage mix is based on forage seed weight and is comprised of 74% alfalfa (*Medicago sativa* var. Nordica), 14.8% Italian rye grass (*Lolium multifolum* var. Royal), 7.4% orchard grass (*Dactylis glomeratu* var. Glacier) and 3.7% timothy (*Phleum pretense L.* var. Tuukka). When applied, the hay forage mix received 33 kg N ha^{-1} as 46-0-0, 8 kg N ha^{-1} and 34 kg P ha^{-1} as 12-51-0 and 32 kg K_2O ha^{-1} as 0-0-60 (G. Shiewe personal communication). In 2005 the agricultural land was dominated by volunteer canola, which was cut and silaged at the end of August 2005 (Figure 3.2a). In 2006, the dominant species of vegetation on the agricultural land was alfalfa (G. Chu and L. Townley-Smith personal communication) (Figure 3.2b). The forage mix was cut and silaged in July 2006 and cut and baled in September 2006. No further cultivation or addition of fertilizer occurred in 2006.

Cultivation was conducted on both sides of the creek to within a few meters of the creek or closer, leaving approximately a 1 m strip of native vegetation along the stream bank and pockets of native riparian vegetation on either side. The dominant grass species in both years in the native vegetation plots were reed canary grass (*Phalaris arundinacea),* Kentucky bluegrass (*Poa pratensis L.*), marsh reed grass (*Calamagrostis canadensis)* and common cattail (*Typha latifolia).* The dominant tree/woody shrub species in the native vegetation area were trembling aspen (*Populus tremuloides*), red-osier dogwood (*Cornus stolonifers*), western snowberry (*Symphoricarpos occidentalis*), chokecherry (*Prunus virginiana*), willow (*salix spp.*), Saskatoon (*Amelanchier alnifolia*) and northern gooseberry (*Ribes oxyacanthoides*) (G. Chu and L. Townley-Smith personal communication) (Figure 3.2c).

The site is characterized as having an undulating landscape with low relief. The parent material is glacio-lacustrine (Bowser et al. 1973; Alberta Agriculture, Food and Rural Development 2007). The soil texture (see below for a description of the method used for soil texture analysis) for the top 20 cm of the soil was clay loam to silt loam in the upland position, silty clay loam in the forage riparian position, and a silt loam to silty clay loam to clay loam in the native vegetation riparian position. The soil in the study site was classified as an Orthic Black Chernozem or Eluviated Black Chernozem in the upland position and predominantly Orthic Humic Gleysol in the riparian position according to the Canadian System of Soil Classification (Soil Classification Working Group 1998). Generally, the top 20 cm of the mineral soil profile was an Ap horizon in the upland position and an Ap to Ahg horizon in the forage riparian position. In the forage upland, there was a Bm horizon (45-75 cm), followed by a Cca (75-100 cm) to Ck (100-200 cm) horizons. The forage riparian position had a Bg horizon (40-80 cm) followed by a Cg horizon (80-100+ cm). The native vegetation riparian position had a 10 cm LFH layer, followed by a Bck horizon (0-5 cm) representing a recent accumulation of sand burying the original soil which comprised of an Ahb horizon for the remaining top 20 cm, followed by a Bgb (35-70 cm) and Cg (70+ cm) horizons.

3.2.2 Experimental Design

This study used a randomized complete block design with three blocks. Each block contained one plot each of forage upland (FU), forage riparian (FR) and native riparian vegetation (NR) (Figure 3.1). This study looked at two pre-planned paired comparisons: FU versus FR and FR versus NR. There were two blocks on the east side of Whitemud Creek with the third block split by the creek with the forage plots on the east side and the native plot on the west side of the creek. The third native riparian plot was located on the west side of the creek because there was not a suitable native riparian area of the same size on the east side. The native riparian plot on the west side of Whitemud Creek had a 0.8 ha buffer immediately to the west that was seeded with the same forage hay mix that was on the rest of the study site.

3.2.3 Soil Sampling and Measurements

Soil Sampling: Soil sampling was conducted at multiple points in time: on June 7, July 6, August 6, September 5, and October 5 in 2005; on May 1, May 31, June 30, July 30 and August 29 in 2006. Within each experimental plot, three soil cores (10 cm long and 5 cm diameter) were collected from randomly selected points and combined to form a composite sample for the 0-10 cm and 10-20 cm mineral soil depth increments. Within each experimental unit, colored pin flags were placed where soil samples were taken the previous sampling time to ensure samples were not taken in the same spot consecutively. Soil samples were placed in coolers, transported back to the lab and were immediately put into a refrigerator (4 °C) until further analysis. In the lab, fresh soil samples were sieved to 4-mm and measured for gravimetric soil moisture content and pH. For available P concentrations, soil samples were air dried for one week and then sieved to 2-mm.

Net P Mineralization Rate: For measuring the net P mineralization rate, the buried-bag method was used. It is an *in situ* procedure that provides an index of phosphorus availability to plants (Pastor et al. 1984). The buried-bag method measures the net P mineralization rate by measuring changes in the inorganic P pool size before and after the incubation.

For each experimental unit at each depth increment (0-10 and 10-20 cm) and for each sampling date, six soil cores, length and width described in the soil sampling section above, were taken: three cores were analyzed for soil available P concentrations on that day (T1) and the other three cores were analyzed after being incubated for 30 days in the field (T2). The three T1 soil samples from each plot were taken to the lab, mixed together to make one composite sample, sieved through a 4-mm mesh to remove plant material, air dried for one week, sieved through a 2-mm mesh and measured for available P concentrations at T1 using the Kelowna method described below. The three T2 intact soil samples were placed in polyethylene bags, sealed and buried in the hole from which they originated and incubated in three randomly selected points *in situ* to determine net P mineralization rates at 30-day intervals except a longer period was used for the winter 2005/06 incubation period. The plastic for making the bags was 15 to 30 μm thick and were permeable to gases such as oxygen and carbon dioxide, but impermeable to liquids. After 30 days, incubated soil cores were removed from the field, mixed and sieved to form one composite sample and measured for available P concentrations at T2. The net P mineralization rate was determined using the following calculation:

$$\textbf{Net P mineralization} = [(H_2PO_4\text{-}P)_{(T2)} - (H_2PO_4\text{-}P)_{(T1)}]/(T)$$

where T is the number of days the sample is incubated. Net P mineralization rates can be positive or negative, with negative values indicating net immobilization.

Incubations were conducted in 2005 and 2006: four times in 2005 from June 7 to July 6, July 6 to August 6, August 6 to September 5, and September 5 to October 5. Hereafter, these dates are abbreviated as June 05, July 05, August 05 and September 05, respectively. As well, an over-winter incubation took place from October 5, 2005 to May 1, 2006 and is abbreviated as Winter 05/06. Incubations in 2006 were conducted five times from May 1 to May 31, May 31 to June 30, June 30 to July 30, July 30 to August 29 and August 29 to September 28. Hereafter, these dates are abbreviated as May 06, June 06, July 06, August 06 and September 06.

The available P concentrations in the soil samples were determined using the Kelowna Method. Six grams of air dried soil samples, sieved to 2 mm, were extracted using 60 mL of a solution containing 0.015 mol L^{-1} ammonium fluoride and 0.25 mol L^{-1} glacial acetic acid (Van Lierop 1988). This method is recommended for Canadian prairie soils (Havlin et al. 2005). Samples were filtered through No.5 Whatman filter papers and the extracts were stored in plastic bottles in a freezer (-18 °C) until further analysis. Available P concentrations in the extracts were determined by the ascorbic acid method (Murphy and Riley 1962) where acidic molybdate solution containing ascorbic acid, forms and reduces phosphomolybdic acid and then develops the molybdenum blue color. The absorbance was measured by a spectrophotometer (Genesys 10-S, Thermospectronic, USA) at 880 nm.

Available P Concentrations: Soil available P concentrations were determined using the Kelowna Method as described above. This is a measure of soil P availability and was measured on un-incubated samples.

Soil pH: Air-dried soil samples were sieved to 2 mm for 0-10 and 10-20 cm soil depth increments. The pH was determined with deionized water and a 0.01 mol L^{-1} calcium chloride ($CaCl_2$) solution at a ratio of 1:2 (w:v, 10 g of dry soil:20 mL of deionized water or $CaCl_2$ solution) (Kalra and Maynard 1991). Soil pH was measured using a pH meter (Piccolo® 2 portable pH electrode, Hanna Instruments, Laval, Canada).

Soil Texture: Dried soil samples, sieved to 2-mm, from each experimental unit at each soil depth increment, were sent to ALS Laboratory Group (Alberta, Edmonton, Canada) for particle size distribution and were determined using the hydrometer method (Sheldrick and Wang 1993).

Moisture Content: To obtain a good estimate of soil water content, ten grams of fresh wet soil sample was weighed out into a tin and the water in the soil is removed by drying the soil sample in an oven at 105 °C for 24 hours (Topp and Ferré 2002). After 24 hours, the soil sample is removed from the oven, cooled to ambient room temperature and then reweighed to determine the amount of water removed. The gravimetric water content is defined as the ratio of the mass lost that is attributed to water that was initially present in the soil. Water content on a mass basis is calculated as a percentage of the mass of dry soil:

$$\theta_m = \frac{(mass\ of\ moist\ soil + tin) - (mass\ of\ dry\ soil + tin)}{mass\ of\ dry\ soil}$$

Soil Temperature: Soil temperature at the depths of 10 cm and 20 cm from the mineral soil surface was recorded by HOBO H8 Temp Loggers (Onset Computer Corporation, Bourne, MA, USA) in the two growing seasons; two loggers were buried at each depth randomly in each experimental plot on June 6, 2005 and April 12, 2006. Blue pin flags indicated their locations in the plots. The hourly readings from the loggers were averaged to calculate the daily temperature means for each plot. The temperature means (129 days in 2005 and 170 days in 2006) were calculated and used for statistical analysis.

Potential P Supply Rate of Soils: Plant Root Simulator $(PRS)^{TM}$ probes (Western Ag Innovations Inc., Saskatoon, Canada), equipped with ion-exchange membranes were used to estimate the potential P supply rates of the soils to plants. These membranes also act as an ion sink, which simulate ion adsorption by plant roots. The manufacturer (Western Ag Innovations, Saskatoon, SK) claims that because the plant roots weren't separated from the probes, the measured values are net P supply rates (e.g. total soil supply of P – plant uptake), however, these PRS^{TM} probes are supposed to simulate plant root adsorption and should be able to compete for the same nutrient pools with plant roots. These probes have some advantages over conventional soil extraction methods because they take into account factors such as soil moisture, soil temperature, mineralization and immobilization and ion diffusion that affect nutrient uptake by plants (Qian and Schoenau 2002; Hangs et al. 2004). This method used resins which measured the amount of nutrient adsorbed but did not measure the pool size or flux. Therefore, this method provides an index of ion supply in the soil solution.

Prior to receiving the membranes encased in 15 cm x 3 cm x 0.5 cm plastic frames, Western Ag Innovations Inc. saturated the four anion exchange membranes with bicarbonate (HCO_3^-), by shaking the membranes three successive times in 0.5 mol L^{-1} $NaHCO_3$ for 4 hours (Hangs et al. 2004). The regenerated PRS^{TM}-probes were rinsed with deionized water before delivery. The probes at the 10-20 cm depth increment were inserted vertically by using a spade to cut out a soil wedge to the 20 cm depth. The probes at the 0-10 cm depth increment were placed vertically above the probes at the lower depth increment. To ensure sufficient contact between probes and the soil, the soil wedge is replaced, a spade is inserted approximately 15 cm away from the probe insertion area and the soil is pushed against the probes. A pink pin flag was used to help find the probes again as well as all probes had pink flagging tape tied around their handles. The probes were inserted into the soil in each experimental plot and incubated for one month (Figure 3.3a). Within each NR plot, probes were placed in areas that represented different vegetation types and proximity to the creek (e.g., under tree canopy, under shrub canopy and various distances away from Whitemud Creek).

After a 30-day insertion period, the probes were taken out of the soil and then in the identical place, the same type of anion probe was inserted to start a new incubation. The measurements were made four times in 2005 from June 6 to July 5, July 5 to August 5, August 5 to September 4 and September 4 to October 4, referred to as June 05, July 05, August 05 and September 05 insertions, respectively. Measurements were also made three times in 2006 from May 2 to June 1, June 1 to July 1 and July 1 to July 30, referred to as May 06, June 06 and July 06, respectively. The four sets of anion probes were retrieved from each experimental plot, sprayed with deionized water and as recommended by the supplier, scrubbed with a coarse brush and then rewashed to remove the residual soil (Figure 3.3b). The PRS^{TM} probes were placed into Ziploc$^{®}$ bags, packaged in a cooler and sent to Saskatoon, Canada for analysis. In the Western Ag Labs, the probes were extracted by 17.5 mL of 0.5 mol L^{-1} HCl per probe in Ziploc® bags (140 mL per bag). The probes were gently shaken with the HCl to ensure it covered the membrane surface to eluate the adsorbed ions for analytical measurement (Hangs et al. 2004). After one hour, the eluate is poured off into vials and is analyzed. Phosphorus was measured with a PerkinElmer Optima 3000-DV inductively coupled plasma (ICP) (PerkinElmer Inc., Shelton, Conn.). Data generated from the ICP analytical instrument was reported in units of μg nutrient ion per mL eluate solution (e.g. ppm). More details can be found in the Operations Manual (Western Ag Labs 2006) but the overall equation for determining the potential nutrient supply rates from eluate ppm data was:

$$\frac{\mu g\, H_2PO_4 - P}{mL\, of\, eluate} * \frac{17.5\, mL\, eluate}{probe} * \frac{8\, total\, probes}{bag} * \frac{bag}{4\ anion\, probes} * \frac{probe}{17.5\, cm^2} * 10 = \frac{\mu g\, H_2PO_4 - P}{10\, cm^2}$$

The ion concentration in the eluate solution is multiplied by the volume of eluate used to eluate the probes to obtain the total weight of ions eluted. The total weight of ions eluted was divided by the total membrane surface area of the anion probes eluated in the sample (17.5 cm^2 per PRS™ probe) and then multiplied by the number of probes to obtain the weight of ion adsorbed per unit surface area of ion exchange membrane. Finally, the value was multiplied by a conversion factor of 10 to increase the sample size with numbers greater than 1 for most of the measured nutrients and to standardize reporting protocol.

3.2.4 Statistical Analyses

The PROC MIXED procedure in SAS (SAS Institute Inc. 1999) was used to analyze two one-way ANOVA's with blocking and repeated measures to evaluate the effect of landscape position (forage upland vs. forage riparian) and land use (native riparian vs. forage riparian) for each of the response variables: available P concentration, P mineralization rate, potential P supply rate, gravimetric soil moisture content, soil temperature and soil pH.

Model:

$$Y_{ijk} = \mu + \rho_j + \alpha_i + d_{ij} + \gamma_k + (\alpha\gamma)_{ik} + \varepsilon_{ijk}$$

Where:

Y_{ijk} = rate of response variable

μ = mean rate of response variable (e.g., P mineralization rate)

ρ_j = block factor

α_i = treatment effect (land use or landscape position)

d_{ij} = random error for the whole plot

γ_k = time (month)

$(\alpha\gamma)_{ik}$ = interaction between treatment and time

ε_{ijk} = random error on repeated measures

To compare the covariate variables (soil pH, gravimetric soil moisture content and soil temperature) with the response variables (available P concentration, P mineralization rate and potential P supply rate), regression and the Pearson Product Moment Correlation analyses were used.

The data in 2005 and 2006 were analyzed separately because of the dominant crop in the forage plots were different: volunteer canola in 2005 and an alfalfa forage mixture in 2006. Outliers were assessed by first using the modified Z-score calculation on each treatment effect and then data was plotted on a scatter plot to determine visually if any outliers still remained. The modified Z-score uses the median and the median of the absolute deviation about the median (MAD) (Iglewicz and Hoaglin 1993; Seo 2006) where:

$MAD = median\ \{|x_i - \tilde{x}|\}$, where $\tilde{x}$ is the sample median and x_i is a measurement in the data set where one measurement might be denoted as x_1, another x_2 and so on. The subscript i might be any integer value up to N, the total number of x values in the dataset (Zar 1999).

The modified Z-Score (M_i) is computed as:

$$M_i = \frac{0.6745(x_i - \tilde{x})}{MAD}$$

Observations were labeled outliers when $|Mi| > 3.5$ (Iglewicz and Hoaglin 1993).

Normality tests on the data set were conducted using the PROC UNIVARIATE procedure (the Shapiro-Wilks test) and showed that transformations of data were not required. The Bartlett test using the PROC GLM procedure showed that the data had variances that were not homogenous. The PROC MIXED procedure overcomes this problem. For statistical significance, $\alpha = 0.05$ was chosen.

3.3 Results

3.3.1 Soil Temperature

There were significant time-of-season effects on soil temperature at both depths in 2005 and 2006 (Table 3.1, Figure 3.5). In 2005, average daily temperature was highest in the summer (June – August) (15.6 °C in FU, 15.36 °C in FR and 12.86 °C in NR) but lowest in the fall (September – October) (8.16 °C in FU, 7.96 °C in FR and 8.16 °C in NR).

In 2005 at both depths, the interaction between land use and time on soil temperature was significant, showing that the FR treatment had higher soil temperatures than in the NR in all months except September where it did not affect soil temperature (Table 3.1, Figure 3.5). In 2005 at 10-20 cm, the interaction between landscape position and time on soil temperature was significant, showing that the FU had higher temperatures than in the FR in June but in July the FR had higher temperature than in the FU but did not affect soil temperature in the other sampling dates ($p = 0.004$).

In 2006 at the 0-10 cm depth, the interaction between landscape position and time on soil temperature was significant, showing that the FU had higher temperatures than in the FR on all dates except August and September ($p = 0.002$). The interaction between land use and time was significant, showing that soil temperature at both depths in the NR treatment was lower than that in the FR treatment throughout the growing season.

3.3.2 Gravimetric Soil Moisture Content

In 2005 at the 0–10 cm depth increment, gravimetric soil moisture content in the FR plots increased from 36.1% in June to 55.1% in October (Figure 3.6). The gravimetric soil moisture content in the FU remained the same throughout the growing season at an average of 27.4%. Soil moisture content was higher in the FR than in the FU treatment at the 10-20 cm in both years and 0-10 cm in 2006 ($p < 0.01$ for both years and both depth increments) (Table 3.1, Figure 3.6). In 2005, the interaction between landscape position and time on gravimetric soil moisture content was significant, showing that the lower landscape position, FR, had higher gravimetric soil moisture content than in the FU from May 1 – June 30 but on August 29, the FU had higher gravimetric soil moisture content than in the FR (Table 3.1, Figure 3.6). In 2005 at the 10–20 cm depth increment, soil moisture content was higher in the NR than in the FR treatment.

3.3.3 Soil pH

Soil pH_{CaCl_2} and soil pH_{H_2O} in 2005 and 2006 in both depth increments remained near neutral throughout the growing season. In 2005 at the 0–10 cm and 10–20 cm depth increments, both landscape position and land use treatments significantly affected soil pH_{CaCl_2}. Soil pH_{CaCl_2} was significantly higher in the FR than in the FU and NR treatments (Table 3.2, Figure 3.7). In 2005 in the 10-20 cm depth increment, the interaction between land use and time on soil pH_{CaCl_2} was significant, with the soil pH_{CaCl_2} levels lower in the NR than in the FR on all sampling dates, except on July 7 and August 6 where there was no effect on soil pH levels (Table 3.2, Figure 3.7a-ii). In 2006 at both depth increments, the interaction between landscape position and time was significant, showing that the higher landscape position, FU, had lower soil pH_{CaCl_2} levels than in the FR on May 1 and May 30 but did not affect soil pH_{CaCl_2} levels in other sampling dates (Table 3.2, Figure 3.7a-i, Figure 3.7a-ii).

3.3.4 Potential P Supply Rate

In 2005, land use treatments significantly affected potential P supply rates as supply rates were higher in the NR than in the FR treatment at the 0-10 cm depth increment (p = 0.001) (Table 3.3, Figure 3.8). In 2006, at the 0-10 cm depth increment, landscape and land use treatments significantly affected potential P supply rates. Potential P supply rates were higher in the FR than in the FU treatment (p = 0.020) and were also higher in the NR than in the FR treatment (p = 0.030). At the 10-20 cm depth increment, the interaction between land use and time on potential P supply rates was significant, showing that the NR had higher P supply rates than in the FR in July but it did not affect rates in May and June (p = 0.010, Table 3.3, Figure 3.8). Also at the 10-20 cm depth increment, the interaction between landscape position and time was significant because the potential P supply rates in the FU increased in June but did not affect potential P supply rates in the landscape position treatments in May and July (p = 0.035, Table 3.3, Figure 3.8). In 2006, as soil temperature increased, potential P supply rates decreased linearly at the 0-10 cm depth increment ($R^2 = 0.25, p = 0.009$) (Figure 3.9).

3.3.5 Available P Concentration

In 2005 at the 0-10 cm depth increment, the interaction between landscape and time was significant with increasing available P in the FU than in the FR in July 7 and August 6 but did not affect available P in the other sampling dates (p = 0.038, Table 3.3, Figure 3.10). A significant relationship showed that as gravimetric soil moisture content increased, available P concentrations increased linearly in 2005 ($R^2 = 0.21, p = 0.004$) (Figure 3.11) and a significant correlation was found between the two variables in 2006 at 0-10 cm (R

= 0.39, $p = 0.019$, Table 3.4b). In 2005 at the 10-20 cm depth increment, the interaction between landscape position and time was significant, with increased available P concentrations in the FU than in the FR in June 7 and decreased available P concentrations in the FU than in the FR in October 6, but did not affect available P concentrations in other sampling dates ($p < 0.001$, Table 3.3, Figure 3.10).

In 2006 at both depth increments, with the exception of the land use treatments at the 0-10 cm depth increment, the interaction between landscape position and time and land use and time on available P concentrations were significant because available P concentrations increased in August 29 in all treatments but did not affect available P rates in other sampling dates (Table 3.3, Figure 3.4, Figure 3.5, Figure 3.10). A precipitation event of 10.2 mm occurred several days prior which may have allowed a flush of organic P to be mineralized, however, a more likely reason is that soil sieving and Kelowna Method extractions were done on the August 29th samples in another lab so variation in protocol may have affected the available P concentrations that were reported.

3.3.6 Net P Mineralization Rates

There was a seasonal trend at the 0–10 cm depth increment that showed net P mineralization in 2005 and then net immobilization in winter 05/06 (Figure 3.12). In 2006, across all 3 treatments, the net P mineralization rate increased throughout the growing season and was highest in August. In September 2006, both FU and FR had net immobilization while the NR treatment had net mineralization (Figure 3.12).

In 2005 at the 0-10 cm depth increment, the interaction between land use treatments and time on net P mineralization rates was significant showing that the NR had net P immobilization rates while the FR had higher net P mineralization rates in July but did not affect net mineralization rates in other sampling dates ($p = 0.044$, Table 3.3, Figure 3.12). In 2006 at the 0-10 cm depth increment, the interaction between landscape position and time, and land use and time on net P mineralization rates were significant because both the FU and the FR had net immobilization rates and the NR had a higher P mineralization rate in September, but did not affect net mineralization rates in other sampling dates (Table 3.3, Figure 3.12). In 2005, as net P mineralization rates increased, available P concentrations decreased linearly at both 0–10 cm ($R^2 = 0.24$, $p = 0.004$) and 10–20 cm depth increments ($R^2 = 0.44$, $p < 0.001$) (Figure 3.13a and b).

In 2006, at the 10–20 cm depth increment, the net P mineralization rate was around zero for the majority of the growing season, except in August where all three treatments had a significantly higher P mineralization rate than the rest of the months. The interaction between land use treatments and time on net P mineralization rates was significant, showing that the FR had increased net P immobilization in September but did not affect net mineralization rates in the other sampling dates ($p < 0.001$, Table 3.3, Figure 3.12). At the 10-20 cm depth increment, the interaction between landscape position and time on net P mineralization rates was significant where both the FU and the FR had increasing net P mineralization rates in August but then decreased in September where FR had net immobilization, but did not affect net mineralization rates in the other sampling dates ($p = 0.031$).

3.4 Discussion

3.4.1 All treatments

The seasonal patterns of net P mineralization rates occurred in the spring and summer with net immobilization in the winter. From spring to summer, as soil temperature increased, net P mineralization increased which produced inorganic P that is available for plant uptake (Figure 3.5, Figure 3.12) (Blair and Boland 1978; Fabre et al. 1996). During winter when temperatures have decreased and created unfavorable soil conditions (intermittently frozen and dry), plant growth and mineralization rates were also low. Any remaining litter that was decomposed, may not have sufficient nutrients to meet microbial demands so any soil available P in the soil solution would be immobilized into the microbial tissues.

One possible explanation for the increased net P mineralization rates in August 2006 was the amount of precipitation up to and including the sampling date of July 30. From July 26–30, the research site received 35.8 mm of rain (Figure 3.4). The incubated soil sample would have remained at the higher gravimetric soil moisture content for 30 days in the bag because there was no exchange of water between the soil in the bag and the environment, thus, forms of P that were adsorbed onto clay surfaces or precipitated onto secondary minerals may have increased the available P pool through desorption and dissolution. In comparison, the plots would be subject to processes such as plant uptake of available P and drying and rewetting of the soil during sporadic precipitation events during that same incubation period. During increased soil moisture content, non-labile forms of P such as Ca-P minerals would have increased solubility, increased availability of organic substrates through desorption from soil surfaces and decomposable organic substrates from dead microorganisms from disruption of the soil aggregates may have increased the soil available P pool (Grierson et al. 1998). On August 29, compared to the rest of the 2006 growing season for both 0–10 cm and 10–20 cm depth increments, there was an enrichment of available P concentrations rates across all treatments and depth increments because of the high P mineralization rates in August (Figure 3.10 and Figure 3.12).

In 2005 and 2006, gravimetric soil moisture content had significant relationships with available P (Figure 3.11, Table 3.4b). Although available P concentrations will increase in aerobic conditions, 94% of P is taken up by plants through diffusion so gravimetric soil moisture contents must be enough to allow flow of nutrients towards plant roots in the soil and encourage microbial activity, including mineralization (Wild 1988; Havlin et al. 2005). Roberts et al. (1985) found that along a topographic sequence in the Black Chernozemic soil, the surface soils showed no consistent trend in soil available P distribution which agrees with the data for 2005.

Although soil pH_{CaCl_2} was significantly affected by landscape position and land use treatments and is an important factor in P availability, the soil pH values were not correlated with any P experimental data (Table 3.4). The variability of the soil pH_{CaCl_2}values were within the neutral pH range and the soils at this site are from calcareous parent material (Figure 3.7). Phosphorus can readily precipitate as secondary compounds or adsorb onto mineral surfaces, and as soil pH increases towards 7.0, P adsorption onto calcium oxide increases and P availability decreases (Barrow 1984).

Minimum P adsorption by Fe, Al or Ca oxides is lowest and P availability is highest at a pH 6.0 to 6.5 (Stevenson and Cole 1999). The establishment of beaver dams in 2005 and spring melt in 2006 caused flooding to occur in the FR plots and the minor fluctuations in soil pH throughout the growing seasons, may have resulted from the movement of salts as soil moisture moved up and down through the soil profile (Brady et al. 1996).

