IMPACT OF UPSTREAM DAM ON RIPARIAN ZONE HYDROLOGY &
NITRATE

INFLUENCE OF AN UPSTREAM DAM ON RIPARIAN ZONE HYDROLOGY AND SHALLOW GROUNDWATER NITRATE DYNAMICS

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Abstract

This study used detailed spatio-temporal hydrologic measurements, groundwater chemistry data (dissolved nitrate, chloride, oxygen and sulphate concentrations) and denitrification potential measurements to assess the impact of a dam on shallow (<150 cm) groundwater movement and nitrate patterns in a downstream riparian zone. The results show that the upstream dam management practices supported stream inputs to the riparian zone by maintaining stream stage above the water table levels in the adjacent riparian zone. These stream inputs limited the extent of the summer water table draw-down in the riparian zone. Furthermore, the timing of upstream dam management practices influenced the timing of large shifts in riparian hydrology, including in-bank flood events and a mid-summer water table gradient reversal. This riparian zone experienced three distinct hydrologic regimes in the spring, summer and fall when riparian zone water table gradients were dominated by the hillslope, stream and upstream marsh respectively. These regimes altered nitrate patterns near the field by changing the balance of high nitrate inputs from the field and intermediate nitrate inputs from depth. Stream stage patterns were only one factor influencing hydrology and nitrate patterns at the site. During all three hydrologic regimes, the mid riparian zone was dominated by low nitrate inputs from depth and acted as a hydraulic barrier to field-to-stream groundwater transport. Nitrate removal by denitrification was observed at this site but was limited by low nitrate fluxes. Therefore, this riparian zone's role as a physical barrier to field-to-stream nitrate transport may be more important than its role as nitrate sink. These results can contribute to the enhancement of current conceptual models linking landscape features to riparian zone hydrology and nitrate removal function.

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1 Introduction

1.1 Background

Human nitrogen inputs to terrestrial ecosystems are equivalent to all natural sources combined (Vitousek *et al.*, 1997). These human nitrogen inputs are centred largely on agriculture where nitrogen is added to agricultural soils as nitrate (NO_3^-) and ammonium (NH_4^+) in chemical fertilizer, as ammonium in manure, and by nitrogen fixing legumes such as soy (Vitousek *et al.*, 1997; Mayer, 2007). Ammonium is a cation that is generally attracted to the net negative surface change of most soils and is, therefore, not generally very mobile in the groundwater. Under aerobic conditions, however, it can be converted into nitrate through a process called nitrification (Osaka, 2006). Nitrate (NO_3^-) is "a highly soluble anion repelled by most soils and is highly mobile in water" (Martin, 1999). Consequently, groundwater recharge in agricultural fields is a significant contributor to nitrate pollution in ground and ultimately, surface waters (Maitre, 2003). This nitrate pollution in agricultural catchments has become an issue of environmental concern because it can contaminate well water. For example, studies in southern Ontario (Vidon and Hill, 2004; Cey *et al.,* 1999; Duval and Hill, 2007) show that groundwater nitrate concentrations in agricultural catchments often exceed the Ontario drinking water standards, which require that nitrate be less than 10 mg NO_3^--N /L (Province of Ontario, 2006). Furthermore, along with phosphate, nitrate pollution contributes to eutrophication of surface waters (Carpenter *et al.,* 1998; Vitousek *et al.*, 1997).

Currently, riparian zones are widely recognized for their ability to remove nitrate from groundwater (Hill, 1996; Dosskey, 2001; Osborne and Kovacic, 1993; Haycock and Burt, 1993). Riparian zones are important transitions between terrestrial and aquatic ecosystems (Martin 1999). In agricultural catchments, they are typically uncultivated strips of land located between farmland and adjacent streams. The ability of riparian zones to remove nitrate from groundwater was first identified, in 1984 (Peterjohn and Correll, 1984), when a nitrogen mass balance study conducted on an agricultural watershed revealed that 75% of nitrogen losses in the riparian zone occurred in the groundwater nitrate concentrations. The study hypothesized that these losses were likely associated with biological processes. Indeed, the most common removal mechanism identified in subsequent research has been denitrification (Hill 1996, Hanson *et al.*, 1994, Groffman *et al.*, 1991, Martin *et al.*1999a). In-situ denitrification removal rates in surface riparian soils have been calculated in several studies (Lowrance *et al.*, 1985, Pinay *et al.*, 1993, Hanson *et al.,* 1994) and range from less than 1 to 104 Kg N/ha/yr (Hill, 1996; Groffman and Tiedje, 1989).

As a result of their known capacity for nitrate removal, it is often recommend that riparian zones be conserved and rehabilitated in order to reduce nitrate pollution in ground and surface water in agricultural catchments (Gilliam, 1994; Vought *et al.*, 1994; Dosskey *et al.*, 2005; Osborn and Kovacic, 1993; Muscutt *et al.*, 1993). For example, the Canada-Ontario Environmental Farm Plan encourages farmers to establish, expand and conserve buffer strips to help protect water resources (OMAFRA, 2006). This plan recommends that buffers be at least 5-16 m wide.

In order to support policy development around riparian zone conservation, much research has been conducted to try to understand mechanisms of removal and their biogeochemical and hydrologic controls (Vidon and Hill, 2004a; Devito *et al.,* 2000; Hill, 1990; Tesoriero *et al.,* 2005; Cirmo and McDonnell, 1997, Hill *et al.*, 2000; Hedin *et al.,* 1998). However, this research has largely focused on riparian zones where shallow confining layers simplify hydrology (*i.e.* upland groundwater inputs move laterally through the riparian zone to the stream) (Hill, 1996; Gilliam, 1994; Lowrance *et al.*, 1997). As a result, this body of research does not adequately reflect the wide variety of hydrogeologic settings that riparian zones occupy in the landscape (Vidon & Hill, 2004c).

This study examines riparian hydrology and nitrate patterns in a complex hydrogeologic setting. It explores how stream regulation by an upstream dam impacts hydrology and subsequent field to stream nitrate transport in a riparian zone without a shallow confining layer. The remainder of this chapter summarizes the current understanding of riparian zone nitrate removal mechanisms and the influence of riparian zone hydrology on nitrate removal. Specific knowledge gaps are discussed and finally, the research questions are presented.

1.2 Riparian Zone Nitrate Removal

The major mechanisms of nitrate removal in riparian zones have been identified to be dilution, vegetation uptake, and denitrification (Altman and Parizek, 1995; Hill, 1996; Martin, 1999a, b). Other mechanisms of nitrate removal could be microbial assimilation of nitrate (Davidson *et al.*, 1992) and dissimilatory reduction of nitrate to ammonium (Hill, 1996). However, in a recent review of biochemical processes controlling groundwater nitrate removal, Rivett *et al.* (2008) suggest that, compared to denitrification, these two mechanisms are unlikely to be important.

1.2.1 Nitrate Removal by Dilution and Plant Uptake

Groundwater nitrate "removal" by dilution occurs when nitrate rich groundwater mixes with a lower nitrate groundwater source. In riparian zones with long residence times, rain water infiltration can also dilute nitrate rich groundwater (Davis et al., 2007). Although dilution does reduce nitrate concentrations, is does not reduce the loading of nitrate to the system. Chloride is often used as a conservative tracer to evaluate the extent of dilution along a flow path (Altman and Parizek, 1995).

Groundwater removal by plant uptake requires that water table levels fall within the root zone. Although there has been evidence that plants play a role in riparian zone nitrate retention, researchers have found it difficult to quantify or evaluate the importance of this process (Osborne and Kovacic, 1993; Haycock and Pinay, 1993; Hill, 1996). Some researchers have suggested that, through leaf litter and root decomposition, vegetation may be important in supplying the labile carbon required for riparian zone denitrification (Haycock *et al.*, 1993; Clement *et al.*, 2002). Haycock and Pinay (1993) suggest that, with respect to riparian zone nitrate removal, the support of denitrification by these carbon inputs may be more significant than plant uptake itself.

1.2.2 Nitrate Removal by Denitrification

In many diverse hydrogeologic settings, denitrification has been identified as the primary mechanism of nitrate removal in riparian zones (Hill 1996, Vidon & Hill 2004c). Denitrification is a four step reduction that transforms nitrate (NO_3^-) to nitrite (NO_2^-) to nitric oxide (NO) to nitrous oxide (N_2O) and then finally to dinitrogen gas (N_2) (Einsle, 2004). The general reaction for denitrification that has gone to completion is:

$$2\,NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \qquad \text{Equation 1}$$

Denitrification is an important part of the biological nitrogen cycle as it is the only mechanism that can counteract N_2 fixation and return reactive nitrogen species, such as nitrate, back to N_2 (Martin *et al.,* 1999a). In riparian zones, this is important because the emission of the denitrification products (N_2O and N_2) allow for the nitrogen to be permanently removed from the terrestrial ecosystem (Hill 1996); the nitrate taken up by plants, for example, is only temporarily removed as it may be returned to the groundwater when the plant decomposes (Martin *et al.,* 1999a). Permanent nitrogen removal allows riparian zones to maintain their nitrate removal function; nitrogen saturated systems have been found to be less effective at protecting streams from nitrate pollution (Hefting *et al.*, 2006).

Although denitrification is a permanent way to remove nitrate from groundwater, it may release N_2O, a greenhouse gas with high global warming potential (IPCC, 2007), as a by-product to the atmosphere. As a result, Hefting *et al.* (2006) argue that the water quality protection function of riparian zones should be weighed against their contributions to atmospheric N_2O concentrations.

Theoretically, it is known that suboptimal conditions for denitrification (*i.e.* low temperatures, low moisture content and low amounts of labile carbon) tend to favour N_2O over N_2 as the end product (Hefting *et al.*, 2006). High nitrate concentrations also favour N_2O production as they inhibit N_2O reduction to N_2 (Van Cleemput 1998). In the field however, researchers have found it difficult to link environmental controls to N_2O:N_2 ratios (Groffman, 1998). This is due to multiple factor interactions (Hefting *et al.*, 2006), the spatio-temporal variability of environmental conditions in riparian zones (Davidson, 2006), and the technical difficulties in measuring in-situ denitrification (Groffman *et al.,* 2006).

1.2.2.1 Measurement of Denitrification

A major obstacle to quantifying denitrification rates is that one of its major products is N_2, which is very difficult to accurately quantify against the high concentrations in the atmosphere. This is overcome by the use of acetylene gas, which inhibits the final transformation of N_2O to N_2 (Smith *et al.,* 1978). This allows for denitrification to be more easily measured because the only product is N_2O, which has relatively low ambient concentrations and is able to be accurately quantified with current analytical technology (Groffman *et al.,* 2006). There are limitations to this technique that must be evaluated before it is used. For example, acetylene also blocks the nitrification pathway that can add to the available nitrate pool. Where there is a limited supply of nitrate, this can result in the underestimation of denitrification rates (Groffman *et al.* 2006). In the study of groundwater nitrate removal in riparian zones, this technique is most commonly used as *in-situ* acetylene blocks (Sanchez-Perez *et al.,* 2003; Baker and Vervier, 2004; Martin, 1999b) and in denitrification potential incubation studies (Groffman *et al.,* 2006; Martin 1999a; Burt *et al.*, 1999). Another obstacle which hinders *in-situ* denitrification measurements is that N_2O can be transported by groundwater flows and emitted in a different location from where it was produced (Osaka *et al.*, 2006; Heincke and Kaupenjohann, 1999).

1.2.2.2 Controls on Denitrification Rates

Heterotrophic denitrification is performed by "ubiquitous heterotrophic bacteria" that, in the absence of oxygen, use nitrate as an electron acceptor to oxidize organic carbon (Boyer *et al.*, 2006):

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \qquad \text{Equation 2}$$

Many studies have shown that that electron donor (organic carbon) and acceptor (NO_3^-, DO) supplies are major controls determining where denitrification will occur in the landscape (Bohlke et al., 2002; Davidsson and Stahl, 2000; Burt and Pinay, 2005). In a study of eight riparian zones in contrasting hydrologic settings, Vidon & Hill (2004c) showed that denitrification hotspots occur where oxic flows transporting nitrate reached locations with low dissolved oxygen and a pool of organic carbon. Similarly, Hill *et al.,* (2000) showed that a zone of denitrification occurred at the interface of shallow nitrate-limited organic soils and deeper carbon-limited sediments.

The absence of a labile carbon source at depth is often cited as the limiting control on denitrification in subsurface sediments (Cey *et al.,*1999; Gold *et al.,* 2001; Clement *et al*., 2002; Robertson and Schiff, 2008). Indeed, denitrification potential measurements often show that the population of active denitrifiers is highest in shallow organic soils (Flite *et al.,* 2001; Clement *et al*., 2002; Pinay and Burt, 2001). For example, Burt *et al*., (1999) found that denitrification potential decreased exponentially with depth in a floodplain near Oxford, England. Despite this, some researchers argue that nitrate removal at depth must not be overlooked because although the removal rates might be substantially smaller in deeper sediments, they receive much higher volumes of water compared to surface sediments, which can be dry for several months of the year (Hill *et al*., 2000; Clement *et al*., 2002; Cey, 1999; Rivett, 2008). Furthermore, depending on the residence time, low denitrification rates at depth may still be sufficient to significantly impact groundwater nitrate concentrations. For example, Clement *et al.* (2002) found that, despite having minimal denitrification rates compared to the shallow soil, deeper soils still made important contributions to nitrate removal at their site. Along the deeper groundwater flow paths, groundwater nitrate decreased from 9.32 to 0.98 mg/L.

In addition, studies have found that denitrification hotspots can occur at depth where organic layers are present in relic channel sediments (Haycock and Burt, 1993; Hill *et al.,* 2004) or organic soils buried by erosion of upland soils or by the transport of sediments during flood events (Hill, 1996; Devito, 2000). Unfortunately, the spatial distribution and carbon quality of these buried soil horizons are difficult to determine, making it difficult to evaluate the extent of denitrification occurring at depth (Gurwick *et al*., 2008; Hill and Cardaci, 2004).

As seen above, the presence of a labile carbon pool is often discussed as an important control governing denitrification. However, denitrification can occur in its absence. Reduced sulphur compounds such as pyrite (FeS_2) can act as electron donors in autotrophic denitrification (Aravena & Robertson 1998):

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \qquad \text{Equation 3}$$

Several studies have noted the impact of autotrophic denitrification on groundwater quality (Bottcher *et al.,* 1990; Bohlke *et al*., 2002; Eulenstein *et al.,* 2008; Tartis *et al.,* 2006; Postma *et al*., 1991). Bohlke *et al.* (2002) used isotopic analysis coupled with a mass balance to show that FeS_2 was supporting denitrification in a thick sand aquifer. In Germany, autotrophic denitrification was identified as the main cause for elevated sulphate concentrations in drinking water wells located in an agricultural watershed (Eulenstein *et al.,* 2008). Similarly, Tartis *et al.* (2006) found decreasing groundwater nitrate concentrations coupled with increasing sulphate concentrations in pyrite-bearing fractures in an agricultural watershed in Brittany, France. In a review of the literature, Korom (1992) notes that it is possible for heterotrophic and autotrophic denitrification to occur simultaneously in saturated sediments.

1.3 Influence of Riparian Zone Hydrology on Nitrate Removal

1.3.1 Riparian Zone Hydrology

Hill (1996) identified three major categories of riparian hydrology based on the size and topography of the upland aquifer. These different hydrologic settings predominantly impact seasonal water table dynamics and groundwater flow paths. The first category of riparian hydrology (Figure 1.1a) is dominated by a shallow confining layer, which forces local hillslope inputs to flow laterally through shallow riparian sediments and prevents regional hydrologic inputs to the riparian zone. This type of system has large seasonal changes in water table levels because it relies heavily on local (shallow) groundwater inputs, which are sensitive to seasonal patterns of precipitation and evapotranspiration (Burt *et al.*, 2002). The second category of riparian hydrology applies to riparian zones that do not have such a confining layer. This allows groundwater from the upland aquifer to enter the riparian zone through deeper flow paths (Figure 1.1b). In this type of system, a variety of flow paths are possible: 1) groundwater can bypass zones of nitrate removal at depth and discharge directly into the stream, 2) deep groundwater can be forced upward by changes in the hydrologic properties of subsurface riparian sediments, or 3) groundwater seeps can occur where the water table meets the slope. The third category of riparian hydrology identified by Hill (1996) also lacks a confining layer and occurs when hilly uplands cause several distinct flow systems to develop in a single aquifer (Figure 1.1c). In this case, different scales of groundwater flow (*i.e.* local, intermediate and regional) can interact in the riparian zone resulting in large groundwater inputs and small seasonal water table fluctuations.

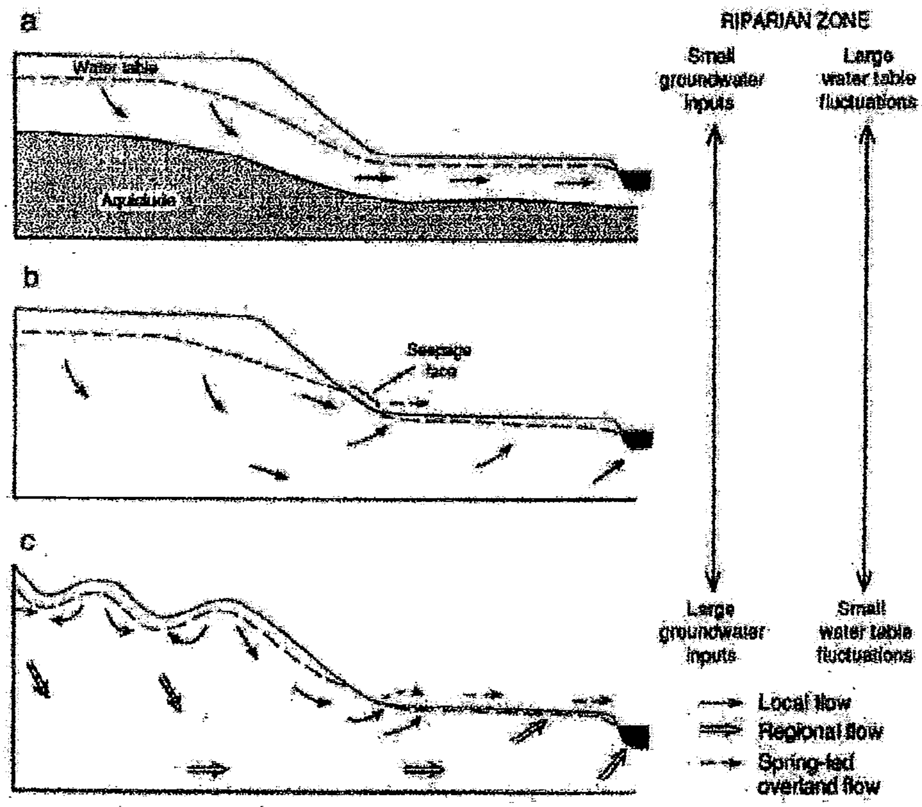

Figure 1.1 Three major categories for riparian hydrology based on the size and topography of the upland aquifer: a) a thin surficial aquifer with horizontal groundwater flow paths, b) a thicker surficial aquifer with a local groundwater flow system originating in the upland and discharging upward in the lowland riparian zone, and c) a thicker surficial aquifer located in a hilly upland with local and larger scale groundwater flow systems discharging in the riparian zone (Hill, 1996).

Evaluation of a riparian zone's role in protecting groundwater resources (and its contributions to N_2O emissions) requires a detailed spatio-temporal understanding of microbial activity, hydrogeology, and water and soil chemistry at the site (Cey *et al.,* 1999). This is a difficult task as riparian zone conditions can vary significantly over space and time. As discussed above, the heterogeneity of subsurface sediments make the location and size of buried carbon sources difficult to predict. Furthermore, other factors driving denitrification rates such as water table levels and soil temperature change over time (Groffman *et al.*, 1996). In surface soils of a forested riparian zone, Groffman and Tiedje (1989) found that high rates of denitrification activity were limited to 3-6 week periods in both the spring and fall. This was driven by high moisture content of the soils and larger pools of available nitrate and carbon during these periods. Furthermore, it was observed that these seasonal patterns coincided with the beginning and end of the growing season, suggesting that the trees may influence denitrification through their impact on soil moisture and nitrate and carbon supplies.

As a result of the spatio-temporal hydrologic and biogeochemical complexity of riparian zones, the literature has largely focused on riparian zones with shallow confining layers (Hill, 1996; Vidon and Hill, 2004b). This feature simplifies hydrologic inputs and flow paths and makes it easier to study the nitrate removal patterns at a given site. For example, a shallow confining layer allowed Maitre *et al.* (2003) to use the stream tube concept to conduct the detailed water, chloride and nitrogen mass balance necessary to quantify the nitrate removal occurring in a river riparian zone.

Although it has allowed for major developments to be made in understanding riparian zone nitrate removal (Ocampo, 2006), this focus on the simplest type of hydrologic setting has limited the development of broadly applicable conceptual models because it does not adequately address the diversity of hydrogeologic settings that riparian zones occupy (Dosskey, 2002). This knowledge gap has limited the ability of scientists to accurately model NO_3^- and N_2O dynamics at the catchment scale (Boyer *et al.*, 2006).

More recently, some researchers have begun to tackle more complex hydrologic systems. For example, Pfeiffer *et al.* (2006) showed that shallow, intermediate and deep flow paths were all important in a riparian zone underlain by a thick sand and gravel aquifer. Furthermore, their study showed that the dynamic nature of these flow paths (*i.e.* the seasonal changes in dominant flow paths observed) allowed for mixing between sources which provided the organic carbon necessary to sustain denitrification at depth. Puckett *et al.* (2002) studied a riparian zone with hillslope inputs flowing down gradient in deep flow paths (>16 m) which discharge in the riparian zone. At that site, nitrate concentrations decrease with distance from the field due to the discharge of progressively older groundwater. Groundwater age and aquifer residence time was important in their study because there was a 20-fold increase in agricultural nitrogen use in the area between 1945 and 2000. Also, long aquifer residence times allowed for slow chemical reactions, such as carbon limited denitrification, to have a noticeable impact on groundwater nitrate concentrations before it reached the riparian zone. The authors warn that, without a detailed understanding of the hydrogeologic setting and groundwater age distribution, these patterns could be falsely attributed to other removal mechanisms, such as denitrification occurring in the riparian zone sediments. Similarly, Bohlke *et al.* (2002) showed that a flood plain wetland underlain by a sand aquifer was a discharge area for groundwater, which increased in age with distance from the field. The study showed that this pattern was related to groundwater age stratification in the upland aquifer. Aquifer residence times ranged from less than one year to over 40 years. Groundwater nitrate concentrations in the riparian zone decreased with distance from the field edge and were attributed to a combination of 1) changes in land use and groundwater recharge patterns over time, and 2) riparian zone denitrification (Bohlke *et al.,* 2002).

1.3.2 Hydrologic Controls on Riparian Zone Nitrate Removal

1.3.2.1 Residence Time and Flow Paths

Site hydrology is a key factor influencing nitrate removal because it determines the amount of nitrate input into the riparian zone, its residence time and the flow path it takes (Hill 1996). Ocampo *et al.* (2006) reviewed data from nine studies to show that longer residence times can have a significant impact on nitrate removal rates by allowing time for removal processes to occur and by promoting the development of the low oxygen conditions required for denitrification. McClain *et al.* (2003) and Cirmo and McDonnell (1997) emphasize the importance of flow paths in riparian nitrogen cycling. Denitrification hotspots are often found where flow paths bring all necessary conditions (low DO) and reactants (labile carbon and nitrate) together (McClain *et al.*, 2003). For example, Devito *et al.* (2000) showed that downward hydrologic gradients created by microtopography facilitated the transport of organic carbon from surface peat layers to underlying carbon limited sand sediments, thus providing the electron donors necessary for denitrification.

1.3.2.2 Water Table Levels

As discussed above, hydrologic inputs also impact the extent and duration of water table draw-down in the riparian zone. In temperate climates, research has shown a clear seasonal water table cycle (Burt *et al.*, 2002). In a Pan-European study, Burt *et al.* (2002) found that water tables are generally highest during the winter and spring. During the growing season, evapotranspiration losses surpass precipitation inputs, causing a soil moisture deficit and associated decrease in water table levels. Fall rains accompanying the end of the growing season (*i.e.* reduced evapotranspiration) allow for the soil moisture deficit to be replenished and water tables to rise. Typically, snow melt also contributes to elevating water table levels.

Water table levels are a significant control on nitrate removal because saturated sediments are required to develop the redox conditions necessary for denitrification (low DO) (Hefting *et al.,* 2004). In Europe, Pinay *et al.* (2007) showed that soil moisture was an important control on denitrification in riparian zones with a wide range of climatic conditions and hydrologic regimes. Furthermore, nitrate removal rates are often higher at the top of the soil profile where there are typically large pools of labile carbon and also there is access to plant roots (Hill 1996). Therefore, when the water table drops too low, riparian zones may lose nitrate removal capacity as groundwater nitrate cannot interact with these shallower soils with their higher potential for nitrate removal (Burt *et al.,* 1999).

Because of their position in the landscape, riparian zones can have multiple and dynamic hydrologic inputs including subsurface flows from adjacent hillslopes, stream inputs, direct precipitation inputs, and regional groundwater inputs (Robertson and Schiff, 2008). This can obscure hydrologic analysis and interpretation of water chemistry data because the relative importance of the different sources can change over time. For example, Molenat *et al.* (2008) found that seasonal nitrate patterns in the stream were related to seasonal water table dynamics along the hillslope. During the winter, when water table levels were high in the upland, the stream had higher nitrate concentrations because the hydraulic gradient promoted the rapid transport of nitrate-rich hillslope inputs to the stream. In the summer, stream nitrate concentrations dropped because a deeper upland water table limited upland hydrologic inputs to the riparian zone. This allowed for upward flow of deep low-nitrate groundwater to dominate groundwater chemistry in the riparian zone and adjacent stream. Clement (2003) also found that hydrologic inputs from the unconfined aquifer below the riparian zone were more significant when hillslope inputs declined in the summer. To further complicate matters, the chemical signature of the same source can change over time due to changes in fertilizer application rates and atmospheric deposition (Boelke and Denver, 1995).

1.3.2.3 Conceptual Models Linking Hydrology and Nitrate to Landscape Controls

Based on research conducted in a variety of hydrologic settings in southern Ontario Vidon and Hill (2004b) developed a conceptual model linking landscape features to riparian hydrology. Specifically, their framework uses the depth of the upland aquifer (*i.e.* distance to impermeable sediments) and topography at the riparian-upland interface to predict hydrologic variables in the riparian zone such as the continuity of upland connectivity, seasonal water table variation and groundwater flow direction. This model uses sediment depth as a measure of the upland aquifer size and uses topography to approximate the water table gradient, which is then used to infer flow paths and hillslope hydrologic fluxes into the riparian zone.

By adding depth of permeable riparian sediment and riparian sediment texture, this framework was expanded to evaluate nitrate removal variables such as nitrogen input flux, distance required for 90% removal and size of nitrogen sink (Vidon and Hill, 2004c). The framework uses the depth of permeable riparian sediment to predict whether shallow or deep flow paths will dominate. When depth of permeable riparian sediment is too small or too large, there is a risk that the nitrate-rich hillslope inputs can bypass the riparian zone as overland flow or in deep flow paths, respectively. Soil texture is used to evaluate groundwater residence times in the riparian zone. This model suggests that the largest riparian sinks are fed by moderate to steep sloping uplands with over six meters of permeable sediments (which allow for continuous large nitrogen fluxes into the riparian zone) and have permeable riparian sediments that are between two and six meters deep (which ensures that the flux does not bypass the riparian zone at depth or as overland flow).

In a later paper, Vidon and Hill (2006), show that this framework is widely applicable in humid temperate landscapes by comparing it to the results of studies conducted in a variety of hydrologic settings across the United States and Europe.

1.3.3 Influence of Streams on Riparian Zone Hydrology and Nitrate Removal Capacity

1.3.3.1 Hyporheic Exchange and Flood Events

In general, discussion of the influence of the stream on riparian hydrology has been limited to hyporheic exchange in the stream banks and isolated flood events. Hyporheic exchange in the stream bank is known to be important in terms of promoting stream and groundwater mixing (Bencala, 2000) and has been identified as a common hotspot for biogeochemical cycling (Duff and Triska, 1990). Flood events have been found to disrupt field-to-stream hydraulic gradients (Bates *et al.*, 2000; Burt., 2001). Bates *et al.* (2000) showed that reverse groundwater ridging caused by over-bank floods can block (nitrate rich) hillslope inputs to the riparian zone. Furthermore, Burt *et al.* (2001) found that depending on antecedent moisture conditions, flood stage and local rainfall-runoff patterns, in-bank flood events can also cause significant reverse groundwater ridging in the riparian zone. In both these studies (Bates *et al.*, 2000; Burt *et al.*, 2001), field-to-stream gradients were re-established soon after the flood event. Wigington Jr *et al.* (2005) showed that during the wet winter season in Oregon (USA), when the stream expands into the riparian zone floodplain, hillslope inputs have the opportunity to bypass the riparian buffer zone as overland flow.

In a study comparing eight riparian zones in southern Ontario, Vidon and Hill (2004b) found the stream can become a dominant control on riparian water table gradients, particularly in flat floodplains. During dry periods, they observed that water table gradients could reverse from field-to-stream to stream-to-field. In a Pan-European study, Burt *et al.* (2002), found that, when hillslope inputs were reduced in the mid-summer, flood plain water tables often "hinge" around stream bank inputs resulting in a reversal of hydraulic gradients. Similarly, Duval and Hill (2006), observed a four month flow reversal when hillslope hydraulic inputs were limited by the summer water table draw-down. During this period, stream-origin groundwater extended all the way to the field edge, effectively extending the hyporheic zone throughout the riparian zone. At a second site, where hillslope inputs were permanently limited by an upslope spur, stream seepage persisted throughout the year (Duval and Hill, 2006). In a complementary paper, Duval and Hill (2007) showed that these stream seepage patterns had an impact on riparian zone nitrogen cycling. They found that in addition to disrupting nitrate inputs from the hillslope, extensive stream seepage also allowed biogeochemical processing of nitrate rich stream water in the riparian zone. Tracking nitrate injections with a bromide tracer indicated that denitrification may be responsible for some of the observed nitrate losses as stream water moved inland. These studies demonstrate that baseflow stream-seepage can be a dominant control on riparian hydrology and biogeochemistry.

1.3.3.2 Streams Regulated by Upstream Dams

Dams are often installed along low order streams in agricultural catchments to control flooding and store water to help maintain summer flows. By controlling discharge rates into streams, they regulate stream levels and can therefore play an important role in controlling hydrology in downstream riparian zones. Duke *et al.* (2007) found that, during dry ("low rainfall") periods, a dam-regulated stream played an important role in groundwater recharge in the riparian zone. The hydraulic head difference between the constant stream stage and lower adjacent water table levels provide an important linkage between stream flow and riparian groundwater levels, allowing stream water to contribute 44% of hydraulic inputs to the site. Hill and Duval (2009) studied the impact of beaver dams on riparian zone hydrology and nitrogen cycling at a riparian zone in southern Ontario. Comparing riparian hydrology and water chemistry before and after the construction of a beaver dam on the adjacent stream reach, they showed that the beaver dam led to a decrease in the extent of seasonal water table draw-downs. The resulting increase in saturated sediment depth enhanced anaerobic conditions, which had consequences for nitrogen cycling.

1.4 Information Gaps and Study Purpose

Given the hydrologic controls on riparian zone nitrate dynamics discussed above, stream regulation by upstream dams could have a significant influence on riparian zone nitrate removal capacity. The literature has not yet examined these impacts. Understanding this relationship is important to ensure that dam management practices do not compromise this important ecological function in downstream riparian zones. Furthermore, this understanding is necessary to evaluate whether or not current models, such as the one presented by Vidon and Hill (2004b, c), are applicable to riparian zones located along streams regulated by upstream dams.

This study begins to address this knowledge gap by examining the impact of dam management practices on a downstream riparian zone's nitrate "buffering" function. To accomplish this, the study seeks to answer the following two questions:

1. How do dam management practices influence water table levels, hydrologic regimes and shallow groundwater flow paths in the riparian zone (Chapter 4)?

2. How does the dam influence shallow groundwater nitrate patterns in the riparian zone (Chapter 5)?

These questions will be examined by testing the following hypotheses:

1. Dam management practices will result in the stream being influent to the riparian zone, which will

    a. help maintain elevated riparian zone water tables, and will

    b. disrupt field-to-stream transport of nitrate rich groundwater from the uplands.

2. The conceptual models developed by Vidon and Hill (2004b,c) to evaluate riparian zone hydrology and nitrate removal capacity will not be applicable to this study site because of the impact of the stream regulation on riparian zone hydrology.

2 Research Site

2.1 Overview

The study site is located approximately 30 km North West of Hamilton in an agricultural watershed in Flamborough, Ontario (Figure 2.1). It is a forested riparian zone located in between a naturally-drained agricultural field and Spencer Creek (Figure 2.2).

The adjacent agricultural field has been farmed for over 100 years using conventional tillage and crop rotation between soy, corn, grains and hay. Depending on the needs of the crop, a combination of manure, potash and chemical fertilizer is used. In 2006, the field adjacent to the study site was planted with barley and was fertilized with a 19-19-19 mass fraction nitrogen-phosphorus-potassium mixture at the rate of 180 lbs per acre. In 2007, this field was planted with soybeans and was fertilized with potash and phosphorus. With the exception of some manure spread in the south-east corner of the field, no nitrogen fertilizer was applied to the field in the year of this study.

2.2 Topography and Surficial Geology

The adjacent agricultural field slopes steeply toward the riparian zone at an average topographic gradient of 0.04. Figure 2.3 shows a conceptual diagram of a cross section from the top of the field to the stream. The upper portion of the field is steeper than the lower portion, which begins to flatten out before the riparian zone. At the field edge, there is a "step" into the riparian zone (Figure 2.3), which appears to be the result of long-term erosion from the field and farming activities. The riparian zone is between 30 and 50 m wide and is relatively flat, with an average gradient of 0.01.

At the study site, the depth to the bedrock is unknown both in the field and the riparian zone. In the surrounding area, depth to bedrock ranges between 0 m and 40 m and overburden is typically made up of sandy gravelly Wentworth till (Heagy, 1993). Indeed, drill records and photos from this site show that, at the upland well (UPL-W) located at top of the field, there is at least 7 m of sandy overburden material below 30 cm of topsoil (Figure 2.3). In the middle of the field, core photos showed evidence of sandy till to at least 4.2 m depth (Private communication from Dr. Rick Bourbonniere: School of Geography and Earth Sciences, McMaster University).

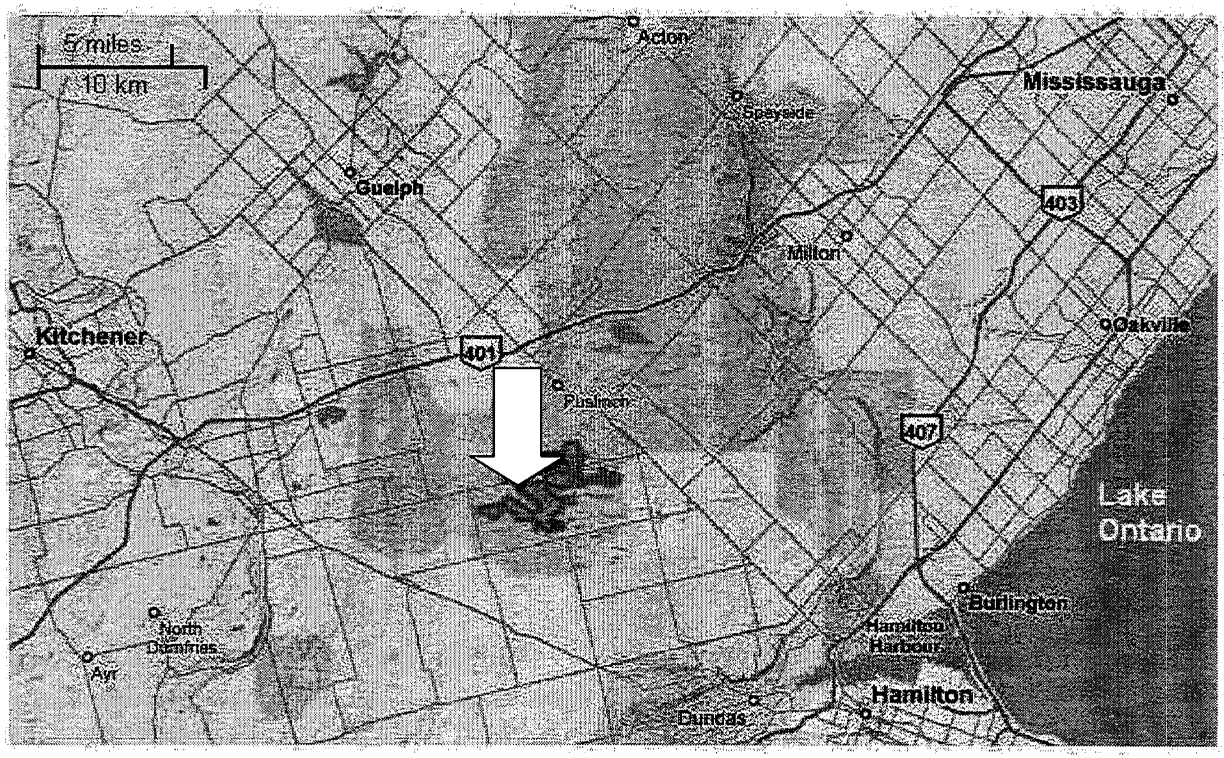

Figure 2.1 Location of the study site in southern Ontario (marked with the white arrow). Beverly swamp is outlined in grey.

Figure 2.2 Location of the study site in relation to Valens Reservoir, Beverly Swamp and the surrounding agricultural fields. This image was taken from Google Maps. Markers 1, 2, 3 and 4, show the respective locations of the upland well (UPL-W), the meteorological station, the stilling well in the stream (S9) and the field edge well (W32). The star indicates the location of a nearby research site.

2.3 Hydrologic Setting

In this region, groundwater generally moves laterally along the impermeable bedrock surface (Heagy, 1993). The bedrock in this region is known to be dolostone. It is part of the Guelph formation, which is part of the Lockport-Amabel-Guelph Hydrologic Unit, a high capacity aquifer, which runs between Hamilton and Owen Sound (Singer *et. al.,* 2003). Local overburden groundwater flow is reported to sustain wetlands in the area (Heagy, 1993).

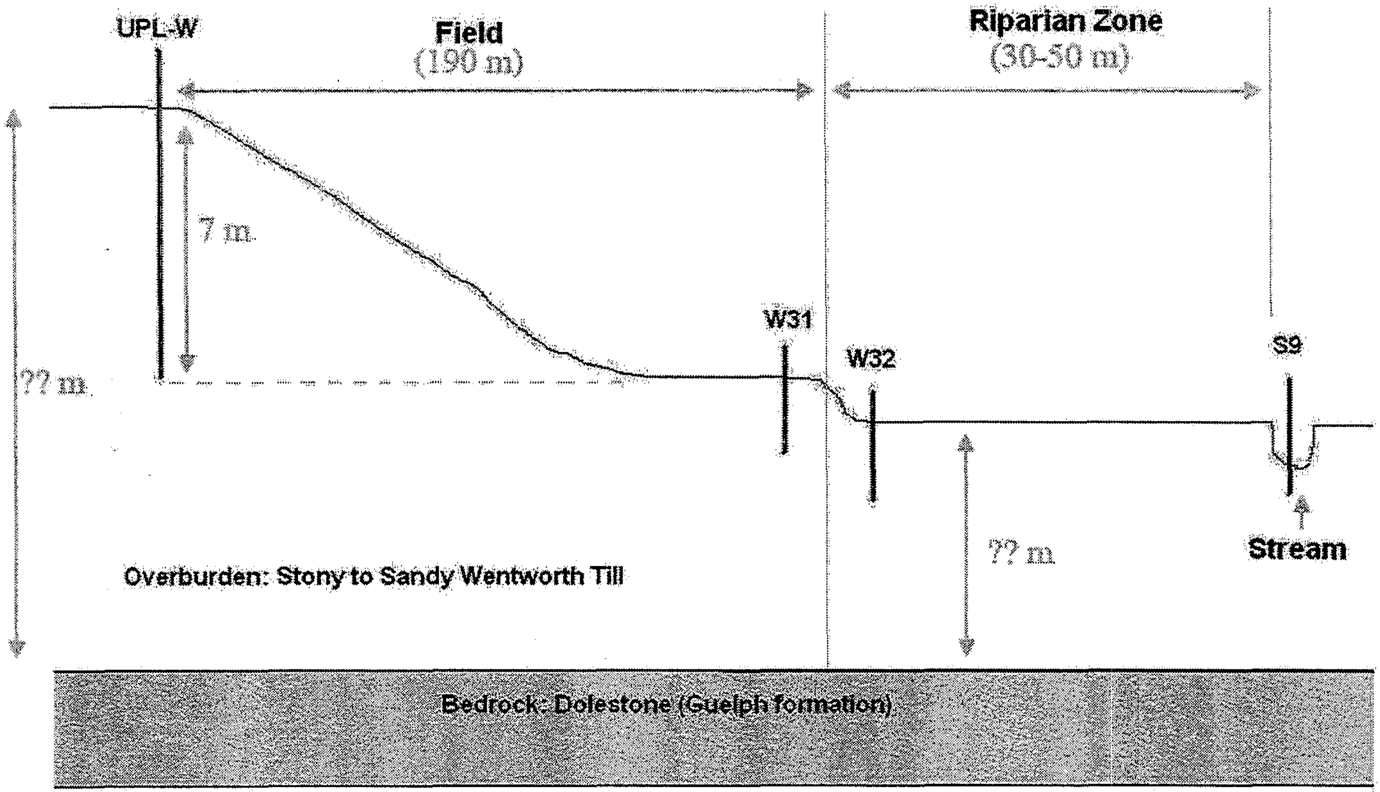

Figure 2.3 Conceptual drawing summarizing the general topography and geology of the study site. Some key wells (UPL, W31, W32 and S9) are shown to illustrate their relative positions in the landscape. The UPL-W is 190 m from the field edge (W31). The distance from the field to the stream ranged from 30-50 m. Note that there is considerable vertical exaggeration on this figure.

Spencer Creek discharge rates are controlled by Valens Dam and Reservoir, located approximately 0.7 km upstream of the site (Figure 2.2). This 76 ha reservoir is managed by the Hamilton Conservation Authority and was installed in 1966 for flood control, maintenance of creek flow in the summer and recreational purposes (Heagy, 1993). The dam consists of a series of stoplogs on top of a concrete drop inlet structure. A valve in the bottom portion of the dam provides control over discharge from the reservoir into the stream. Every fall, in preparation for the winter and subsequent spring melt, the stoplogs are removed and the valve is opened all the way to lower the reservoir water levels. The resulting increase in stream discharge typically causes extensive flooding in the riparian zone. In the summer, in order to maintain appropriate water levels for recreation and downstream users, the conservation authority will reduce discharge to the stream to increase reservoir water levels, or temporarily increase discharge rates to draw-down the reservoir water levels in a "dam release".

Between the reservoir outlet and the riparian zone, is a marsh (Figure 2.2), which is dominated by Reed Canary Grass (*Phalaris arundinaceae*). When water table levels in the marsh are close to the surface, a side channel running parallel to Spencer Creek forms between the upland marsh and the riparian zone.

2.4 Climate

This study site has a humid continental climate (Woo and Valverde, 1981). Long-term climate normals for the area were obtained from the Cambridge Galt weather station, located 14.2 km from the site (Meteorological Services of Canada, 2008). The thirty-year (1971-2000) annual precipitation average was 831 mm, with 85% falling as rain, and for the months of the study period (March to November) was 723.5 mm. The 30-year average daily temperature recorded at the Cambridge Galt station was 7.6 °C, with a daily average high of 20.6°C in July and a daily average low of –6.0°C in January.

2.5 Vegetation

A detailed vegetation survey of the site was conducted in 2008 (Cymbaly, 2009). This survey found that the riparian zone canopy has mean basal area of 17 m^2 ha^{-1} and is largely composed of large Silver Maple (*Acer saccharinum L).* Other significant canopy species include Black Ash (*Fraxinus nigra* Marsh.) and White Elm (*Ulmus americana* L.). The subcanopy is irregular in density and includes small trees and shrubs such as Choke Cherry (*Prunus virginiana* L.), Elderberry (*Sambucus canadensis* L.), Sweet Viburnum (*Viburnum lentago* L.), and Common Buckthorn (*Rhamnus cathartica* L.).

At the field edge, the understory is primarily composed of grasses (e.g. Smooth Brome - *Bromis inermis,* Reedcanary Grass – *Phalaris arundinacea*), Wild Red Raspberry (*Rubus idaeus var. strigosus*) and herbaceous flora (eg. Goldenrod - *Solidago* spp., Aster - *Aster* spp., Canada Anemone -*Anemone canadensis*, Wild Cucumber - *Dryopteris spinulosa*, Cow Parsnip - *Heracleum lanatum* Michx.) and Ostrich Fern (*Matteuccia struthiopteris*).

In the mid riparian zone (flood-plain), the understory vegetation includes Jewelweed (*Impatiens capensis*), Tall Meadow Rue (*halictrum polygamum*), Virginia Creeper (*Parthenocissus quinquefolia*), Marsh Merigold (*Caltha palustris*), Dewberry (*Rubus flagellaris*), nettles (e.g. *Laportea Canadensis* and various *Urtica* spp.), violets (*viola* spp.), ferns (predominantly *Onoclea sensibilis*, and *Dryopteris* spp.), and sedges (*Carex* spp., especially *Carex comosa*). An assortment of aquatic grasses (e.g. *Scirpus* spp.), Smartweeds (*Polygonum* spp.), and native loosestrifes (e.g. *Lysimachia ciliate* and *Lysimachia thyrsiflora*) are the dominant vegetation found along the stream banks.

2.6 Piezometer and Well Network

In the riparian zone, nests of piezometers installed at 50 cm, 100 cm and 150 cm depth are concentrated along three transects (T3, T4 and G23, see Figure 2.4). Off-transect piezometers are located in a more intensive sampling zone located less than 11 m from the field, between transects T3 and T4.