Additions of P by fertilizer or mineralization from organic P from plant residues will likely be adsorbed onto mineral surfaces or precipitated until the potential of adsorption decreases and adsorption sites are saturated, thus an available P concentration would occur. When there is a depletion in soil available P concentration because of plant uptake or adsorption to mineral surfaces or immobilization, the labile and the non-labile pools will dissolve to resupply $H_2PO_4^-$ and HPO_4^{-2} in the soil solution P by dissolution of mineral P or release of adsorbed P to re-establish the P equilibrium so there is a constant soil available P concentration (Havlin et al. 2005). This may explain the significant inverse relationship between net P mineralization and available P concentrations in 2005 at the 0–10 cm ($R^2 = 0.24$, $p = 0.004$) and 10–20 cm soil depth increments ($R^2 = 0.44$, $p < 0.001$) (Figure 3.13a and b). Where there were low available P concentrations, organic P was mineralized to increase the soluble P pool and once there were sufficient available P concentrations, the mineralization rate shifts towards immobilization due to the equilibrium between soil adsorption, soil solution and precipitation of P (Havlin et al. 2005).

3.4.2 Landscape Treatments

Although it was hypothesized that potential P supply rates would be higher in the FU than in the FR because of higher soil temperature and lower gravimetric soil moisture content, the opposite occurred. In 2006, lower soil temperature and higher gravimetric soil moisture content were found where potential P supply rates were higher in the FR than in the FU (Table 3.3, Figure 3.8) which is also different from other research (Qian and Shoenau 2002; Johnson et al. 2005). The FR plots were on Gleysolic soils with slightly more clay than the FU plots on Chernozemic soils which may have contributed to the increase in potential P supply rates in the FR. In addition, potential P supply rates decreased linearly as soil temperature increased at the 0-10 cm depth increment ($R^2 = 0.21, p = 0.004$) (Figure 3.9). The potential P supply rates for FR in May and June 2006 may have been underestimated while the gravimetric soil moisture content may have been overestimated which could explain why no significant relationship could be determined between the two. In both months at the beginning of each insertion period, some of the probes were inserted into muddy and waterlogged soils. In a month's time, when the probes were removed, soil moisture had decreased and the soil had contracted to the point that there was poor contact between the soil and the membrane, affecting the potential P supply rate measurement (Johnson et al. 2005). Gravimetric soil moisture content for the burial period was only measured at the initial time of the burial period which did not represent the soil moisture content of the entire burial period. To ensure sufficient probe to soil surface contact, probes should be checked during the burial period and repositioned if necessary. Gravimetric soil moisture content could also be measured during the burial period in order to capture changes in soil moisture content.

Net P immobilization occurred at both depth increments in the FU and in the FR in September 2006 and a possible explanation may be the addition of residues from the alfalfa-grass forage stand. Although the predominantly alfalfa forage crop was cut and then silaged the week of July 6th, not all the material was removed from the site. As the decomposition of the cut alfalfa-grass residue continued throughout the summer, there is an increase in the number of organisms which used the new material for their own energy source and may have caused net immobilization to occur (Vitousek 1982).

According to Manunta et al. (2000), the majority of non-irrigated agricultural land in Alberta has a mean extractable P range of 25-30 kg ha^{-1} in the top 15 cm of the soil surface and based on the study by the Alberta government, soil in this range are generally deficient or marginal for crop production. The available P concentrations at this site were in this range (Table 3.5).

Agronomic thresholds for P in Alberta were established by Alberta Agriculture, Food and Rural Development (AAFRD) to provide a soil test P (STP) level. Howard (2001) defines STP as methods that are based on using chemicals to dissolve enough P from the soil to estimate the amount of P the soil can supply to a crop and to determine an index of the amount of additional P needed to prevent crop value loss due to P deficiency. For most crops, any more than 60 kg ha^{-1} STP would not be economically practical or give any further crop yield response to add P from inorganic and organic fertilizers based on a Norwest modified Kelowna extraction (McKenzie et al. 1995; Howard 2001). The Norwest modified Kelowna Extraction developed by Ashworth and Mrazek (1989), is one of the two most commonly used for determining soil test P levels in Alberta (Howard 2001). According to McKenzie et al. (1995), agronomic thresholds for canola in Alberta for STP are between 20 to 60 kg ha^{-1}. Averaging the 2005 field data over the field season and calculating the equivalent STP values using a regression equation (Equation 1) derived by McKenzie et al. (1995), it was determined that the values were in the lower range of providing adequate yield for canola and an addition of P fertilizers may increase the canola yield without affecting soil and water quality (Table 3.5). STP levels for my site were derived from the relationship between the Kelowna Test, which was used to extract available P concentrations for this study and a modified Kelowna Method (Norwest) that is commonly used in laboratories in Alberta.

$$y = 1.915 + 1.137x \qquad \text{(Equation 1)}$$

where x = Norwest Modified Kelowna Method, y = Kelowna Test

(McKenzie et al. 1995)

According to the Alberta Fertilizer Guide published by Alberta Agriculture, Food and Rural Development (2004), the P_2O_5 fertilizer recommendations for canola for the black soil zone is between 17 – 39 kg ha^{-1}. Annual soil testing of this site would best determine the appropriate rate of fertilization depending on the crop grown.

For alfalfa, there have not been any clearly defined agronomic thresholds for P (Howard 2001). Following the AAFRD recommendations of the upper limit 60 kg ha^{-1}, however, the 2006 field data averaged over the growing season and calculated using a regression equation derived by McKenzie et al. (1995) (Equation 1), found STP values were within the limits for providing adequate yield for alfalfa, in particular, the forage riparian treatment (Table 3.5). According to the Alberta Fertilizer Guide published by Alberta Agriculture, Food and Rural Development (2004), the P_2O_5 fertilizer recommendations for a crop with greater than 60% legumes for the black soil zone is between 0–67 kg ha^{-1}. Increased P fertilizer application in the spring is necessary but it would have to be discussed with the producer to find out what his nutrient management plan is and take into consideration the local conditions, economics, crop history and goals for that field. Annual soil testing of this site would best determine the appropriate rate of fertilization of P and other nutrients depending on the crop grown and should be done to ensure that there are sufficient nutrients for optimal crop yield, however, this test alone does not provide the potential rate for the release of P into the surface water (Pote et al. 1996). Soil testing should be used in association with other measurements to predict that risk, such as measurement of dissolved and/or particulate P. In Alberta, the surface water quality guideline for the protection of freshwater aquatic life for P (total inorganic and organic) is 0.05 mg L^{-1} under chronic conditions (Alberta Environment 1999).

3.4.3 Land Use Treatments

With the diversity of vegetation present and no removal of plant material in the NR treatment for many years, there was constant litter input throughout the growing season. As soil temperatures increase in the spring, organic P from the litter becomes mineralized, evidenced by the increase in potential P supply rates in May 2006 and could be removed from the soil into Whitemud Creek by spring melt events (Figure 3.5, Figure 3.8). In the FR treatment, the volunteer canola and alfalfa crops were removed periodically so litter accumulation was minimal. Vegetation data for the research site showed that in 2005 and 2006, nutrient uptake was highest and accumulation of litter largest in the NR areas (G. Chu and L. Townley-Smith personal communication). In the NR, net immobilization was likely to happen throughout the growing season as different types of litter may not have sufficient nutrient contents for the microbial demand present (e.g. July and August 05) (Figure 3.10).

3.5 Conclusions

Net P mineralization and available P concentrations were dependent on time of season and treatment interactions. The trend of net P mineralization rates throughout the growing season and net P immobilization in the winter was likely affected by soil temperature. Both methods of measurement of P mineralization, the buried-bag and the PRS^{TM} probes, rejected both hypotheses at both depth increments.

According to AAFRD P threshold guidelines, further addition of P fertilizer is recommended because the P levels at this site were deficient or marginal for crop production. Annual soil testing is needed to determine if P levels are adequate for crop growth without over applying fertilizers and manures. In native riparian areas, measurement of P sorption in soils may determine if these areas are functioning as buffers to prevent P runoff into surface waters and preserving water quality. Since soil available P for this area is characteristically low, any additional P from mineralization or fertilizer, may be adsorbed until its capacity becomes saturated.

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Table 3.1 P values from the analysis of variance using repeated measures for soil temperature (°C) and gravimetric soil moisture content (% GS Moisture) as affected by landscape position (LP), land use (LU) and soil depth increment. Highlighted values are significant at $p < 0.05$.

	0–10 cm				**10–20 cm**			
	Soil Temperature (°C)		**% GS Moisture**		**Soil Temperature (°C)**		**% GS Moisture**	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
	Effects of landscape position							
LP	0.470	**0.078**	**<0.001**	**0.002**	0.838	**0.042**	**<0.001**	**<0.001**
Time (T)	**<0.001**	**<0.001**	**0.021**	**<0.001**	**<0.001**	**0.031**	0.498	0.079
LP * T	0.827	**0.002**	0.510	**0.014**	**0.004**	0.474	0.687	0.452
	Effects of land use							
LU	0.245	**0.006**	0.078	0.267	**<0.001**	**<0.001**	**0.006**	0.179
Time (T)	**0.018**	**<0.001**	**0.021**	**<0.001**	**<0.001**	**<0.001**	0.317	**0.022**
LU * T	**0.006**	**<0.001**	0.876	0.526	**<0.001**	**0.004**	0.912	0.926

Table 3.2 P values from the analysis of variance using repeated measures for soil pH using 0.01 mol L^{-1} $CaCl_2$ solution and water as affected by landscape position (LP), land use (LU) and soil depth increment in 2005 and 2006. Highlighted values are significant at $p < 0.05$.

	0–10 cm				**10–20 cm**			
	pH_{CaCl_2}		**pH_{H_2O}**		**pH_{CaCl_2}**		**pH_{H_2O}**	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
	Effects of landscape position							
LP	**<0.001**	0.249	0.053	0.582	**0.004**	0.257	0.139	0.257
Time (T)	0.250	**0.001**	0.101	**<0.001**	0.686	**0.003**	0.580	**0.005**
LP*T	0.806	**0.015**	0.481	0.354	0.603	**0.004**	0.961	0.123
	Effects of land use							
LU	**0.006**	0.350	0.374	0.505	**<0.001**	0.387	0.150	0.483
Time (T)	0.218	**0.014**	0.104	**<0.001**	**0.008**	0.321	**0.009**	**<0.001**
LU*T	0.229	0.934	0.565	0.371	**0.024**	0.312	0.303	0.264

Table 3.3 P values from the analysis of variance using repeated measures for soil net P mineralization (P Min.), available P concentration (Available P) and potential P supply rate (PRS-P) as affected by landscape position (LP), land use (LU) and soil depth increments in 2005 and 2006. Highlighted values are significant at $p < 0.05$.

	0–10 cm						**10-20 cm**					
	P Min ($kg\ ha^{-1}$)		**Available P ($kg\ ha^{-1}$)**		**PRS-P ($\mu g\ 10\ cm^{-2}\ month^{-1}$)**		**P Min ($kg\ ha^{-1}$)**		**Available P ($kg\ ha^{-1}$)**		**PRS-P ($\mu g\ 10\ cm^{-2}\ month^{-1}$)**	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
	Effects of landscape position											
LP	0.612	0.802	0.652	0.054	0.250	**0.020**	0.283	0.510	0.255	**0.006**	0.182	0.120
T	0.333	**<0.001**	0.173	**<0.001**	0.119	**0.004**	0.579	**<0.001**	**<0.001**	**<0.001**	**0.035**	**0.009**
LP * T	0.097	**0.014**	0.997	**0.038**	0.863	0.377	0.087	**0.031**	**<0.001**	**<0.001**	0.827	**0.035**
	Effects of land use											
LU	0.210	0.085	0.679	0.779	**0.001**	**0.030**	0.786	**0.037**	0.602	0.140	0.070	0.110
T	0.324	**<0.001**	0.255	**0.005**	0.480	0.100	0.969	**<0.001**	0.126	**<0.001**	**0.040**	**0.002**
LU * T	**0.044**	**0.001**	0.927	0.912	0.272	**0.010**	0.794	**<0.001**	0.270	**0.012**	0.06	**0.018**

Table 3.4 Correlation coefficient (r value) among soil properties: soil temperature (TEMP), gravimetric soil moisture (MOIST), soil $pH_{(H2O)}$, soil $pH_{(CaCl2)}$, potential P supply rate (PRS- P), P mineralization (PMIN) and available P (AVAIL P) at the a) 0–10 cm in 2005, b) 0-10 cm depth increment in 2005, c) 10–20 cm in 2005 and d) 10–20 cm depth increment in 2006. Highlighted correlation coefficients were significant at $\alpha = 0.05$. P values are in brackets.

(a) 0–10 cm in 2005

Variable	TEMP	MOIST	$pH(H_2O)$	$pH(CaCl_2)$	PRS- P	PMIN
AVAIL P	0.37	0.34	-0.26	-0.04	0.01	-0.21
	(0.06)	(0.09)	(0.21)	(0.828)	(0.966)	(0.277)
	n = 26	n = 27	n = 26	n = 28	n = 26	n = 29
PMIN	-0.09	-0.10	0.11	0.12	-0.17	
	(0.648)	(0.600)	(0.579)	(0.528)	(0.398)	
	n = 26	n = 27	n = 26	n = 28	n = 26	
PRS- P	-0.08	0.38	-0.23	-0.17		
	(0.665)	(0.079)	(0.217)	(0.353)		
	n = 29	n = 28	n = 30	n = 32		

(b) 0–10 cm in 2006

Variable	TEMP	MOIST	$pH(H_2O)$	$pH(CaCl_2)$	PRS- P	PMIN
AVAIL P	-0.25	**0.39**	0.08	0.11	0.26	0.05
	(0.085)	**(0.019)**	(0.631)	(0.476)	(0.250)	(0.718)
	n = 47	**n = 36**	n = 43	n = 45	n = 22	n = 46
PMIN	0.20	-0.26	-0.26	-0.20	0.11	
	(0.194)	(0.126)	(0.096)	(0.205)	(0.646)	
	n = 45	n = 35	n = 41	n = 43	n = 20	
PRS- P	**-0.49**	-0.22	-0.07	-0.05		
	(0.015)	(0.377)	(0.770)	(0.826)		
	n = 24	n = 18	n = 21	n = 23		

(c) 10-20 cm in 2005

Variable	TEMP	MOIST	pH(H_2O)	pH($CaCl_2$)	PRS- P	PMIN
AVAIL P	0.23	0.05	-0.23	-0.06	**0.49**	**-0.74**
	(0.214)	(0.810)	(0.219)	(0.743)	**(0.008)**	**(<0.001)**
	n = 32	n = 28	n = 31	n = 28	**n = 28**	**n = 31**
PMIN	-0.27	0.21	0.24	0.27	-0.16	
	(0.149)	(0.284)	(0.194)	(0.173)	(0.412)	
	n = 31	n = 27	n = 31	n = 27	n = 27	
PRS- P	0.31	0.25	-0.04	0.09		
	(0.093)	(0.204)	(0.832)	(0.647)		
	n = 31	n = 27	n = 30	n = 27		

(d) 10-20 cm in 2006

Variable	TEMP	MOIST	pH(H_2O)	pH($CaCl_2$)	PRS- P	PMIN
AVAIL P	-0.18	-0.08	-0.06	0.11	-0.27	-0.13
	(0.284)	(0.631)	(0.732)	(0.536)	(0.228)	(0.405)
	n = 39	n = 37	n = 37	n = 34	n = 21	n = 43
PMIN	0.21	-0.06	-0.11	0.14	0.03	
	(0.185)	(0.732)	(0.503)	(0.422)	(0.883)	
	n = 40	n = 38	n = 38	n = 35	n = 21	
PRS- P	**0.45**	-0.26	-0.37	-0.23		
	(0.033)	(0.238)	(0.092)	(0.339)		
	n = 23	n = 22	n = 22	n = 45		

Table 3.5 Calculation of equivalent soil test P (STP) derived from a regression equation between the Kelowna method which was used to extract available P concentration in this study and the modified Kelowna method (Norwest) that is commonly used in Alberta for canola in 2005 and alfalfa in 2006 (McKenzie et al. 1995). Available P concentration values were averaged over the growing season.

$y=1.915 + 1.137x$ where x = modified Kelowna method (Norwest), y = Kelowna method

Crop	**Treatment**	**Soil Depth Increment**	**Kelowna Method (y) (kg P ha^{-1})**	**STP – (x) Modified Kelowna (kg P ha^{-1})**
Canola	Forage Upland	0–10 cm	22.62	18.21
	Forage Riparian		28.96	23.79
	Forage Upland	10–20 cm	17.01	13.27
	Forage Riparian		19.76	15.69
Alfalfa	Forage Upland	0–10 cm	29.36	24.14
	Forage Riparian		59.06	50.26
	Forage Upland	10–20 cm	13.75	10.41
	Forage Riparian		44.28	37.26

Figure 3.1 Layout of experimental plots. Comparisons are between landscape position (Forage Upland vs. Forage Riparian) and land use (Forage Riparian vs. Native Riparian).

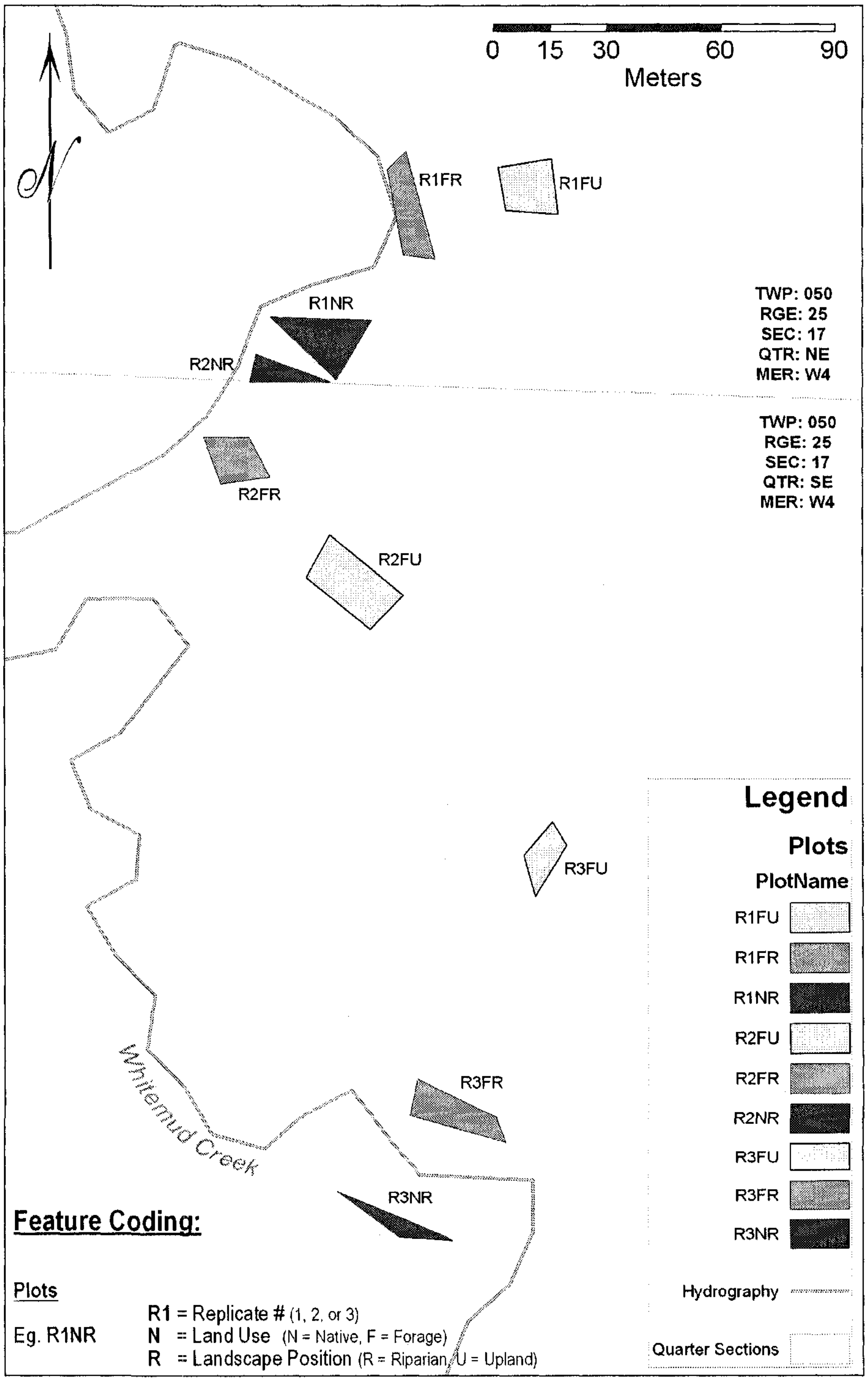


Figure 3.2 Land uses in 2005 and 2006 on the forage upland (FU), forage riparian (FR) and native vegetation riparian (NR) plots: a) in 2005, the land use on the FU and FR was volunteer canola, b) in 2006, the land use on the FU and FR was an alfalfa grass mixture and c) in 2005 and 2006, the land use on the NR plots was native riparian vegetation.

a) In 2005, volunteer canola in the FU and FR plots.

b) In 2006, alfalfa-grass mixture in the FU and FR plots.

c) In 2005 and 2006, native riparian vegetation (in the background) in the NR plots.

Figure 3.3 The installation and removal of PRS^{TM} probes: a) Installation of PRS probes in the soil. To facilitate locating them after the 30-day incubation, pink flagging tape was tied around the handles and pink pin flags were used. b) After incubation, PRS^{TM} probes were sprayed with deionized water and scrubbed with a coarse brush to removal residual soil in order to be analyzed.

a) Installation of PRS^{TM} probes

b) Spraying the PRS^{TM} probes after incubation.

Figure 3.4 Total daily precipitation, mean daily air temperature and land use and landscape position effects on soil temperature during the 2005 and 2006 growing seasons at the (a) 0–10 cm and (b) 10–20 cm soil depth increments.

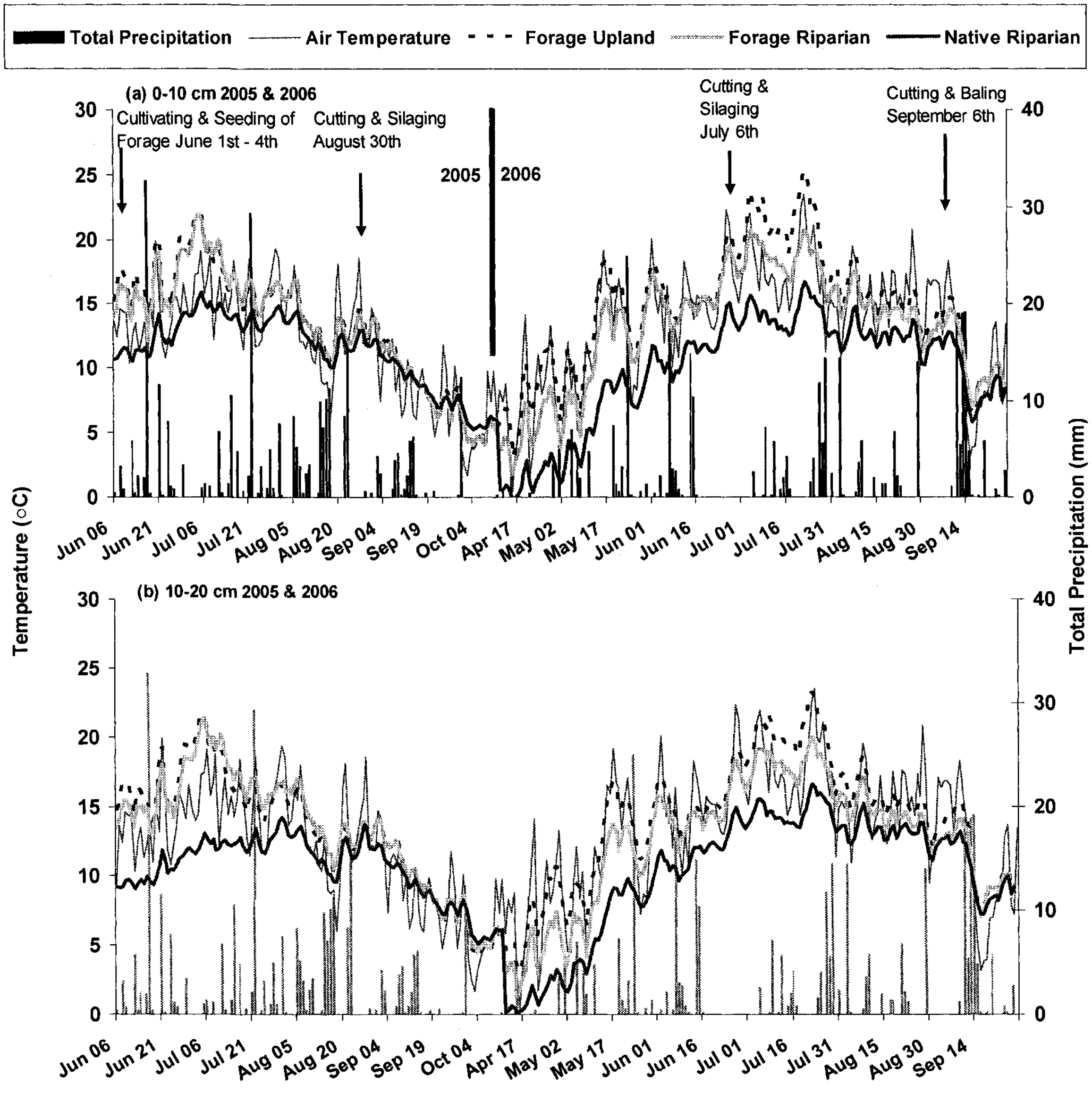


Figure 3.5 Land use and landscape position effects on average daily soil temperature during the 2005 and 2006 growing seasons at the (a) 0–10 cm and (b) 10–20 cm soil depth increments.