The research site has a network of 26 wells, which are concentrated along transects T3 and T4 (Figure 2.4). At the field edge, there is a well above (W31) and below (W32) the step into the riparian zone. These wells were complimented with a well at the top of the adjacent agricultural slope (UPL-W) and stilling well (S9), used to measure the stream stage. Figure 2.3 shows the position of these different wells in relation to topographic features in the landscape. Figure 2.2 shows the position of these wells relative to each other and the sampling site. It should be noted that the stilling well is located upstream of the study site, at the interface between the riparian zone and the marsh.

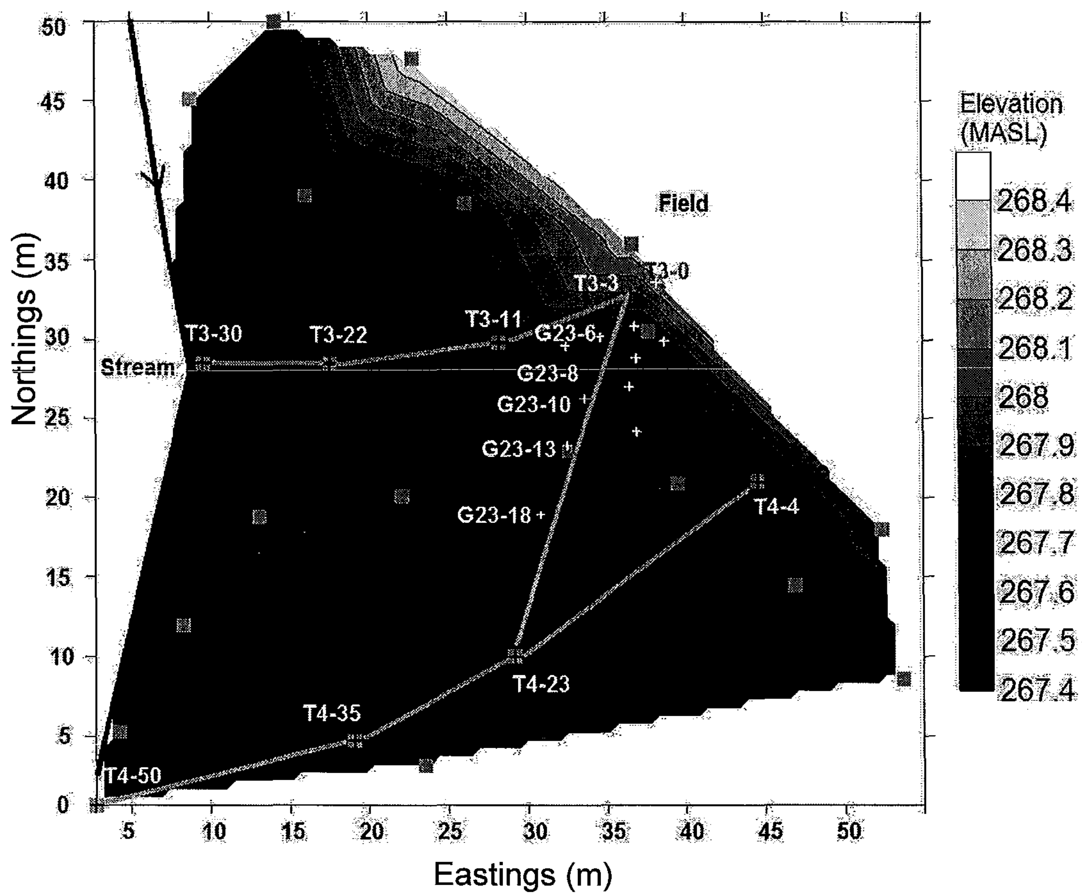

Figure 2.4 Site topography and location of the well network (grey squares), single depth piezometers (white crosses) and piezometer nests (black crosses) along transects T3, T4 and G23 (thick grey lines). The stream (thick black line) flows downward in the figure and dictates the data boundary between T3-30 and T4-50). The contour lines are spaced at 0.1 m intervals.

3 Methods

3.1 Meterological Data Collection

Rainfall and atmospheric pressure measurements were logged at 15 minute intervals by a Hobo Weather Station (Onset Computer Inc.), located at the top of the adjacent agricultural field (Figure 2.2 in Chapter 2).

3.2 Piezometer Construction and Installation

Piezometers were constructed out of 3.4 cm (outside diameter) PVC piping, with a polyethylene cap at the bottom. A 10 cm reservoir was left at the bottom and the next 15 cm (10-25 cm from the bottom) were drilled with 1cm holes approximately every 2.5 cm. This drilled area was covered with layers of polyester window screen, triple wrapped, to protect the piezometer from filling with sediment (Figure 3.1).

To install the piezometers, 3.81 cm diameter hand-held auger was used to drill a hole of the appropriate depth (sampling depth + 17.5 cm) and the piezometer was pounded in using a mallet. This method of installation allowed for a snug fit between the piezometer and the surrounding soils, so no bentonite clay was required to seal the sides. Piezometer depths were measured from the ground surface to the mid-point of the screen (Figure 3.1). During piezometer installations, notes were taken on the characteristics (i.e. colour and texture) of the soil removed.

Wells were constructed in the same way as the piezometers but had holes and screening along the entire length of the pipe. Locations of all wells and piezometers used in this study were determined using a Wild Leitz Total Station surveying instrument.

Transects T3 and T4 extend from the field edge to the stream and were installed previously for earlier research at the site. Transect G23 was installed for this study based on 2006 water table data which showed the water table following the topographic gradient during periods of high water table levels (Zhang, 2007).

Preliminary water chemistry data collected in 2006 showed that riparian zone nitrate concentrations generally fell below 2 mg/L within 11 m of the field-edge. To better understand these near field nitrate patterns, additional piezometers were installed between 0 and 11 m from the field edge, between transects T3 and T4.

It was difficult to install piezometers in this area because of the accumulation of boulders that have been thrown off the field over the years. Because of this, individual piezometers were installed wherever possible, rather than along a defined grid as originally planned.

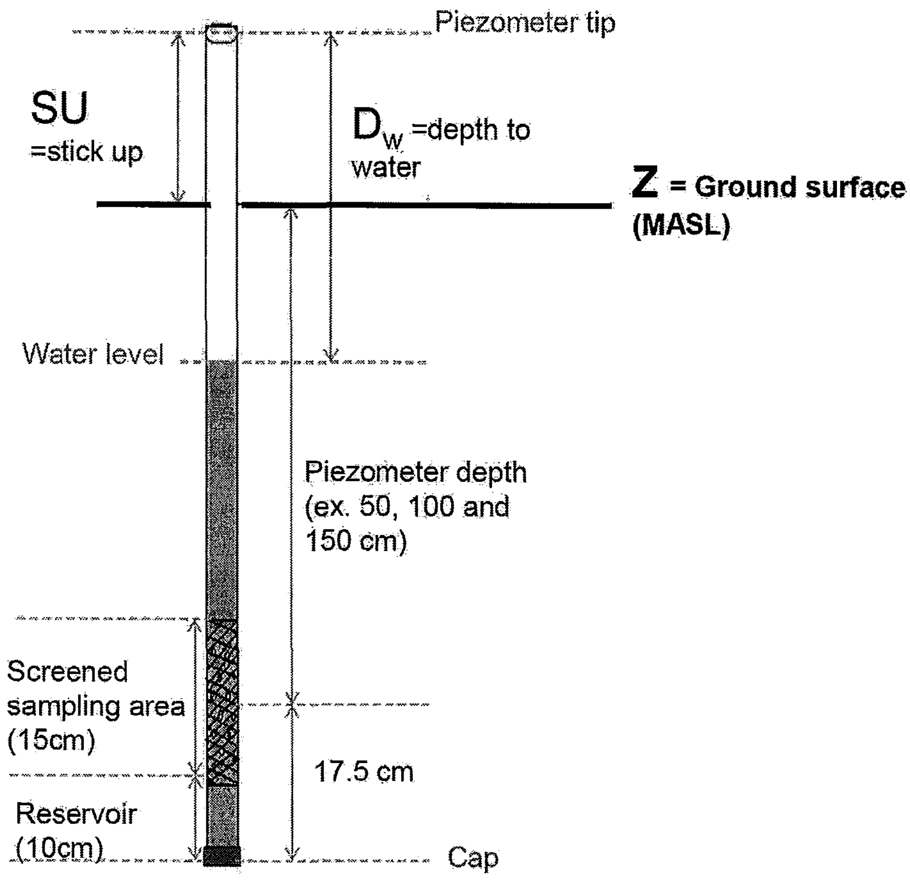

Figure 3.1 Schematic of piezometer construction and installation. The 15 cm screened sampling area is located above the 10 cm reservoir, which is capped at the bottom of the piezometer. The sampling depth is measured to the middle of the screen (17.5 cm from the bottom). The stick up (SU) is measured from the tip of the piezometer to the ground surface (Z) and depth to water (D_W) is measured from the piezometer tip to the water level in the piezometer.

3.3 Hydrologic Measurements

The distance of piezometer and well water levels below the tip (D_w) were measured using an electronic water level sensor (±3 mm). This measurement was used along with ground surface elevation (Z) and stick up (SU) data to calculate hydraulic head, in meters:

$$h = Z + SU - D_w \quad \text{Equation 4}$$

Four wells (S9, UPL-W, W32, T4-50) were instrumented with HOBO U20 Water Level Logger (Onset Computer Inc.) that recorded absolute pressure (kPa) and temperature (°C) every 15 minutes. These data were processed into water table levels using HOBOware ® Pro software (Version 2.3.1 – Onset Computer Inc.) and with barometric pressure data from the meteorological station logger and a manual water table reference point (*i.e.* D_w recorded at a specific time). All loggers were downloaded approximately once a month.

Saturated soil hydraulic conductivities (K_{sat}) were determined through Hvorslev analysis of piezometer bail test data (Freeze and Cherry, 1979). Specific discharge rates were calculated using Darcy's law (Freeze and Cherry, 1979):

$$q = -K_{sat}(\Delta h/\Delta l) \quad \text{Equation 5}$$

where, Δh is the change in hydraulic head between two points and Δl is the change in distance between the points. For vertical specific discharge rates, Δl was the vertical distance between the sampling screens of piezometers at different depth in the same nest. For lateral specific discharge rates, Δl was the horizontal distance between piezometers at different locations.

Manual well water level measurements at key wells (W31, W32, T4-50 and S9) were taken frequently over the March-November 2007 study period (at least once every two weeks, but typically twice a week), to monitor site water table levels, responses to hydrologic events and shifting hydrologic regimes. Measurement of water levels in the complete well network occurred on all water sampling days. To fill important gaps, additional wells were added to the network in July 2007. Also, it should be noted that several wells were dry during low water table conditions.

Water table elevation maps and groundwater flow nets were created using the triangulation and linear interpolation tool in the Surfer Surface Mapping System program (Golden Software Inc., Version 8.05).

3.4 Groundwater Sampling and Water Chemistry Analysis

Groundwater sampling occurred at least once every two weeks between May and September of 2007. Hydrologic events, such as rain and flood events guided additional sampling (*i.e.* sampling attempted during rising and receding limbs of the hydrograph) during this period. There was a break in sampling between the middle of September and the end of October. Between the end of October and the end of November, three more groundwater samplings were completed. Between samplings, all piezometers were loosely covered (but not sealed) with heavy plastic cups in order to protect them from contamination (rain water, leaves, etc.). A peristaltic pump and silicone tubing were used to purge the piezometers the day before sampling.

Water samples were collected from the piezometers using the peristaltic pump to pump the water from the piezometer into a 250 mL Nalgene ® HDPE sample bottle. To avoid cross contamination, the silicone tube was flushed with sample water before samples were collected in the bottle. Grab samples from the stream were obtained by holding an empty bottle in the top 20 cm of the stream with the opening facing upstream. In the field, all water samples were kept cold in coolers.

On the day of sampling, before water samples were taken, dissolved oxygen (DO) was measured in the piezometer using a YSI Model 57 instrument (Yellow Springs Instruments Inc.). Immediately on return to the lab, water samples were suction filtered through 0.45 μm cellulose acetate membrane filters and transferred into sterile 20 mL scintillation vials. In the lab, samples were stored in the fridge until they were analyzed. Samples were analyzed for nitrate (NO_3^-), sulphate (SO_4^{-2}) and chloride (Cl^-) by ion chromatography (DIONEX) at Wilfred Laurier University (Department of Geography and Environmental Studies). All samples were analyzed within two weeks of collection.

3.5 Denitrification Potential Measurements

Soil samples were taken at three depths (0-30 cm, 30-60 cm and 80-110 cm) and three locations (2.5, 8.0 and 15.0 m) from the field edge, between transects T3 and T4) during the spring (May 29th-- DOY 149), summer (August 13th-- DOY 225) and fall (October 28-- DOY 301). At each sampling location, one sampling hole was made for each of the three different sampling days. At each sampling location, the sampling holes were no more than 30 cm apart. After the samples were taken, piezometers were installed in the sampling holes.

Shallow samples (0-0.6 m depth) were collected using an Oakfield sampler. Deep samples (0.6-1.6 cm depth) were collected using an auger. To avoid soil contamination from shallower depths, the outside layer of soil was removed before the augured soil was collected for the incubation. Soil samples from each depth were placed in separate Ziplock bags and kept cold in a cooler until they could be placed in the laboratory fridge.

Soil slurries amended with nitrate and glucose were incubated under an acetylene-helium atmosphere according to the Nova Scotia Agricultural College (NSAC) Standard Operating Procedure (NSAC, 2007). The incubations were carried out in 250 mL Mason® jars. To allow for headspace gas sampling, the Mason® jar lids (86 mm Wide Mouth SNAP Lids) were punched with ¼ inch holes and were fitted with rubber grommets and polycarbonate Luer 2-way stopcocks (Cole-Palmer Canada). The grommet-lid and grommet-stopcock seams were sealed with General Electric Silicone 2 to prevent gas leakage. A photograph of the experimental apparatus is shown in Figure 3.2.

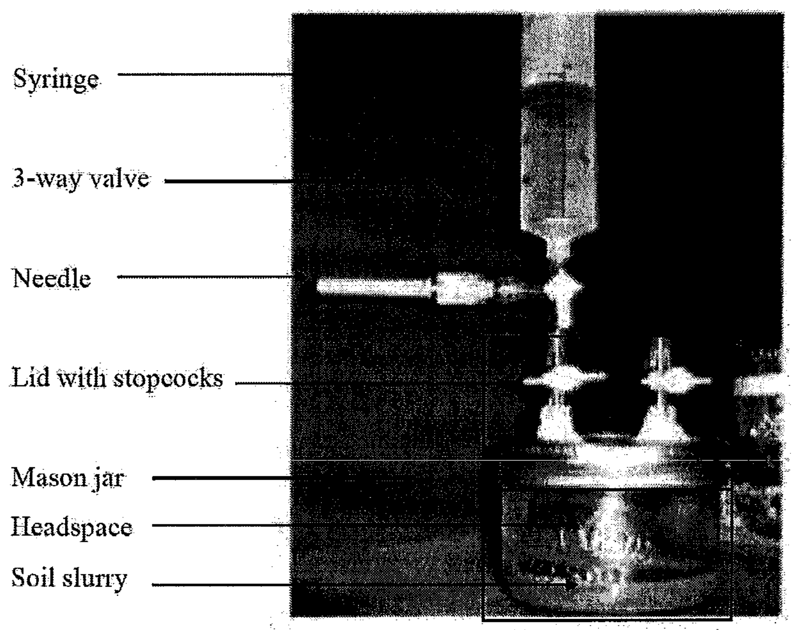

Figure 3.2 Incubation apparatus which includes 250 mL Mason ® jar with lid fit with stopcocks valves and a 60 mL syringe fit with a 3-way valve and a 25 ga needle.

Headspace gas samples (30 mL) taken every hour for six hours were analyzed on an SRI 8610C Gas Chromatograph (GC) optimized for N_2O (NWRI Biogeochemistry Lab) and results were managed using the Peak Simple chromatography software package (SRI Instruments, Torrance, CA, USA).

During the incubation, air temperature and headspace sample volumes were recorded. After the incubation, the headspace volume and dry soil mass were measured. Along with the GC results, these measurements were used to calculate a denitrification potential (DEA) value, which is the production rate of N_2O normalized by the mass of soil. Incubations were done in triplicate for each soil sample to facilitate statistical analysis.

4 Riparian Zone Hydrology and Hydrogeologic Setting

This chapter addresses Objective 1 of this thesis: How does stream regulation influence water table levels and shallow groundwater movement in the riparian zone? In addition, it provides the hydrologic framework necessary to evaluate the spatio-temporal nitrate dynamics (Objective 2) presented in Chapter 5.

Results in this chapter are organized and presented in four main sections: First, spatio-temporal stream stage and water table patterns are examined to understand the relative importance of the stream, field and upland marsh on water table levels at the site (Section 4.1). Spatial patterns of hydraulic conductivities (K_{sat}) along the three transects are subsequently discussed to provide context for the analysis of shallow groundwater movement in the riparian zone (Section 4.2). In Section 4.3, chloride concentrations (which are considered to be a conservative tracer at this site) are used to examine the changing importance of different groundwater sources to the riparian zone over the study period. Next, specific discharge rates were used to understand shallow groundwater movement during the different regimes (Section 4.4).

Finally, the results are discussed to evaluate the impact of stream regulation by the upstream dam on riparian zone hydrology and to test the applicability of Vidon and Hill's conceptual model (2004a) at this site (Section 4.5).

Results

4.1 Temporal Patterns in Stream Stage and Water Table Position

Figure 4.1a shows precipitation data for the 2007 study period. From March to November, only 353.2 mm of rain fell at the site. This is 49% less than the long term average (723.5 mm) for the same months recorded at the Cambridge Galt weather station, located 14.2 km from the site. During the study period, most rain events were less than 10 mm and the largest rain event (41.6 mm) occurred on DOY 279.

Figure 4.1 shows stream stage (Figure 4.1a) and water table dynamics in the marsh and upland wells (Figure 4.1b). Before DOY 279, stream stage was largely controlled by the reservoir discharge set by the Hamilton Conservation

Authority. A reduction in reservoir discharge to the stream on DOY 93, 128 and 166 caused abrupt stream stage decreases on these days. On DOY 176 and 235, dam releases (see description in Chapter 2) caused in-bank floods (*i.e.* stream stage pulse that does not overflow the stream banks) in the riparian zone, which lasted five and nine days, respectively. The dam release on DOY 327 caused both the marsh and riparian zone to be inundated by the stream. Aside from changes in reservoir discharge, stream stage was relatively constant between DOY 128 and 279.

Prior to the large rain event on DOY 279, the conservation authority removed the stoplogs from the top portion of the dam in preparation for the winter (Private Communication from Patrick Ragaz: Hamilton Conservation Authority). As a result, the large rain event on DOY 279 caused the water in the reservoir to reach the top of the remaining concrete portion of the dam and overflow into the stream. The reservoir water level remained at the top of the dam after this event. Thus, subsequent rain-events caused unregulated discharge to the stream for the remainder of the study period.

Similarities between the marsh water table (T1-7 in Fig 4.1(b)) and the stream stage indicated that the hydrology in the marsh was strongly controlled by stream discharge patterns in the spring (DOY < 128), before the second decrease in stream stage. Between DOY 128 and 279, the marsh and upland water tables showed seasonal patterns associated with evapotranspiration driven soil-moisture deficits (water table decreased over the summer and increased in the fall). No diurnal water table patterns where seen at the upland (UPL) well, likely due to the depth of the water table, which remained over three metres deep for the entire study period. The beginning of the UPL-W water table increase in the fall coincided with the visual observations of plant senescence (mid September). This provides a point of reference for the start of the wet-up period, which is more difficult to indentify in the riparian zone and upstream marsh where water table dynamics are more complex.

The rain event on DOY 279 caused the marsh water table to jump by over 0.6 m but the stream only increased by approximately 0.2 m during this rain event. This suggests that hillslope run-off was important in this initial water table increase and makes it difficult to assess the relative importance of stream inputs during this period.

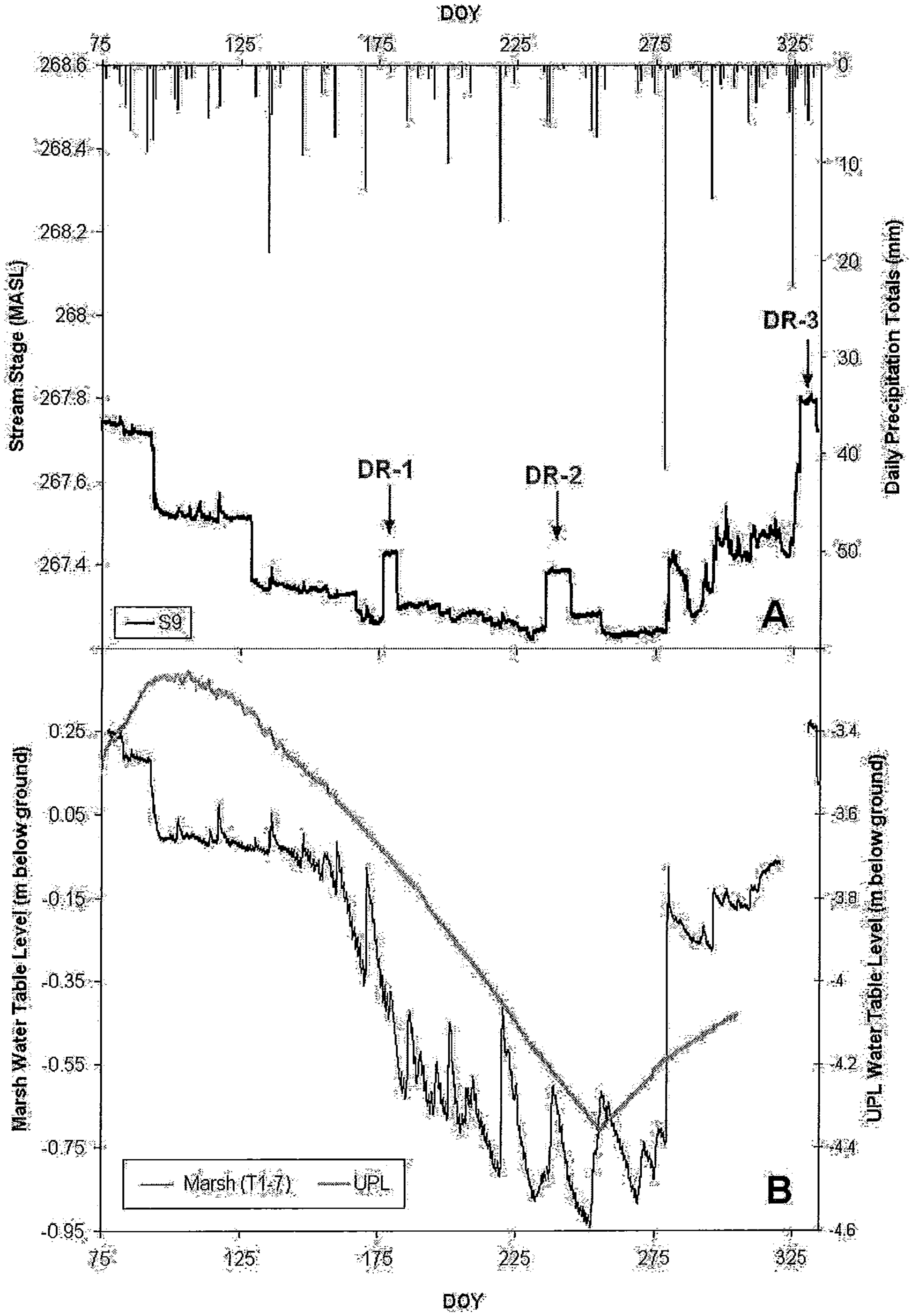

Figure 4.1 (a) Daily precipitation totals and stream stage (S9) over the study period and (b) water table dynamics at the upland well (UPL) and in the upstream marsh (T1-7). The three dam releases (DR-1, DR-2, DR-3) are highlighted with arrows.

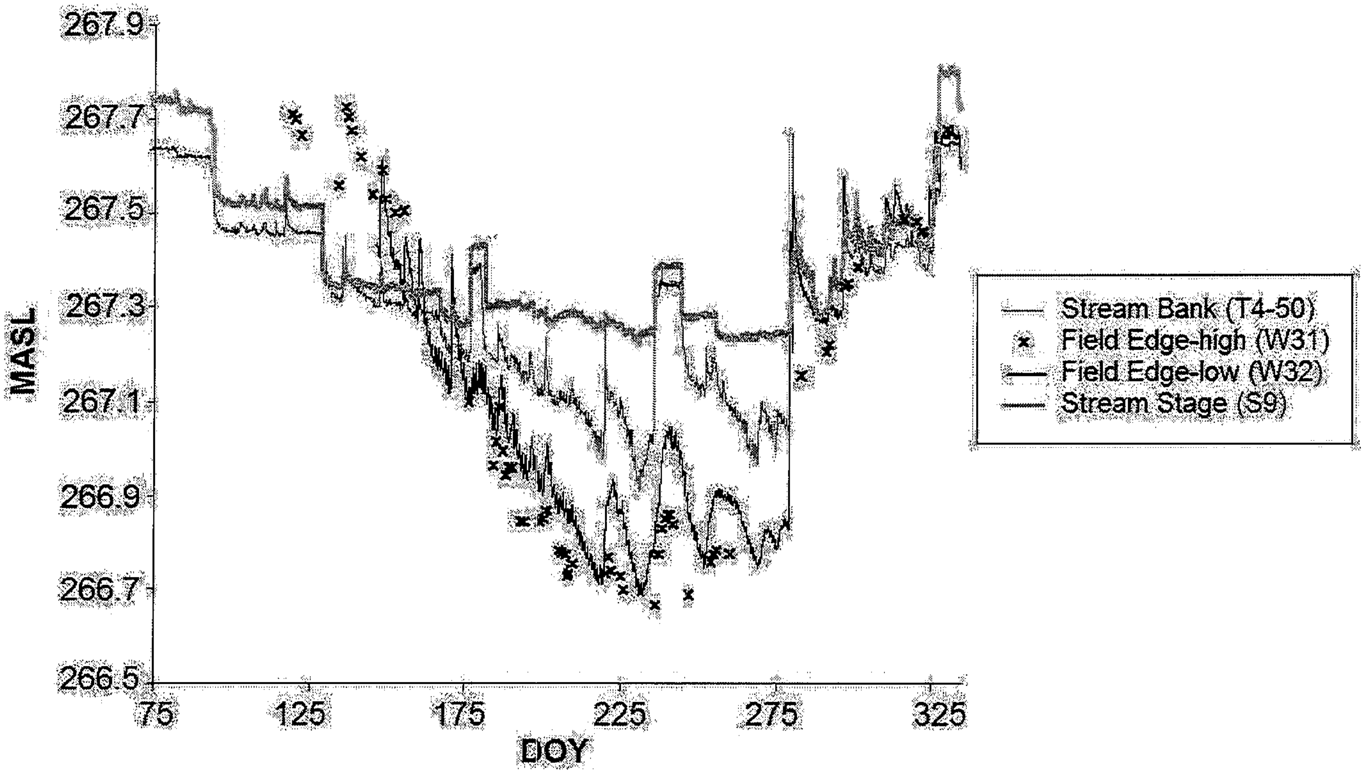

Figure 4.2 Riparian zone water table dynamics at the field edge (W31 and W32) and at the stream bank (T4-50). Measurements at W31 were taken manually, while the other measurements were obtained from data loggers recording at 15 minute intervals. Stream stage levels (S9) are included in this figure for comparison with the water table patterns.

Water tables at both the stream bank and field edge in the riparian zone (Figure 4.2) showed similar seasonal water table patterns to those in the marsh, decreasing gradually in the summer and increasing rapidly during the fall wet-up. Responses to all three dam releases were seen in the riparian zone both in the stream bank and at the field edge. Notably, the extent of water table draw-down at the field edge (1.1 m below ground surface) was greater than that at the stream bank (0.6 m below ground surface). From DOY 165 to 279, the field edge well (W32) dropped below the stream bank well (T4-50-W), indicating a sustained water table gradient reversal towards the field.

In both the riparian zone and the marsh, water table increases associated with rain events suggest that hillslope runoff influences both the marsh and riparian water table levels. The DOY 279 rain event resulted in a large (and sustained) water table increases in the marsh and across the riparian zone. The water table at these locations continued to increase with subsequent rain events.

These water table dynamics suggest that major hydrologic shifts occur around DOY 165, when the water table at the field edge (W32) drops below that near the stream (T4-50-W), and around the 41.6 mm rain event on DOY 279.

Water table profiles along transects T3 and T4 provide more information about the water table dynamics in the riparian zone. Figure 4.3 shows water table profiles for several representative dates during the water table draw-down in summer and the fall wet-up. At both transects, stream–to-field gradients were always seen in the near-stream zone. However, elsewhere in the riparian zone, water table gradients changed direction under different moisture conditions. Field-to-stream gradients were observed at both T3 and T4 in the early summer (Figure 3a, c). As the summer progressed and the water table at the field edge decreased, transect T4 wells show that the water table "hinged" near the stream, and the overall water table reversed, producing a dominant stream-to-field gradient. Although the majority of the T3 wells were dry over this period, the near field wells showed evidence of the flow reversal. When wet conditions returned in the autumn (Figure 4.1), the field-to-stream gradients did not rapidly re-establish, and stream-to-field gradients were still present.

The progression of the wet-up along T3 (Figure 4.3(b)), shows that the mid riparian water table increased more rapidly than the water table at the field edge. This hindered the re-establishment of field-to-stream water table gradients and resulted in a very low water table gradient during the fall. These wet-up patterns, along with the flatness of the water table in the mid riparian zone (despite stream-bank and field edge water table differences), suggests that a source other than the field may be dominating riparian zone hydrology during this period.

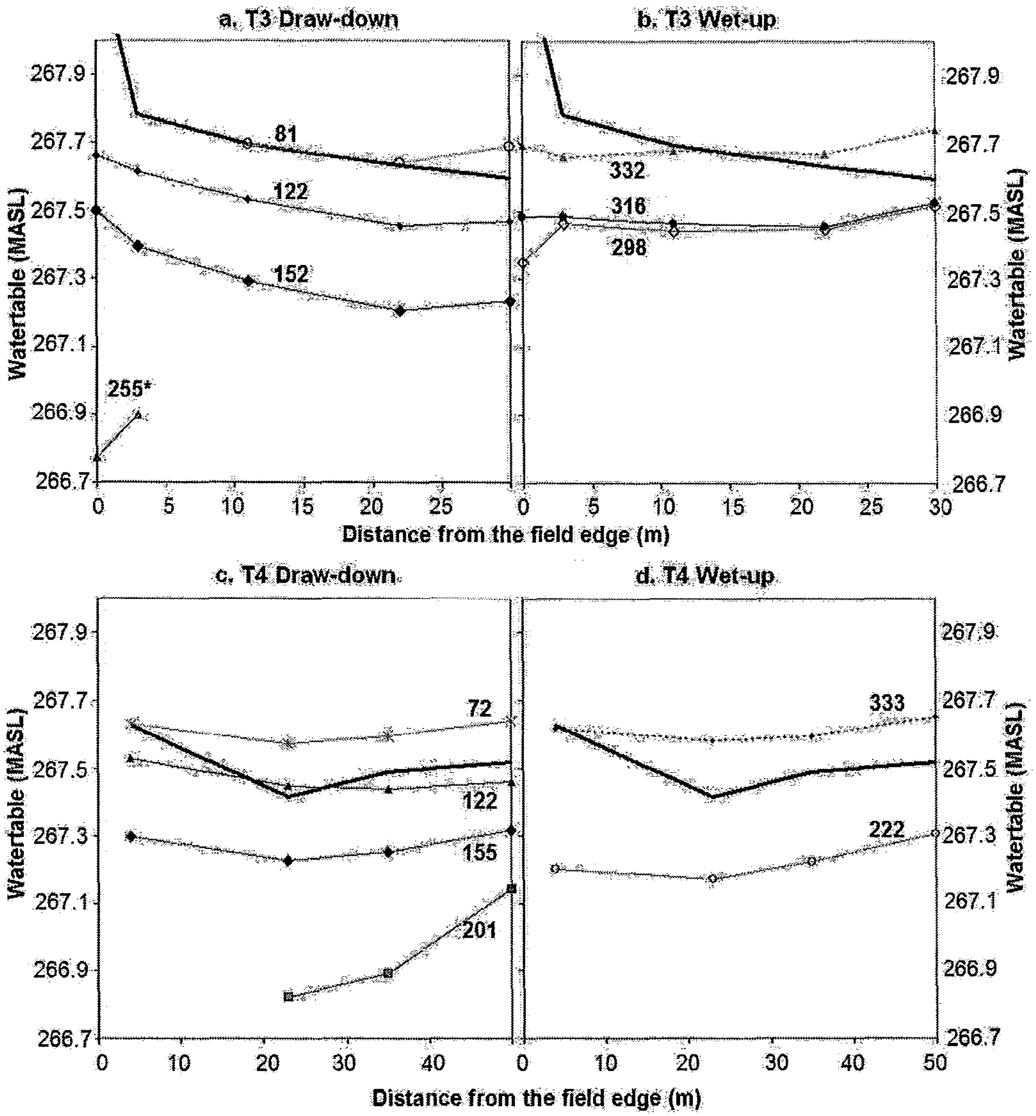

Figure 4.3 Water table profiles for representative days (DOY is marked on the graph) during water table draw-down and wet-up along Transect 3 (a and b) and Transect 4 (c and d). The thick black line shows the ground surface. In the mid-summer, T3 wells became dry, so water table data at T3-11, T3-22 and T3-30 is not available during that time.

Burt *et al.* (2002) have suggested that field-to-stream transects are often limited in their ability to capture complex water table patterns and promote the use of monitoring grids to generate water table elevation maps. Indeed, water table elevation maps were an important tool in understanding the controls driving water table patterns --particularly the importance of the upstream marsh --at this site.

The days for which these potentiometric surfaces were created and the regimes that they were grouped into are shown on Figure 4.4. Note the days in the same group had the same general water table elevation pattern. During Regime R2, Figure 4.2 and Figure 4.3c showed that there was a water table gradient reversal, as the field-edge water table dropped well below that at the stream bank. During this period, many wells at the study site went dry; therefore, there were not enough water table measurements to construct a contour map. Thus, the Regime R2 markers on Figure 4.4 indicate where the water table at the field edge well (W32) is at least 0.2 m less than that at the stream bank (T4-50).

Figure 4.5 shows examples of potentiometric surfaces for dates representative of three of the observed hydrologic regimes. During Regime R1, the water table gradient at the field edge followed the topographic gradient (compare Figure 4.5a to Figure 2.4). In the mid riparian zone, however, the hydraulic gradient ran perpendicular to the topographic gradient, roughly parallel to the stream. This mid riparian gradient is likely caused by the channel that forms between the marsh and the riparian zone during high water table conditions (*i.e.* when the water table is close to the ground surface but not necessarily flooded)

During Regime R3, water table gradients were dominated by inputs from the upstream marsh (Figure 4.5b). As a result, the water table gradient was parallel to stream flow.

During the first dam-release, which began on DOY 176, the water table elevation map shows clear a stream-to-field gradient (Figure 4.5c). Comparing the regime R2 relationship between the water table levels at T4-50 and W32 (Figure 4.4) with those during this event suggests that the water table elevation map for regime R2 may be similar to that seen here, but with lower stream-to-field gradients.

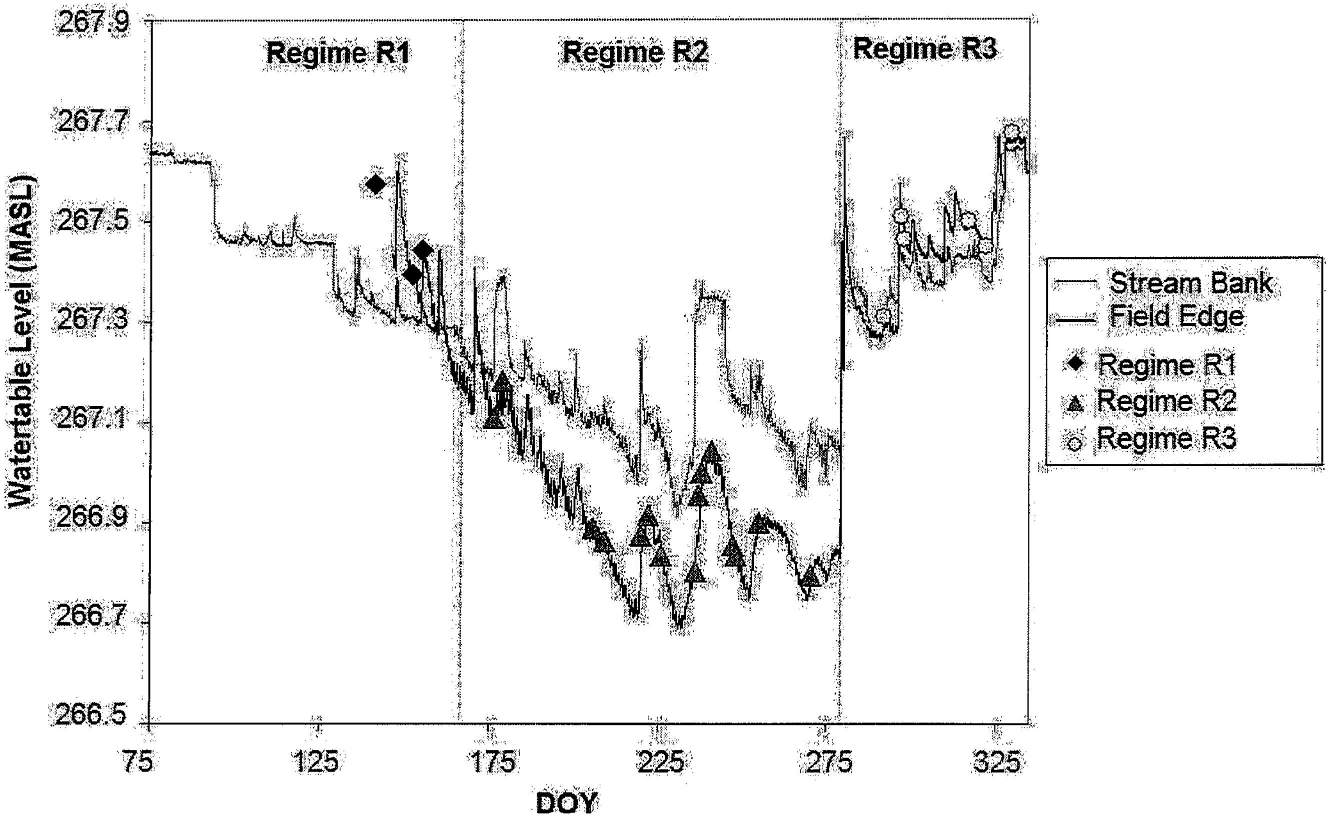

Figure 4.4 Categorization of the different water table elevation map patterns seen with respect to water table levels at the field edge (W32) and in the stream bank (T4-50). Days marked with the same symbol had similar water table elevation maps. The three regimes were allocated by comparing these water table pattern groupings with the temporal water table patterns at the field edge (W32) and stream bank (T4-50).

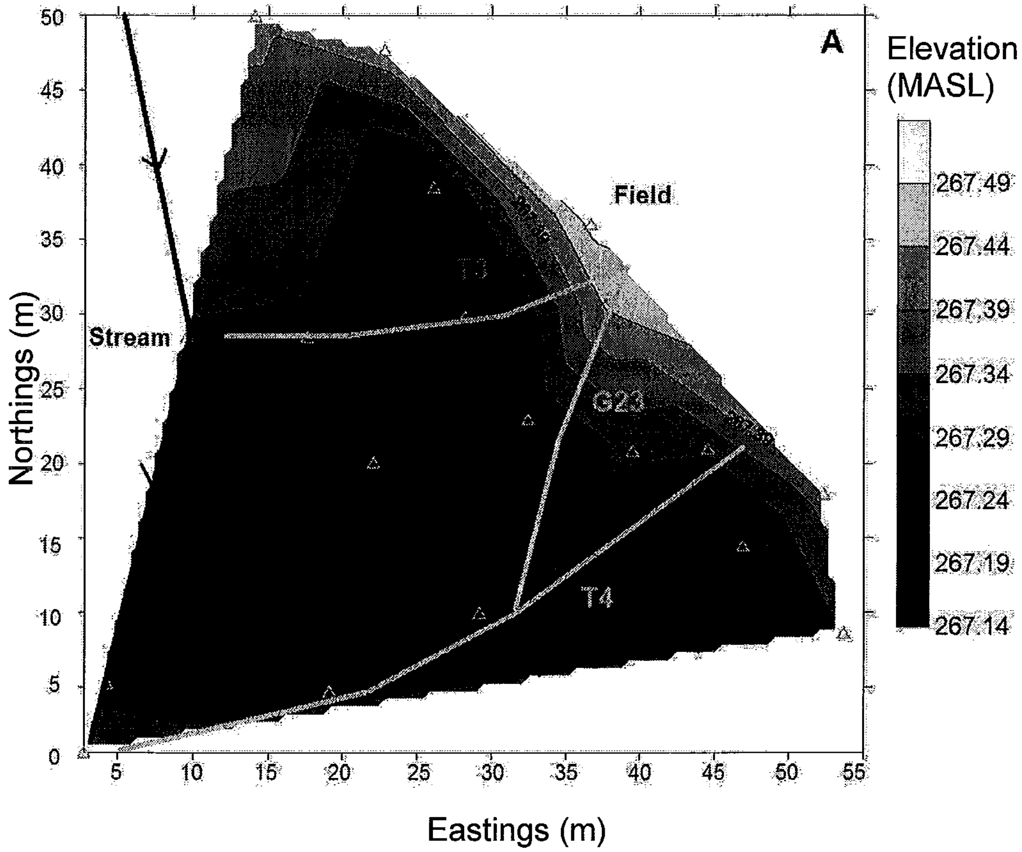

Figure 4.5a Water table elevation map for a date representative of Regime R1 (DOY 155). Equipotential lines are at 5 cm intervals and the water table elevations decrease from light to dark. The triangles show the wells that were used to create the map. A different number of wells were used in each of the maps due to wells drying out in the summer and additional wells being installed over the study period.

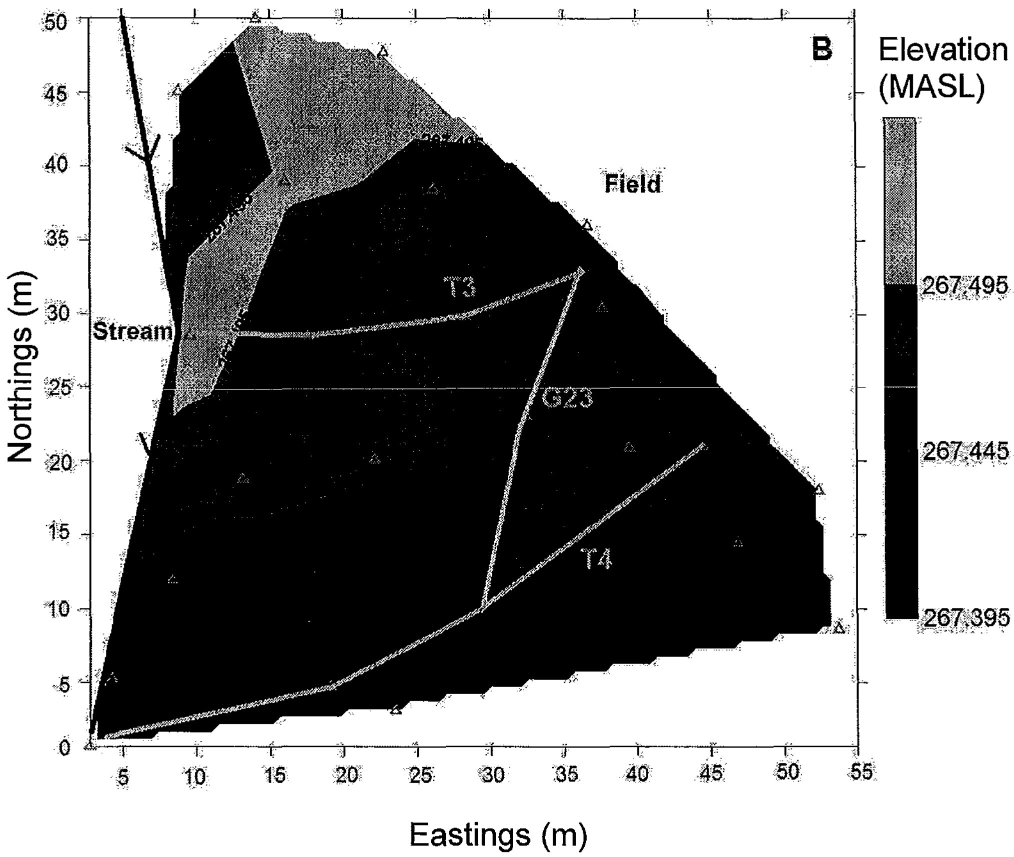

Figure 4.5b Water table elevation map for a date representative of Regime R3 (DOY 317). Equipotential lines are at 5 cm intervals and the water table elevations decrease from light to dark. The triangles show the wells that were used to create the map. A different number of wells were used in each of the maps due to wells drying out in the summer and additional wells being installed over the study period.