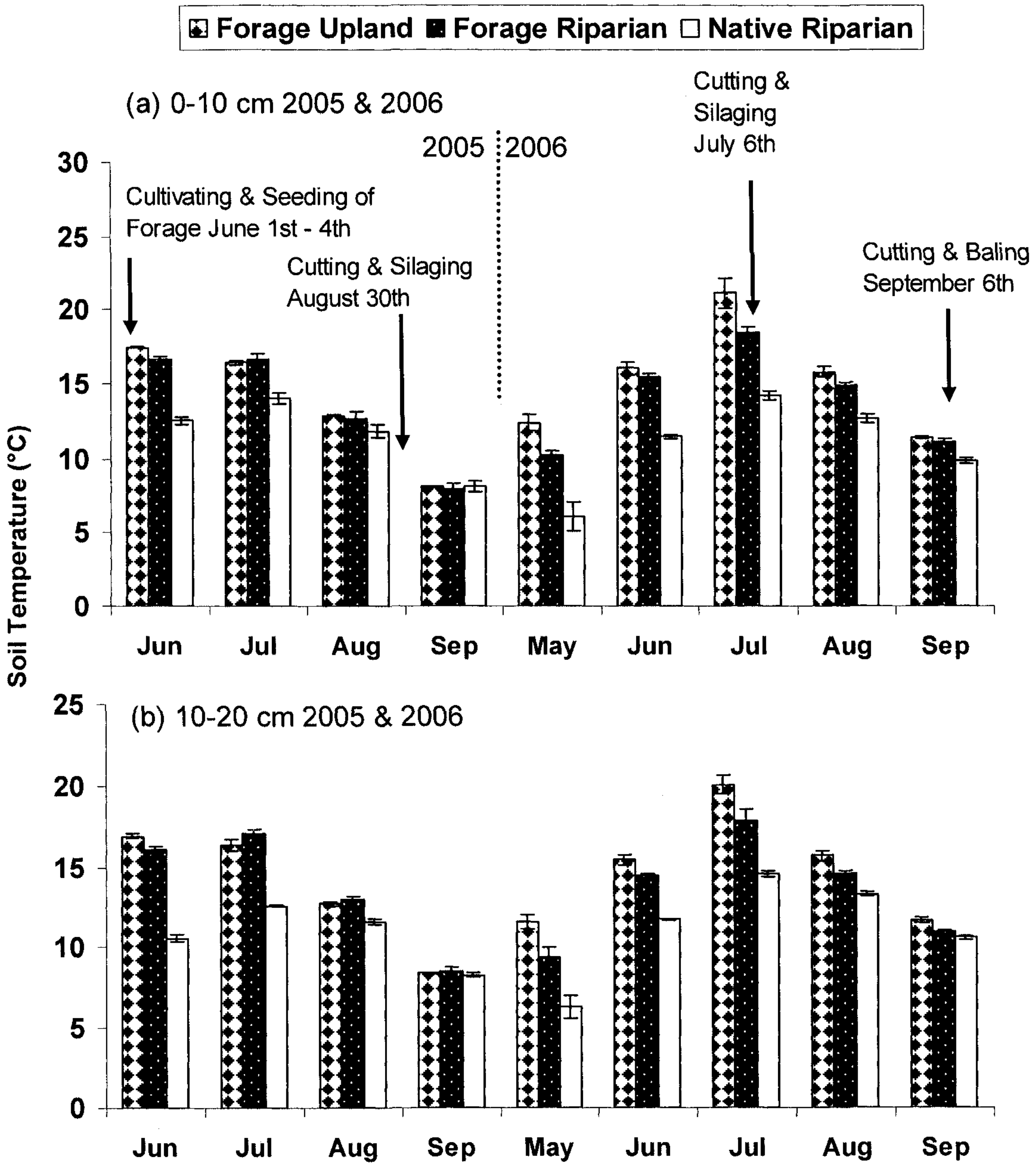


Figure 3.6 Land use and landscape position effects on gravimetric soil moisture content for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

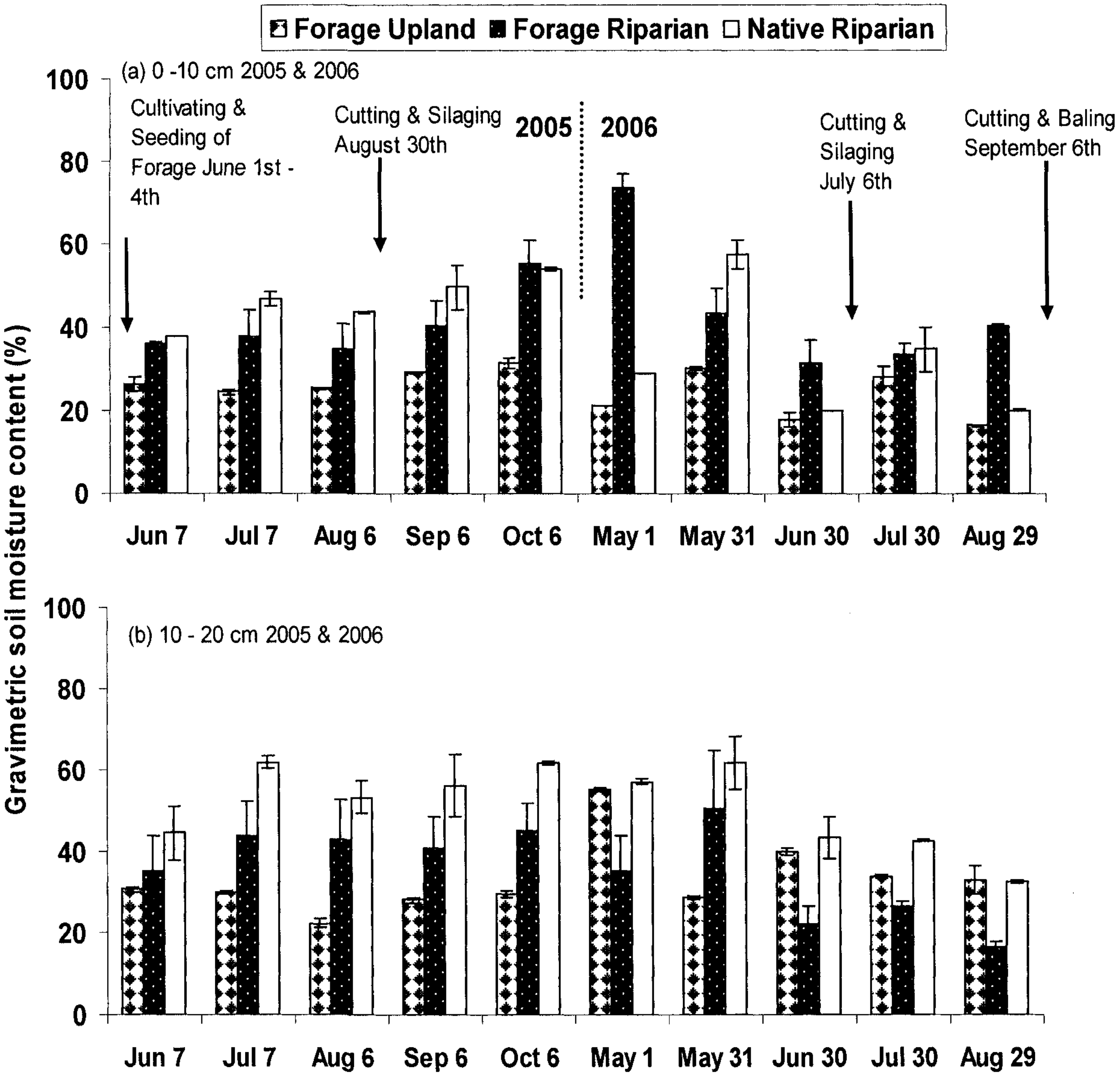


Figure 3.7 Land use and landscape position effects on soil pH for the 2005 and 2006 growing season using (a) 0.01 mol L^{-1} $CaCl_2$ and (b) water at (i) 0–10 cm and (ii) 10–20 cm soil depth increments. Error bars are SEs.

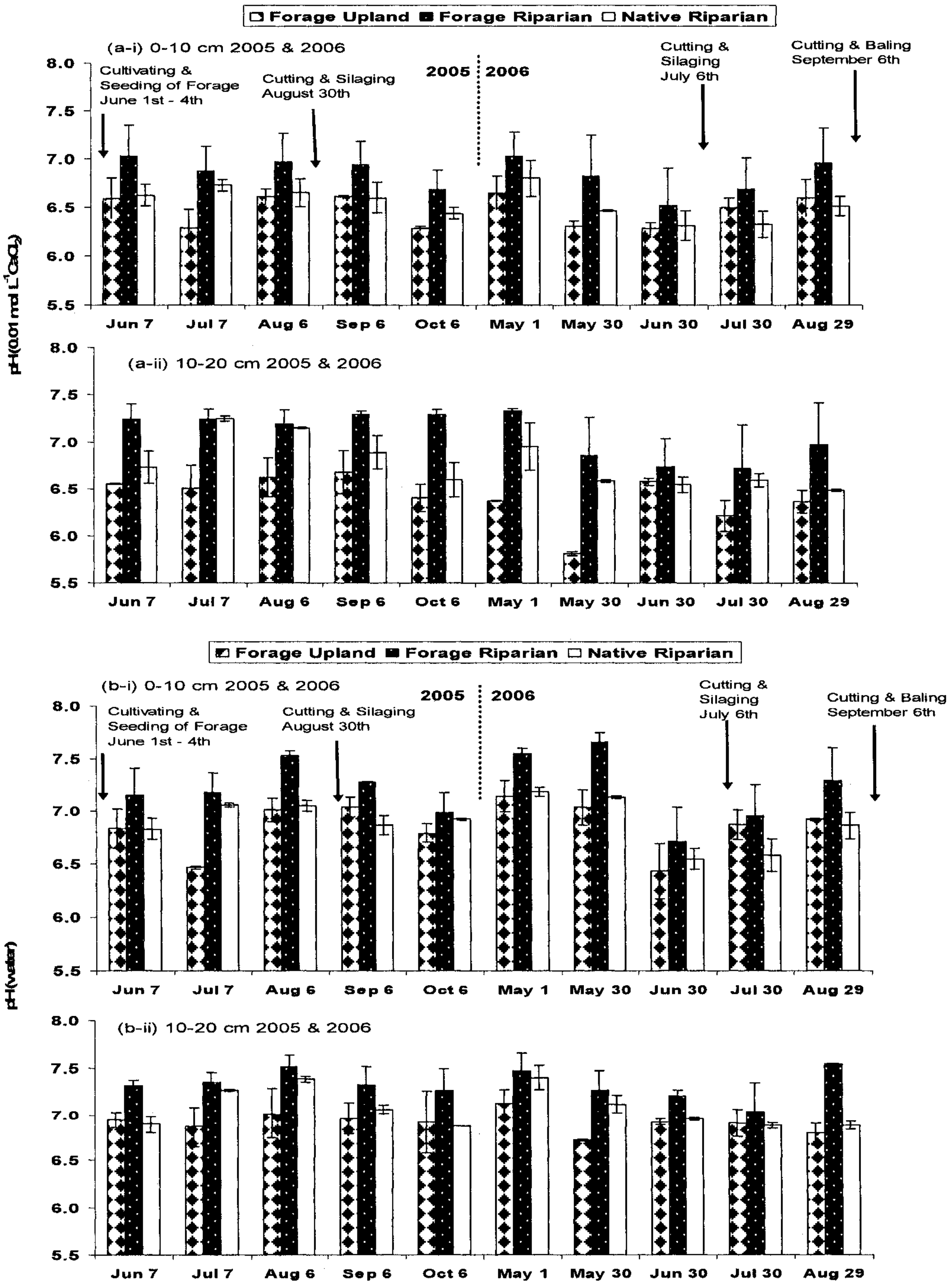


Figure 3.8 Land use and landscape effects on potential P supply rates measured by PRS™ for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10-20 cm soil depth increments. Error bars are SEs.

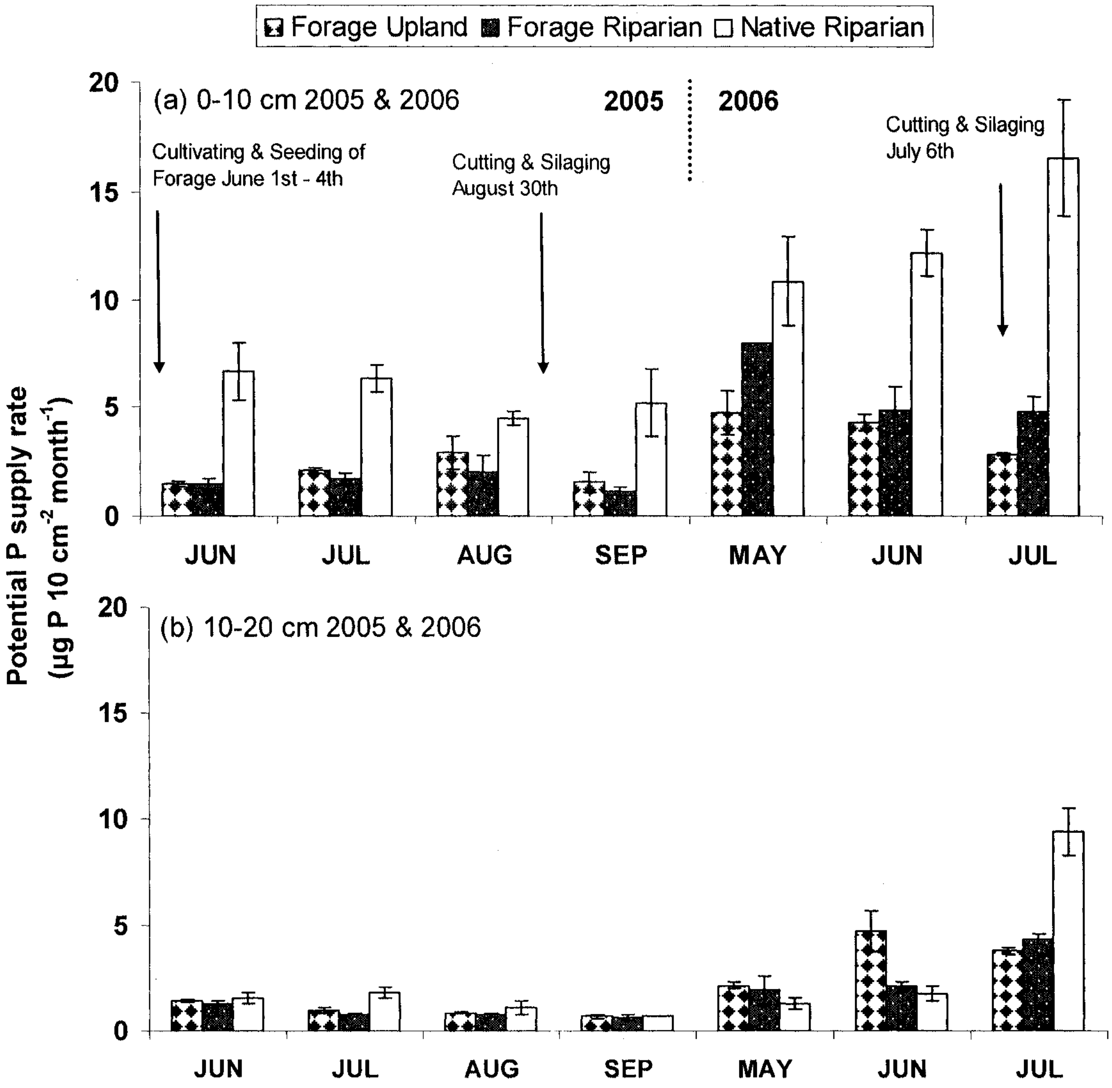


Figure 3.9 Regression of potential P supply rate with soil temperature at the 0-10 cm soil depth increment in 2006 (n=24).

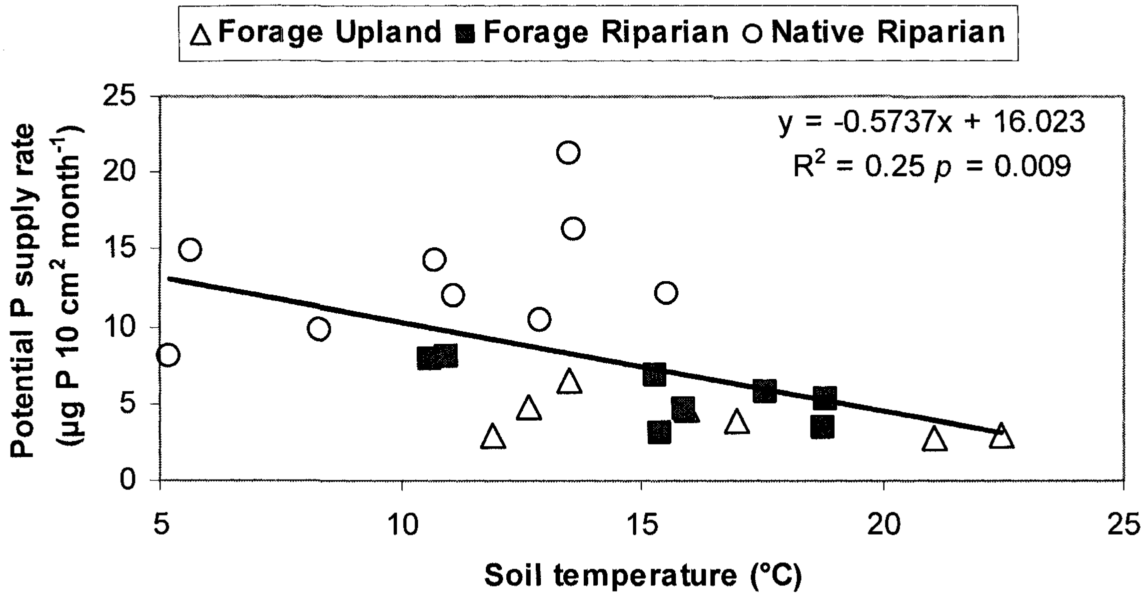


Figure 3.10 Land use and landscape position effects on soil available P concentrations for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

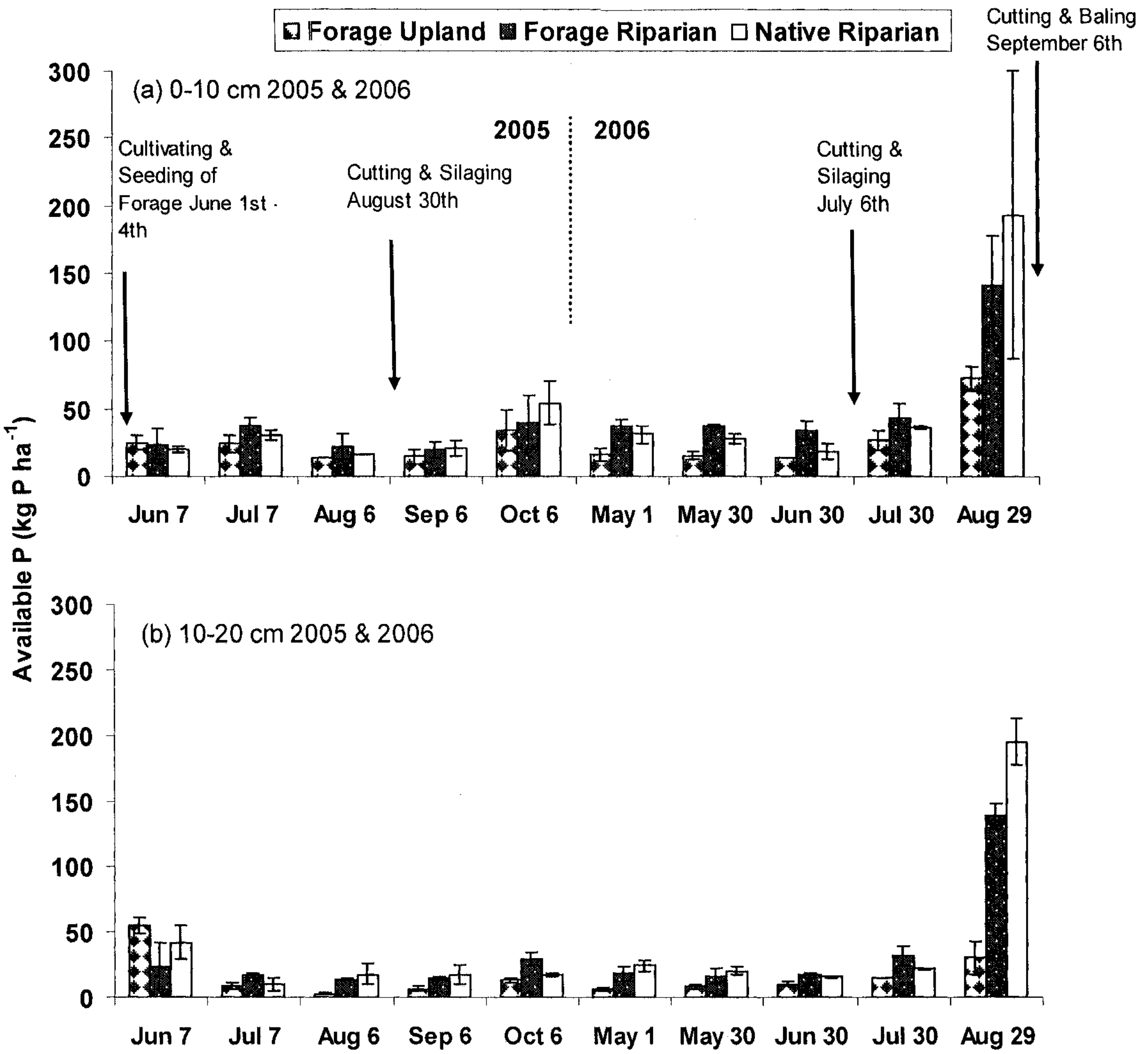


Figure 3.11 Regression of soil available P concentrations with gravimetric soil moisture content at the 0-10 cm soil depth increment in 2005 (n=35).

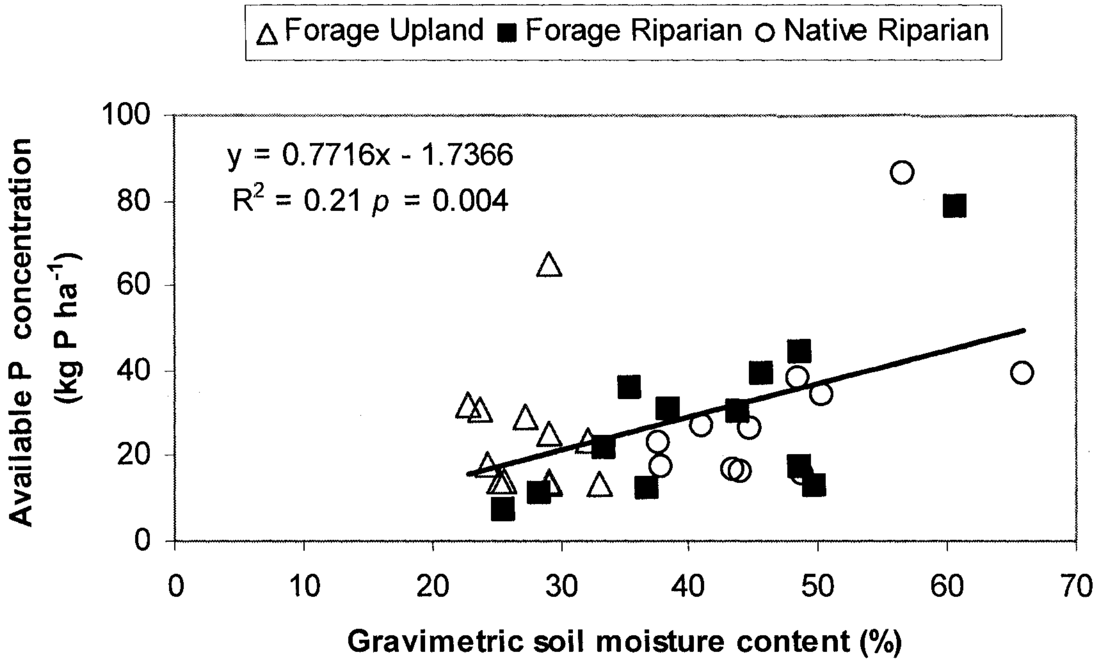


Figure 3.12 Land use and landscape position effects on net P mineralization for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

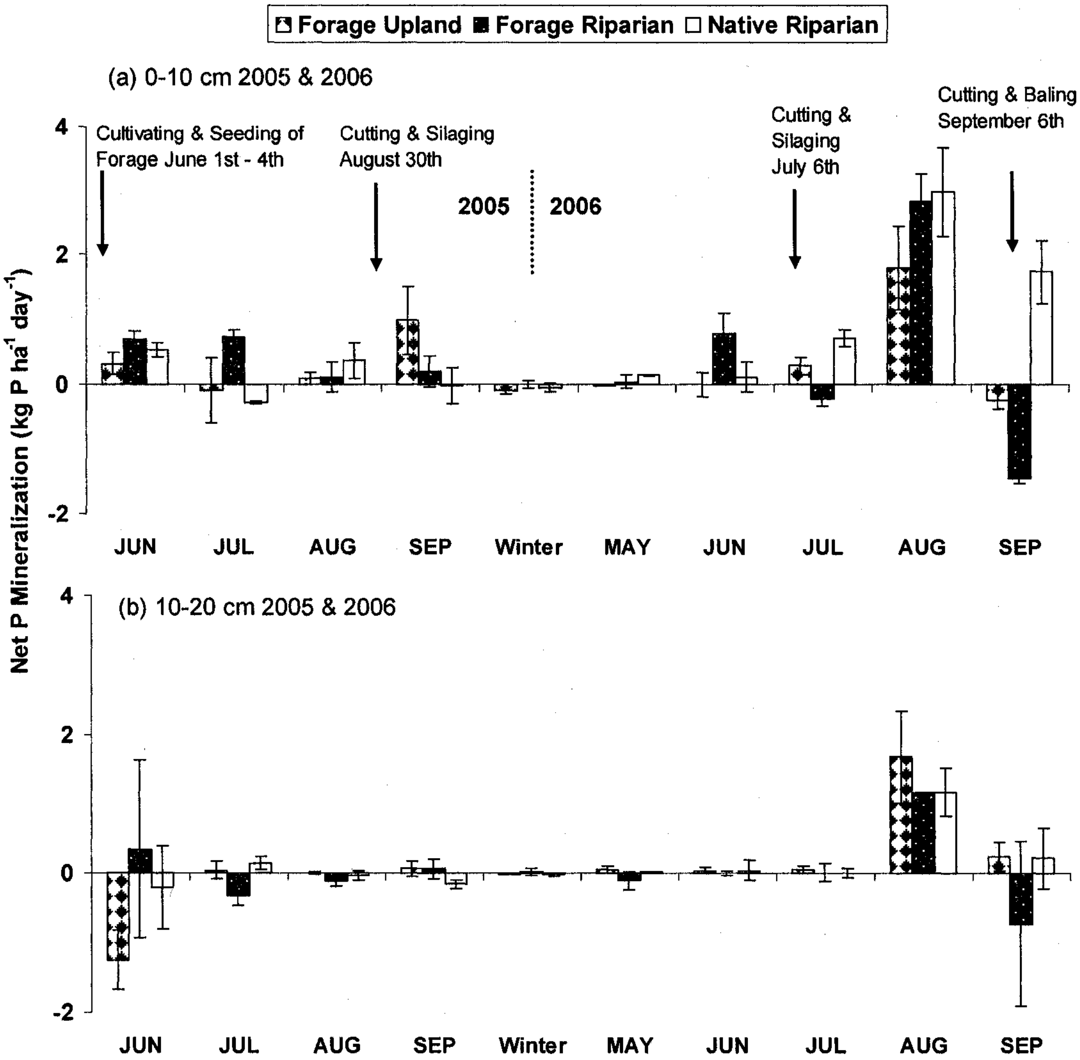
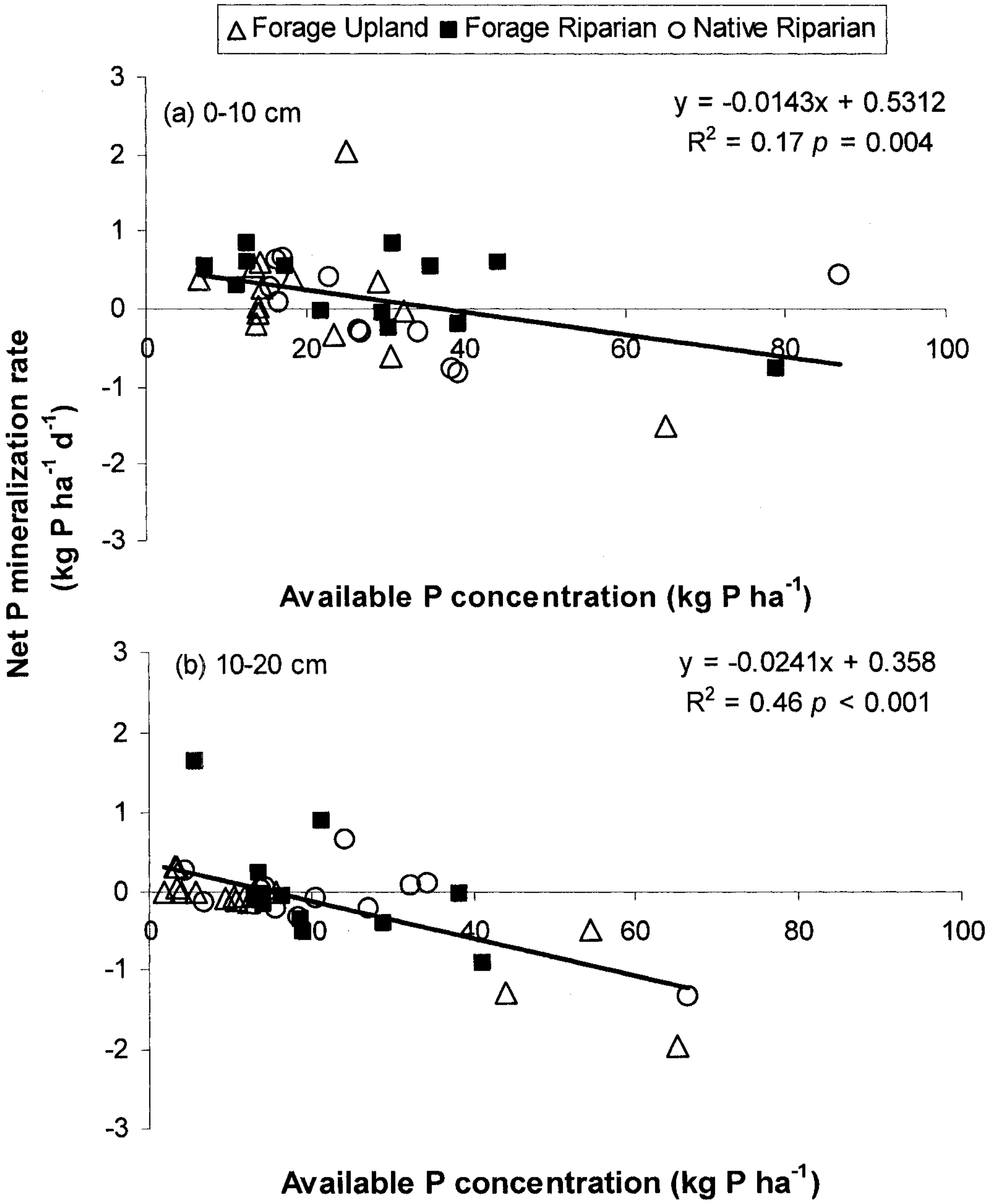


Figure 3.13 Regression of soil available P concentration with net P mineralization rates in 2005 at a) the 0-10 cm (n = 38) and b) the 10-20 cm soil depth increments (n = 39).



Chapter 4: Landscape Position and Land Use Effects on Net Nitrogen Mineralization Rates within a Riparian-Agricultural System

4.1 Introduction

N mineralization is an essential process in maintaining soil quality, fertility and therefore, agricultural sustainability (Raiesi 2006). In riparian ecosystems, N mineralization requires more study in order to understand the amount of available N that is released in managed and unmanaged areas; especially where manures and fertilizers may be placed on intensive agricultural areas that are adjacent to surface water bodies.

Ettema et al. (1999) suggested that riparian areas act as an effective buffer, immobilizing N in the biologically active portion of the soil profile. Some riparian areas have been converted to agricultural activities, leaving only patches of native vegetation that provide important habitat and protection for wildlife, stabilize stream banks, reduce air pollution, reduce nutrient and pesticide runoff and protect water quality (Moffatt et al. 2004).

Studies across the Canadian prairies and worldwide have been carried out to determine the effects of topography and land use on net N mineralization and discovered that forested riparian sites have greater extractable N than a grassland riparian site and that N mineralization rates are higher in the lower slope position than in the upland (e.g. Burke et al. 1995; Entry and Emmingham 1996; Manning et al. 2001; Zhang et al. 2004; Soon and Malhi 2005). Entry and Emmingham (1996) discovered that in comparisons between forest and grassland sites within a riparian area in Oregon, U.S.A., the forest site had more extractable nutrients, including N, in its soil than the grassland site because forest woody debris slowly decomposed, creating a litter layer that held nutrients in the vegetation and organic matter. Soon and Malhi (2005) showed that net N mineralization rates were lower in the upper slope because of lower soil moisture content and organic matter content than at the lower slope position in a field experiment on a Black Chernozem soil near Prince Albert, SK, Canada. Burke et al. (1995) found N mineralization increased from the upslope to the down slope in Eastern Colorado because of the transport of organic matter and clay. However, Manning et al. (2001) found that N mineralization was lower in the wetter lower slopes than at the upper slope position because N was lost via denitrification in a wet growing season on a Black Chernozem soil near Minota, MB, Canada. In an effort to understand the spatial variability of N mineralization in Alberta, Zhang et al. (2004) found that in the Aspen Parkland Ecoregion of Alberta, where this study is located, the soil released potential mineralized N was released in the lower slopes than the upper slopes.

It is important to understand the factors controlling net N mineralization rates on different landscape positions and land uses in agricultural areas that have a riparian component. Such understanding will help in the design and development of nutrient management planning strategies for agricultural systems that include riparian areas. The objectives of this study were to determine the effects of landscape position (upland vs. riparian) and land use (native vegetation vs. forage) on the net N mineralization rate in an agricultural landscape within the Whitemud Creek watershed in central Alberta. This chapter focuses on the following two hypotheses: I hypothesized that landscape positions (forage upland versus forage riparian) affected soil net N mineralization rates in that the rates in the 0-10 cm and 10-20 cm depth increments are greater in the forage upland than the forage riparian position. Greater net N mineralization rates could occur under aerobic conditions in the upland compared to anaerobic conditions that can be found in the riparian area. I further hypothesized that land uses (forage riparian versus native vegetation) affect soil net N mineralization rates so that the rates in the 0-10 cm and 10-20 cm depth increments are greater in the forage riparian than in the native riparian land use. Greater net N mineralization rates could occur in the forage riparian treatments because of N inputs such as inorganic fertilizers placed on the forage riparian plots and higher soil temperatures due to less vegetation cover than in the riparian plots with native vegetation.

4.2 Materials and Methods

4.2.1 Study Site

The details of the study site and soil characteristics are described in Chapter 3.

4.2.2 Experimental Design

This study used a randomized complete block design with three blocks. Each block contained one plot each of forage upland (FU), forage riparian (FR) and native riparian vegetation (NR) (Figure 3.1). This study looked at two pre-planned paired comparisons: FU versus FR and FR versus NR. There were two blocks on the east side of Whitemud Creek with the third block split by the creek with the forage plots on the east side and the native plot on the west side of the creek. The third native riparian plot was located on the west side of the creek because there was not a suitable native riparian area of the same size on the east side. The native riparian plot on the west side of Whitemud Creek had a 0.8 ha buffer immediately to the west that was seeded with the same forage hay mix that was on the rest of the study site.

4.2.3 Soil Sampling and Measurements

Soil Sampling: Soil sampling was conducted at multiple points in time: on June 7, July 6, August 6, September 5, and October 5 in 2005; on May 1, May 31, June 30, July 30 and August 29 in 2006. Within each experimental plot, three soil cores (10 cm long and 5 cm diameter) were collected from randomly selected points and combined to form a composite sample for the 0-10 cm and 10-20 cm mineral soil depth increments. Within each experimental unit, colored pin flags were placed where soil samples were taken the previous sampling time to ensure samples were not taken in the same spot consecutively. Soil samples were placed in coolers, transported back to the lab and were immediately put into a refrigerator (4 °C) until further analysis. In the lab, fresh soil samples were sieved to 4-mm and analyzed for available NH_4^+ and NO_3^- concentrations and water soluble carbon.

Soil Net N mineralization And Nitrification Rates: For measuring the N mineralization rate, the buried-bag method was used. It is an *in situ* procedure that provides an index of nitrogen availability to plants in the forms of NH_4^+ and NO_3^- (Binkley and Hart 1989; Eno 1960). For each experimental unit at each depth increment (0-10 cm and 10-20 cm) and for each sampling period, six soil cores, (10 cm long and 5 cm in diameter), were taken: three that were analyzed for inorganic N concentrations on that day (T1) and three that were incubated for 30 days in the field

(T2). The T1 soil samples from each plot were taken to the lab and for each plot and depth increment, the T1 soil samples were mixed together to make one composite sample, sieved through a 4-mm mesh to remove plant material and analyzed for inorganic N concentrations at T1. The T2 intact soil samples were placed in polyethylene bags, tied shut and were buried in the hole from which they originated and incubated *in situ* to determine net N mineralization rates at 30-day intervals, except for the winter 2005/2006 incubation period. The polyethylene bags used for this method were permeable to gases such as oxygen and carbon dioxide, but impermeable to liquids.

Incubations were conducted in 2005 and 2006, four times in 2005 from June 7 to July 6, July 6 to August 6, August 6 to September 5, and September 5 to October 5. Hereafter, these dates are abbreviated as June 05, July 05, August 05 and September 05 respectively. As well, an over winter incubation took place from October 5, 2005 to May 1, 2006 and is abbreviated as Winter 05/06. Incubations in 2006 were conducted five times from May 1 to May 31, May 31 to June 30, June 30 to July 30, July 30 to August 29, and August 29 to September 28. Hereafter, these dates are abbreviated as May 06, June 06, July 06, August 06 and September 06.

After 30 days, the bags were removed from the field. The three T2 soil samples from each depth increment for each plot were mixed and sieved together to make one composite sample. Each composite sample was then analyzed for inorganic N concentrations at T2. The difference in the amount of N mineralized (T2-T1) is the net N mineralization rate. The net N mineralization rate was calculated using the following equation:

$$\textbf{Net N Mineralization} = [(NH_4^+\text{-}N+NO_3^-\text{-}N)_{(T2)} - (NH_4^+\text{-}N+NO_3^-\text{-}N)_{(T1)}] / (T)$$

where T is the number of days the sample is incubated. A negative value using the above equation indicates net immobilization.

The net nitrification rate was determined using the following equation:

$$\textbf{Net Nitrification} = [(NO_3^-\text{-}N)_{(T2)} - (NO_3^-\text{-}N)_{(T1)}] / (T)$$

Fresh moist soil samples before and after incubation (10-15 g of fresh weight soil) were extracted using 50 mL of 2 mol L^{-1} KCl, filtered using Fisherbrand™ Q2 filter papers. Extracts were stored in plastic bottles in a freezer (-18 °C) until further analysis. Ammonium concentration in the extracts was determined by the indophenol blue method where ammonium with phenol and hypochlorite at high pH forms a blue color (Keeney and Nelson 1982); nitrate concentration was determined by the vanadium (III) chloride method where vanadium(III) in acid solution reduces nitrate to nitrite and produces a pink color when reacted with N-(1-naphthyl)ethylenediamine (NED) (Doane and Horwath 2003); and the absorbance was measured by a spectrophotometer at 636 nm for NH_4^+ and 540 nm for NO_3^- (Genesys 10-S, Thermospectronic, USA).

Water Soluble Carbon: From each experimental unit and from each depth increment, fresh composite soil samples (10-15 g of fresh weight soil) were extracted using 50 mL distilled water. The samples were put in a centrifuge (Thermo IEC-MultiRF 2003, Needham Heights MA USA) at 10,000 rpm for 10 minutes and then filtered using No. 5 Whatman filter papers. Extracts were stored in plastic bottles in a freezer (-18 °C) until further analysis. The concentrations of water soluble C in the extracts were determined by a Shimadzu TOC-V CSH/CSN Total Organic Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan).

Total C and N Concentrations: Air-dried soil samples were used to determine total C and N concentrations using a Shimadzu TOC-V CSH/CSN Total Organic Carbon and Total N Analyzer and SSM-5000A Solid Sample Module (Shimadzu Corporation, Kyoto, Japan). Carbon concentration was divided by N concentration to obtain the C:N ratio (Table 4.1).

Potential N Supply Rate of Soils: Plant Root Simulator (PRS)^{TM} probes (Western Ag Innovations Inc., Saskatoon, Canada), equipped with ion-exchange membranes, were used to estimate the potential N supply rates of the soils to plants. These membranes also act as an ion sink, which simulate ion adsorption by plant roots. The manufacturer (Western Ag Innovations, Saskatoon, SK) claims that because the plant roots were not separated from the probes, the measured values are net N supply rates (e.g., total soil supply of N – plant uptake), however, these PRS^{TM} probes are supposed to simulate plant root adsorption and should be able to compete for the same nutrient pools with plant roots. The resin membrane probes have been recommended for use on the Canadian prairies to understand mineralization contribution on prairie soils and to measure conservation management practices that influence N mineralization

(Schoenau et al. 1998).

Prior to receiving the membranes encased in 15 cm x 3 cm x 0.5 cm plastic frames, Western Ag Innovations Inc. saturated the cation and anion probes with sodium (Na^+) and bicarbonate (HCO_3^-), respectively, by shaking the membranes three successive times in 0.5 mol L^{-1} $NaHCO_3$ for 4 hours (Hangs et al. 2004). The regenerated PRS^{TM} probes were rinsed with deionized water before delivery. The probes at the 10-20 cm depth increment were inserted vertically by using a spade to cut out a soil wedge to the 20 cm depth. The probes at the 0-10 cm depth increment were placed vertically above the probes at the lower depth increment. To ensure sufficient contact between probes and the soil, the soil wedge is replaced, a spade is inserted approximately 15 cm away from the probe insertion area and the soil is pushed against the probes. A pink pin flag was used to help find the probes again as well as all probes had pink flagging tape tied around their handles (Figure 3.3a). The probes were inserted into the soil in each experimental plot and incubated for one month. Within each FU and FR plot, PRS^{TM} probes were inserted into the soil in random locations. Within each NR plot, probes were placed in areas that represented different vegetation types and proximity to the creek (e.g., under tree canopy, under shrub canopy, distance away from Whitemud Creek).

After a 30-day insertion period, the probes were taken out of the soil and then in the identical place, the same type of anion or cation probe was inserted to start a new incubation. The measurements were made four times in 2005 from June 6 to July 5, July 5 to August 5, August 5 to September 4 and September 4 to October 4. Hereafter those dates will be referred to as June 05, July 05, August 05 and September 05 insertions.

Measurements were also made three times in 2006 from May 2 to June 1, June 1 to July 1 and July 1 to July 30, referred to as May 06, June 06 and July 06 samplings below.

The NH_4^+ and NO_3^- ions captured by the ion-exchange membranes of the four sets of cation and anion probes were retrieved from each experimental plot, sprayed with deionized water, scrubbed with a coarse brush and then rewashed to remove the residual soil (Figure 3.3b). The PRS™ probes were placed into polyethylene containers, packed in a cooler and sent to Western Ag Innovations Inc. in Saskatoon, Canada for analysis. In the Western Ag Labs, the probes were extracted by 17.5 mL of 0.5 mol L^{-1} HCl per probe in Ziploc® bags (140 mL per bag). The probes were gently shaken with the acid to ensure it covered the membrane surface to eluate the adsorbed ions for analytical measurement (Hangs et al. 2004). After one hour, the eluate is poured off into vials and the eluate is analyzed. The NH_4^+ and NO_3^- eluates were determined colorimetrically by an autoanalyzer (The Technicon Autoanalyzer II 1977) with NO_3-N analysis modified by adding NaOH to the NH_4Cl reagent in order to neutralize the sample solution before it enters into the Cd-reduction column (Western Ag Labs 2006). Data generated from the autoanalyzer was reported in units of μg nutrient ion per mL eluate solution (e.g. ppm). More details can be found in the Operations Manual (Western Ag Labs 2006) but the overall equation for determining potential PRS™-probe nutrient supply rates from eluate ppm data for my site was:

$$\frac{\mu g\ nutrient}{mL\ of\ eluate} * \frac{17.5\ mL\ eluate}{probe} * \frac{8\ total\ probes}{bag} * \frac{bag}{4\ anion\ or\ cation\ probes} * \frac{probe}{17.5\ cm^2} * 10 = \frac{\mu g\ nutrient}{10\ cm^2}$$

The ion concentration in the eluate solution is multiplied by the volume of eluate used to eluate the probes to obtain the total weight of ions eluted. In this study, 4 anions and 4 cations were used in each plot so the total volume would be 140 mL. The total weight of ions eluted was divided by the total membrane surface area of the anion or cation probes eluated in the sample (17.5 cm^2 per PRS^{TM} probe) and then multiplied by the number of probes to obtain the weight of ion adsorbed per unit surface area of ion exchange membrane. Finally, the value was multiplied by a conversion factor of 10 to increase the sample size with numbers greater than 1 for most of the measured nutrients and to standardize reporting protocol.

4.2.4 Statistical Analyses

The PROC MIXED procedure in SAS (SAS Institute Inc. 1999) was used to analyze two one-way ANOVA's with blocking and repeated measures to evaluate the effect of landscape position (forage upland vs. forage riparian) and land use (native riparian vs. forage riparian) for each of the response variables: available NH_4^+ and NO_3^- concentrations, net nitrification rate, net N mineralization rate, potential NH_4^+ and NO_3^- supply rates, gravimetric soil moisture content, soil temperature, soil pH and water soluble carbon.

Model:

$$\mathbf{Y_{ijk} = \mu + \rho_j + \alpha_i + d_{ij} + \gamma_k + (\alpha\gamma)_{ik} + \varepsilon_{ijk}}$$

where:

Y_{ijk} = total rate of response variable

μ = mean rate of response variable (e.g. N mineralization rate)

ρ_j = experimental blocking

α_i = treatment effect (land use or landscape position)

d_{ij} = random error for the whole plot

γ_k = time (month)

$(\alpha\gamma)_{ik}$ = interaction between treatment and time

ε_{ijk} = random error on repeated measures

To compare the covariate variables (soil pH, gravimetric soil moisture content, water soluble carbon and soil temperature) with the response variables (available NH_4^+ and NO_3^- concentrations, potential NH_4^+ and NO_3^- supply rates, nitrification and N mineralization), regression and the Pearson Product Moment Correlation analyses were used.

The data in 2005 and 2006 were analyzed separately. Outliers were assessed by first using the modified Z-score calculation on each treatment effect and then data was plotted on a scatter plot to determine visually if any outliers still remained. The modified Z-score uses the median and the median of the absolute deviation about the median (MAD) (Iglewicz and Hoaglin 1993; Seo 2006):

$$MAD = median \ \{| x_i - \tilde{x} |\},$$

where $\tilde{x}$ is the sample median and x_i is a measurement in the data set where one measurement might be denoted as x_1, another x_2 and so on. The subscript i might be any integer value up to N, the total number of x values in the dataset (Zar 1999).

The modified Z-Score (M_i) is computed as:

$$M_i = \frac{0.6745(x_i - \tilde{x})}{MAD}$$

Observations were labeled outliers when |Mi| > 3.5 (Iglewicz and Hoaglin 1993).

Normality tests on the data set were conducted using the PROC UNIVARIATE procedure (the Shapiro-Wilks test). Most of the time data were normally distributed and when it was not, the data was transformed to lognormal and was found to be normally distributed. This transformation The Bartlett test using the PROC GLM procedure showed that the data had variances that were not homogeneous. The PROC MIXED procedure overcomes this problem. For statistical significance, $\alpha = 0.05$ was chosen.

4.3 Results

4.3.1 Water Soluble Carbon

In all three treatments at both depth increments, water soluble carbon (WSC) followed a seasonal pattern of increasing WSC from the spring into the later summer months (Figure 4.1). In 2005 at the 0–10 cm depth increment, the interaction between land use and time was significant showing that the NR had higher WSC concentrations than did the FR on all sampling dates except September 6 ($p = 0.014$, Table 4.2, Figure 4.1). At the 10–20 cm depth increment in 2005 and 2006, the land use treatment significantly affected WSC, which was higher in the NR than in the FR treatment ($p < 0.001$). At the 10-20 cm depth increment in 2006, the interaction between landscape position and time was significant, showing that the FU had higher WSC concentrations than in the FR on July 30 but did not affect WSC concentrations in the other sampling dates ($p = 0.029$). In 2006 at the 0-10 cm depth increment, the interaction between landscape position and time was significant, showing that the lower landscape position, FR, had higher WSC concentrations than in the FU on May 1, May 31, July 30 and August 29 but on June 30, the FU had higher WSC concentrations than in the FR.

4.3.2 Potential NH_4^+ Supply Rate

In 2005, the potential NH_4^+ supply rate at both depth increments in all three treatments was highest in June and July and then decreased in August and September (Figure 4.2). The interaction between land use and time was significant, showing that the NR had the higher potential NH_4^+ supply rates than in the FR in June 05 at the 0-10 cm and 10-20 cm soil depth increments and July 05 at the 10-20 cm but the interaction did not affect supply rates in the other sampling dates (Table 4.3, Figure 4.2). In 2006, landscape position and land use treatments did not significantly affect potential NH_4^+ supply rates. Potential NH_4^+ supply rates were negatively correlated with gravimetric soil moisture content, WSC, available NO_3^-, soil $pH_{(CaCl_2)}$, net nitrification and net mineralization in 2005 and 2006 (Table 4.5).

4.3.3 Potential NO_3^- Supply Rate

In 2005 and 2006 at both depth increments, landscape position treatments significantly affected potential NO_3^- supply rates as NO_3^- was higher in the FU than in the FR treatment (Table 4.3, Figure 4.3). In 2005 at 10-20 cm, the interaction between land use and time was significant, showing that the FR treatment had higher potential NO_3^- supply rates than the NR in June but there were no significant interactions between land use and time in the other sampling dates (Table 4.3, Figure 4.3). In 2006 at both depth increments, the opposite was found where land use treatments significantly affected potential NO_3^- supply rates where NO_3^- was higher in the NR than in the FR ($p = 0.004$). Gravimetric soil moisture content and potential NO_3^- supply rates in 2005 at both depth increments showed a significant relationship where gravimetric soil moisture content increased but potential NO_3^- supply rates decreased (Figures 4.4a and b). Figures 4.5a and 4.5b showed that the FR treatments had a real response across all gravimetric soil moisture contents. The NR treatments either had no response (Figure 4.4b) or were found at the highest soil moisture contents and lowest potential NO_3^- supply rates (Figure 4.4a) while the FU treatments were on the other end of the regression line with the highest rates of potential NO_3^- supply rates and lowest gravimetric soil moisture contents. Potential NO_3^- supply rates were also positively correlated with available NO_3^- and NH_4^+ concentrations and negatively correlated with soil $pH_{(H_2O)}$ in 2005 and negatively correlated with gravimetric soil moisture content in 2006 (Table 4.5).

4.3.4 Available Ammonium Concentrations

The highest available NH_4^+ concentrations in all three treatments occurred from June 7 to September 6, 2005 (Figure 4.5). On October 6, 2005 available NH_4^+ concentrations then decreased to below 2 kg N ha^{-1} and maintained that concentration level for the 2006 growing season. In 2005 at both depth increments, land use treatments significantly affected available NH_4^+ concentrations (Table 4.4, Figure 4.5). Available NH_4^+ concentrations were higher in the NR than in the FR treatment with the exception of October 6 at the 10–20 cm depth increment where NH_4^+ was higher in the FR than in the NR treatment ($p = 0.013$). In 2006 at the 0–10 cm depth increment, the landscape position treatment significantly affected available NH_4^+ concentrations, which was higher in the FR than in the FU treatment ($p = 0.009$). In 2006, the interaction between land use and time was significant, showing that the FR had higher available NH_4^+ concentrations than in the NR on August 29 at 0-10 cm and June 30 at both depth increments and the reverse occurred on May 30 at 0-10 cm and 10-20 cm depth increments and July 30 at 10-20 cm depth increment where NR had higher available NH_4^+ than in the FR. Available NH_4^+ concentrations were positively correlated with WSC in 2005 ($r = 0.48$, $p = 0.003$), net nitrification ($r = 0.47$, $p = 0.002$) and net N mineralization rates ($r = 0.33$, $p = 0.034$) in 2006 (Table 4.5).

4.3.5 Available Nitrate Concentrations

In 2005, the highest available NO_3^- concentrations were as high as 55 kg N ha^{-1} on June 7 and July 7 (Figure 4.6). Available NO_3^- concentrations then decreased to an average of 10 kg N ha^{-1} for the remaining 2005 and the entire 2006 growing seasons. The exception was in the NR on July 7 which was at its lowest concentrations (1.7 kg N ha^{-1} at 0–10 cm and 1.8 kg N ha^{-1} at 10–20 cm) (Table 4.4, Figure 4.6). In 2005 at the 0–10 cm depth increment, the interaction between land use treatments and time was significant, showing that the FR had higher available NO_3^- than in the NR on all dates except August 6 ($p = 0.010$). The reverse occurred in 2006, where the interaction between land use and time was significant, showing that the NR had higher NO_3^-

concentrations than in the FR treatment on May 1 and May 31 but did not affect NO_3^- concentrations in the other sampling dates ($p = 0.009$). In 2006 at the 10–20 cm depth increment, land use treatments significantly affected available NO_3^- concentrations where NO_3^- was higher in the NR than in the FR treatment ($p = 0.019$). At both depth increments, the interaction between landscape position and time was significant, showing that the FU had higher available NO_3^- concentrations than in the FR on June 7 at 0-10 cm, July 7 and October 6 at 10-20 cm in 2005 and May 1 and July 30 at 10-20 cm in 2006 but did not affect NO_3^- concentrations in the other sampling dates. The opposite occurred in 2006 where the interaction between landscape position and time was significant, showing that the FR had higher available NO_3^- concentrations than in the FU on June 30 but did not affect NO_3^- concentrations in the other sampling dates (Table 4.4, Figure 4.6).

4.3.6 Net Nitrification Rates

In 2005, with the exception of NR at both depth increments, net nitrification rates decreased from June to September (Figure 4.7). At the 10–20 cm depth increment in 2005, land use treatments significantly affected net nitrification rates as nitrification was higher in the FR than in the NR treatment ($p = 0.01$). The interaction between land use and time was significant, showing that the FR treatment had higher net nitrification rates than in the NR in June 05 at the 0-10 cm depth increment but did not affect nitrification rates in the other sampling dates ($p = 0.014$) (Table 4.4, Figure 4.7). The lowest rates of net nitrification among all 3 treatments occurred in Winter 05/06 at both depth increments. Net nitrification rates then gradually increased from Winter 05/06 until June 06. In 2006 at the 0–10 cm depth increment, landscape position treatments significantly affected net nitrification rates as the nitrification rates were higher in the FR than in the FU treatment ($p = 0.003$). The interaction between land use and time was significant, showing that the NR had higher net nitrification rates than in the FR on June and August 06 at the 10-20 cm depth increment but did not affect nitrification rates in the other sampling dates ($p = 0.024$) (Table 4.4, Figure 4.7). At the 0–10 cm depth increment in both years, net nitrification was positively correlated with net N mineralization but negatively correlated with WSC (Table 4.5).

4.3.7 Net N Mineralization Rates

The net N mineralization rates (Figure 4.8) and the net nitrification rates (Figure 4.7) had similar patterns of increase and decrease within treatments and depth increments across both growing seasons. With the exception of June 05 and Winter 05/06, at the 0–10 cm depth increment, net N mineralization rates were fairly consistent throughout the 2005 and 2006 growing seasons (Figure 4.8). In 2005 at the 10-20 cm depth increment, the land use treatments significantly affected net N mineralization rates as mineralization was higher in the FR than in the NR treatment ($p = 0.036$) (Table 4.4). The interaction between land use and time was significant, showing that the FR had net N mineralization while the NR had net immobilization in June 05 but did not affect mineralization rates in the other sampling dates ($p = 0.022$). The Winter 05/06 had the lowest net N mineralization rates while June and July had the highest net N mineralization rates (Figure 4.8). In 2006 at the 0–10 cm depth increment, the landscape position treatments significantly affected net N mineralization rates as mineralization rates were higher in the FR than in the FU treatments ($p = 0.010$). In both years, net N mineralization rates were positively correlated with available NO_3^-

concentrations, soil $pH_{(H_2O)}$ and net nitrification rates but were negatively correlated with WSC (Table 4.5).