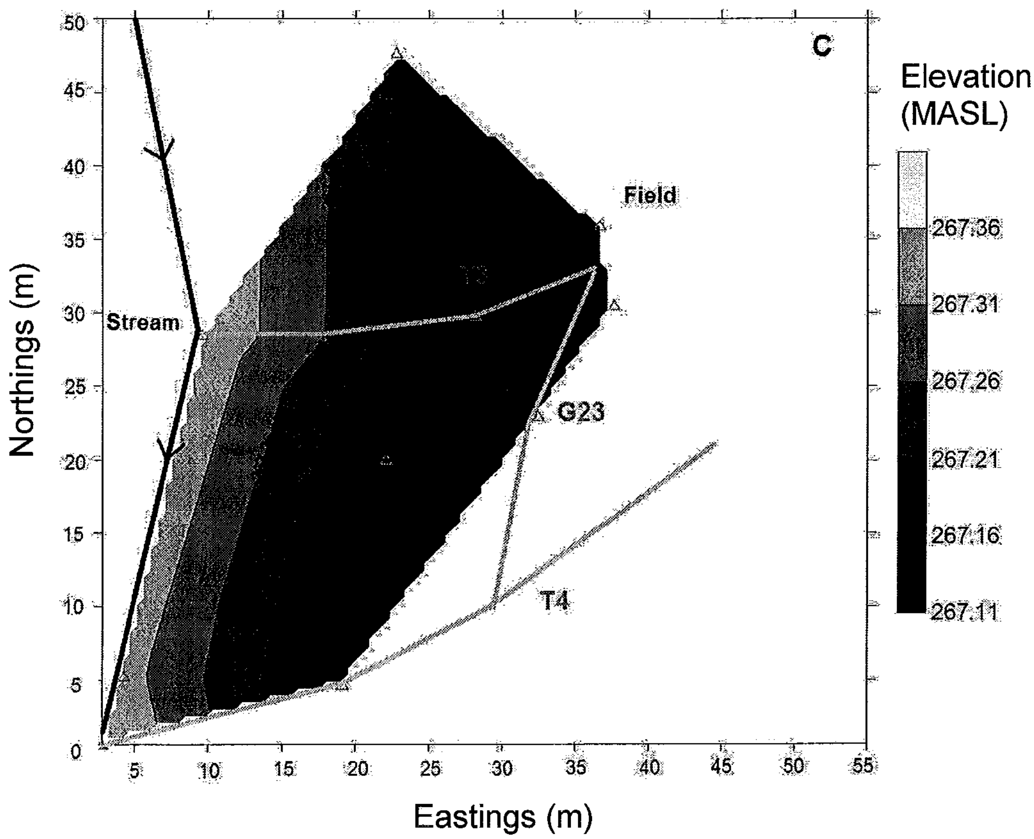

Figure 4.5c Water table elevation map for a date representative of the first dam release DR-1 (DOY 179). Equipotential lines are at 5 cm intervals and the water table elevations decrease from light to dark. The triangles show the wells that were used to create the map. A different number of wells were used in each of the maps due to wells drying out in the summer and additional wells being installed over the study period.

The temporal water table patterns presented above suggest there are at least three different hydrologic regimes during the study period:

1) Field dominated (DOY < 165), when the water table is dominated by slope discharge

2) Stream dominated (DOY 165 –279), during the flow reversal

3) Marsh dominated (DOY > 279), during the fall wet-up when groundwater recharge rates in the marsh were greater than those in the field

These regimes suggest that the relative importance of different hydrologic inputs changed significantly over the study period. In order to understand how these hydrologic shifts affect shallow nitrate patterns (Chapter 5), it is important to understand how these hydrologic shifts impacted upland connectivity (*i.e.* nitrate inputs), as well as shallow groundwater flow paths and flow rates in the riparian zone.

4.2 Saturated Hydrologic Conductivity of Subsurface Sediments

Groundwater discharge rates and the direction of groundwater flow depend on subsurface hydraulic gradients as well as the hydraulic conductivity of the subsurface sediments (Freeze and Cherry, 1979). Figure 4.6 shows saturated hydraulic conductivity (K_{sat}) measured at piezometers along transects T3 and T4. K_{sat} values along transects T3 and T4 ranged from 10^{-4} to 10^{-5} cm/s and 10^{-2} to 10^{-5} cm/s, respectively. K_{sat} values along G23 (Figure 4.7) ranged four orders of magnitude (10^{-2} to 10^{-6} cm/s), and generally increased moving into the riparian zone along the topographic gradient from transects T3 to T4. Overall these K_{sat} values indicate that the subsurface sediments range from being highly conductive to practically non-conductive; Vidon and Hill (2006) define a confining layer as having a K_{sat} of less than 10^{-6} cm/s.

These K_{sat} patterns corresponded with the grain size analysis results (also shown on Figure 4.7), which indicate a range of sediment textures from poorly sorted sand-silt-clay at the field edge to 97% sand at depth in the mid riparian zone (Leoni, 2008). These patterns show that there is a large degree of heterogeneity in the hydraulic properties of shallow soils at the study site and suggest that groundwater flow patterns may be complex.

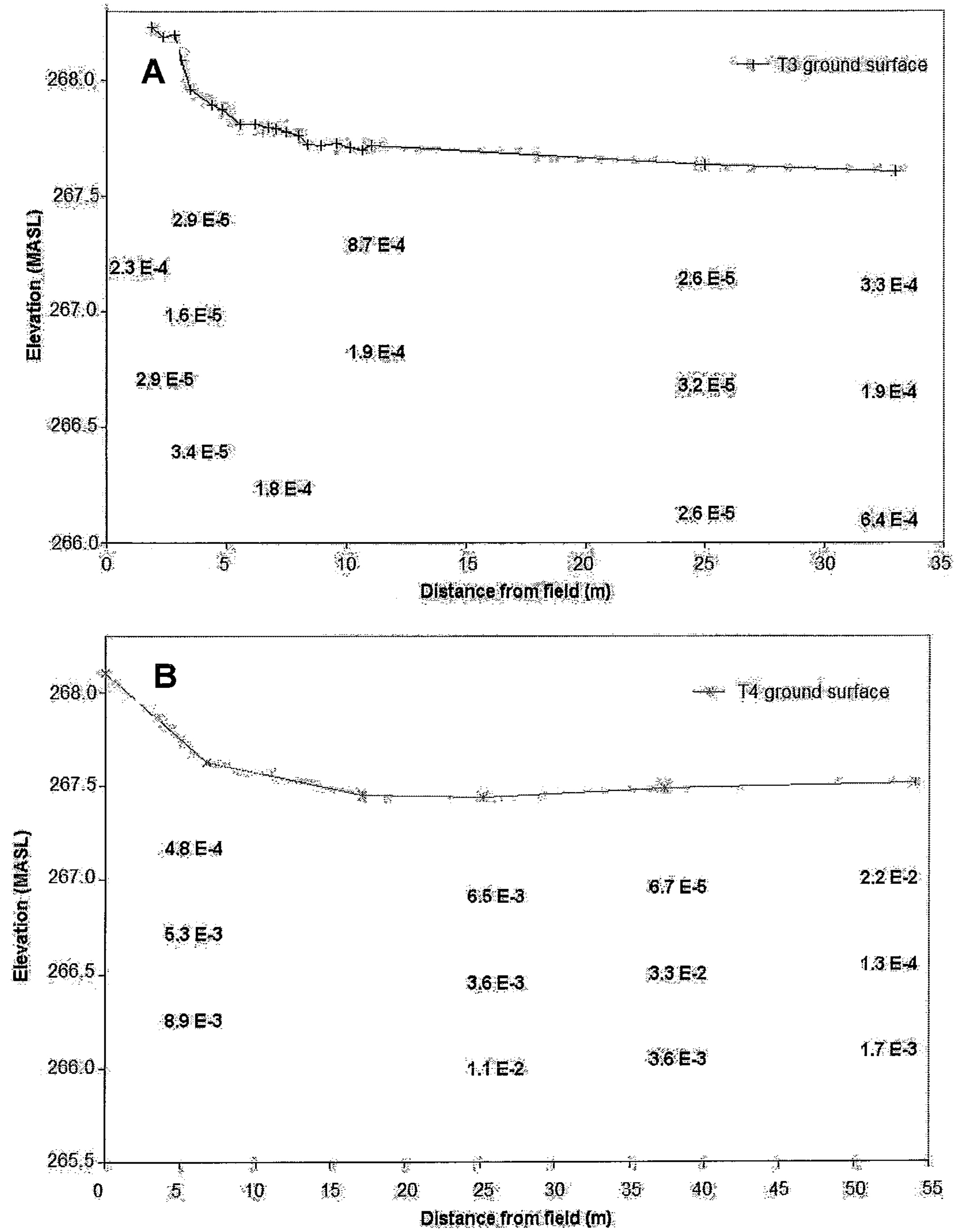

Figure 4.6 K_{sat} values (cm/s) measured at piezometers along transects a) T3 and b) T4.

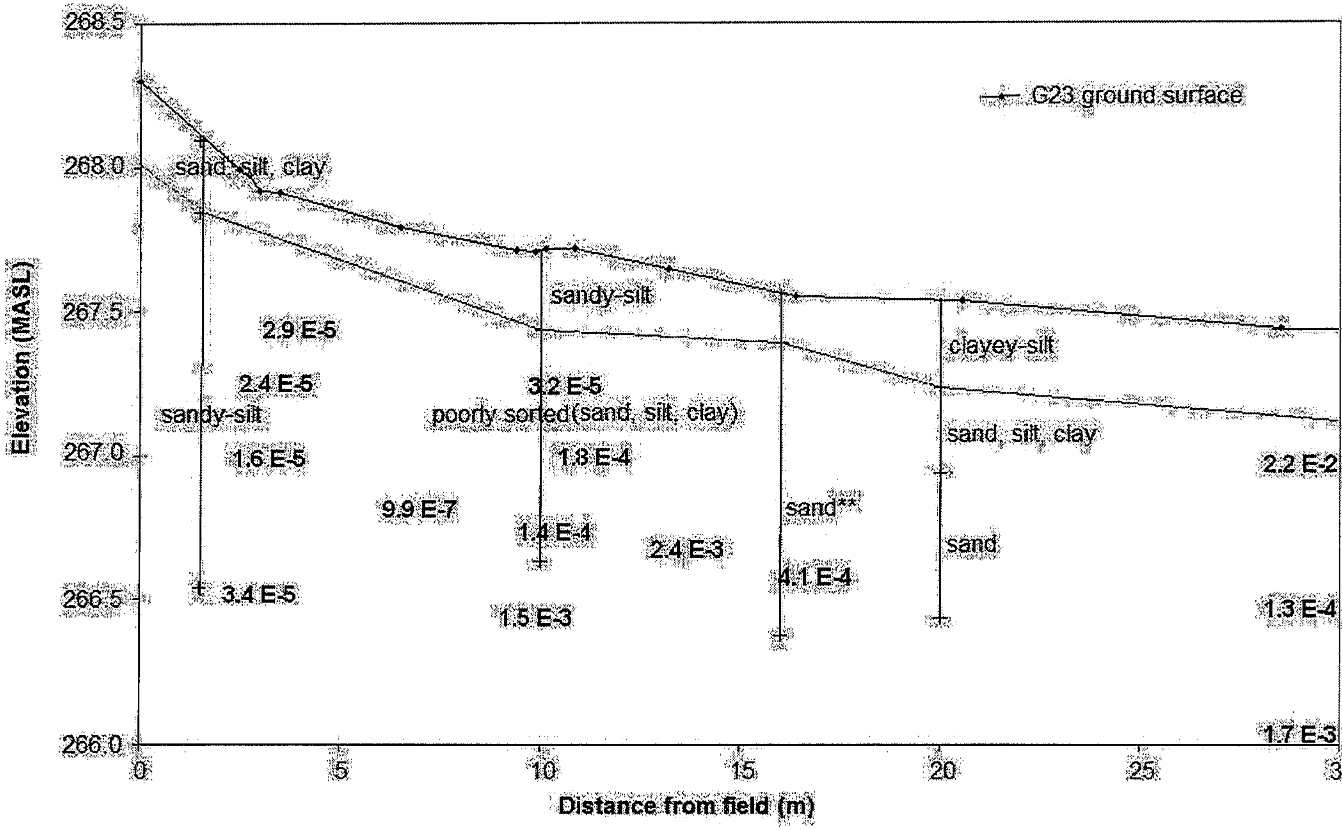

Figure 4.7 K_{sat} values (cm/s) measured at piezometers along transect G23 along with particle size analysis results from cores taken at three locations along the transect (Leoni, 2008). Visual observations are denoted with astericks (**).

In homogeneous systems with relatively constant K_{sat} values, flow lines are drawn perpendicular to the equipotential lines. In heterogeneous systems, such as this, flow lines are "refracted" as they move though media with different K_{sat} values (Freeze and Cherry, 1979). As a result, in this study, subsurface hydraulic gradients shown by equipotential lines were used to determine the general direction of groundwater flow (*i.e.* field-to-stream, stream-to field, up welling, down welling) but were not used to determine specific flow paths through the riparian zone.

4.3 Spatio-temporal Changes in Riparian Zone Groundwater Sources

In evaluating the nitrate buffering function of riparian zones, upland connectivity is an important factor as it is often a dominant control on nitrate inputs to the riparian zone. Table 4.1 lists the average chloride concentrations found in the field and stream adjacent to the riparian zone. The chloride concentrations in the groundwater beneath the field are expected to be influenced by the use of fertilizer in this agricultural catchment. Potassium chloride (KCl) is a common component of agricultural fertilizers. It is highly soluble in water and readily dissociates into K^+ and Cl^- ions. Chloride anions are repelled by the negative charge of soils; therefore groundwater recharge in agricultural areas often contributes to elevated groundwater chloride concentrations

A one-tailed t-test (α=0.05) showed that the high chloride concentrations in the stream were significantly different than those in the field. This is likely due to additional chloride inputs to the stream from road salt applied in the area (Warren *et al.*, 2001). These differences in water chemistry between the stream and field permit the use of chloride as a tracer to determine dominant hydrologic sources at different points in the riparian zone.

Table 4.1 Chloride concentrations in the stream water (S9) and in groundwater at 100 cm depth at the field-edge (T3-0).

		Chloride (mg/L)			
Location	**Number of samples**	**Average**	**Stdev**	**Max**	**Min**
Stream (S9)	10	27.9	5.16	35.23	20.12
Field (T3-0)	11	8.82	2.00	13.76	7.15

To explore the different hydrologic sources feeding this riparian zone, hydraulic gradients and chloride concentrations measured at piezometers along transects T3 and T4 on DOY 86 were plotted (Figure 4.8). This day was chosen because it had both high stream stage and high water table levels below the field and clearly showed all sources observed over the study period.

Notably chloride concentrations in the mid riparian zone along transect T4 were much lower than the minimum concentrations measured at the field edge (7.15 mg/L) and in the stream (20.1 mg/L) shown in Table 4.1. Combined with the apparent upward hydraulic gradient in the mid riparian zone, these low (3-5 mg/L) chloride concentrations suggest that there is an additional groundwater source discharging in the riparian zone. This mid riparian discharge zone is consistent with Hill's (1996) categories of riparian hydrology which suggests that hilly uplands cause several distinct flow systems to develop in a single aquifer. A more detailed discussion of the origin of these mid riparian inputs is included in Chapter 5.

Piezometer nests T4-50 and T4-35, were inundated with stream water on DOY 86. Therefore, the elevated chloride concentrations seen in the top 50 cm of the soil profile at these locations was likely the result of mixing between surface (stream) water and groundwater. At both transects T3 and T4, at the field edge, intermediate chloride concentrations at depth (150 cm) indicate that mixing may have occurred between field inputs and the low chloride source coming from beneath the riparian zone. Evidence of mixing between field inputs and deeper flow paths was also seen in the mid riparian zone of transect T3, where a decrease in chloride concentration is seen. The distinct chloride concentration distributions between transects T3 and T4 indicate a difference in the dominance of low chloride inputs upwelling from below. This makes sense given the variability of K_{sat} values along these two transects (Figure 4.6). Lower hydraulic conductivity along transect T3 (than at T4) may hinder upward discharge in this area.

At both transects, low chloride concentrations in the shallow (50 cm) piezometers combined with low specific discharge rates (indicating long residence times) at the field edge indicate that dilution by rain water infiltration may have an impact on shallow water chemistry at these locations. Rain water dilution may also occur further into the riparian zone but it is difficult to evaluate because of mixing with other sources. Furthermore, at the field edge, there is no canopy cover so rain water infiltration is expected to be greater there than at locations further into the riparian zone. Other studies conducted near this research site in Beverly Swamp have found canopy interception to range from 15 to 25% (Valverde, 1978; Young, 2001).

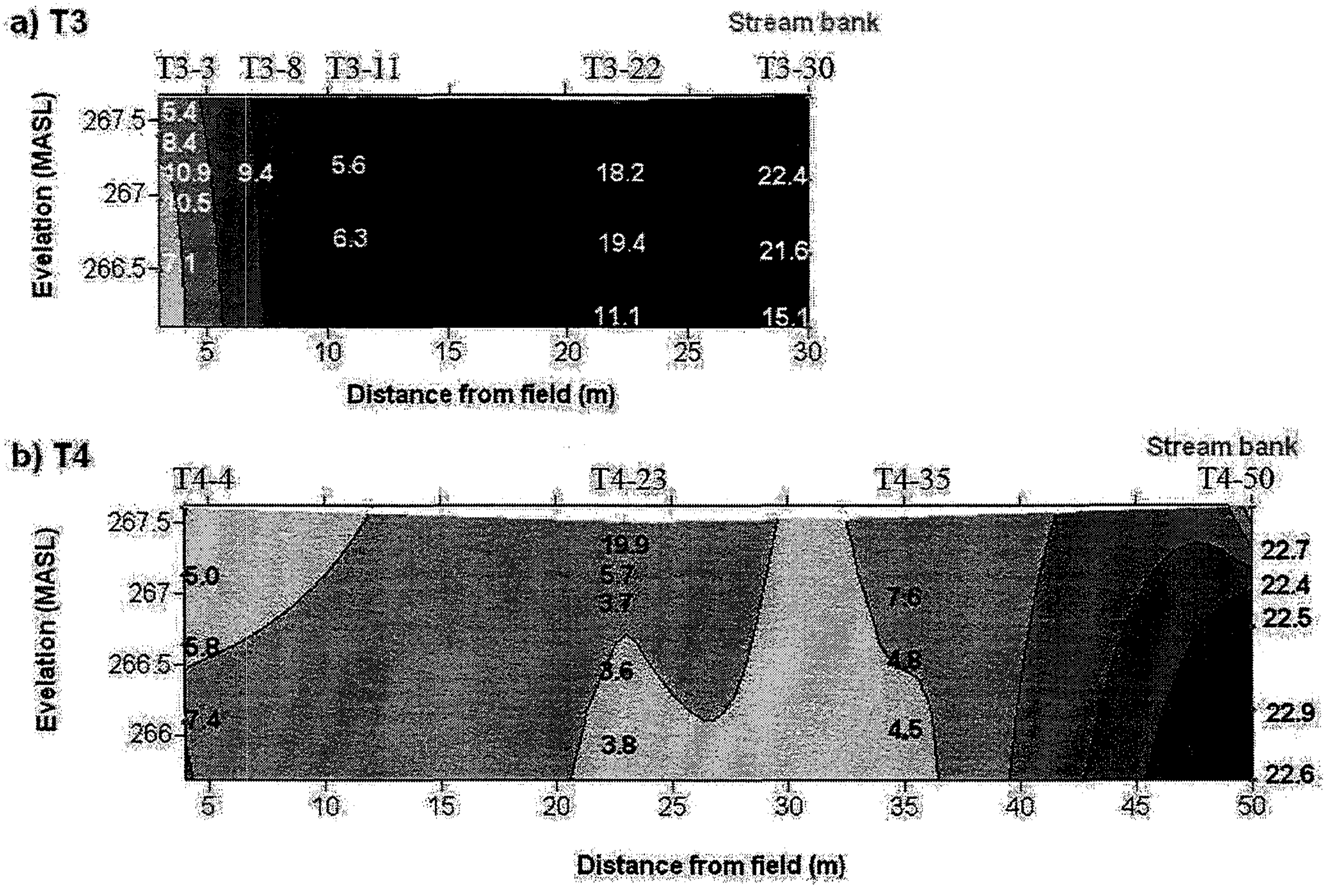

Figure 4.8 Chloride concentrations and hydraulic gradients along transects a) T3 and b) T4 on DOY 86 (high stream stage and high field edge water table levels). Equipotential lines are at 5 cm intervals and hydraulic heads decrease from light to dark. Stream chloride concentration on DOY 86 was 24.5 mg/L. Note that stream was inundating T4-50 and T4-35 on this day.

At both transects, elevated chloride in the stream bank piezometers show that they are dominated by stream inputs. However, equipotential lines suggest different groundwater flow behaviour at the stream bank end of each transect. Equipotential lines at the transect T4 stream bank indicate a strong downward gradient, in the stream bank. In contrast, the gradient at T3 appears to radiate into the riparian zone. With no hydraulic data in the stream or below 1.5 m in the stream bank, it is difficult to confirm the apparent downward gradient at transect T3. The lateral flow suggested by the gradient between T3-30 and T3-22 is supported by high chloride concentrations at T3-22. This shows that stream origin water has traveled at least 8 m into the riparian zone and is not limited to the stream bank. These patterns are consistent with the different distribution of K_{sat} values measured in the near stream zone of these two transects (Figure 4.6) which show that the soils in the stream bank at T3 and T4 have very different hydraulic properties.

At both T3-30 and T3-22, there was an abrupt drop in chloride between groundwater between 100 cm and 150 cm, which was not easily explained by the hydraulic gradients. This type of drop was not seen at T4-50, which suggests that the different hydraulic properties at these two stream banks influence the extent of their hyporheic zone. These patterns may also suggest that stream inputs may be traveling along preferential flow paths along T3. In a floodplain in southern Ontario, Duval (2006) used a bromide tracer to show that stream inputs followed preferential flow paths into the riparian zone.

In summary, the hydraulic gradients and the distribution of groundwater chloride concentrations along transects T3 and T4 suggest that there were three principal groundwater sources in the riparian zone on DOY 86:

1) the stream, which had chloride concentrations of 24.5 mg/L on DOY 86

2) up welling of low chloride (3-5 mg/L) groundwater, and

3) subsurface inputs from the hillslope (field), characterized by intermediate (8-10 mg/L) chloride concentrations.

Considering the large changes in site hydrology described above (Section 4.1), it is not surprising that changes in these groundwater source patterns were observed over the study period. Figure 4.9 shows the dominant source at each of the 100 cm piezometers at the site during regime R1 and indicates the locations where chloride concentrations indicated a shift in the dominant hydrologic source during regimes R2 and R3. High chloride groundwater concentrations, which are indicative of stream origin water, were always seen at the T3-22 nest and at the stream bank nests (T3-30 and T4-50). This suggests that the extent of stream inputs did not change significantly over the study period. However, the spatio-temporal resolution of sampling near the stream may simply have not been detailed enough to capture it.

In the mid riparian zone, chloride concentrations remained constant throughout the study period, indicating a constant source. In contrast, a change in hydrologic source was observed at the field edge. During regime R1, field inputs extended up to 11 m into the riparian zone. During the flow reversal (regime R2), groundwater chemistry indicated that field inputs were reduced to the first three meters of the riparian zone. During regime R3, the only piezometer that changed sources was the one at the field edge (T3-3), which switched back to its original (R1) source.