4.4 Discussion

4.4.1 All treatments

Potential NH_4^+ supply rates and available NH_4^+ concentrations in 2005 and 2006 at both depth increments were similar across all three treatments (FU, FR and NR) per 30-day incubation, suggesting stable ammonification rates across landscape position and land use treatments (Figure 4.2). Available NH_4^+ concentrations were lower than available NO_3^- concentrations in 2005 and 2006 at both depth increments because of well-aerated soils where net nitrification dominate N mineralization (Figure 4.5 and Figure 4.6) (Stevenson and Cole 1999). A positive relationship was found between available NH_4^+ concentrations and net nitrification and between potential NH_4^+ supply rates and net nitrification (Table 4.5). The dominant form of available N in the soil was NO_3^- which is supported by a strong correlation by between net nitrification and net N mineralization at both depth increments and both years (Table 4.5) and was also found in a study by Robertson and Vitousek (1981). Nitrifiers can draw on NH_4^+ pools present at the beginning of the incubation and also when NH_4^+ becomes available during the buried-bag incubation (Pastor et al. 1984). Lower net nitrification rates in September 05 and Winter 2005/2006 could mean nitrifier populations were low at the beginning of the incubations and lag in growth because of low nutrient availability due to lower soil temperatures and decreased nitrifier activity (Vitousek et al. 1982).

4.4.2 Landscape Position Treatments

Available NH_4^+ concentrations were higher in 2005 compared to 2006 because of the agronomic activities taking place on the landscape. The 2005 and 2006 growing seasons had differences in vegetation cover that may explain the available NH_4^+ results. The NH_4^+ concentrations in the soil may not have been fully utilized in 2005 because in June and July bare soil dominated in the FU and in the FR plots and in later months, the alfalfa and forage grasses were not well established as volunteer canola became the dominant vegetation. In 2006, lower NH_4^+ concentrations in the soil may reflect the established forage stand utilizing the available NH_4^+ when no additional cultivation or fertilization occurred and/or the net nitrification rate was proceeding quicker than the ammonification rate as suggested in the previous section.

The potential NO_3^- supply rates were higher in the FU than in the FR in 2006, which could be explained by the alfalfa vegetation, soil type and the gravimetric soil moisture content. Ta et al. (1986) and Rochette et al. (2004) suggested that alfalfa contributes to raising the N concentration by excreting N compounds and that high soil available N in early spring comes from the decomposition of labile soil organic matter and plant material that did not survive the winter. For my research site, the main contribution of available N from plant material in the FU and FR treatments in 2006 would be canola stubble and residues from the 2005 crop. In a grass mixture site similar to this site in 2006, Rochette et al. (2004) suggested that the roots of alfalfa released large amounts of available N that was fixed by rhizobia throughout the growing season and transferred a significant amount of N from the legumes to the grasses.

A negative relationship was found between potential NO_3^- supply rates and gravimetric soil moisture content in 2005 (Figure 4.4). There were other negative correlations between gravimetric soil moisture content and the potential N supply rates which explains that N availability was higher in the FU than the FR treatment because of lower gravimetric soil moisture content due to the Chernozemic soil found in the higher position landscape position (Chapter 3, Figure 3.5). Johnson et al. (2005) found that the PRS^{TM} probes had a greater sensitivity to soil moisture content than mineral soil N measurements, which suggests that the probes related well to plant uptake. Thus, microbial activity and potential N supply rates may be limited by very wet soils, such as the FR plots during spring melt that are Gleysolic soils, due to anaerobic soil conditions and also, denitrification may be the dominant N process removing NO_3^- from the system.

In the FR plots, the potential NO_3^- supply rates in May and June 2006 may be attributed to the warming of the soil and fluctuating soil moisture contents (Figure 4.4). The soils were waterlogged by spring melt in early May and spring rains in early June (52.2 mm). As the incubations periods continued, soil temperatures increased, gravimetric soil moisture content decreased and the soils contracted as they dried out, causing insufficient PRS^{TM} probe membrane to soil surface contact. The probes were affected by soil moisture content and without adequate soil to membrane surface contact, the probes do not provide accurate potential N supply rates in dry conditions as was cautioned by Johnson et al. (2005).

Not having sufficient soil moisture content can also decrease the available N mineralized. Soon and Malhi (2005) found that soil moisture was controlled by topography and that landscape positions had a predominant effect on soil N levels where both available NO_3^- and NH_4^+ were greater in the lower slope than the upper slope. At this site, landscape position affected net nitrification and mineralization rates as was found by Hook and Burke (2000) because of the differences in soil moisture content. On June 30, 2006, for example, the FU had lower NO_3^- concentrations than in the FR thus, lower soil moisture content might have resulted in the lower nitrification rate found in July 06 and August 06 at the 0–10 cm depth increment in the FU than in the FR (Table 4.4, Figure 4.7, Figure 4.8, Chapter 3, Figure 3.5). Net nitrification and net mineralization rates could not proceed as quickly compared to the rest of the growing season without sufficient soil solution (Stevenson and Cole 1999).

4.4.2 Land Use Treatments

Potential N supply rates (NO_3^- in 2006 and NH_4^+ in June and July 05 only) and soil available NH_4^+ concentrations (all of 2005 and May 30, 2006) were higher in the NR than in the FR since the diversity of plant species present had different decomposition rates due to their varying C:N ratios in the NR plots, thus creating a continuous amount of organic N that is mineralized and made available for plant uptake (Table 4.3, Table 4.4, Figure 4.2, 4.3 and 4.5). G. Chu and L. Townley-Smith (personal communication) reported that at the research site in 2005, nutrient uptake was highest and accumulation of litter higher in the NR areas compared to the forage areas. Entry and Emmingham (1996) also found similar results where the riparian forest site had more extractable N than the riparian grassland site because the forest woody debris slowly decomposed to create a litter layer that held nutrients in the vegetation and organic matter.

In June and July 2005 with the exception of the 10-20 cm depth increment available NO_3^- measurement, the FR treatment had higher NO_3^- supply rates and available NO_3^- concentrations than in the NR in June because cultivation and fertilizer application occurred in the FR treatment prior to soil sampling from June 1-4, 2005 (Table 4.3, Figure 4.3). These results were also found on June 7 and July 7, 2005, where available NO_3^- concentrations in all 3 treatments were highest because of tillage, fertilizer and time of season (Figure 4.6). Rovira and Greacen (1957) and Pierzynski et al. (2005) concluded that tillage and cultivation increased mineralization rates because soil disturbance leads to more available carbon substrates. These carbon substrates support greater microbial activity in the soil because of the breakdown of soil aggregates and therefore increased net N mineralization rates. The increased net N mineralization is only temporary and with continued annual cultivation, it will likely decrease soil organic matter and total N and therefore, crop productivity and yield (Rovira and Greacen 1957; Havlin et al. 2005).

In 2005 at the 0–10 cm depth increment, available NO_3^- concentrations were greater in the FR than in the NR treatment because of the higher soil temperatures found in the FR treatment. The FR treatment had no tree cover and less plant litter in comparison to the NR treatment (Table 4.4, Figure 4.6) because of the removal of canola in 2005 and alfalfa in 2006 and therefore, created a higher surface heat flux compared to tree canopy covered soils (Sharratt 1998). The reverse occurred on May 1 and May 31, 2006, at both depth increments where NR had greater available NO_3^- concentrations than FR because FR was waterlogged due to spring thaw, with the possibility of NO_3^- becoming denitrified (Vought et al. 1995). Although in the same landscape position, waterlogging did not occur in the NR but did occur in the FR. A difference of a couple of centimeters in elevation may have been enough for waterlogging to occur in the FR plots and not the NR plots (S. Chang personal communication).

In June 05 at the 0–10 cm depth increment, there was net N immobilization in the NR treatment because with increased temperatures and declining soil moisture contents in late spring, the microorganisms were likely quickly decomposing the litter material in the NR (Figure 4.8). The NR had the highest soil C:N ratio and WSC concentrations compared to the FR (Table 4.1, Figure 4.1), which created a large demand for available N by the microbes (Vitousek 1982) (Table 4.1, Figure 4.1). Both net nitrification and net N mineralization in 2005 and 2006 had negative correlations with WSC (Table 4.5) which was in agreement with a study by Zeller et al. (2000) in a comparison between abandoned and managed pastures. As the ratio of available carbon (the microbes energy source) to available nitrogen (the microbes protein source) increased, the microbes immobilized N and incorporated N from the soil solution into their biomass. Although soil temperature is an important factor in net N mineralization rates, no strong correlation was found because according to Schmidt et al. (1999), any increase in gross N mineralization due to soil temperature changes would either lead to N immobilization in the microbes or would be released into the soil inorganic N pool.

The buried-bag method provided an index of the net N mineralization rate, however, there were some difficulties with this method such as soil disturbance and a representative soil moisture content for the duration of the incubation. The buried-bag method can provide an index of soil net N mineralization rates when the soil moisture content is constant throughout the entire incubation period. If the surrounding environment had fluctuating soil regimes, such as precipitation or evaporation, it would make interpretation of net N mineralization results difficult (Raison et al. 1987; Abril et al. 2001). According to Raison et al. (1987), soil disturbance, including sieving to remove roots and other plant material prior to analysis of N, could increase net N mineralization, immobilize N or alter the proportion of inorganic N during incubation causing an incorrect measurement.

4.5 Conclusions

Seasonal trends of potential N supply rates, available N and net N mineralization rates were dependent on soil moisture and to a lesser extent by WSC, soil pH and soil temperature. Seasonal trends were apparent across all treatments and both depth increments. Regardless of method of measurement, all treatments appeared to follow a seasonal pattern of increased N mineralization and availability during the summer months compared to decreasing mineralization rates in the winter months. Summer is the period of increased N mineralization and active plant uptake. During late fall, nutrients are cycling back into available forms via replenishment through litter. Although N availability tended to be elevated in the riparian treatments compared to the upland, these effects varied through time and were frequently absent.

Vegetation type may have also affected N availability in the forage treatments as canola residue from the 2005 growing season appeared to decompose more slowly than alfalfa grass residue in the 2006 growing season and therefore N availability improved for plant growth during the alfalfa cropping system. With the exception of potential

NO_3^- supply rates in both years and both depth increments, the buried-bag method and the PRS^{TM} probes, rejected both hypotheses for N mineralization in 2005 and 2006 at both depth increments.

Based on the results on N mineralization and N availability for plant uptake, the development of a nutrient management plan for this site would need to understand that the current year's crop nutrient requirements may or may not differ at different landscape positions within a field. Soil testing after spring melt and prior to seeding would ensure that the appropriate amount of nutrients is applied for the specific crop with minimal risk of N loss through denitrification, leaching or runoff.

4.6 Literature Cited

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Table 4.1 Total C and Total N concentrations and C:N ratio of soils at the study site (n=3; mean ± SE).

Treatment	Soil depth increment (cm)	Total C (Mg C ha^{-1})	Total N (Mg N ha^{-1})	C:N ratio
Forage	0 – 10	56.3 ± 3.42	5.46 ± 0.30	10.29 ± 0.08
Upland	10 – 20	47.1 ± 10.0	4.55 ± 0.90	10.26 ± 0.25
Forage	0 – 10	70.0 ± 11.0	6.68 ± 0.97	10.46 ± 0.12
Riparian	10 – 20	66.2 ± 16.3	6.35 ± 1.45	10.35 ± 0.17
Native	0 – 10	10.4 ± 9.71	8.42 ± 0.65	12.37 ± 0.26
Riparian	10 – 20	82.2 ± 9.80	7.32 ± 0.67	11.17 ± 0.46

Table 4.2 P values from the analysis of variance using repeated measures for water soluble carbon as affected by landscape position (LP) and land use (LU) in 2005 and 2006 at 0–10 cm and 10–20 cm soil depth increments. Highlighted values are significant at $p < 0.05$.

	0–10 cm		10-20 cm	
Effect	**2005**	**2006**	**2005**	**2006**
	Effects of landscape position			
Landscape Position (LP)	0.185	**0.038**	0.123	0.395
Time (T)	**<0.001**	**<0.001**	0.345	**<0.001**
LP*T	0.779	**<0.001**	0.145	**0.029**
	Effects of land use			
Land Use (LU)	**<0.001**	0.320	**<0.001**	**<0.001**
Time (T)	**<0.001**	**<0.001**	0.225	**<0.001**
LU*T	**0.014**	0.516	0.091	0.120

Table 4.3 P values from the analysis of variance using repeated measures for potential NH_4^+ and NO_3^- supply rates for measured by PRS^{TM}-probes as affected by landscape position (LP) and land use (LU) in 2005 and 2006 at two soil depth increments. Highlighted values are significant at $p < 0.05$.

	0–10 cm				**10–20 cm**			
	PRS- NH_4^+		**PRS- NO_3^-**		**PRS- NH_4^+**		**PRS- NO_3^-**	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
	Effects of landscape position							
LP	0.164	0.666	**<0.001**	**0.005**	0.438	0.600	**<0.001**	**<0.001**
Time (T)	**0.037**	0.086	**0.001**	0.052	**<0.001**	0.056	**<0.001**	**0.001**
LP*T	0.355	0.351	0.896	0.801	0.182	0.289	**0.018**	**0.004**
	Effects of land use							
LU	0.061	0.953	0.282	**0.004**	0.059	0.906	0.174	**0.004**
Time (T)	**<0.001**	**0.001**	**0.016**	0.100	**<0.001**	0.061	**0.009**	0.144
LU*T	**0.020**	0.275	0.053	0.070	**0.035**	0.674	**0.006**	0.094

Table 4.4 P values from the analysis of variance using repeated measures for soil available NH_4^+ and NO_3^- concentrations, net nitrification and net N mineralization rates as affected by landscape position (LP) and land use (LU) in 2005 and 2006 at a) 0–10 cm and b) 10–20 cm soil depth increments. Highlighted values are significant at $p < 0.05$.

(a) 0–10 cm

	Available NH_4^+		**Available NO_3^-**		**Net Nitrification**		**N Mineralization**	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
			Effects of landscape position					
LP	0.295	**0.009**	0.155	0.264	0.257	**0.003**	0.145	**0.010**
T	**0.017**	**0.010**	**<0.001**	0.574	**0.004**	**<0.001**	**0.006**	**<0.001**
LP * T	0.576	0.240	0.153	**<0.001**	0.435	0.206	0.505	0.082
			Effects of land use					
LU	**0.013**	**<0.001**	**<0.001**	**0.009**	**0.034**	0.774	**0.017**	0.522
T	**0.045**	**0.031**	**<0.001**	**<0.001**	0.095	**0.002**	0.266	**<0.001**
LU * T	0.465	**0.040**	**0.010**	**0.008**	**0.014**	0.195	**0.022**	0.113

(b) 10–20 cm

	Available NH_4^+		**Available NO_3^-**		**Net Nitrification**		**N Mineralization**	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
			Effects of landscape position					
LP	0.426	0.379	0.180	0.213	0.280	0.547	0.620	0.810
T	**0.040**	**0.015**	**0.004**	0.761	**0.012**	**0.005**	**0.008**	**0.004**
LP * T	0.321	0.522	0.148	**0.011**	0.229	0.365	0.082	0.855
			Effects of land use					
LU	**0.013**	**<0.001**	0.068	**0.019**	**0.010**	0.169	**0.036**	0.965
T	**0.015**	**0.003**	**0.020**	**<0.001**	0.061	**<0.001**	0.380	**<0.001**
LU * T	0.446	**0.037**	0.630	0.204	0.572	**0.024**	0.985	0.235

Table 4.5 Correlation coefficient (r value) among soil properties: water soluble carbon (WSC), soil temperature (TEMP), gravimetric soil moisture (MOIST), soil $pH_{(H2O)}$, soil $pH_{(CaCl2)}$, potential N supply rates (PRS-NH_4^+ and PRS-NO_3^-), net N mineralization (NMIN), net nitrification (NNIT), available NH_4^+ and NO_3^- concentrations at the a) 0–10 cm in 2005, b) 0-10 cm in 2005, c) 10–20 cm in 2005 and d) 10–20 cm depth increments in 2006. Highlighted correlation coefficients were significant at α = 0.05. P values are in brackets.

(a) 0–10 cm in 2005

Variable	WSC	TEMP	MOIST	pH(H_2O)	pH($CaCl_2$)	PRS- NO_3^-	PRS-NH_4^+	NMIN	NNIT	NH_4^+
NO_3^-	**-0.66** **(<0.001)** **n = 36**	**0.40** **(0.020)** **n = 34**	**-0.43** **(0.012)** **n = 34**	-0.01 (0.960) n = 35	0.21 (0.209) n = 37	0.29 (0.108) n = 32	**0.57** **(0.002)** **n = 28**	**0.51** **(0.003)** **n = 32**	**0.52** **(0.002)** **n = 32**	-0.12 (0.464) n = 32
NH_4^+	**0.48** **(0.003)** **n = 37**	0.20 (0.251) n - 34	0.28 (0.113) n = 33	0.09 (0.618) n = 35	0.05 (0.786) n = 37	**0.45** **(0.011)** **n = 32**	-0.33 (0.082) n = 28	-0.02 (0.990) n = 31	0.17 (0.348) n = 31	
NNIT	**-0.36** **(0.050)** **n = 29**	0.28 (0.144) n = 28	-0.05 (0.791) n = 28	0.31 (0.073) n = 35	**0.44** **(0.066)** **n = 37**	-0.12 (0.532) n = 32	-0.14 (0.489) n = 28	**0.95** **(<0.001)** **n = 32**		
NMIN	**-0.44** **(0.018)** **n = 37**	0.13 (0.513) n = 28	-0.08 (0.704) n = 28	**0.33** **(0.050)** **n = 35**	**0.45** **(0.005)** **n = 37**	0.28 (0.129) n = 31	0.27 (0.167) n = 27			
PRS-NH_4^+	**-0.67** **(<0.001)** **n = 27**	0.23 (0.241) n = 29	**-0.72** **(<0.001)** **n = 27**	-0.33 (0.088) n = 27	-0.12 (0.509) n = 30	0.28 (0.130) n = 31				
PRS- NO_3^-	-0.29 (0.097) n = 33	0.10 (0.580) n = 32	-0.19 (0.309) n = 31	**-0.54** **(0.001)** **n = 32**	-0.29 (0.096) n = 35					

(b) 0–10 cm in 2006

Variable	WSC	TEMP	MOIST	pH(H_2O)	pH($CaCl_2$)	PRS- NO_3^-	PRS-NH_4^+	NMIN	NNIT	NH_4^+
NO_3^-	-0.30	**-0.59**	0.09	0.07	-0.02	<0.01	0.01	0.23	0.17	0.23
	(0.065)	**(<0.001)**	(0.625)	(0.690)	(0.910)	(0.993)	(0.970)	(0.156)	(0.274)	(0.139)
	n = 39	**n = 41**	n = 29	n = 36	n = 40	n = 18	n = 21	n = 41	n = 41	n = 41
NH_4^+	0.07	-0.27	0.02	-0.18	0.07	<0.01	-0.29	**0.33**	**0.47**	
	(0.646)	(0.087)	(0.910)	(0.360)	(0.676)	(1.00)	(0.200)	**(0.034)**	**(0.002)**	
	n = 40	n = 41	n = 29	n = 36	n = 40	n = 18	n = 21	**n = 41**	**n = 41**	
NNIT	**-0.44**	0.10	0.01	0.23	0.05	-0.34	**-0.54**	**0.92**		
	(0.002)	(0.491)	(0.971)	(0.172)	(0.748)	(0.163)	**(0.012)**	**(<0.001)**		
	n = 46	n = 47	n = 35	n = 36	n = 40	n = 18	**n = 21**	**n = 48**		
NMIN	**-0.50**	0.11	0.01	**0.36**	0.16	-0.36	**-0.58**			
	(<0.001)	(0.444)	(0.992)	**(0.029)**	(0.318)	(0.143)	**(0.006)**			
	n = 47	n = 48	n = 36	**n = 36**	n = 40	n = 18	**n = 21**			
PRS-NH_4^+	-0.12	-0.03	-0.41	-0.35	-0.09	0.18				
	(0.575)	(0.889)	(0.102)	(0.130)	(0.686)	(0.486)				
	n = 23	n = 23	n = 17	n = 20	n = 22	n = 18				
PRS- NO_3^-	-0.17	-0.25	-0.07	0.10	0.06					
	(0.483)	(0.291)	(0.824)	(0.705)	(0.803)					
	n = 19	n = 20	n = 13	n = 18	n = 19					

(c) 10-20 cm in 2005

Variable	WSC	TEMP	MOIST	pH(H_2O)	pH($CaCl_2$)	PRS- NO_3^-	PRS-NH_4^+	NMIN	NNIT	NH_4^+
NO_3^-	-0.23	0.23	-0.12	-0.21	0.10	**0.59**	**0.42**	0.23	0.31	**0.47**
	(0.197)	(0.161)	(0.519)	(0.210)	(0.570)	**(<0.001)**	**(0.030)**	(0.229)	(0.095)	**(0.003)**
	n = 32	n = 37	n = 33	n = 33	n = 33	**n = 28**	**n = 27**	n = 30	n = 30	**n = 37**
NH_4^+	0.13	0.24	0.20	0.15	0.04	**0.63**	-0.02	0.15	**0.41**	
	(0.494)	(0.145)	(0.272)	(0.390)	(0.815)	**(<0.001)**	(0.926)	(0.417)	**(0.026)**	
	n = 32	n = 37	n = 33	n = 35	n = 33	**n = 28**	n = 27	n = 30	**n = 30**	
NNIT	-0.36	0.35	0.28	0.14	0.21	0.162	**0.49**	**0.83**		
	(0.075)	(0.058)	(0.159)	(0.422)	(0.231)	(0.411)	**(0.009)**	**(<0.001)**		
	n = 26	n = 30	n = 27	n = 35	n = 33	n = 28	**n = 27**	**n = 30**		
NMIN	-0.35	0.06	-0.24	0.27	0.34	0.20	**0.57**			
	(0.081)	(0.771)	(0.224)	(0.119)	(0.056)	(0.308)	**(0.003)**			
	n = 26	n = 30	n = 27	n = 35	n = 33	n = 28	**n = 25**			
PRS-NH_4^+	**-0.48**	0.24	**-0.62**	-0.33	**-0.40**	0.21				
	(0.010)	(0.181)	**(<0.001)**	(0.071)	**(0.037)**	(0.269)				
	n = 28	n = 32	**n = 28**	n = 30	**n = 28**	n = 30				
PRS- NO_3^-	-0.123	-0.27	0.13	-0.33	-0.17					
	(0.518)	(0.127)	(0.487)	(0.063)	(0.370)					
	n = 30	n = 34	n = 30	n = 32	n = 30					

(d) 10-20 cm in 2006

Variable	WSC	TEMP	MOIST	$pH(H_2O)$	$pH(CaCl_2)$	PRS- NO_3^-	PRS-NH_4^+	NMIN	NNIT	NH_4^+
NO_3^-	-0.25 (0.148) n = 36	-0.18 (0.321) n = 34	0.02 (0.907) n = 32	0.10 (0.592) n = 33	-0.04 (0.845) n = 32	-0.29 (0.246) n = 18	0.23 (0.324 n = 20	-0.05 (0.761) n = 38	0.05 (0.762) n = 38	0.06 (0.713) n = 37
NH_4^+	0.27 (0.122) n = 35	-0.21 (0.229) n = 34	0.14 (0.442) n = 31	0.10 (0.953) n = 33	0.14 (0.458) n = 31	-0.37 (0.124) n = 19	-0.25 (0.301) n = 19	0.32 (0.055) n = 37	**0.49** **(0.022)** **n = 37**	
NNIT	-0.14 (0.360) n = 42	0.15 (0.343) n = 41	0.13 (0.426) n = 38	-0.23 (0.208) n = 33	-0.28 (0.115) n = 32	-0.23 (0.338) n = 19	-0.36 (0.118) n = 20	**0.94** **(<0.001)** **n = 45**		
NMIN	-0.24 (0.121) n = 42	0.22 (0.167) n = 41	0.11 (0.524) n = 38	-0.29 (0.102) n = 33	-0.31 (0.079) n = 32	-0.25 (0.300) n = 19	-0.34 (0.142) n = 20			
PRS-NH_4^+	0.03 (0.884) n = 23	-0.09 (0.708) n = 22	**-0.58** **(0.005)** **n = 22**	-0.05 (0.817) n = 21	-0.02 (0.940) n = 20	0.31 (0.179) n = 20				
PRS- NO_3^-	-0.33 (0.157) n = 20	0.17 (0.493) n = 19	**-0.50** **(0.031)** **n = 19**	-0.248 (0.338) n = 17	-0.23 (0.365) n = 18					

Figure 4.1 Land use and landscape position effects on water soluble carbon for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

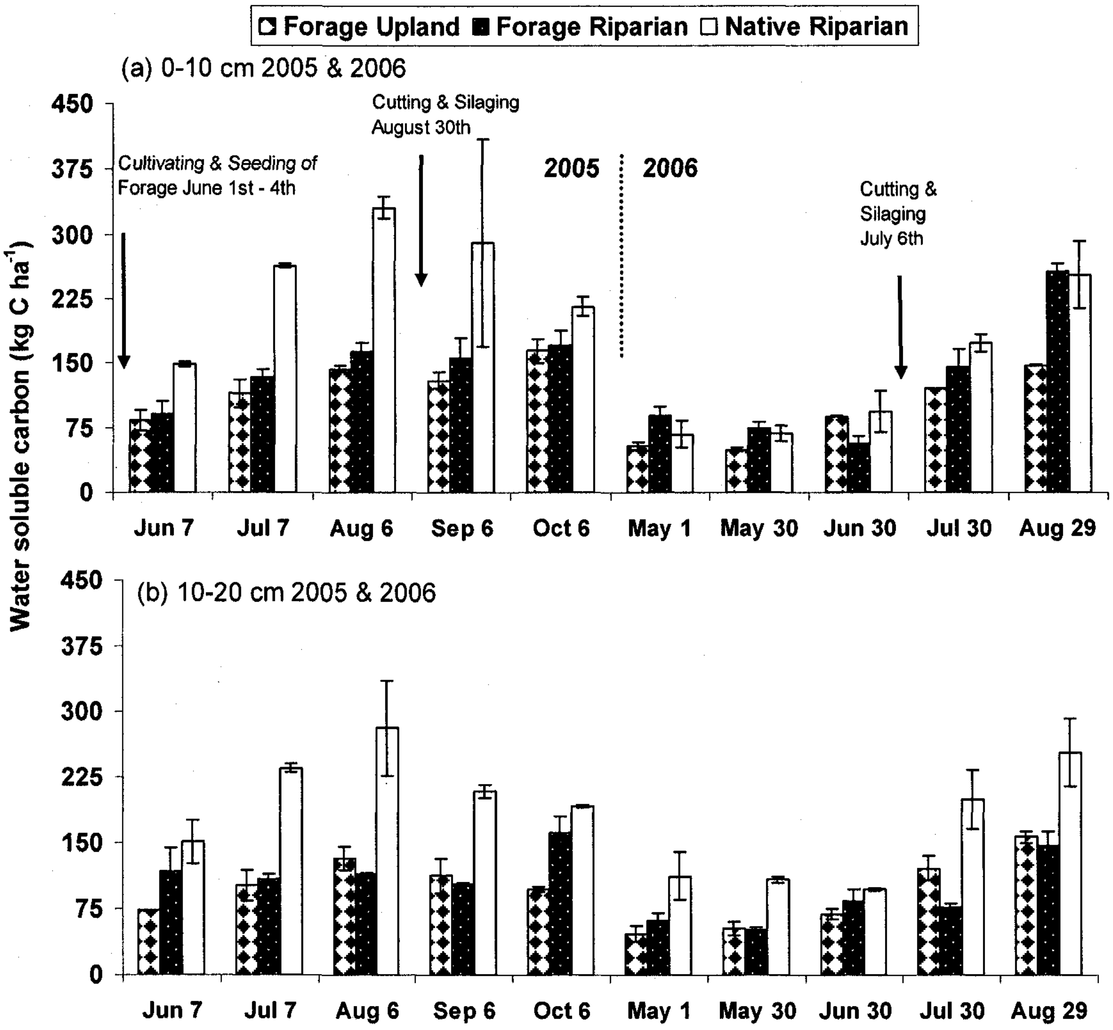


Figure 4.2 Land use and landscape position effects on potential N supply rates for NH_4^+ measured by PRS™ for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