Interestingly, piezometers closer to the field changed sources during regime R2, while 2 piezometers further into the riparian zone continued to have intermediate chloride concentrations indicative of field inputs. These patterns are a bit counterintuitive as it would be expected that locations further from the field would first experience a source change related to a flow reversal. These patterns demonstrate the complexity of the flow paths and upland connectivity at the field-riparian interface. Another possible explanation for these patterns is the low K_{sat} values at the locations that appear to remain connected to the upland during the flow reversal (ex. 9.9×10^{-7} cm/s at G23-3). Recall that Vidon and Hill (2006) define a confining layer as having a K_{sat} of less than 10^{-6} cm/s, so perhaps these locations become disconnected from the upland but have low enough hydraulic conductivities that the field origin water is not replaced by water from other hydrologic sources during the reversal.

Table 4.2 lists the day of year that hydrologic source changes were observed at the near-field piezometers. All of the observed source changes occurred between DOY 190 and 206, more than a month after the regime change from R1 to R2. This lag time between the change in water table regime and the shift in groundwater sources might be related to the rain events during that period (which would promote slope-discharge) or may simply be related to the time it takes for the subsurface flows to respond to the shift in the hydrologic regime.

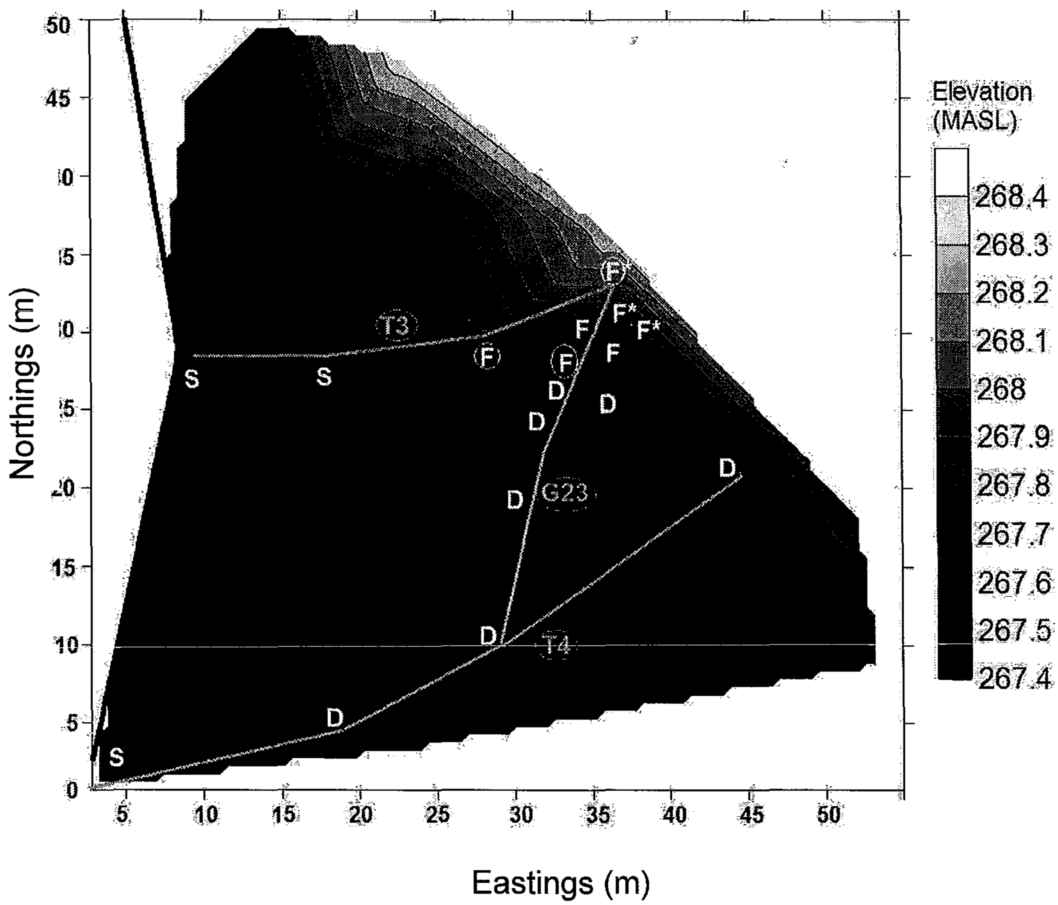

Figure 4.9 Hydrologic sources indicated by chloride concentrations at the 100 cm piezometers across the study site. F=field (8-12 mg-Cl^{-}/L), S=stream (20-30 mg-Cl^{-}/L), D=deep (3-5 mg-Cl^{-}/L), F with a circle indicates a switch to sources from depth during Regime 2. Astericks (*) indicate piezometers that went dry during regime R2.

4.4 Shallow Groundwater Movement in the Riparian Zone

Although specific flow paths through this riparian zone are expected to be complex, specific discharge rates between different points in the riparian zone are useful in understanding the dominant subsurface flow patterns at the site and how they change overtime.

Table 4.2 Date of riparian zone source change for 100 cm piezometers located near the field.

Location	**Day of recorded R2 source change (DOY)**
T3-3	201
G23-3	n/a
G12-4	n/a
G23-5	200
T3-11	190-206

Lateral specific discharge rates (q) at the field edge, in the mid riparian zone and at the stream bank along the three transects are shown in Table 4.3. Positive q values correspond with field-to-riparian groundwater flows and negative q values correspond with stream-to-riparian groundwater flows. Overall, the lateral discharge rates indicated that groundwater was not moving very quickly through the riparian zone; maximum (absolute value) lateral discharge rates in the riparian zone ranged from 1.1 x 10^{-4} to 1.2 x 10^{-6} cm/s. The largest lateral discharge rate (-1.1 x 10^{-4} cm/s) was observed in the mid riparian zone (T4-23 to T4-4 at 150 cm) during the second dam release (DR-2). This is particularly notable because outside of these events the mid riparian zone generally had very low specific discharge rates (Table 4.3). Thus, although the stream stage rises associated with the dam release occurred for brief periods of time, the elevated stream-to-field specific discharge rates that they induce may have an important impact on lateral nitrate transport through the riparian zone.

The lowest lateral specific discharge rate was observed at 150 cm at the field edge (T3-0 to T3-3) during regime R3, when inputs from the upland marsh dominated riparian hydrology and obstructed the development of strong field-to-riparian water table gradients. The largest field-to-riparian specific discharge rates at the field edge (T3-0 to T3-3) were observed during regime R1. This is not surprising, as this coincides with the time when the field-to-riparian water table gradients where highest. At the stream edge (T3-30 to T3-22), the largest stream-to-riparian specific discharge rates were observed in the spring (regime R1), when a high stream stage supported high stream-to-riparian water table gradients (Figure 4.3).

Table 4.3 Summary of maximum lateral specific discharge rates. Positive values indicate discharge from field to the riparian zone; negative values indicate discharge from the stream to the riparian zone.

Transect	End Points (m)	Depth (cm)	q (cm/s) Max (Regime)
T3	0-3	100	1.1 E-5 (R1)
		150	1.2 E-6 (R3)
	3-11	100	3.3 E-6 (R1)
	11-22	100	-4.4 E-5 (DR-2)
	22-30	100	-1.4 E-6 (R1)
		150	-4.8 E-6 (R1)
G23	3-8	100	1.1 E-5 (R1)
T4	4-23	100	-2.9 E-5 (R2)
		150	-1.1 E-4 (DR-2)

Table 4.4 shows the maximum and average vertical specific discharge rates between 150 cm and 100 cm depth at the riparian zone piezometer nests. Thus, positive and negative discharge rates are indicative of up welling and down welling groundwater, respectively (note: T3-11 is excluded because it has no piezometers at 150 cm depth). Maximum vertical specific discharge rates at the nests at the field edge and mid riparian zone along T3 were comparable to the low lateral specific discharge rates presented above. They ranged from 2.4 x 10^{-5} to 5.8 x 10^{-6} cm/s. However, at nest G23-5 and the T4 nests, the vertical specific discharge rates were orders of magnitude higher, ranging from 1.2 x 10^{-3} to 1.2 x 10^{-4} cm/s (Table 4.4). These comparatively high positive vertical specific discharge rates supports the earlier hypothesis that low chloride groundwater from depth is discharging in the mid riparian zone. These upward specific discharge rates, combined with the constant low-chloride concentrations presented above, suggest that the vertical up welling in the mid riparian zone may dominate shallow groundwater movement at this site.

Table 4.4 also shows average vertical specific discharge rates at T3-3, T4-4 and G23-8 for the different regimes. These sites are all located close to the field-riparian zone interface (see Figure 2.4 for the location of these different nests). At nest T3-3, average discharge rates were negative during regime R1, indicating downward flow, but became positive during regimes R2 and R3, which indicates an expansion of the discharge zone towards the field. This coincides with the regime R2 shift from field to other hydrologic sources that was indicated by chloride concentrations at this location (Figure 4.9). The negative discharge rates in regime R1 suggest that subsurface inputs from the upland may be diverted downward at the field edge. This is not surprising considering there is an order of magnitude drop in the maximum lateral discharge rate between 0-3 m and 3-11 m at transect T3. It is likely that lateral flow through the riparian zone is impeded due to low hydraulic conductivity soils at the field edge, which results in subsurface runoff from the field being forced downward. At nest T4-4, average discharge rates were negative for all of the regimes. This constant down welling may be due to the elevated discharge rates further along this transect. For example, in southern Ontario, Cey *et al.* (1999) found that the hydrologic contrast in discharge rates between the uplands and the riparian zone caused hydrologic flows to be diverted downward at their interface.

In contrast, the mid riparian zone was dominated by positive (upward) vertical discharge rates, whose averages ranged from 2.6 x 10^{-6} cm/s at nest T3-22 during regime R1 to 5.8 x 10^{-4} cm/s at nest G23-8 during regime R1 (Table 4.4).

Table 4.4 Vertical specific discharge rates calculated using the hydraulic heads measured at 150 and 100 cm depth at the same piezometer nest. Positive and negative values are indicative of up welling and down welling groundwater, respectively.

Nest	Regime	q (cm/s)	
		Average	Max
T3-3	R1	-1.9E-06	3.0E-06
	R2	2.5E-06	3.7E-06
	R3	1.0E-07	5.8E-06
T3-22	ALL	2.6E-06	2.4E-05
T3-30	ALL	4.6E-05	8.8E-04
T4-4	R1	-1.5E-03	-5.6E-03
	R2	-1.9E-04	-4.4E-04
	R3	-1.3E-03	-1.6E-03
T4-23	ALL	2.0E-04	3.6E-04
T4-35	ALL	2.1E-04	1.3E-03
T4-50	ALL	1.2E-04	-1.0E-03
G23-5	R1	5.8E-04	9.8E-04
	R2	2.3E-04	8.4E-04
	R3	7.8E-05	8.0E-05

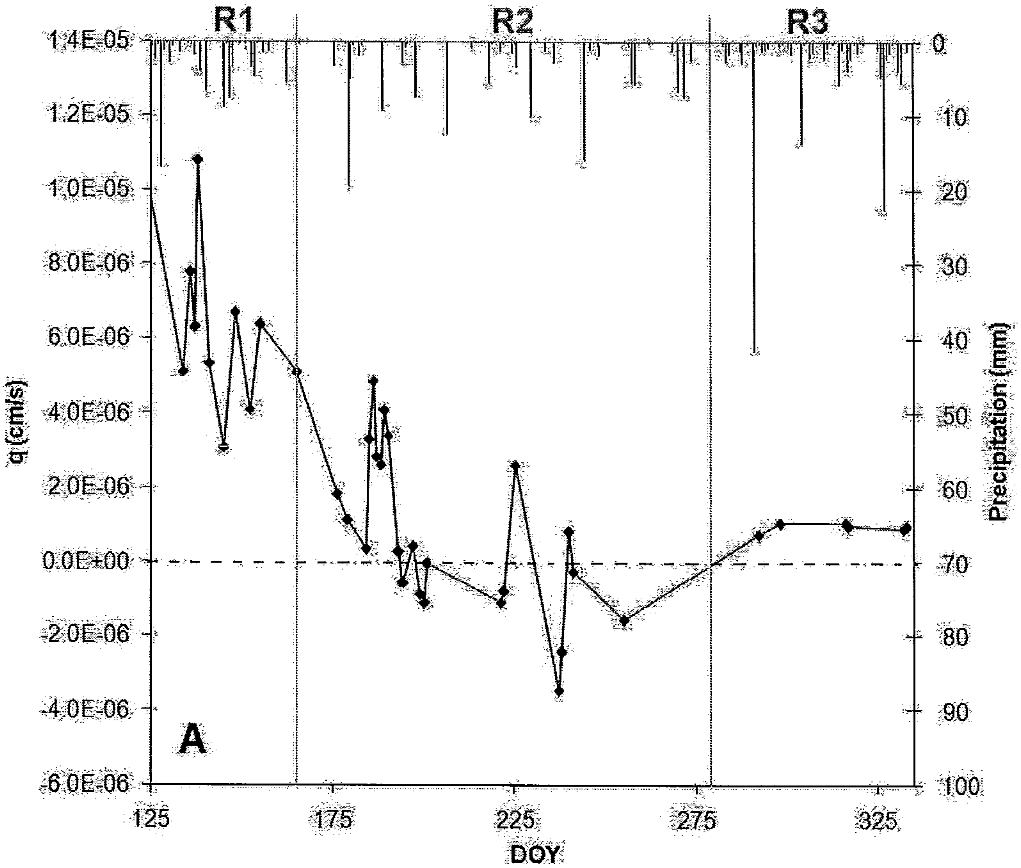

Figure 4.10a Temporal patterns in lateral (between 100 cm piezometers at T3-3 and G23-8) specific discharge rates (cm/s). Daily precipitation totals are displayed on the top of the figure. R1, R2 and R3 label the time periods of the three hydrologic regimes.

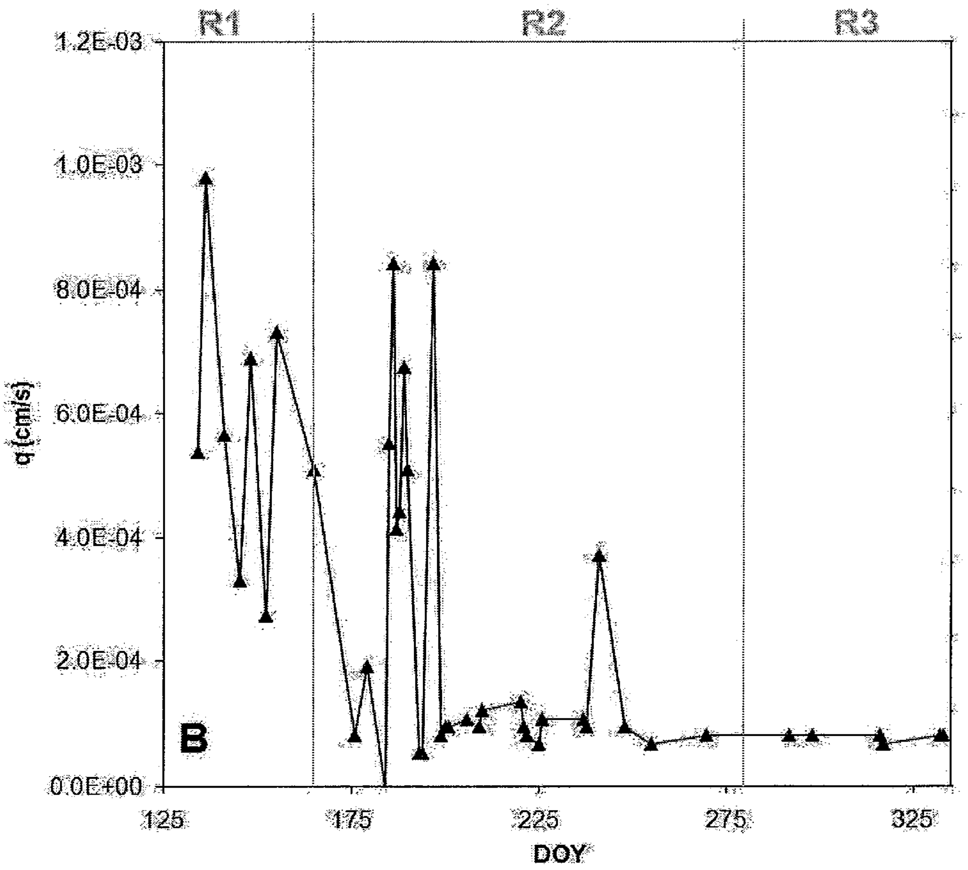

Figure 4.10b Temporal patterns in vertical (between 150 and 100 cm at G23-8) specific discharge rates (cm/s). R1, R2 and R3 label the time periods of the three hydrologic regimes.

Figure 4.10 shows an example of how the lateral and vertical specific discharge rates changed near the field over the course of the study period. The lateral discharge rates calculated between the 100 cm piezometers T3-3 and G23-8 (Figure 4.10a) started out positive (field-to-riparian flow) in regime R1, became negative (riparian-to-field flow) during the regime R2 flow reversal. During regime R3, the lateral discharge rates became positive again, but were less than those in regime R1. The vertical discharge rates at G23-8 remained positive (upward discharge) over the entire study period, but dropped in magnitude during regime R2 and remained low in R3. The fact that, during regime R3, there was a shift in the lateral discharge rates but not the vertical ones shows that this regime change impacted the field inputs and deep flow paths upwelling in the mid riparian zone differently.

The vertical and lateral discharge rates followed similar temporal patterns during regimes R1 and R2 and appeared to be influenced by rain events during this time. This is not surprising considering the hillslope response expected from the sloping uplands (Brown *et al.*, 1999; Inamdar and Mitchell, 2007). Notably the shifts in both these subsurface hydraulic gradients occur between DOY 195 and 200, which corresponds with the observed shift in hydrologic sources (Table 4.2). This further supports the hypothesis that small rain events may have delayed the timing of the source changes observed and the field edge during regime R2.

Discussion

4.5 Influence of Dam Management on Riparian Zone Hydrology

Dam management practices were an important control governing stream discharge. This research showed that the stream discharge had an important impact on the riparian zone hydrology at this site.

4.5.1 Maintenance of Stream-to-Riparian Hydraulic Gradients

At sites with unregulated streams (*i.e.* no upstream dam), it is typical for zones of groundwater discharge to extend beneath the stream and influence stream water chemistry (Puckett *et al.*, 2002; Bohlke *et al.*, 2002). At this site, water chemistry data and stream-to-riparian water table gradients showed that the stream was influent to the riparian zone throughout the study period. This corresponds to what has been found by other studies conducted along this stretch of Spencer Creek. Comparing discharge rates above and below the current study area, Young (2001) found that between April and November 2000, the section of Spencer Creek adjacent to the study site was discharging into the riparian zone.

Warren *et al.* (2001) also characterized this section of Spencer Creek as a losing stream.

In the context of this site, where regulated stream levels are maintained higher than the water table in the surrounding riparian zone, these patterns of stream discharge to the riparian zone make sense. The negative gradient that is maintained between the stream stage and riparian water table drives stream-to-riparian fluxes. These results indicate that stream regulation by the upstream dam may have an important impact on downstream groundwater systems by artificially creating a losing stream. Indeed, Duke *et al.* (2007) found that the impoundment of a second-order stream resulted in increased riparian zone groundwater recharge by the stream.

4.5.2 Reduced Water Table Draw-down

In this region, it is typical for water tables to decrease in the summer months due to high evapotranspiration rates (Warren *et al.*, 2001; Macrae, 2003). In this study, the maximum water table draw-down at the stream edge was 0.5 m less than that at the field edge. This difference, along with the "hinging" of the water table around the stream during regime R2, suggests that stream inputs limited the water table draw-down in the riparian zone. Flow reversals were also observed at this site in 2006 (Zhang, 2007), which was a normal year for precipitation compared to the long-term average. This suggests that stream seepage is an important hydrologic control at the site under a variety of conditions and not only during very dry years. Furthermore, with drier conditions expected as a result of climate change (Shriner and Street, 1998), these dry conditions may be more representative of what will be seen in the future.

4.5.3 Timing of Major Hydrologic Shifts

Several significant hydrologic shifts seen in the riparian zone were directly related to the timing of different upstream reservoir management practices. First, the start of the water table reversal was delayed by the Hamilton Conservation Authority's decision to reduce stream discharge rates on DOY 128. During this period, water table dynamics (Figure 4.2) indicated that stream stage was a dominant control on stream bank water table levels. Therefore, if the discharge rates had not been lowered, the water table in the stream bank would not have dropped and the flow reversal would have occurred earlier.

Second, the strongest stream-to-field hydraulic gradients occurred during the regime R2 in-bank floods. In non-regulated streams, in-bank floods generally correspond with large rain events (Bates *et al.,* 2000; Burt *et al.,* 2002). At this site, during regime R2, the in-bank floods only occurred when the conservation authority decided to reduce the water level in the reservoir by releasing a pulse of water in to the stream.

Third, during the fall wet-up, the Hamilton Conservation Authority lowered the dam by removing the stoplogs, which resulted in water spilling over the dam into the stream when it rained (at other times of year, stream discharge was regulated by a valve and was not responsive to rain events). This unregulated stream discharge had a significant influence on temporal water table patterns in the riparian zone; however, it is unclear how important it was in establishing the dominance of the marsh on riparian zone hydrology during this period.

These results suggest that spatio-temporal hydrology patterns at this riparian zone could be vastly different depending on the management practices followed at the upstream reservoir.

4.5.4 Field-to-Stream Flow Paths

Specific discharge rates and groundwater chloride concentrations showed that the extent of field inputs to the riparian zone were reduced during the regime R2 flow reversal. Despite this, the changing hydrologic regimes did not substantially alter shallow field-to-stream flow paths. Throughout the study period, upward specific discharge rates were orders of magnitude higher than lateral specific discharge rates. Furthermore, regardless of hydrologic regime, the mid riparian zone was dominated by the upwelling of groundwater, which had a chloride signature distinct from the field and stream inputs. This robust mid riparian discharge zone acts as a hydraulic barrier to the lateral transport of field inputs through the riparian zone to the stream (Figure 4.9). Cey *et al.* (1999) also found that the riparian zone can act as a hydraulic barrier to the transport of field inputs to the stream. These patterns suggest that the hillslope and stream would have been hydrologically disconnected regardless of flow reversals and the influent stream caused by the maintenance of an elevated stream stage.

4.6 Complex Hydrogeologic Setting

There were three major hydrologic regimes observed over the study period: 1) field dominated, 2) stream dominated, and 3) marsh dominated. Many other studies have reported riparian zone flow reversals when upland inputs are limited (Burt *et al.*, 2004; Vidon and Hill, 2004a). Furthermore, other riparian studies have shown that water table gradients can run oblique rather than perpendicular to the stream (*e.g.* Duval and Hill, 2006). However, this is the first study to report three distinct hydrologic regimes in the same riparian zone.

The impact of the upstream marsh on riparian zone hydrology as well as the major influence of the stream regulation on major hydrologic shifts at the site demonstrate the need to understand the hydrogeologic context of the riparian zone under study. Cey *et al.* 1999 emphasized this concept in their paper that found that tile drainage in an adjacent field had a large impact on groundwater flow paths in the riparian zone.