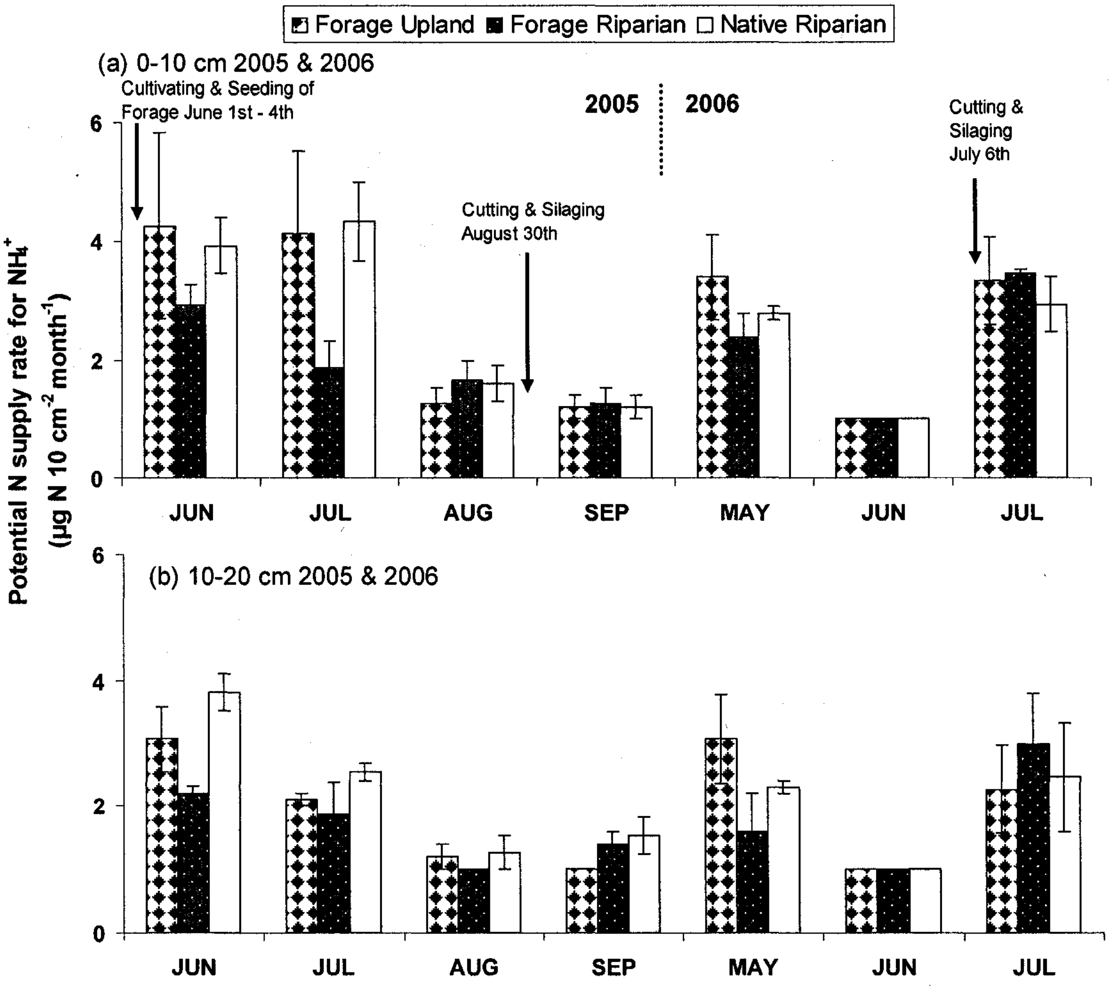


Figure 4.3 Land use and landscape position effects on potential N supply rates for NO_3^- measured by PRS™ for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

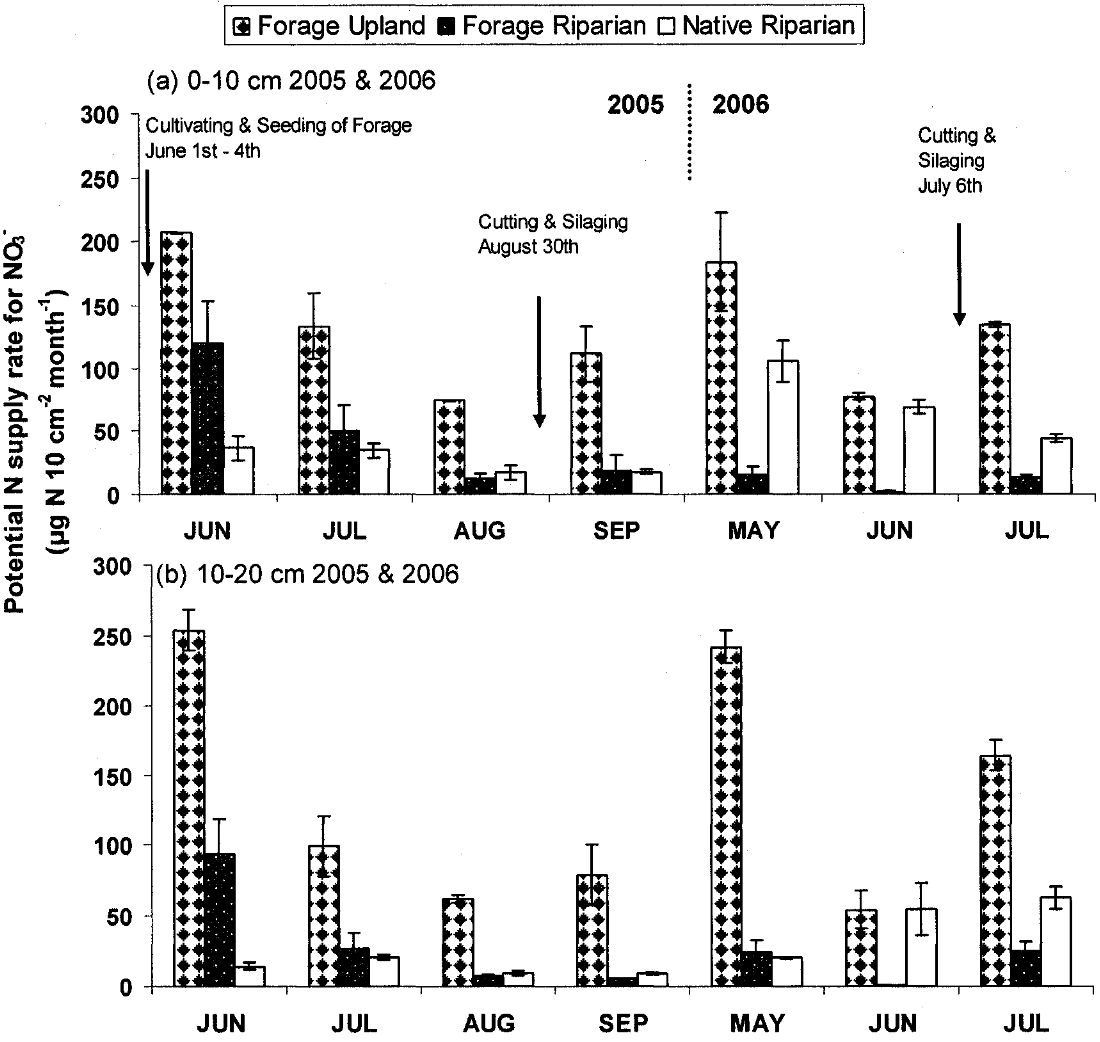


Figure 4.4 Regression of potential N supply rate for NO_3^- with gravimetric soil moisture content in 2005 at the (a) 0-10 cm (n = 27) and (b) 10–20 cm soil depth increments (n=28).

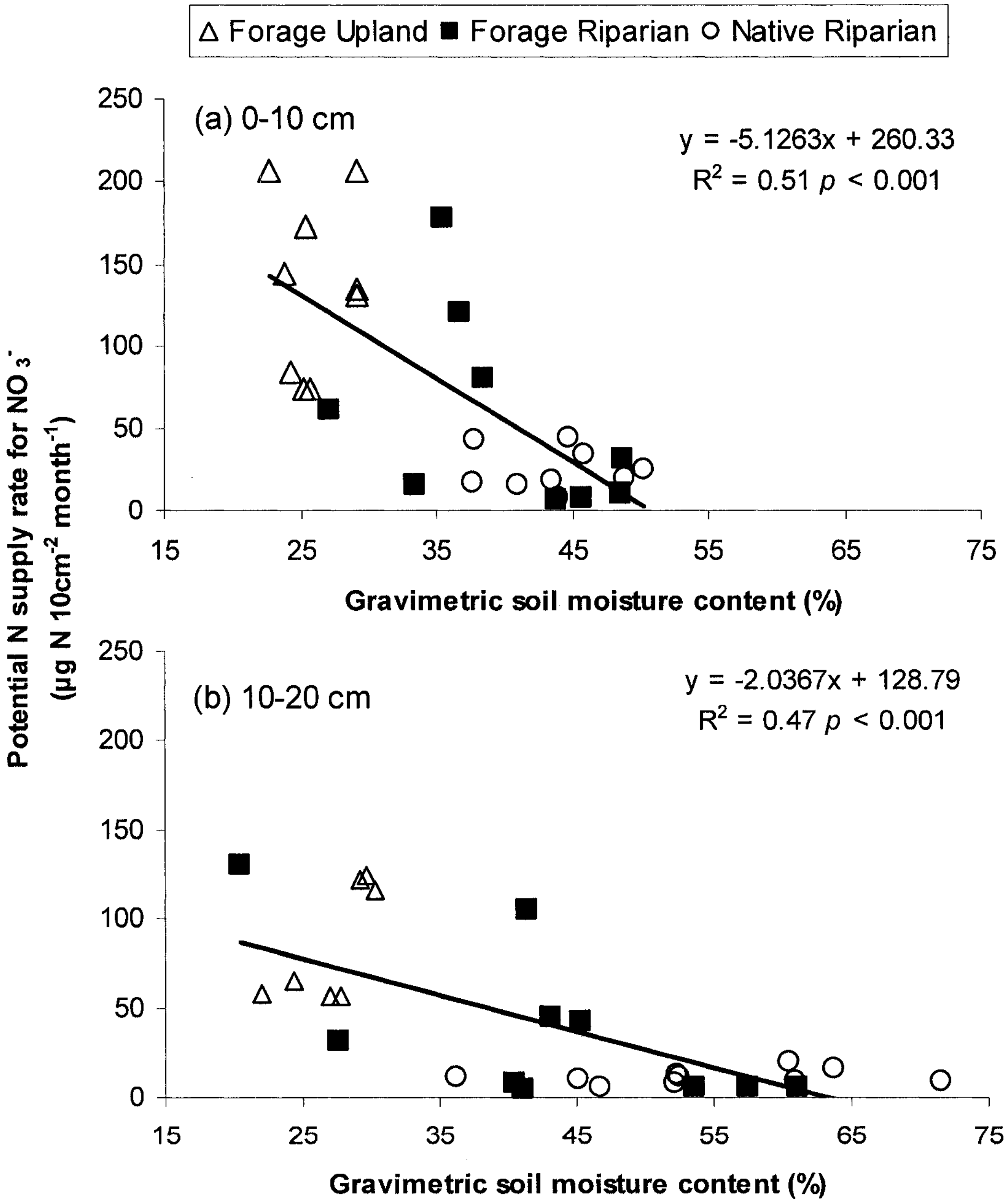


Figure 4.5 Land use and landscape position effects on available NH_4^+ concentrations for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

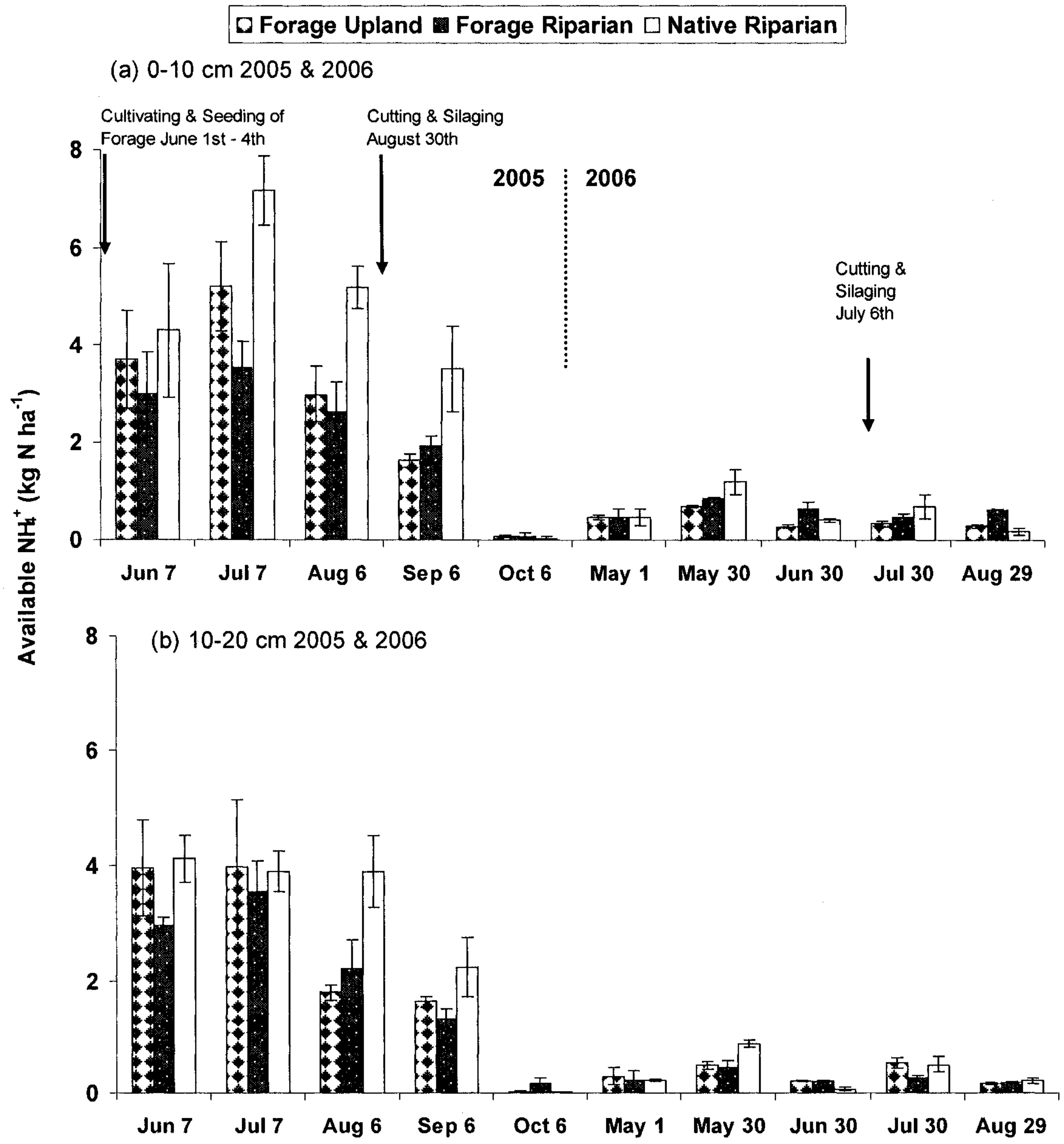


Figure 4.6 Land use and landscape position effects on available NO_3^- concentrations for the 2005 and 2006 growing season at the (a) 0–10 and (b) 10–20 cm soil depth increments. Error bars are SEs.

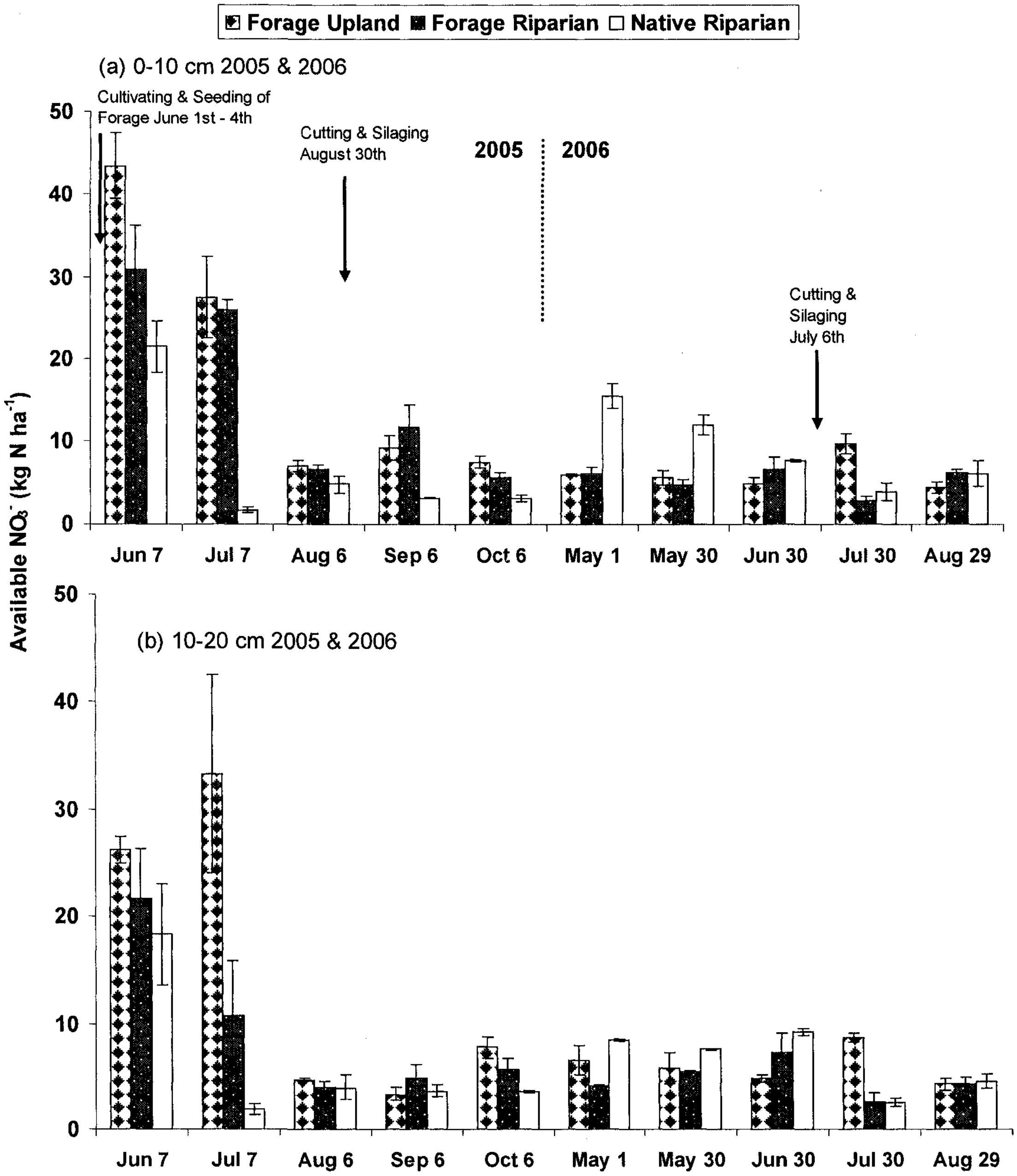


Figure 4.7 Land use and landscape position effects on net nitrification rates for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

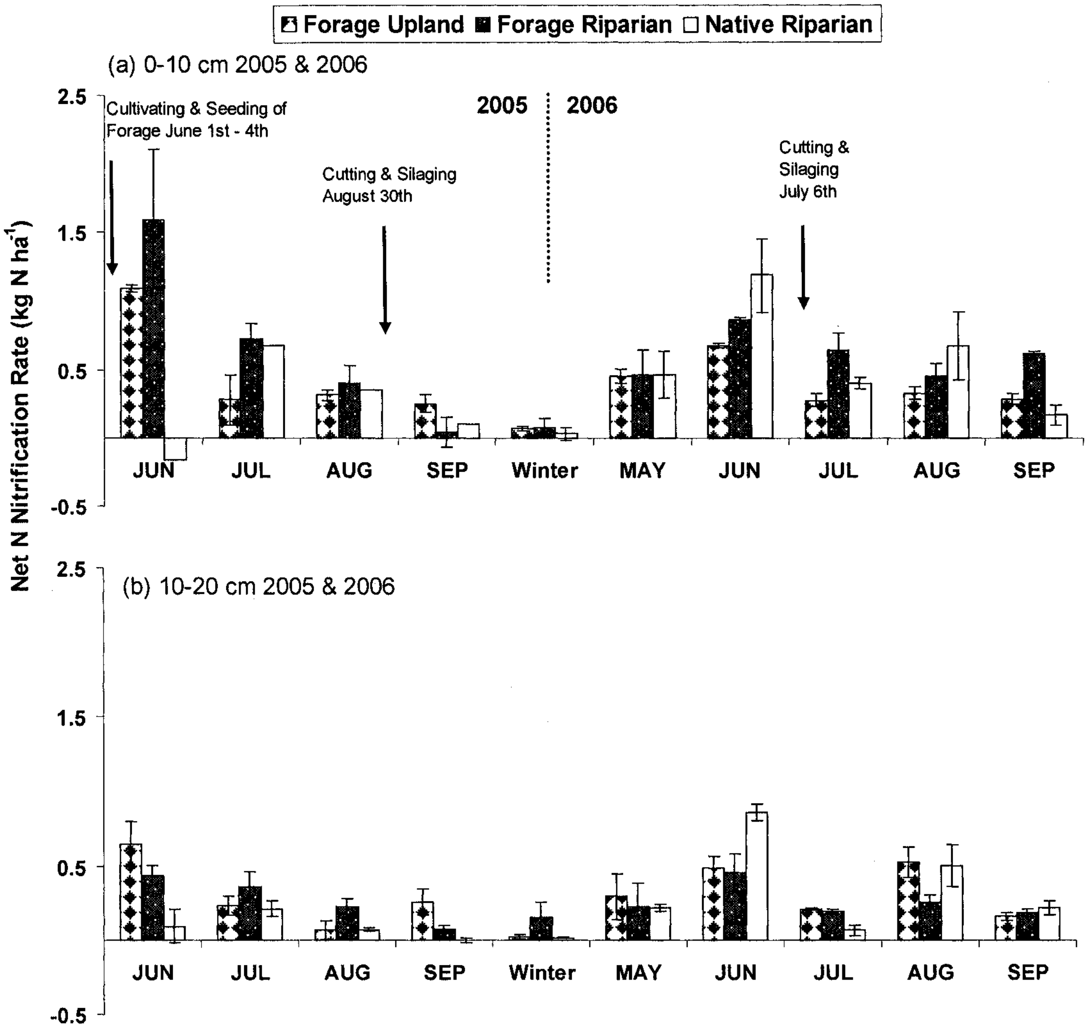
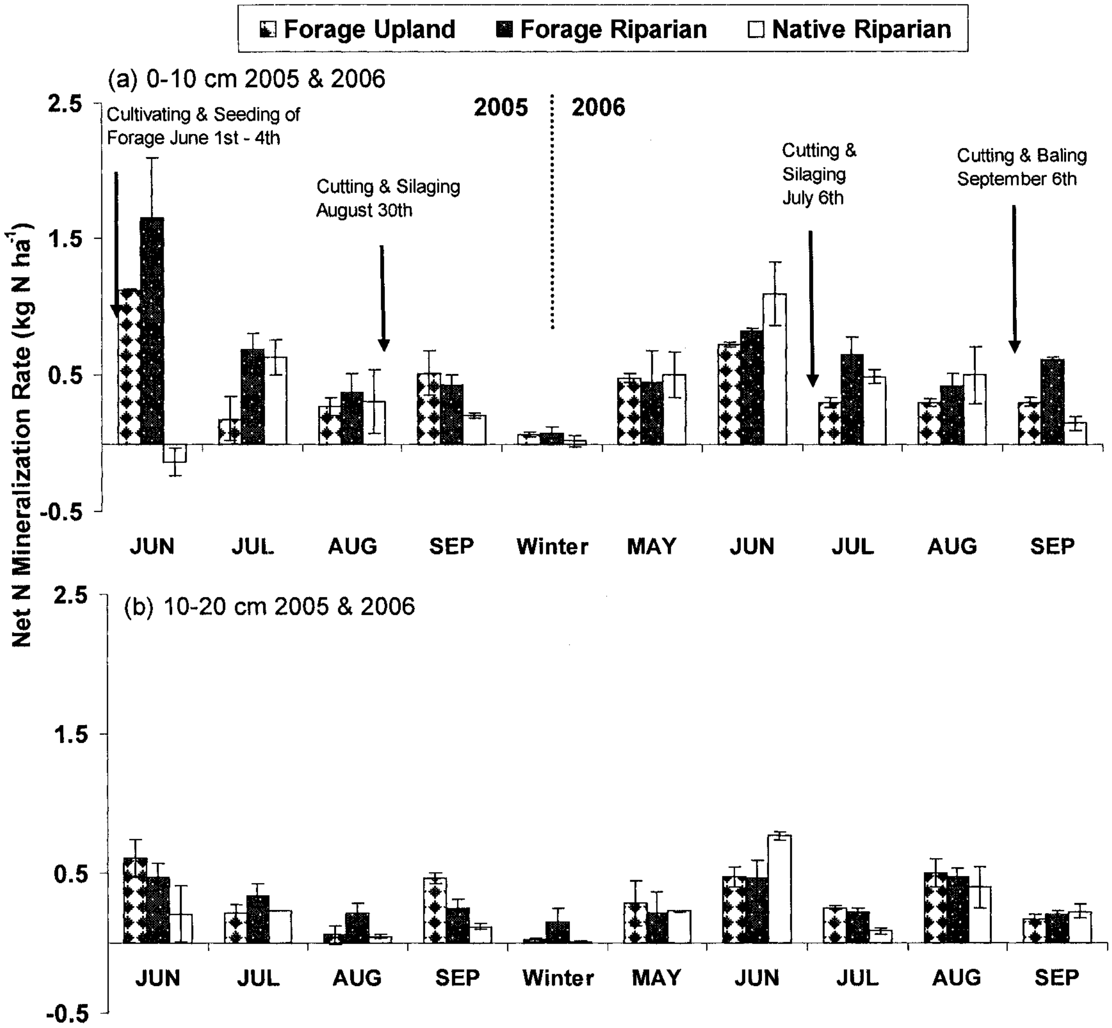


Figure 4.8 Land use and landscape position effects on net mineralization rates for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.