Vidon and Hill (2004) defined hydrogeologic setting as "...surface and groundwater flows as well as geologic characteristics such as topography, stratigraphy and hydraulic properties of soils and underlying materials that influence water flow and chemistry". The results presented in this chapter show that this reach of Spencer Creek is located in a complex hydrogeologic setting. For example, groundwater inputs varied much in space and time, and hydrologic properties of the subsurface materials (*e.g.* K_{sat}) showed high spatial variability. Furthermore, linkages to the upland marsh, rain events and management practices at the upstream reservoir add to the hydrologic variability of the site. Thus, it seems appropriate that the definition of hydrogeologic setting should be expanded to explicitly consider the impact of human manipulation of surface and groundwater flows (*e.g.* dams, tiled drainage) and connectivity to other nearby hydrologic features (*e.g.* marsh).

4.7 Conceptual Model Evaluation

As described in Chapter 1, Vidon and Hill (2004) developed a conceptual model linking upland depth of permeable sediments and topography to riparian zone hydrologic functioning (Figure 4.11).

This study site has more than 6 m of permeable upland soils and topography less than 5% at the riparian-upland interface. Therefore, it falls in the upper left-hand quadrant of the conceptual model diagram (Figure 4.11); which describes the expected hydrological characteristics of the site:

- variable groundwater flows with no flow reversals,
- upland inputs are continuous small to moderate flows, and
- water table variations ranging from 0.5 to 1.5 m.

Observations at this study site do not support such characterizations. First, this site had an extended (3.5 month) flow reversal during this study period (2007). Second, during the flow reversal, hillslope inputs were switched off at some locations. Thus, upland inputs were not continuous throughout the study period.

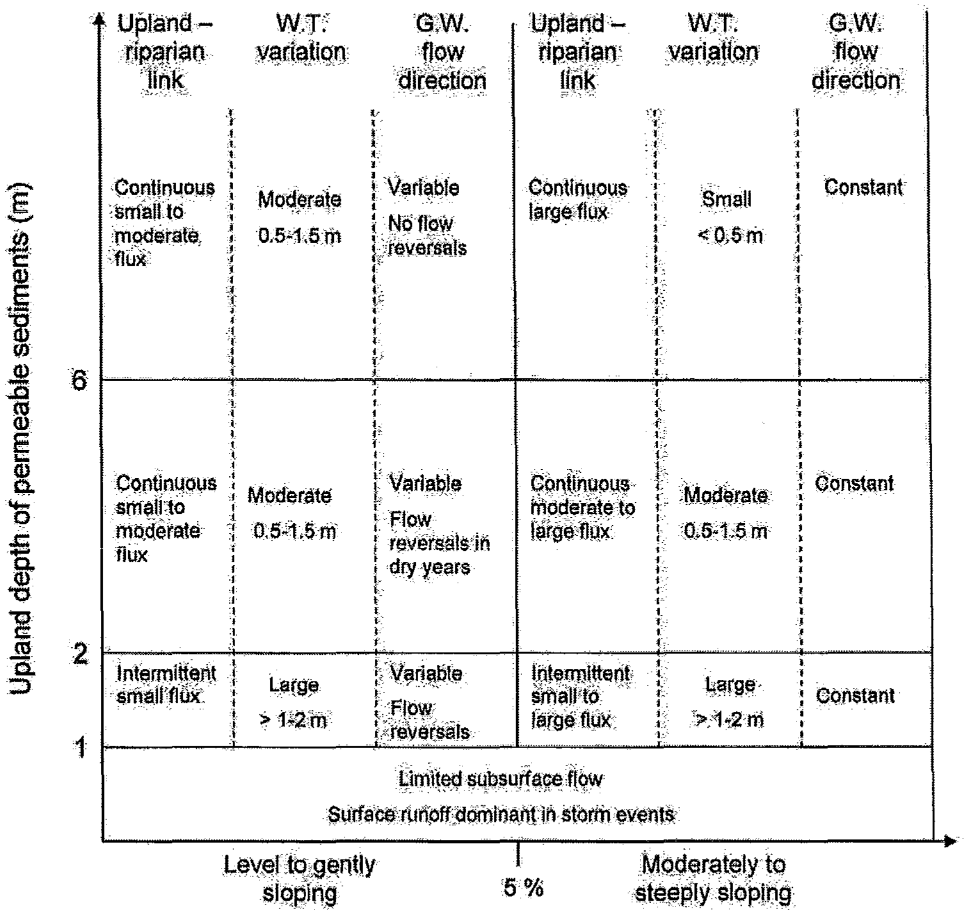

Figure 4.11 Conceptual model linking upland depth of permeable sediments and topography to riparian zone hydrologic functioning (from Vidon and Hill (2004b)).

The water table draw-down did fall within the range observed by Vidon & Hill (2004b); however, the extent of the draw-down was not controlled by the connection to a large upland aquifer, but by stream water inputs into the riparian zone.

Comparing the hydrologic categorizations of Vidon & Hill with the hydrologic results of the present study shows that there is an opportunity to improve this model by including other significant hydrologic controls in the landscape such as upstream dams.

4.8 Summary

These results suggest that management practices at the upstream dam had a significant impact on riparian hydrology. Furthermore, in addition to field and stream inputs, the results showed that there were also deeper flow paths discharging in the mid riparian zone. Three distinct hydrologic regimes were observed in the riparian zone, depending on the relative hydrologic importance of the stream, field and marsh during the study period. These hydrologic shifts impacted groundwater flow patterns and the spatial distribution of hydrologic sources in the riparian zone—particularly the extent of field inputs to the riparian zone. Regardless of hydrologic regime, however, the mid riparian discharge zone remained a dominant control on riparian zone hydrology and acted as a hydrologic barrier to field-to-stream connectivity.

5 Influence of Stream Regulation on Spatio-Temporal Riparian Zone Nitrate Patterns

This chapter builds on the hydrology presented in Chapter 4 to address the second question of this thesis: Does the upstream dam influence shallow groundwater nitrate patterns in the riparian zone?

The results are presented in four main sections. First, nitrate, chloride, sulphate and dissolved oxygen (DO) concentrations are examined along a key study transect (G23) to explore how redox conditions and hydrologic flow paths influence nitrate concentrations in shallow groundwater under the first hydrologic regime (R1) (Section 5.1). Next, plots comparing sulphate and nitrate concentrations in groundwater are used to understand what is driving the temporal nitrate patterns at the site (*i.e.* biological removal *vs.* change in hydrologic source) (Section 5.2). The distribution of the different nitrate patterns measured at all the piezometers at the site are subsequently presented to place these patterns in the physical context of the site (Section 5.3). Following this, to help identify possible denitrification hot spots at the site, denitrification potential incubation results are presented and discussed in the context of the nitrate removal patterns seen at the site (Section 5.4).

Finally these results are discussed in terms of nitrate inputs to the riparian zone, groundwater nitrate removal and the riparian zone's role in protecting the stream from upland nitrate inputs. The applicability of Vidon and Hill's (2004c) conceptual model linking landscape features to riparian zone nitrate removal patterns is also evaluated.

Results

5.1 Spatial Groundwater Chemistry Patterns

Groundwater chemistry (nitrate, sulphate, chloride and DO) is spatially variable throughout the riparian zone. This is demonstrated by examining the regime R1 groundwater chemistry at 100 cm depth along transect G23 (Figure 5.1), which follows the topographic gradient from the field edge to the mid riparian zone. From the figure, it can be seen that there are distinct water chemistry signatures at the field edge, mid riparian zone and the stream. Recall that transect G23 does not extend all the way to the stream bank (Figure 2.4), which is why the influence of stream inputs is not seen in the groundwater chemistry presented here. In the following discussion, the term "mid riparian zone" will be used to refer to the piezometers from 10 m to 30 m along transect

G23, and the term “transition zone” will be used to refer to the piezometers at 6 m and 8 m from the field.

At the field-riparian zone boundary, average nitrate, chloride, and sulphate concentrations were 94.3, 9.5, and 10.7 mg/L, respectively. DO concentrations were >3 mg/L, indicating that groundwater is oxic in this section of the riparian zone. Several changes were observed over the distance from 3 m to 8 m from the field edge. Chloride and sulphate concentrations remained constant within this section of the transect; however, nitrate concentrations decreased by over 30 mg/L across this zone.

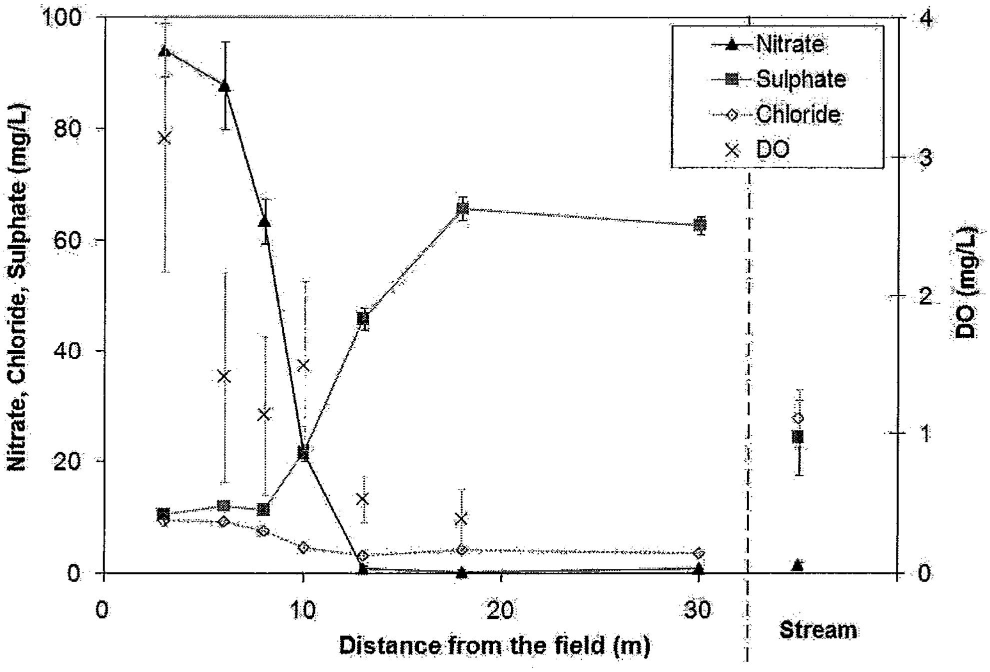

Figure 5.1 Average regime R1 groundwater chemistry (nitrate, chloride, sulphate and DO) at the 100 cm piezometers along transect G23 compared to average stream water chemistry (nitrate, chloride and sulphate) for all three regimes. The error bars show standard deviation and are sometimes too small to be seen over the data point markers. Note that DO concentrations are on the right-hand axis.

Hydrometric data (presented in Chapter 4, Figure 4.8) demonstrates that there was a field-to-stream gradient between 3 and 8 m during regime R1. These groundwater chemistry patterns suggest that biological nitrate removal may have occurred as field inputs traveled into the riparian zone. Indeed, DO concentrations <2 mg/L at 6 m and 8 m show that that redox conditions could support denitrification along this flow path. At the field edge (3 m), average DO concentrations were >3 mg/L, thus the decrease in DO below 2 mg/L at 6 m suggests that residence times were long enough for microbial respiration to use up DO in the groundwater. This coincides with the low lateral specific discharge rates (10^{-5} cm/s) calculated between 3 and 8 m in Chapter 4 (Table 4.3).

At a distance of 10 m from the field edge, chloride concentrations dropped below 5 mg/L, suggesting a change in hydrologic source. This is consistent with the spatial distribution of high and low chloride hydrologic sources presented in Chapter 4 (Figure 4.9). Interestingly, despite the change in source indicated by the drop in chloride, nitrate concentrations at 10 m remained above 20 mg/L. This suggests that the field may not be the only source of nitrate inputs to this riparian zone.

Between 10 and 18 m from the field edge, sulphate concentrations increased by over 50 mg/L, while chloride concentrations remained in a relatively constant low range. Low nitrate and DO concentrations from 13 m to 30 m suggest that redox conditions would support the reduction of sulphate. This is supported by the smell of H_2S observed during water sampling at this portion of the transect. Therefore, it is unlikely that sulphate was being produced in the riparian zone at this time.

The data shown here demonstrate a large degree of spatial variability in groundwater chemistry that appears to be driven by a combination of variable hydrologic sources and biological processes. Spatial variability across floodplains and riparian zones has been observed in other systems. For example, studies at other locations have found that groundwater discharging closer to field edges had shorter aquifer residence times than those closer to the stream banks (Bohlke *et al.*, 2002; Puckett *et al.*, 2002). In those studies, groundwater chemistry patterns were largely explained by the different ages and flow paths of the groundwater discharging in different locations in the riparian zone. The high vertical specific discharge rates measured at the nests at 8 and 30 m indicate that this portion of the G23 transect is likely a discharge zone. Thus, these mid riparian zone sulphate patterns may indicate different flow paths discharging at different distances into the riparian zone.

Furthermore, Boelke (2002) found that increased sulphate concentrations in the mid riparian zone in their study were the result of pyrite (FeS_2) supported (autotrophic) denitrification in the up-gradient aquifer. If the constant range of chloride concentrations between 10 and 30 m indicates a shared groundwater recharge zone, then the nitrate concentrations above 20 mg/L at 10 m suggest that, although nitrate concentrations are less than 2 mg/L from 13 m to 30 m, they may have been higher at the beginning of the flow path. Indeed it would not be surprising for groundwater recharge in an agricultural catchment such as this to have elevated nitrate concentrations. After 150 years of farming, groundwater in the area is often contaminated with nitrate concentrations greater than the 44.3 mg/L drinking water standard (Robertson, 1996). Furthermore, the sulphur content in Wentworth till at several study sites in southern Ontario (0.03% sulphur by weight) has been found to support autotrophic denitrification, which resulted in increased pore water sulphate concentrations (Robertson *et al.*, 1995). Furthermore, in a nearby riparian zone that shares the same upland area (Figure 2.2), $Fe(OH)_3$ deposits were observed on the outside of a piezometer that had overflowed. The groundwater samples collected from this piezometer had similar low chloride, low nitrate and high sulphate concentrations as that seen in the groundwater upwelling in the mid riparian zone in this study (DeSimone, 2009). This provides evidence of elevated Fe^{2+} concentrations in deep flows, which would be consistent with groundwater chemistry impacted by autotrophic denitrification (Equation 3). More research is required to confirm autotrophic denitrification at this site, but these results suggest that this process could be an important control on nitrate concentrations in the deep flow paths upwelling in the mid riparian zone.

Figure 5.2 presents a conceptual diagram of the dominant subsurface flow paths that appear to be discharging in the riparian zone. The riparian zone received hydrologic inputs from the hillslope, the stream, and deep flows discharging in the floodplain. Specific discharge rates at the field edge suggested that a portion of the hillslope groundwater fluxes might be diverted downward at the field-riparian boundary.

5.2 Temporal Nitrate Patterns in Shallow Groundwater

A wide range of temporal nitrate concentration patterns were observed at the study site. At different locations, nitrate concentration changes were controlled by either shifting hydrology, biogeochemical transformations (denitrification), or a combination of the two. The large differences in sulphate concentrations (compared to chloride) between different sources and between different deep flows discharging in the mid riparian zone (Figure 5.1) made sulphate an important tool for understanding these complex temporal nitrate patterns.

The spatial patterns presented above suggest that a change in chloride and sulphate concentrations will indicate a shift in hydrologic source (*i.e.* intermediate chloride discharge from the field *vs.* low chloride discharge from deeper flow paths), but that only a change in sulphate will accompany shifts between the

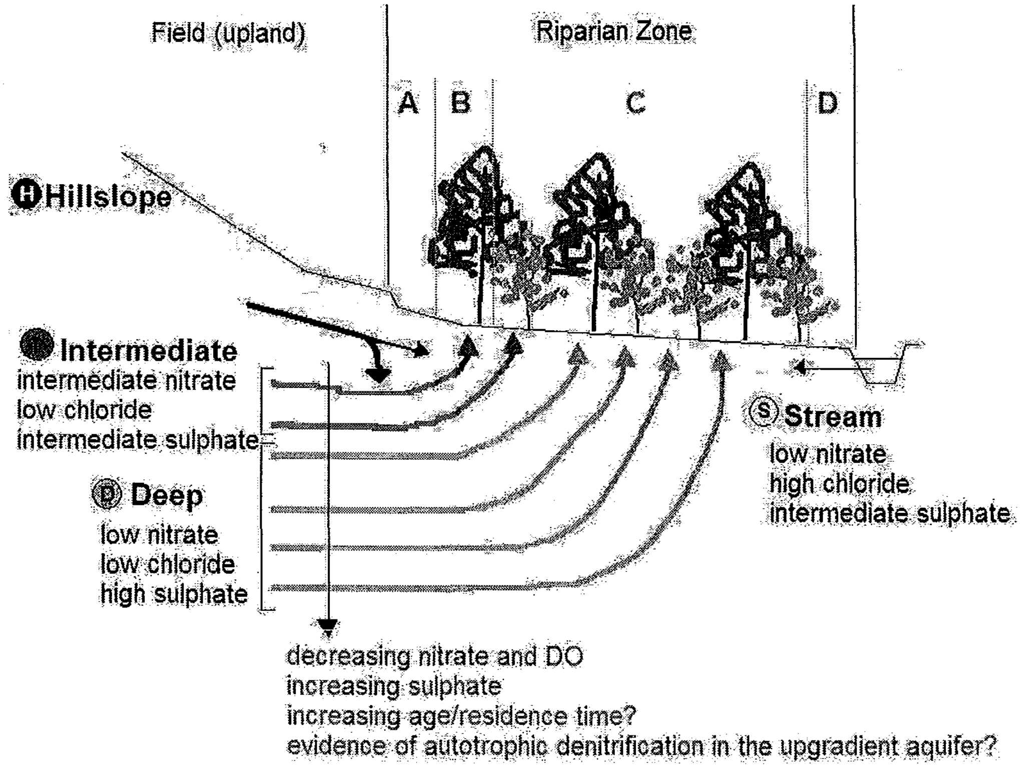

Figure 5.2 A conceptual diagram of the dominant subsurface flow paths that appear to be discharging in the riparian zone. H=hillslope inputs (black), i=intermediate flows (dark grey), D=deep flows (light grey), S=stream inputs (white). The riparian zone is divided into 4 sections: field edge (A), transition zone (B), mid riparian zone (C), and stream bank (D).

deeper flow paths. This is important because some of the deeper low chloride flows discharging in the riparian zone have elevated nitrate concentrations (*e.g.* G23-10) and others do not (*e.g.* G23-13). Thus, if nitrate dynamics were only analyzed using chloride as a tracer, nitrate decreases resulting from a change from a intermediate to low nitrate flow paths could be incorrectly attributed to biological removal processes such as denitrification (a decrease in nitrate would be observed with relatively constant chloride). At this site, considering the groundwater concentration patterns discussed above (Section 5.1), denitrification would be indicated by decreasing nitrate concentrations with constant sulphate and chloride concentrations. It should be noted that, at this research site, constant sulphate concentrations in space or time always coincide with constant chloride concentrations.

Sulphate-nitrate plots have been used in other studies to analyze water chemistry evolution with timc in complex hydrologic settings (*e.g.* Tarits *et al.*, 2006; Grimaldi *et al.*, 2004) and also proved useful in evaluating complex nitrate patterns at this site. To analyze the different nitrate patterns observed along the topographic gradient from the field edge to the mid riparian zone, Figures 5.3 , 5.4 and 5.5 present the temporal nitrate-sulphate dynamics observed at the 100 cm piezometers located along transect G23. The following section uses the sulphate-nitrate plots to demonstrate five distinct temporal nitrate concentration patterns that will be summarized after the data are presented.

Figure 5.3 shows the nitrate and sulphate averages and standard deviations for regimes R1-R2 (black crosses) and for regime R3 (grey crosses) at the 100 cm piezometers located at the field edge (T3-3) and in the mid riparian zone (G23-10, G23-13 and G23-18). Dashed squares are used to group water chemistry data from the same location. During regimes R1 and R2, the sulphate and nitrate patterns followed the same patterns seen in Figure 5.1 (*i.e.* sulphate increasing and nitrate decreasing with distance from the field). As per the discussion above, these ranges represent the sulphate-nitrate signatures of field inputs (T3-3) and of distinct flow paths upwelling in the mid riparian zone (G23-10, G23-13 and G23-18).

As expected from the chloride patterns described in Chapter 4 (Table 4.2), source change was observed at T3-3 on DOY 201. This source change resulted in a decrease in nitrate concentrations from 91.7 to 28.1 mg/L and an increase in sulphate concentrations from 12.0 to 17.1 mg/L (Figure 5.3). These water chemistry patterns appear to be moving toward those seen at G23-10. There is only one data point available for this period of disconnection from field inputs because the DOY 201 water sample was the last taken before the piezometer (T3-3) became dry. On DOY 238, which corresponds with the second dam release (DOY 235-244) and a 12 mm rain event (DOY 235-237), water table levels at the field edge increased enough for groundwater samples to be taken at T3-3. On this day, nitrate and chloride concentrations increased to 70.2 mg/L and 8.0 mg/L, respectively, while sulphate concentrations decreased to 11.0 mg/L. Thus, the water chemistry moves closer to that seen at T3-3 during regime R1-R2, which suggests that this location received field inputs during this water table rise. This corresponds with the increase in lateral specific discharge rates observed on this date (see Figure 4.10 in Chapter 4), and suggests that the hillslope groundwater runoff processes associate with the rain event dominated groundwater inputs at this location despite the in-bank flood event. During Regime R3, the increase in chloride and nitrate concentrations showed that T3-3 became reconnected to hillslope inputs.

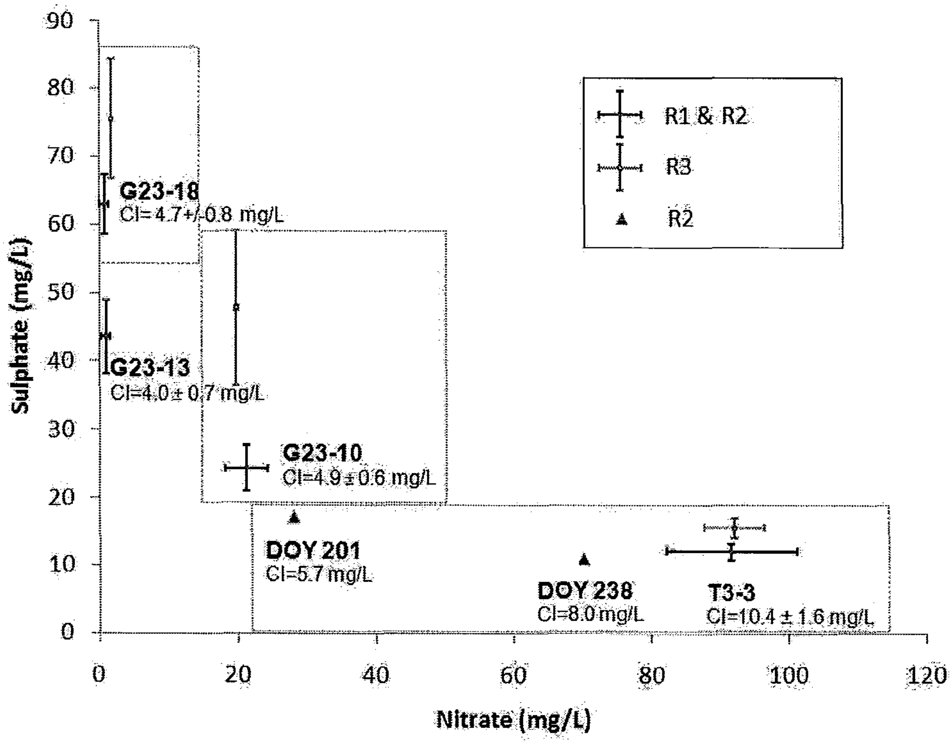

Figure 5.3 Average nitrate and sulphate concentrations for regimes R1-R2 (black crosses) and regime R3 (grey crosses) at T3-3, G23-10, G23-13 and G23-18 (100 cm depth). Error bars show standard deviation. Dashed squares group water chemistry data from the same location. Regime R1-R2 chloride concentration averages with standard deviations (mg/L) are provided to help interpret the nitrate-sulphate patterns. Single data points (black triangles) are used to show regime R2 changes observed at R3. Note that during regime R3, G23-13 sulphate concentrations were over 100 mg/L and are not shown on this figure.