Chapter 5: Landscape Position and Land Use Effects on Denitrification Rates within a Riparian-Agricultural System

5.1 Introduction

A riparian ecosystem is a transitional area between streams or wetlands and uplands that can potentially influence nutrient cycling in both soil and water (Gregory et al. 1991; Davis et al. 2007). As excess fertilizers and manures are applied over time, plants and microbial pools become enriched or saturated with N and their N absorption capacity decreases. This increases the possibility of N leaching, especially nitrate, from the soil into surface and ground waters (Aber et al. 1989). There are a lot of unknowns about the mechanisms of N retention in the riparian ecosystem so the potential use and effective management of these areas are not fully realized. Ettema et al. (1999) stated that N is effectively buffered in riparian areas because of several processes in the biologically active portion of the soil profile. The two main biological processes involved in removing NO_3^- from the soil are by plant and microorganism uptake which only removes N temporarily from the soil and denitrification which is the removal of N into the atmosphere (Clément et al. 2003). Groffman et al. (1992) and Martin et al. (1999) suggested that denitrification is the preferred method of NO_3^- removal from the land including stream riparian zones because NO_3^- removed by plant uptake and microbial immobilization is subject to remineralization and is released back into the soil solution. However, one of the products produced by denitrification is N_2O, a known greenhouse gas that contributes to global warming (Machefert and Dise 2004).

Denitrification can be microbial or chemical, but the microbial process dominates in most soils through the dissimilatory reduction of NO_3^- and NO_2^- to produce NO, N_2O and N_2 gases by a diverse group of bacteria (Mosier et al. 2002). Denitrification is one of the principal mechanisms of nitrous oxide(N_2O) entering the atmosphere as a greenhouse gas and thus, a contributor to global warming (Piernzeski et al. 2005). In Canada, approximately 10% of soluble N entering agroecosystems as fertilizer, atmospheric inputs, and readily available N in manure, may be lost via denitrification and an additional 10% of N mineralized from organic matter is also denitrified (Janzen et al. 2003). In riparian zones there is also a lack of data on N gas emissions (Oehler et al. 2007). Denitrification can occur in microsites within many ecosystems including well-drained soils in forests, grasslands and agricultural lands; partially to fully water-saturated soils; groundwater aquifers and riparian sediments and surface waters (Seitzinger et al. 2006). Rates of denitrification can be very variable because it is influenced by spatial heterogeneity, time of year, time of day and other factors including moisture content, organic matter, temperature and NO_3^- supply.

Riparian soils denitrified NO_3^- at higher rates due to saturated conditions and greater quantities of microbially available C in comparison to upland soils (Ettema et al. 1999; Machefert and Dise 2004). Ettema et al. (1999) had denitrification rates of 83.5 *n*g N g^{-1} d^{-1} in the riparian area in comparison to 8.8 *n*g N g^{-1} d^{-1} in the upland and Machefert and Dise (2004) reported 71.7 kg N ha^{-1} in the riparian and 4.8 kg N ha^{-1} in the upland. On the Canadian prairies, the studies of denitrification in a riparian-agricultural system are few, but there have been studies of denitrification along topographic gradients. Denitrification was highest in the level-concave, depressional and footslope areas and lowest on the shoulder position (Pennock et al. 1992; Izaurralde et al. 2004).

Understanding the factors controlling denitrification rates on different landscape positions and land uses in agricultural areas that have a riparian component will help with the design and development of nutrient management planning strategies. The objectives of this study were to determine the effects of landscape position (upland vs. riparian) and land use (native vegetation vs. forage) on the denitrification rate in an agricultural landscape within the Whitemud Creek watershed in central Alberta. This chapter focuses on the following two hypotheses:

1) landscape positions affect denitrification rates in that the rates in the top 20 cm of the soil are greater in the forage riparian than the forage upland because soil properties, specifically soil moisture content, increase the rate of denitrification; and

2) land uses affect denitrification rates in that the rates in the top 20 cm of the soil are greater in the native riparian vegetation than in the forage riparian because there would be greater biomass, organic matter and soil moisture content in the native riparian vegetation.

5.2 Materials and Methods

5.2.1 Study Site

The details of the study site and soil characteristics are described in Chapter 3.

5.2.2 Experimental Design

This study used a randomized complete block design with three blocks. Each block contained one plot each of forage upland (FU), forage riparian (FR) and native riparian vegetation (NR) (Figure 3.1). This study looked at two pre-planned paired comparisons: FU versus FR and FR versus NR. There were two blocks on the east side of Whitemud Creek with the third block split by the creek with the forage plots on the east side and the native plot on the west side of the creek. The third native riparian plot was located on the west side of the creek because there was not a suitable native riparian area of the same size on the east side. The native riparian plot on the west side of Whitemud Creek had a 0.8 ha buffer immediately to the west that was seeded with the same forage hay mix that was on the rest of the study site.

5.2.3 Soil Sampling and Measurements

Moisture Content: Gravimetric soil moisture contents were determined on samples taken on the dates of denitrification measurements. Please see Chapter 3 for a description of the method used to determine gravimetric soil moisture contents.

Denitrification – Acetylene Inhibition Method: For each experimental unit at each depth increment (0-10 cm and 10-20 cm) and for each sampling period, 3 soil cores were taken at random locations to measure denitrification rates. Acetylene, C_2H_2, inhibits the reduction of N_2O to N_2 during denitrification and provides a value of total N via denitrification by measuring the amount of N_2O produced (Yoshinari et al. 1977). There are many different variations of the technique that are used for the acetylene inhibition method and this project used intact cores for the measurement.

The C_2H_2 inhibition method is an *in situ* technique that uses intact cores that are incubated with acetylene (Tiedje et al. 1989). The cores were encased in a PVC pipe to protect the soil core from being destroyed and to maintain the soil structure (Figure 5.1a). The 10 cm long PVC pipe (3.5 cm internal diameter) had 72 holes (7 mm diameter) to allow diffusion of C_2H_2 in and N_2O out of the intact soil core (Mosier and Klemedtsson 1994). Each core was placed in an incubation glass jar with a lid. The glass jar had a rubber stopper (0.95 cm long) on the lid through which a needle can be inserted for sampling the gas inside. A coating of silicone was applied between the stopper and lid to ensure a secure seal. Acetylene was added to the headspace above the soil to a final concentration of 5 to 10% vol vol^{-1} (5 - 10 kPa) (Figure 5.1b). The final concentration was calculated by determining the headspace volume by subtracting the total volume of the jar from the total volume of the core (Equation 1) with soil (Equation 2 and 3). The final acetylene concentration was approximately 8.8% vol vol^{-1} (kPa) or 16.5 mL. This concentration was used to account for higher or lower soil bulk densities that may increase or decrease the total volume of headspace in the jar (Equation 4).

Total volume of core:

$$Vc = \pi r^2 h \qquad \text{Equation 1}$$

$$Vc = (3.14)(0.035\ m/0.020\ m)^2(0.100\ m) = 0.962\ m^3$$

Where:

Vc = total volume of core

r = radius of core

h = height of core

Total pore space in core:

$Vp = (Bd/Pd)*Vc$ Equation 2

$Vp = (1.3 \times 10^{-4}\ Mg\ m^{-3}/2.65 \times 10^{-4}\ Mg\ m^{-3})(0.962\ m^3) = 0.472\ m^3$

Where:

Bd = Soil bulk density. Average is assumed to be 1.3×10^{-4} Mg m^{-3}

Pd = Soil particle density. Average is assumed to be 2.65×10^{-4} Mg m^{-3}

Total volume of headspace in jar:

$Vh = Vj - (Vc - Vp)$ Equation 3

$Vh = 2.366\ m^3 - (0.962\ m^3 - 0.472\ m^3) = 1.876\ m^3$

Where:

Vj = total volume of glass jar (2.366 m^3)

Amount of acetylene gas:

$AA = (Vh)(8.8\%)$ Equation 4

$AA = (1.876\ m^3)(8.8\%) = 0.165\ m^3 = 16.5\ cm^3 = 16.5\ mL$

Acetylene gas was brought to the field in a Tedlar 2-mm thick PVF Gas Sampling Bag (38 x 38 cm) and was secured in a cardboard box lined with expanded polystyrene (EPS). The C_2H_2 mixed with the gas in the macropores in the soil by reducing and increasing the pressure by pumping with a large gas tight 50 mL syringe (Mosier and Klemedtsson 1994). Headspace atmosphere samples of 5 mL were taken at 0, 3 and 6 hours and injected into 3 mL vials to provide a positive pressure for successful analysis on the GC (Figure 5.1c). The cores were incubated *in situ* in a hole slightly larger than the glass jar at the study site for 6 hours (Figure 5.1d). After 6 hours, the gas samples were taken back to the lab to be analyzed using a Varian CP-3800 gas chromatograph (GC, Varian Canada, Mississauga, Canada) equipped with an Electron Capture Detector (ECD) for quantification of N_2O. To determine the amount of N_2O produced in μg N_2O-N m^{-2} d^{-1}, the following linear model equation was used (Equation 5) (Metivier *In Prep.*). The linear model was adopted since it is often used to approximate a relationship between the observed concentrations and time for short deployment periods where the rate of change is nearly constant (Anthony et al. 1995). There were a few instances during the study where the measurement at 6 hours was much lower than the measurement at 3 hours which may suggest the nitrate supply had decreased after 3 hours. In those instances, the measurement at 3 hours was used.

Equation 5:

$$\mu g\, N_2O - N\, m^{-2} d^{-1} = \frac{(N_2O\ (\mu mol\, mol^{-1}) - Ambient\, (\mu mol\, mol^{-1})) * Mv\, (mol\, m^{-3}) * V(m^3) * Mm(28)(g\, mol^{-1})}{A(m^2) * 4 * 1000000\, \mu g\, g^{-1} * 10^{-6}\ mol\, \mu mol^{-1}}$$

Where:

N_2O is the volume of N_2O in the sample measured by the GC at 6 hours

Ambient is the volume of N_2O in the sample measured by the GC at 0 hours

Mv is the molar volume of air

V is the volume of jar

Mm is the mass of N in N_2O

A is the area of jar

*4 (to convert sample time of 6 hours to 24 hours)

Denitrification measurements were taken on the following dates in 2005: July 28, September 1, September 21, and October 12 and in 2006: April 12, May 3, May 30, June 6, July 10, July 27, August 23, September 15, and September 25.

5.2.4 Statistical Analyses

The PROC MIXED procedure in SAS (SAS Institute Inc. 1999) was used to analyze two one-way ANOVA's with blocking and repeated measures to evaluate the effect of landscape position (forage upland vs. forage riparian) and land use (native riparian vs. forage riparian) for each of the response variables: denitrification rate, gravimetric soil moisture content, soil temperature, soil pH and water soluble carbon.

Model:

$$\mathbf{Y_{ijk} = \mu + \rho_j + \alpha_i + d_{ij} + \gamma_k + (\alpha\gamma)_{ik} + \varepsilon_{ijk}}$$

Where:

Y_{ijk} = total rate of response variable

μ = mean rate of response variable (e.g. denitrification rate)

ρ_j = experimental blocking

α_i = treatment effect (land use or landscape position)

d_{ij} = random error for the whole plot

γ_k = time (month)

$(\alpha\gamma)_{ik}$ = interaction between treatment and time

ε_{ijk} = random error on repeated measures

To compare the covariate variables (soil pH, gravimetric soil moisture content, water soluble carbon, soil temperature and nitrate) with the response variable (denitrification), regression and the Pearson Product Moment Correlation analyses were used.

The data in 2005 and 2006 were analyzed separately. With the exception of the denitrification dataset, outliers were assessed by first using the modified Z-score calculation on each treatment effect and then data was plotted on a scatter plot to determine visually if any outliers still remained. The modified Z-score uses the median and the median of the absolute deviation about the median (MAD) (Iglewicz and Hoaglin 1993; Seo 2006) where:

$$MAD = median \ \{|x_i - \tilde{x}|\},$$

where $\tilde{x}$ is the sample median and x_i is a measurement in the data set where one measurement might be denoted as x_1, another x_2 and so on. The subscript i might be any integer value up to N, the total number of x values in the dataset (Zar 1999).

The modified Z-Score (M_i) is computed as:

$$M_i = \frac{0.6745(x_i - \tilde{x})}{MAD}$$

Observations were labeled outliers when |Mi| > 3.5 (Iglewicz and Hoaglin 1993).

Normality tests on the data set were conducted using the PROC UNIVARIATE procedure (the Shapiro-Wilks test) and showed that most of the time, transformations of data were not required. The denitrification data were log transformed and no outliers were removed because of the heterogeneity of the denitrification rate in the soils (Tiedje et al. 1989). The Bartlett test using the PROC GLM procedure showed that the data had variances that were not homogeneous. The PROC MIXED procedure overcomes this problem. For statistical significance, $\alpha = 0.05$ was chosen.

5.3 Results

5.3.1 Gravimetric Soil Moisture Content

Gravimetric soil moisture content was measured on the days when denitrification measurements were taken (Figure 5.2). For each treatment in 2005, the two soil depth increments had similar gravimetric soil moisture contents throughout the growing season averaging at 29.9 % for FU, 41.5 % for FR and 51.1 % for NR at the 0–10 cm depth increment and 28.0 % for FU, 41.10 % for FR and 56.0 % for NR at the 10–20 cm depth increment. At both depth increments in 2005, landscape position and land use treatments significantly affected gravimetric soil moisture content as moisture was higher in the FR than in the FU treatment ($p = 0.001$ in 2005 and $p < 0.001$ in 2006 at 0-10 cm and $p = 0.004$ in 2005 and $p < 0.001$ in 2006 at 10-20 cm) and it was higher in the NR than in the FR treatment ($p = 0.005$ in 2005 and $p = 0.006$ in 2006 at 0-10 cm and $p = 0.008$ in 2005 and $p = 0.001$ in 2006 at 10-20 cm) (Table 5.1). In 2006, gravimetric soil moisture contents were highest in the three measurements in April and May, then gradually decreased in July and slowly increased in late summer/early fall (Figure 5.2).

5.3.2 Soil Temperature

Since denitrification measurements commenced at the end of July 2005, soil temperature decreased from July 28 from an average of 15.5 °C, 15.7 °C and 12.7 °C for the FU, FR and NR respectively at the 0–10 cm and 15.2 °C, 15.7 °C and 12.6 °C for the FU, FR and NR respectively at the 10–20 cm to October 12 to an average of 5.9 °C, 5.4 °C and 6.0 °C for the FU, FR and NR respectively at the 0-10 cm depth increment and 5.7 °C, 5.9 °C and 6.5 °C for the FU, FR and NR respectively at the 10–20 cm (Chapter 3, Figure 3.3). At both depth increments, the interaction between land use treatment and time was significant, showing that FR had higher soil temperatures than did the NR treatment on July 28 and September 01 but the reverse occurred on October 12 when temperature was higher in the NR than in the FR treatment.

In 2006, measurements were taken before, during and after the growing season and soil temperatures were, on average, 10.3 °C, 9.0 °C and 4.5 °C for the FU, FR and NR respectively at the 0–10 cm and 9.6 °C, 8.0 °C and 5.2 °C for the FU, FR and NR respectively at the 10–20 cm for the spring denitrification measurement period (April 12 – June 6). Soil temperature was at its highest in July at 21.7 °C, 18.9 °C and 14.1 °C for the FU, FR and NR respectively at the 0–10 cm and 20.9 °C, 18.5 °C and 15.0 °C for the FU, FR and NR respectively at the 10–20 cm. Soil temperature then decreased in late summer – early fall: 11.2 °C, 11.2 °C and 10.1 °C for the FU, FR and NR respectively at the 0–10 cm and 11.8 °C, 11.3 °C and 10.9 °C for the FU, FR and NR respectively at the 10–20 cm from August 23 – September 25. Landscape position and land use treatments significantly affected soil temperature where temperature was higher in the FU than in the FR treatment and FR was higher than in the NR treatment in both 0–10 cm and 10–20 cm soil depth increments in 2006 (Table 5.1, Figure 5.3).

5.3.3 Denitrification Rate

In both 2005 and 2006 at both depth increments with the exception of the July 28, 2006 measurement, the highest denitrification rates occurred in the FR treatment (Figure 5.4). In 2005 at the 0–10 cm soil depth increment, land use treatments significantly affected the denitrification rate where denitrification was higher in the FR than in the NR treatment ($p = 0.001$) (Table 5.1). At the 10–20 cm depth increment in 2005 and at both depth increments in 2006, landscape position and land use treatments significantly affected the denitrification rate as denitrification was higher in the FR than in the FU and NR treatments. The following seasonal trend became apparent where all three treatments had their highest denitrification rates in the spring (April 12 – June 23, 2006), lowest in the summer (July 10, 2006 and July 27, 2006) and moderate in late summer/early fall (September 1 – October 12, 2005 and August 23 – September 25, 2006).

The only significant correlation to denitrification in 2005 was soil temperature with $r = 0.44$ ($p = 0.023$) and $r = 0.55$ ($p < 0.001$) at 0–10 cm and 10–20 cm respectively (Table

5.2). The reverse was found in 2006 when there was a negative correlation with soil temperature (r = -0.29, $p = 0.011$ and r = -0.31, $p = 0.010$ at 0–10 cm and 10–20 respectively). In 2006, soil $pH_{(CaCl_2)}$ and $pH_{(H_2O)}$ and gravimetric soil moisture content were positively correlated to denitrification at 0–10 cm and 10–20 cm (Table 5.2). Soil temperature at both depth increments and WSC at 10–20 cm in 2006 were negatively correlated to denitrification. A relationship was found between the denitrification rate and soil $pH_{(H_2O)}$ where the denitrification rate increased with increasing pH at the 0–10 cm depth increment in 2006 ($R^2 = 0.26, p < 0.001$) (Figure 5.5a).

5.4 Discussion

The highest denitrification rates were found in the spring/early summer because of spring thaw that caused increased soil moisture content and higher availability of NO_3^- from nutrient sources such as litter decomposition. The highest denitrification rates in agroecosystems on the Canadian prairies have been reported to occur during spring snowmelt and early summer (Nyborg et al. 1997; Lemke et al. 1998). In spring 2006, it was wet and waterlogged in 2 out of 3 FR plots which increased the chance of anaerobic conditions and denitrification rates (Tate 2000). Land use and landscape position treatments significantly affected denitrification rates as denitrification was lowest in the NR and in the FU compared to in the FR because there was lower gravimetric soil moisture content in the FU and there may be a slight elevation increase in the NR plots in comparison to the FR plots which may explain why no waterlogging occurred in the NR plots (Figure 5.2).

The lowest denitrification rates were found in the summertime during low soil moisture content providing insufficient anaerobicity for microbes (Figure 5.4) and the denitrifying microbes would also be competing with higher plant uptake of NO_3^- (July 28, 2005 and July 10 and July 27, 2006). Groffman and Tiedje (1989), Pinay et al. (1993) and Lowrance et al. (1995) also found the lowest periods of denitrification in summer when rainfall was low and vegetation growth was occurring. At the Mundare, AB site, Izaurralde et al. (2004) showed that in the perennial cover (alfalfa), denitrification rates were smaller during summer and concluded that the moisture regime was affected by slope position.

Denitrification rates in late summer/early fall were in between the first and second trends. Lower plant uptake after the forage was cut in the FU and FR plots and a return of plant residue to the soil in the NR plots would allow for higher available NO_3^- concentrations to be present in the soil in comparison to the summertime. Increasing soil moisture content due to precipitation events would likely increase anaerobic conditions than in the summertime (September 1 – October 12, 05 and August 23 – September 25, 06) (Figure 5.4). The seasonal pattern present in this study was also found by Izaurralde et al. (2004) near Mundare, AB about 60 km east of this study site on Black Chernozemic soils. Pinay et al. (1993) and Groffman and Tiedje (1989) also found denitrification rates to be lowest in the summer and highest in spring and autumn.

The denitrification rates in 2005 were positively correlated with soil temperature because denitrification measurements were only taken in the latter half of the growing season when temperatures are typically higher than in the spring (Table 5.2). There was a negative correlation between denitrification and soil temperature in 2006 as was also found by Pinay et al. (1993). Higher soil temperatures occurred when water tables and soil moisture content in the plots were low (summer) and therefore, low soil moisture was limiting the denitrification rates (Figure 5.3). Lower soil temperatures occurred in the spring, where there was increased soil moisture and anoxic conditions because which enhanced the opportunity of denitrification to occur. Correlations between denitrification and NO_3^- and WSC, with the exception at 10-20 cm depth increment in 2006, were not significant because NO_3^- and WSC were sampled on different dates and denitrification rates were highly variable with time and space, as was also reported by Horwath et al. (1998) (Table 5.2).

Denitrification rates were higher in the FR than in the FU treatments because FR had significantly higher soil moisture content (Figures 5.2 and 5.4) which is in agreement with other studies (e.g. Hanson et al. 1994; Oehler et al. 2007). The high soil moisture content in the FR treatment was partly caused by waterlogging of the plot due to beaver activity that began in late July 2005. The denitrification rates measured in the drier FU treatment was likely caused by the anaerobic micro-sites that are found in unsaturated soils. According to Parkin et al. (1985), rapid diffusion of oxygen through gas-filled pore spaces confine denitrification to anaerobic micro-sites such as detritus and aggregates of soil particles where oxygen levels might be low, allowing for denitrification to happen.

In both years and at both depth increments, the higher denitrification rates in the FR than in the NR treatment was related to the higher soil moisture content, soil temperature and soil $pH_{(H_2O)}$ in the FR than the NR treatment (Table 5.1, Figure 5.4, Figure 5.5a). According to Hanson et al. (1994), rates of denitrification in natural soils, such as those in the NR treatment, do not respond to rain or water during the growing season because plant and heterotrophic microbes were taking up available N and kept available NO_3^- concentrations low (Figure 5.4). Although a linear relationship was found between soil $pH_{(H_2O)}$ and denitrification in 2006 (Figure 5.5a), the upper end of the trend was dominated by soil $pH_{(H_2O)}$ values that were greater or equal to 7.5 and found in the FR treatment. The relationship between denitrification and soil $pH_{(H_2O)}$ may explain that for this soil, a range between $pH_{(H_2O)}$ 7.0 – 8.0 with anaerobic conditions is optimal for denitrifying microbes at this site (Koskinen and Keeny 1982; Šimek et al. 2002). The higher soil pH may promote denitrification in waterlogged conditions like riparian areas (Dhondt et al. 2002) because with an increase in pH, there can be an increase in organic carbon availability and thus microbial activity.

From September 12 -15, 2006, inclusive, there was 62.6 mm of rainfall (Chapter 3, Figure 3.1). The September 15, 2006 measurement had the highest denitrification rates for the late summer/fall season because denitrification can occur in bursts in response to rainfall as aeration decreases and anaerobic conditions increased (Tate 2000). With increased soil moisture content, the diffusion of NO_3^- and solubility of carbon in the soils was facilitated into sites of denitrification (Luo et al. 1998). Although the NR plots had similar or higher gravimetric soil moisture contents for most of 2006, soil temperature, which is also an important factor for denitrification, was higher in the FR than the NR which would aid in the higher denitrification rates than in the NR.

5.5 Conclusions

The rate of denitrification is influenced by a variety of factors. Soil temperature, soil moisture content, soil pH and, to a lesser extent, water soluble carbon were the factors that were significantly correlated to denitrification rates. No relationship was found, however, between NO_3^- and denitrification in any treatment. Although it is clear that the denitrification rate was influenced strongly by landscape position and land use, soil moisture content appears to be the most important factor influencing denitrification rates.

Comparing landscape positions, the hypotheses at both depth increments was supported by increased denitrification rates in the FR than in the FU because of higher soil moisture content. Between land use treatments, the NR treatment was expected to have higher denitrification rates than in the FR, but the forage riparian soils demonstrated the capacity to denitrify at higher rates because of higher soil temperatures and soil moisture contents.

Although landscape position and land use affected denitrification rates, the magnitude of the denitrification rates varied seasonally. The denitrification rate and gaseous losses of N were dependent on the time of year and amount of soil moisture present. Overall, the denitrification rates were largest in both depth increments during spring melt in 2006 and were controlled primarily by the soil moisture content. As the growing season progressed with increased plant uptake, increased soil temperatures and evaporation of moisture in the soil, more oxygen circulated within the soil and inhibited denitrification. Soil moisture is the main constraint on denitrification for it affects the activity of anaerobic denitrifiers.

The importance of an undisturbed riparian area such as the NR plots to reduce NO_3^- pollution into Whitemud Creek from the surrounding forage upland remains unclear. Further investigation into the role of groundwater movement and denitrification will provide a better approach in understanding the movement and removal of NO_3^- through denitrification and other processes such as plant uptake, leaching and runoff.

Since the highest losses of N occurred during spring melt, especially in the FR plots, it may be advisable to apply enough fertilizer for the current year based on crop needs to avoid excess fertilizer N loss the following spring. The National Farm Stewardship Program promotes beneficial management practices (BMPs) such as the use of precision farming applications that use a GPS and a variable rate fertilizer applicator to apply less fertilizer in the riparian areas and more fertilizer in the upland areas. Producers who complete an environmental farm plan are eligible to receive financial and technical assistance for BMPs such as precision farming to encourage adoption of these practices (Agriculture and Agri-Food Canada 2007).

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Table 5.1 P values from the analysis of variance using repeated measures for gravimetric soil moisture content (GS Moisture), soil temperature and denitrification rates as affected by landscape position (LP) and land use (LU) at a) 0-10 cm and b) 10-20 cm depth increments in 2005 and 2006. Highlighted values are significant at $p < 0.05$.

(a) 0–10 cm

	GS Moisture		Temperature		Denitrification Rates	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
			Effect of landscape position			
LP	**0.001**	**<0.001**	0.257	**0.021**	0.335	**<0.001**
T	0.451	**<0.001**	**<0.001**	**0.026**	0.233	**0.001**
LP * T	0.847	0.163	0.271	0.12	0.592	0.453
			Effect of land use			
LU	**0.005**	**0.006**	**0.029**	**<0.001**	**0.001**	**0.016**
T	0.621	**<0.001**	**<0.001**	**0.028**	0.112	0.413
LU* T	0.406	0.070	**<0.001**	0.065	0.611	0.790

(b) 10–20 cm

	GS Moisture		Temperature		Denitrification Rates	
Effect	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
			Effect of landscape position			
LP	**0.004**	**<0.001**	0.288	**0.004**	**0.002**	**<0.001**
T	0.531	**<0.001**	**<0.001**	**<0.001**	**0.004**	**0.009**
LP * T	0.665	0.564	0.802	**0.029**	0.166	0.530
			Effect of land use			
LU	**0.008**	**0.001**	**<0.001**	**<0.001**	**0.003**	**0.005**
T	0.621	**<0.001**	**<0.001**	**<0.001**	0.471	**0.002**
LU * T	0.792	0.658	**<0.001**	**<0.001**	0.932	0.653

Table 5.2 Correlation coefficient (r value) between the log denitrification rate (Den) and soil properties that affect the denitrification rate: soil pH$_{(H_2O)}$, soil pH$_{(CaCl_2)}$, water soluble carbon (WSC), nitrate (NO_3^-), soil temperature (TEMP), gravimetric soil moisture (GMOIST) at the a) 0–10 cm and b) 10–20 cm depth increments in 2005 and 2006. Highlighted correlation coefficients were significant at $\alpha < 0.05$. P values are in brackets.

a) 0–10 cm

Variable	pH$_{(H_2O)}$	pH$_{(CaCl_2)}$	WSC	NO_3^-	TEMP	GMOIST
Den	-0.09	-0.09	-0.24	0.15	**0.44**	0.06
2005	(0.608)	(0.640)	(0.243)	(0.483)	**(0.023)**	(0.685)
	n = 30	n = 32	n = 25	n = 24	**n = 26**	n = 31
Den	**0.52**	**0.37**	-0.12	-0.13	**-0.29**	**0.39**
2006	**(<0.001)**	**(0.007)**	(0.467)	(0.418)	**(0.011)**	**(<0.001)**
	n = 58	**n = 62**	n = 41	n = 43	**n = 73**	**n = 75**

b) 10–20 cm

Variable	pH$_{(H_2O)}$	pH$_{(CaCl_2)}$	WSC	NO_3^-	TEMP	GMOIST
Den	0.07	0.09	-0.13	-0.14	**0.55**	0.12
2005	(0.690)	(0.636)	(0.545)	(0.480)	**(0.001)**	(0.509)
	n = 33	n = 32	n = 24	n = 27	**n = 31**	n = 35
Den	**0.28**	**0.27**	**-0.38**	0.05	**-0.31**	**0.43**
2006	**(0.030)**	**(0.045)**	**(0.014)**	(0.784)	**(0.010)**	**(<0.001)**
	n = 58	**n = 55**	**n = 42**	n = 39	**n = 68**	**n = 75**

Figure 5.1 The acetylene inhibition method: a) soil core, b) insertion of acetylene gas into glass jar, c) gas sampling of headspace, and d) incubation of jars in the soil.

a) Soil core was 10 cm x 3.5 cm with 72 holes

b) Acetylene being inserted into jar with soil core

c) Gas sampling of headspace

d) Incubation of jars in the soil for 6 hours.

Figure 5.2 Land use and landscape position effects on gravimetric soil moisture content in 2005 and 2006 at the (a) 0–10 cm and (b) 10–20 cm soil depth increments in 2006. Error bars are SE.

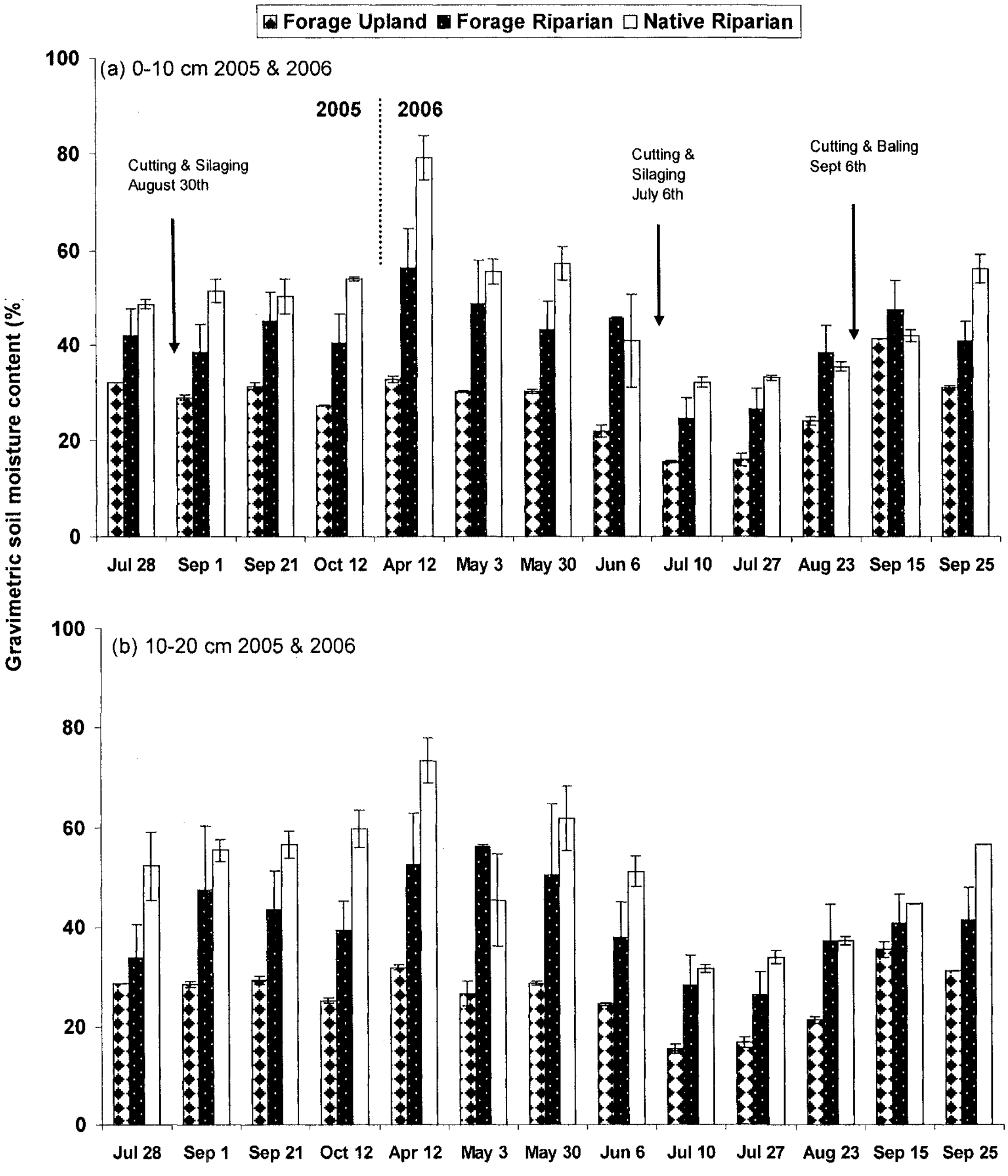


Figure 5.3 Land use and landscape position effects on soil temperature for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

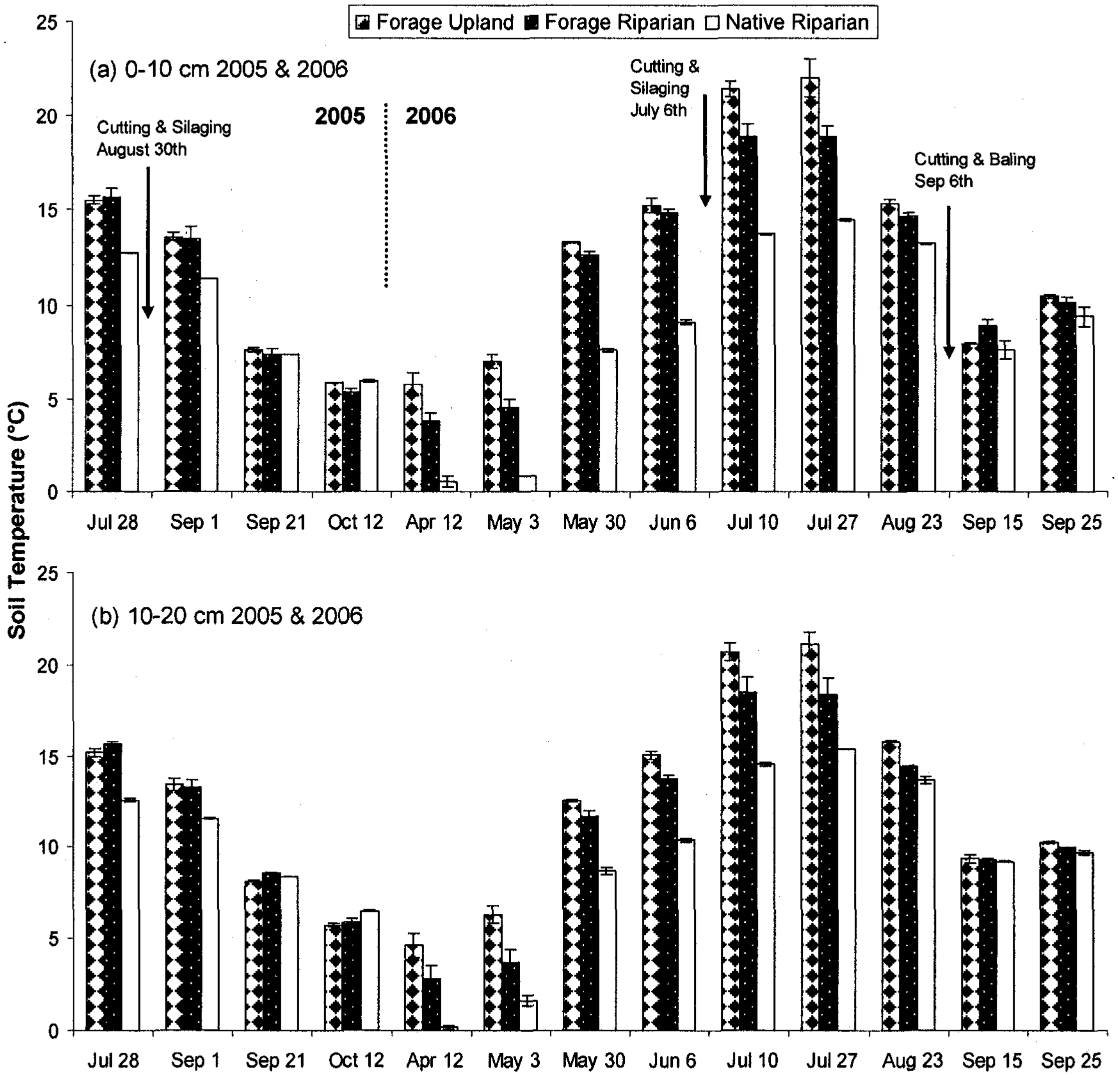


Figure 5.4 Land use and landscape position effects on denitrification for the 2005 and 2006 growing season at the (a) 0–10 cm and (b) 10–20 cm soil depth increments. Error bars are SEs.

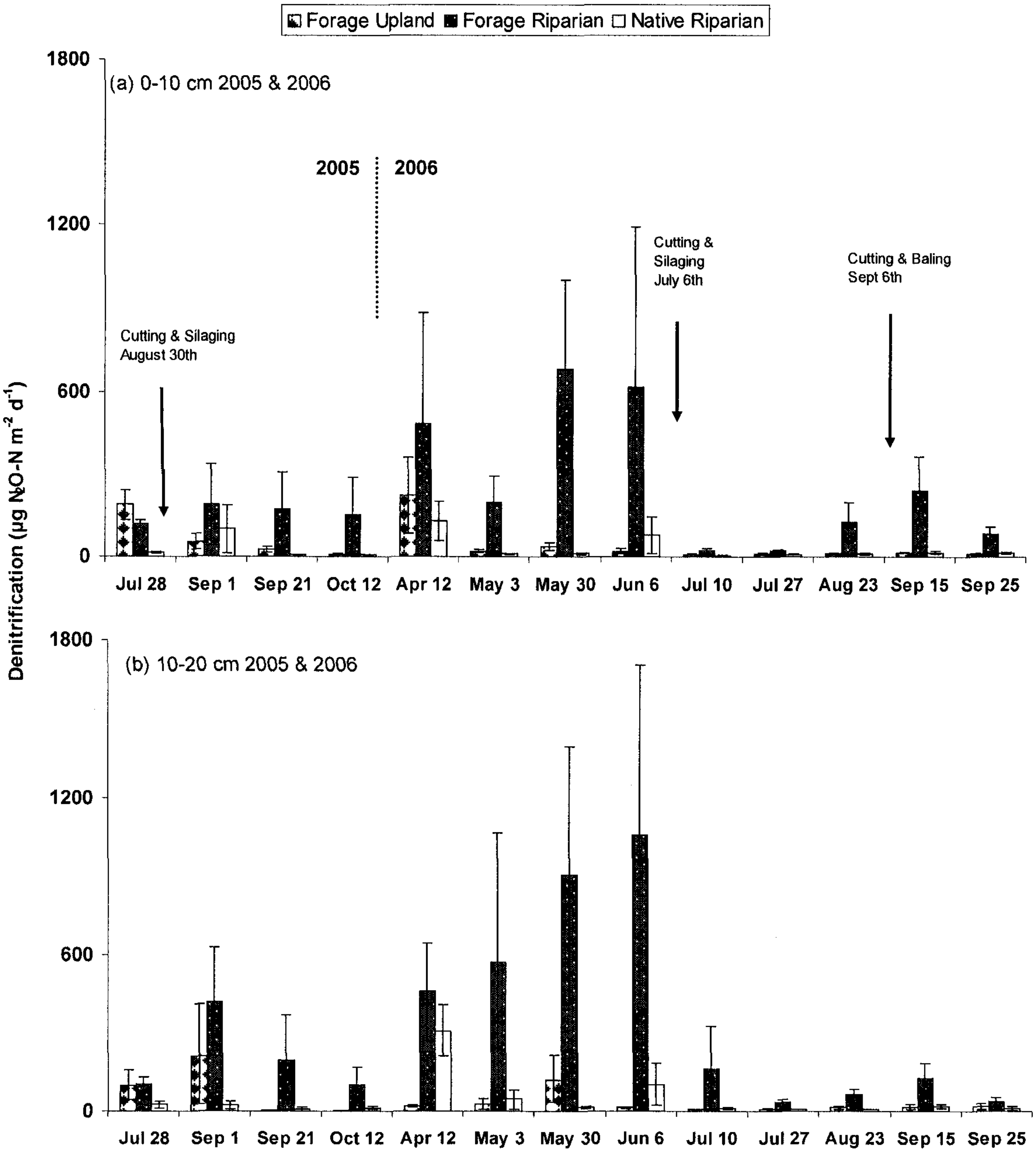
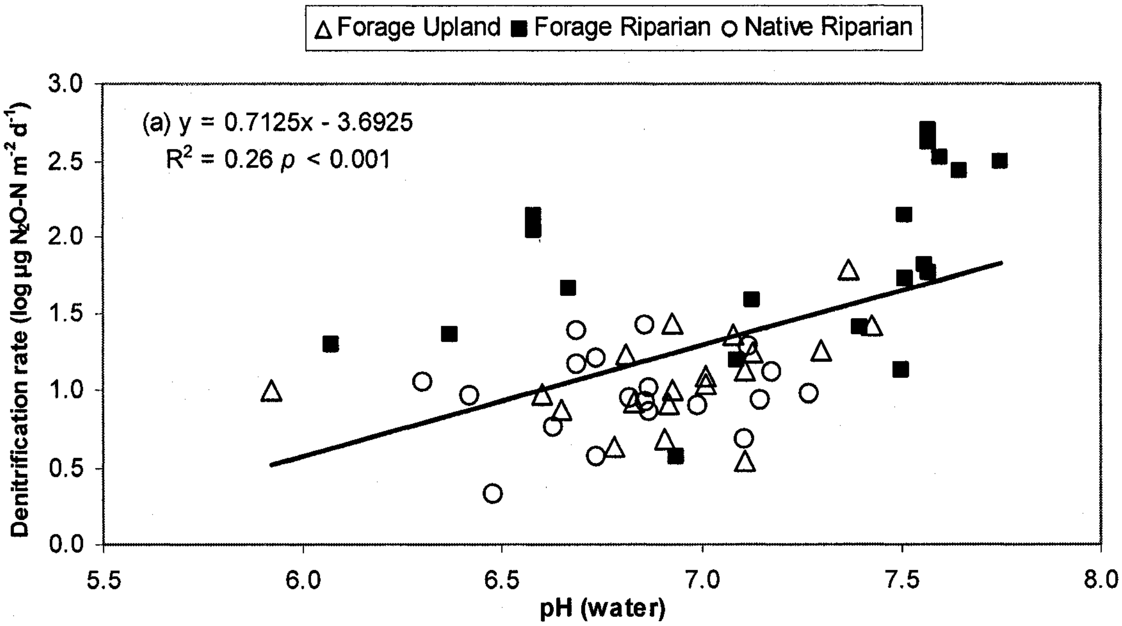


Figure 5.5 Regression of the denitrification rate and soil $pH_{(H_2O)}$ in 2006 at the 0–10 cm soil depth increment (n = 58).



Chapter 6: Synthesis and Conclusion

6.1 Synthesis and Conclusion

This research set out to quantify denitrification, net N and P mineralization rates in two different landscape positions (upland vs. riparian) for two different land uses (forage vegetation vs. native riparian vegetation) within a riparian-agricultural system in Central Alberta during the 2005 and 2006 growing seasons.

Soil moisture content, especially during flooding events in the forage riparian treatment, was one of the most important influences on N and P availability for plants and denitrification rates. It was also found to be an important controlling factor on N and P availability and loss in studies on the Canadian Prairies (e.g., Roberts et al. 1985; Lemke et al. 1999; Soon and Malhi 2005).

Denitrification, net nitrification and net N mineralization rates were highest in the FR in comparison to NR in 2005 and FU in 2006. There were significant correlations between net nitrification and denitrification, and between net N mineralization and denitrification, in the landscape position treatments. In 2005, there was a significant correlation between net nitrification and denitrification at the 10 – 20 cm depth increment (R = 0.51, p = 0.016). In 2006 using the landscape treatment data, there was a significant relationship between net N mineralization and denitrification (R = 0.52, p = 0.005) and net nitrification and denitrification (R = 0.53, p = 0.005) at the 0 – 10 cm depth increment. These correlations may explain that when N is mineralized in the FR treatment, available N is likely to be denitrified, especially during periods of high soil moisture content such as waterlogging that occurred in mid-summer to early fall of 2005 and during spring melt in 2006. Soils had slightly less sand from the upland to the riparian landscape position (silty clay loam in the upland versus clay loam to silt loam in the riparian), which would follow a typical topographic gradient. With less sand in the FR, moisture would remain in the soil longer and anaerobic conditions are possible. Anaerobic conditions in the soil are optimal for denitrification to occur (Tiedje et al. 1989).

Soil pH_{CaCl_2} was higher in the FR treatment and closer to neutral which may be the optimal pH level for denitrifying bacteria at this site (Table 3.3, Figure 3.5a, Šimek et al. 2002). Lowrance et al. (1995) agreed that riparian soils do denitrify at high rates because factors such as saturated soil conditions and greater quantities of available C, but often NO_3^- is the limiting source in native areas. An external source of NO_3^- is needed, such as fertilizer or agricultural runoff inputs. In the FR treatment, any available N (NH_4^+ or NO_3^-) would have likely undergone denitrification as evidenced by a significant negative correlation of potential NO_3^- supply rates with denitrification rates in the landscape position treatments in 2006 at 0-10 cm (R = -0.62 p = 0.023) and 10-20 cm (R = -0.54 p = 0.044). In the FU treatment, the primary removal of soil available N would likely not be through denitrification but through vegetation uptake, which was not measured, as suggested by Ettema et al. (1999).

Few trends were found for denitrification and net P mineralization results between land use treatments. Potential P supply rates had a significant negative correlation with denitrification in 2005 (R = -0.68 p = 0.003) and 2006 (R = -0.57, p = 0.017). There have been investigations by other research projects about the effect of additional soil available

P on decreasing the activity of denitrifying microbes (Ullah and Zinati 2006). However, since soil available P is naturally low in this region of Alberta, this does not appear to be a reason for this correlation. High gravimetric soil moisture content would be one explanation for the negative correlation as potential P supply rates would decrease and denitrification increase under these circumstances.

Potential P and NO_3^- supply rates had similar trends along both landscape position and land use treatments. The potential NO_3^- supply rates within the NR treatment and all three treatments lower in 2005 compared to 2006. In 2006, there is a marked increase in nutrients present in those treatments. Soil temperatures and soil moisture content were similar between both years (Figures 3.4 and 3.5). Potential P and NO_3^- supply rates were higher in the NR than in the FR in 2006. A correlation between both nutrient supply rates for the land use treatments in 2006 showed a positive correlation at the 0 – 10 cm (R = 0.66, p = 0.019) and 10 – 20 cm (R = 0.76, p = 0.002). Although a significant relationship was found between potential N and P supply rates, this does not likely represent a cause and effect relationship. Further studies are needed to define the relationship between these potential N and P supply rates in riparian soils. The increase from 2005 to 2006 in potential N and P supply rates might be an indication that other factors are acting on the landscape positions and land use treatments that need to be further investigated, such as plant nutrient uptake and litter decomposition. Main differences between the two growing seasons could be agronomic practices in the FU and FR treatments (volunteer canola in 2005 and alfalfa grass mix in 2006) and a comparatively smaller runoff during spring melt in 2006 than 2005 (S. Reedyk personal communication) allowing the accumulation of litter material in the treatments to remain in the soil instead of being removed by spring melt or runoff into Whitemud Creek.

The two methods used for measuring net N and P mineralization rates, the buried-bag method and the PRS^{TM} probes, often had contrasting results within the same depth increment or growing season (Table 6.1). No consistent trends were evident to explain the differences. The variability of the growing seasons and flooding of some replications may have affected measurements by the two methods. Waterlogged soils within the polyethylene bags for the buried-bag method may not have reflected soil moisture contents within a 30 day burial period. Soils were flooded in summer 2005 and also flooded and then dried out during spring 2006, thus, observed net mineralization rates may not be the actual rate. Raison et al. (1987) and Abril et al. (2001) discovered differences between soil water content where the soil water content did not change inside the bag but there were significant changes in the soil outside the bag. As well, Abril et al. (2001) showed that in their study, nitrifier activity decreased due to oxygen depletion in the bags, which suggests that the net N mineralization rate was underestimated. Fluctuating soil moisture content occurred at the study site, especially during times of flooding and drying. When the soil dries, contracts, and shrinks, there is insufficient surface to PRS^{TM} probes membrane contact, which may have caused an underestimation of supply rates during events of flooding and subsequent drying. Johnson et al. (2005) showed that PRS^{TM} probes had a greater sensitivity to soil moisture than mineral N concentrations which suggests that soil solution is a major vector of contact between soil exchange sites and the resin surfaces. Thus, the probes would not be accurate indications of mineral N in dry conditions.

The study site is a groundwater recharge area for most of the growing season (S. Reedyk personal communication) and the soil texture at the site ranged from silt loam to silt clay loam to clay loam, therefore, nutrient leaching into the groundwater and nutrient movement into Whitemud Creek does not appear to be a major concern at this site. Two potential times of year when nutrients may enter the groundwater or surface waters are: 1) overland flow from the upland and riparian landscape positions into the creek during high precipitation events and 2) during spring thaw when water levels in both the creek and groundwater are high in the riparian areas. Further research should focus on how to limit nutrient runoff during those times.

For overland flow and erosional events due to occurrences such as spring snow melt, BMPs must also be developed and adopted by producers that will prevent N and P losses from the field including nutrient management plans and riparian buffers to sequester or eliminate N and P before discharge to surface waters. In the case of buffer strips as a BMP in riparian areas, these should be designed for each specific location and recognizes nutrient movement in sediment and surface flow. A “Cookie cutter” or “one-size-fits” all type of buffer design by government recommendations or regulations will not always work for every landscape. It is important to understand the function of particular riparian systems through tools such as a Geographic Information System (GIS) to delineate and classify riparian systems and through site-specific research, demonstration and application of riparian zones and buffers (Naiman and Décamps 1997).

6.2 Suggestions for Future Research

The results from this thesis may have implications for improving Beneficial Management

Practices (BMPs) on the agricultural landscape in Alberta, especially for nutrient management in cropping systems incorporating a riparian component.

Based on the higher potential NO_3^- and P supply rates in the NR treatment compared to the FR treatment in 2006, how widely applicable are the effects observed throughout the Whitemud Creek watershed? Whitemud Creek is a managed watershed (i.e., agricultural, industrial and municipal activities) and the native riparian vegetation areas in the watershed are not. Would the periodic removal of vegetation material decrease the amount of NO_3^- and PO_4^{3-} in the native vegetation treatment?

At this study site, nutrients could be built up in riparian native vegetation areas because of the vegetation present and from other sources (i.e. agricultural upland). Dorioz et al. (2006) suggested that organic P found in the form of litter, can enrich the soil surface with labile forms of P that can be released seasonally as dissolved-P or as fine particles very rich in P. Dorioz et al. (2006) and Sheppard et al. (2006) proposed that this release could be limited by harvesting the biomass, modififying the timing and the form of export of part of the P but the effects of harvesting biomass has not been well documented and researched. Further research is needed to study the soils, vegetation and litter of this site and others along the Whitemud Creek that are under typical agricultural land uses for the watershed such as cereal production, oilseed production and livestock to measure if the nutrient levels are common and what is the potential of these nutrients to be removed during events such as spring snow melt into surface waters. Determination of P sorption of soils in areas where available P levels are naturally low as in the Whitemud Creek watershed, is also a suggestion for further research. Further addition of P fertilizer would increase crop production for this site because the STP levels were deficient, with an of average 24 kg STP ha^{-1}(Table 3.5) based on AAFRD P threshold guidelines (Howard et al. 2001). The amount of additional P would be based on annual soil testing, crop intended to be grown, local conditions and economics.

The release of nitrous oxides via soil processes such as nitrification and denitrification and especially from inorganic N fertilization, has increased the amount of N_xO emitted to the atmosphere because the reduction of NO_3^- to N_2O is energy efficient and favored by denitrifying bacteria (Breitenbeck et al. 1980). To decrease these emissions, N use efficiency through a nutrient management plan must be a readily adopted BMP to not only decrease N_xO emissions but also leaching and pollution of N into water sources. Denitrification was found to be highest in the FR treatment when waterlogging occurred (Chapter 5, Figure 5.3) and further research could look at conversion of the FR into a permanent riparian vegetation stand that can be used for economically viable hay production and to investigate if denitrification losses would decrease over time as the stand matured.

Research and refinement of groundwater measurements to understand nutrient movement and retention throughout the growing season is also needed. Groundwater N isotope research was undertaken for this thesis, but due to high variability in the dataset, it is not included. Further intense sampling of groundwater and vegetation sampling for N isotope analysis might increase the power to detect treatment effects on N cycling processes at research site.

Riparian systems, acting as a management tool for stewards of the land, are expected to fulfill a multitude of ecological (biodiversity, habitat, biogeochemical cycles, microclimate and resistance to disturbance) and social (recreation, culture, aesthetics and resources) functions but no one riparian system can serve them all (Naiman and Décamps 1997). Actions in the upland can affect the function of the riparian area and a systems approach is needed to target areas of concern for excess nutrients on the landscape in relation to the water quality of surface and groundwater. The economic and environmental impact of nutrient management issues are obviously important aspects of the current re-evaluation of nutrients flowing and cycling in sustainable agricultural systems, including those with a riparian component (Magdoff et al. 1997). A multitude of philosophies and practices that farmers follow abound, that take into consideration their effects on nutrient movement on and off their farm. Studying, emphasizing and promoting economically and environmentally sound practices that enhance the farmer's quality of life will be one of the ways that BMPs such as nutrient management plans will be adopted.

6.3 Literature Cited

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Table 6.1 P values from the analysis of variance using repeated measures for potential P and NO_3^- supply rates measured by PRS^{TM}-probes and net P and N mineralization rates measured by the buried-bag method in 2005 and 2006 at two soil depth increments. The three treatments were forage upland (FU), forage riparian (FR) and native riparian vegetation (NR). Highlighted values are significant at $p < 0.05$. NS means no significant difference.

	Phosphorus				**Nitrogen**			
	Potential P Supply Rates (μg P 10 cm^{-2} month^{-1})		**Net P Mineralization (kg ha^{-1})**		**Potential NO_3^- Supply Rates (μg N 10 cm^{-2} month^{-1})**		**Net N Mineralization (kg ha^{-1})**	
Depth (cm)	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
	Effects of landscape position							
0–10	NS	**0.020** **FR > FU**	NS	NS	**< 0.001** **FU > FR**	**0.005** **FU > FR**	NS	**0.010** **FR > FU**
10–20	NS	NS	NS	NS	**< 0.001** **FU > FR**	**< 0.001** **FU > FR**	NS	NS
	Effects of land use							
0–10	**0.001** **NR > FR**	**0.03** **NR > FR**	NS	**0.037** **NR > FR**	NS	**0.004** **NR > FR**	**0.017** **FR > NR**	NS
10–20	NS	NS	NS	NS	NS	**0.004** **NR > FR**	**0.036** **FR > NR**	NS