At the field edge (T3-3) and in the mid riparian zone (G23-10, G23-13 and G23-18), Figure 5.3 shows that sulphate concentrations increased during regime R3, while nitrate concentrations remained in a similar range to those in regime R1-R2. On DOY 292 (regime R3), sulphate at G23-13 was 125 mg/L, more than double the regime R1-R2 average. Furthermore, a one-tailed t-test (α=0.05) showed that average regime R3 sulphate concentrations at the other locations were significantly different than those in regimes R1-R2. At a nearby location in Beverly Swamp, Warren *et al.* (2001) also reported sulphate increases during the 1999 fall wet up after drought conditions (precipitation was 26% less than the 30-year normal). They attributed these sulphate increases to the mobilization of sulphate that accumulated in unsaturated soils due to the oxidation of sulphide during the water table drawdown. This is a reasonable explanation for the regime R3 sulphate increases observed in this study, as regime R3 corresponds with the fall wet-up period following a dry summer and began with a rapid increase in water table levels.

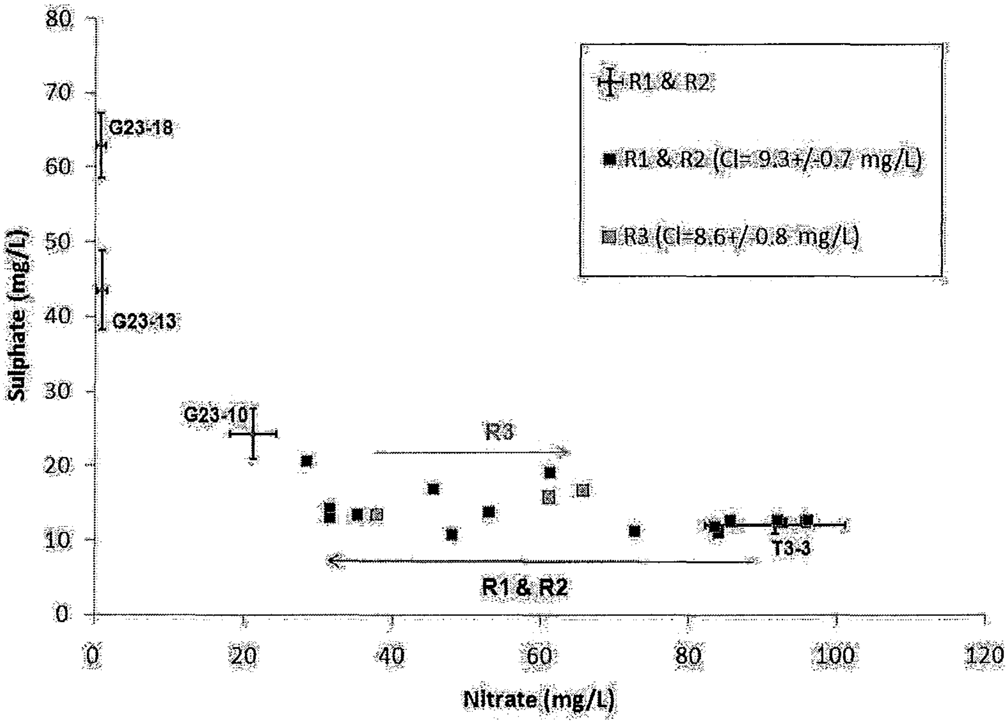

Figure 5.4 Nitrate and sulphate dynamics at G23-6 (100 cm). Individual measurements are shown and arrows are used to show the general temporal trends. Chloride concentration averages and standard deviations over the different hydrologic regimes are provided to support the analysis. To provide context to these patterns, the R1-R2 sulphate-nitrate signatures (black crosses) at the field edge (T3-3) and mid riparian zone (G23-10, G23-13 and G23-18) are also shown on the figure.

Nitrate concentration patterns at piezometers in the transition zone (G23-6, G23-8) were more complex than those at the field edge and mid riparian zone, so individual data points were used along with arrows to show nitrate-sulphate trends over time (Figure 5.4 and Figure 5.5). In order to help distinguish between hydrologic shifts and biological removal, the sulphate-nitrate signatures (*i.e.* R1-R2 averages and standard deviations) of the field inputs (T3-3) and of the different flow paths discharging in the mid riparian zone (G23-10, G23-13, G23-18) were included on the figure. Large changes in field origin nitrate concentrations were observed at G23-6 (Figure 5.4). During regimes R1 and R2, nitrate concentrations at this piezometer dropped from 95.7 to 35.3 mg/L, while chloride and sulphate concentrations remained relatively constant. During regimes R1 and R2, DO concentrations were <2 mg/L, indicating that denitrification may be a removal mechanism affecting nitrate concentrations at this location (recall that this location has very low hydraulic conductivity and thus low specific discharge rates and long residence times).

During regime R3, nitrate concentrations at piezometer G23-6 (Figure 5.4) increased while sulphate and chloride concentrations were not significantly different (t-test, α=0.05) from those measured in regimes R1 and R2. This increase corresponded with an increase in average DO to 5.9 mg/L (data not shown), which may explain why nitrate values did not decrease after their initial increase (*i.e.* redox conditions are not conducive to denitrification). Regime R3 began with the largest rain event of the study period (Figure 4.1); therefore, these patterns suggest that large rain events may be important in moving nitrate and DO rich water from the adjacent field into the riparian zone.

At piezometer G23-8 (Figure 5.5), nitrate decreases were the result of both denitrification and shifting hydrologic sources and flow paths. Before DOY 201, nitrate concentrations decreased while sulphate and chloride concentrations remained constant. During this time, average DO concentrations were <2 mg/L, indicating that these nitrate patterns were being driven by denitrification. On DOY 201, as was discussed in Chapter 4, chloride concentrations dropped indicating a change in hydrologic source. After DOY 201, nitrate decreases corresponded with constant chloride and increasing sulphate (Figure 5.5). These water chemistry patterns followed the signatures of the different flow paths discharging in the mid riparian zone. Therefore, these nitrate-sulphate dynamics suggest that the flow paths discharging at that location are changing over time. A jump in sulphate concentrations was observed with the change from regime R2 to R3, while nitrate and chloride concentrations remained relatively unchanged. These patterns suggesting that this location was also influenced by the mobilization of sulphate during the fall wet up.

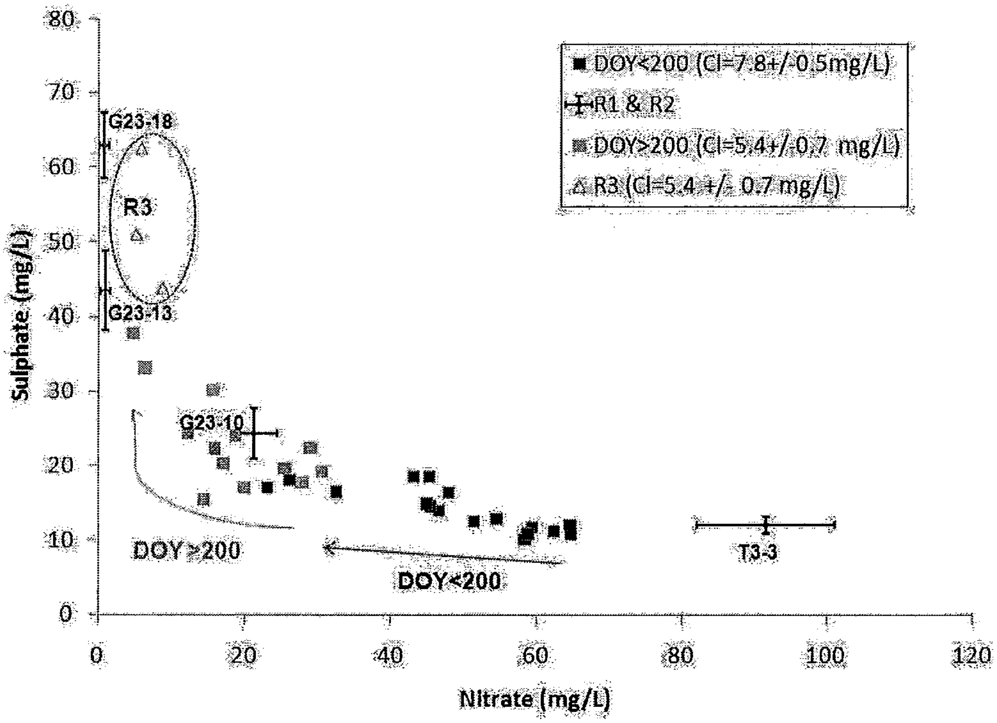

Figure 5.5 Nitrate and sulphate dynamics at G23-8 (100 cm). Individual measurements are shown and arrows are used to show the general temporal trends. Chloride concentration averages over certain time periods are provided to help indentify source changes. Data points that are circled do not show any particular temporal trend. To provide context to these patterns, the R1-R2 sulphate-nitrate signatures (black crosses) at the field edge (T3-3) and mid riparian zone (G23-10, G23-13 and G23-18) are also shown on the figure.

In summary, five distinct temporal nitrate concentration patterns were identified at the 100 cm piezometers along transect G23:

1. Generally high nitrate due to hillslope inputs. Regime R2 nitrate drop due to source change (T3-3) to lower nitrate fluxes from depth.

2. Hillslope nitrate inputs decreasing due to denitrification (G23-6).

3. Hillslope nitrate inputs decreasing due to denitrification. Regime R2 nitrate decreases due to source change followed by changing flow paths discharging at this location (G23-8).

4. Relatively constant intermediate nitrate concentrations throughout the study period due to intermediate nitrate inputs from depth (G23-10).

5. Low nitrate concentrations (< 2 mg/L) throughout the study period due to low nitrate inputs from depth (G23-13, G23-18, G23-30).

The results show that in addition to the shifts in hydrologic sources indicated by chloride concentration patterns (Table 4.2), shifting flow paths and biological removal also impact temporal nitrate patterns at the site. At field edge and transition zone, the relative importance of hydrologic *vs.* biogeochemical controls varied substantially from piezometer to piezometer. This is not surprising given the large differences (*i.e.* over four orders of magnitude) in hydraulic conductivity seen along transect G23. To further investigate different controls on nitrate biogeochemistry, these patterns were examined within the broader context of the study site.

Figure 5.6 summarizes the hydrologic and biogeochemical controls responsible for the five different temporal nitrate patterns observed at the site. The changing hydrologic regimes affected shallow nitrate patterns by changing the nitrate sources at the field edge and transition zone. During regime R1, high-nitrate hillslope inputs dominated. Whereas, during the flow reversal in regime R2, intermediate-nitrate inputs from depth became more important. During regime R3, the dominance of hillslope inputs returned at the field edge but not in the transition zone. Denitrification hot spots were limited to a narrow band in the transition zone (Figure 5.6) and appeared to be influenced by changes in hydrologic sources (evidence of denitrification was only seen with field origin water) and large rain events, which increase discharge rates from the upland and allowed high DO groundwater to reach the denitrification zone. Throughout the study period, regardless of hydrologic regime, the mid riparian zone was dominated by low nitrate inputs from depth (Figure 5.6). This discharge zone provided a robust hydraulic barrier to field-to-stream groundwater transport.

5.3 Spatio-temporal Nitrate Patterns

The five temporal nitrate patterns identified above (Section 5.2) were seen at multiple locations and depths (50 cm, 100 cm, and 150 cm) throughout the riparian zone (Figure 5.7 and Figure 5.8). For all depths, piezometers with similar nitrate patterns were grouped roughly in succession moving away from the field along the topographic gradient. High nitrate groundwater concentrations (Pattern 1) were clustered near the field edge at ground surface elevations >267.8 MASL. Between 267.65 - 267.8 MASL elevation, there was a band of piezometers where field nitrate inputs were removed by denitrification (Patterns 2 and 3) followed by a group of piezometers with intermediate nitrate concentrations (Pattern 4). In the mid riparian zone, where topography flattened out (<267.65 MASL) groundwater nitrate concentrations were always below 2 mg/L (Pattern 5), due to the dominance of a low nitrate source upwelling in this area and the fact that stream inputs also had nitrate concentrations below 2 mg/L (Figure 5.1).

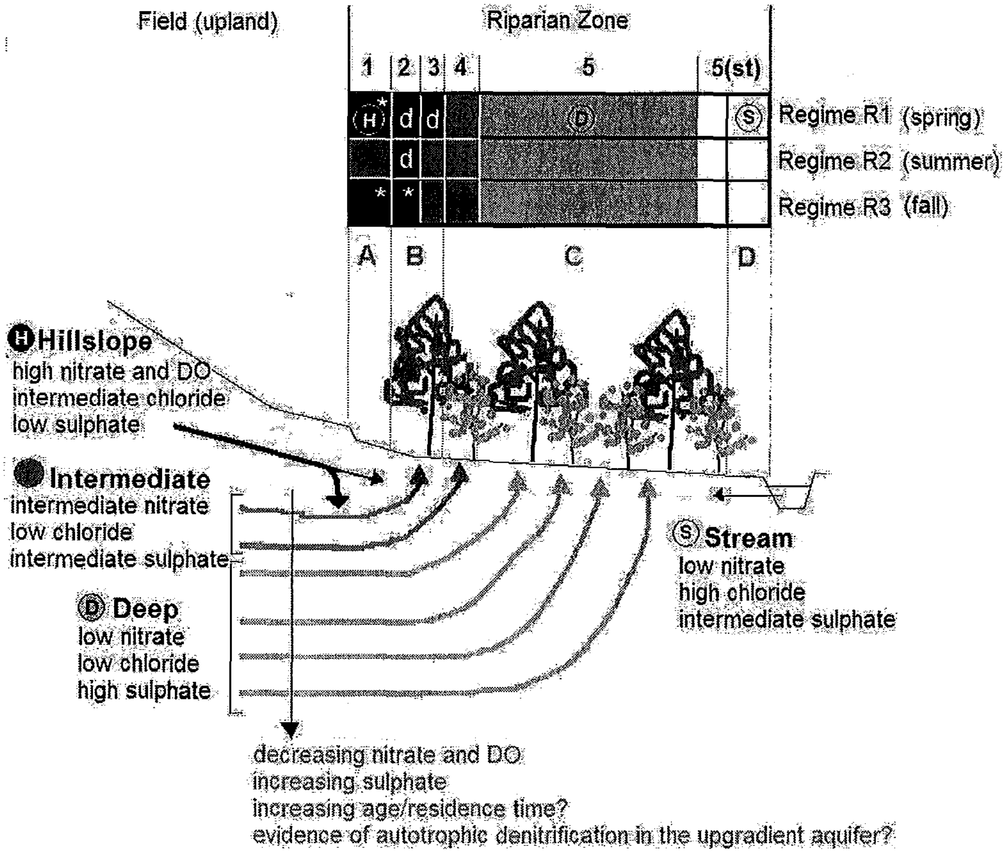

Figure 5.6 Summary of the hydrologic and biogeochemical controls responsible for the five different temporal nitrate patterns observed at the site. H=hillslope inputs (black), i=intermediate flows (dark grey), D=deep flows (light grey), S=stream inputs (white). The five temporal nitrate patterns are labelled across the top and the riparian zone is divided into 4 sections: field edge (A), transition zone (B), mid riparian zone (C), and stream bank (D). The "d" indicates a denitrification hot spot and the * indicates locations where DO > 2mg/L.

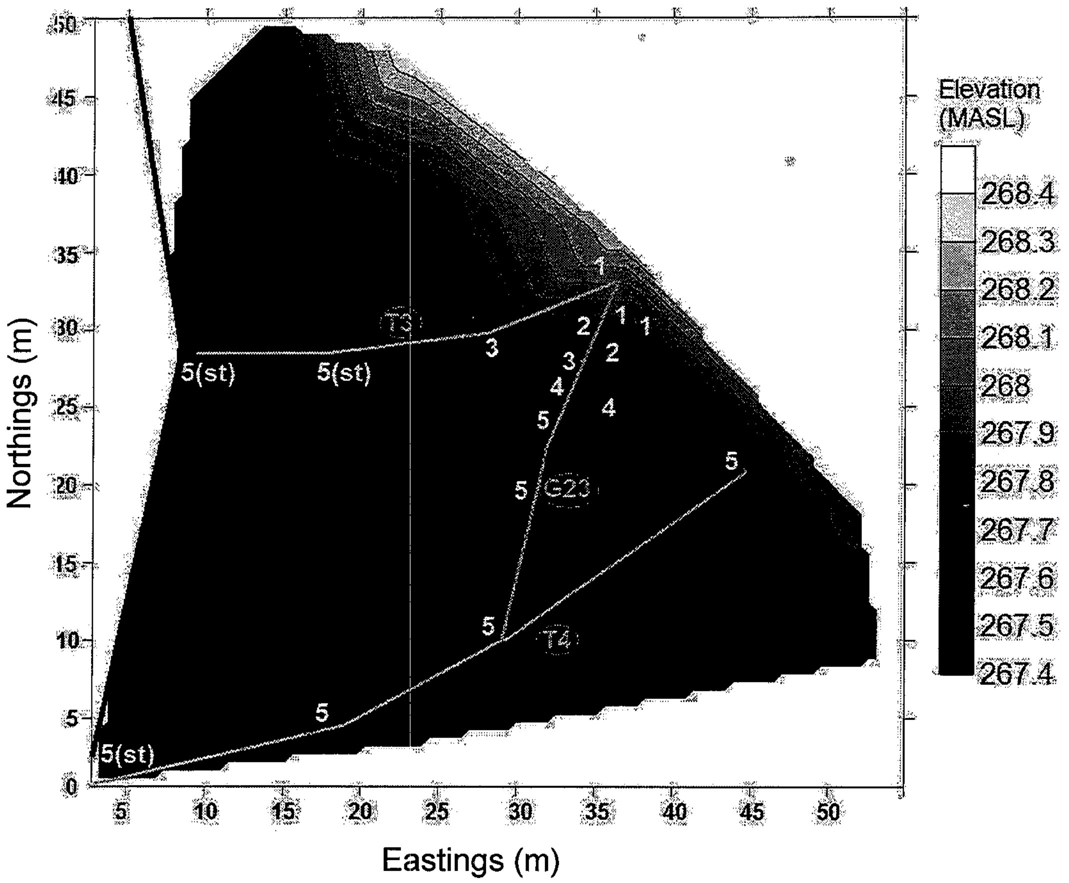

Figure 5.7 Topographic map showing the 100 cm piezometers labelled by their type of nitrate behaviour over the study period (see text for description of the 5 behaviour types). Piezometers that show evidence of stream influence (high Cl concentrations) are marked with "st".

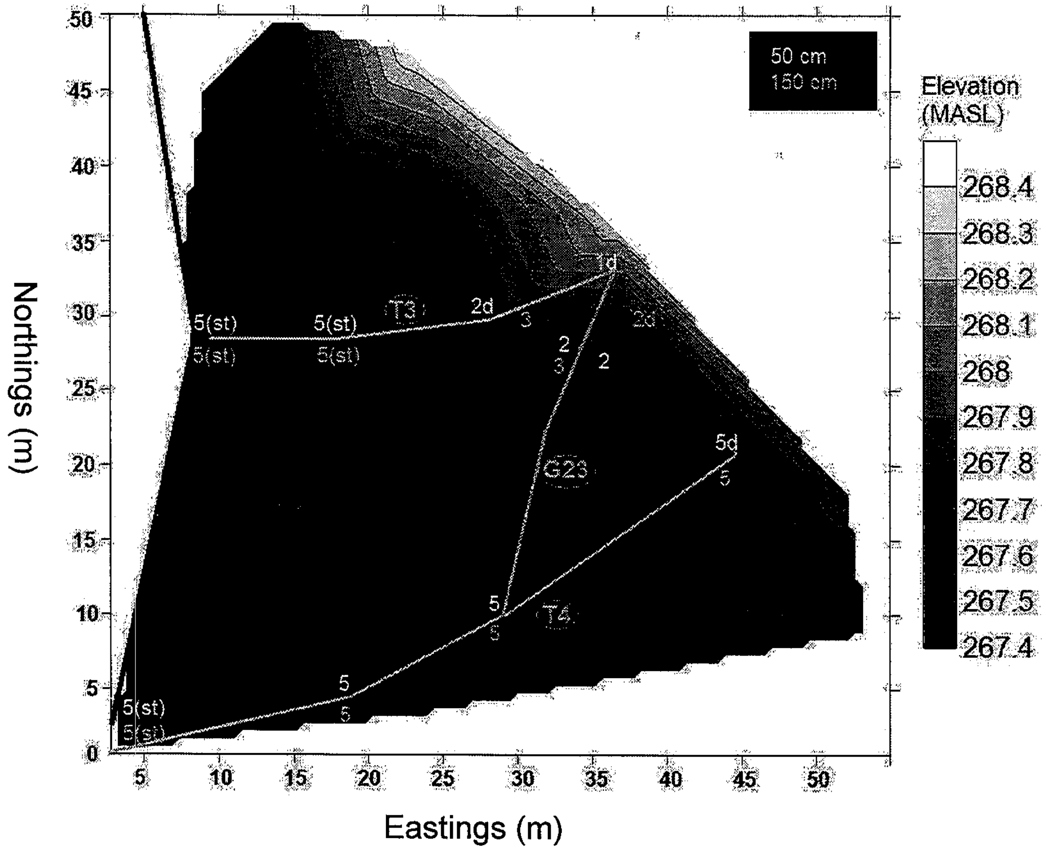

Figure 5.8 Topographic map showing the 50 cm and 150 cm piezometers labelled by their type of nitrate behaviour over the study period (see text for description of the 5 behaviour types). Locations that have evidence of rainwater dilution have a "d" beside their behaviour number. Piezometers that show evidence of stream influence (high Cl concentrations) are marked with "st".

Figure 5.8 also shows the 50 cm piezometers which had evidence of dilution. As was discussed in Chapter 4, rainwater dilution may occur at the field edge where there is no canopy interception. Indeed the 50 cm piezometers near the field edge that did not show evidence of dilution were under the canopy of trees along G23 and those that did were out in the open.

These patterns show that a wide range of hydrologic and biogeochemical controls are influencing nitrate dynamics within a relatively small area near the field edge. This is not surprising considering the high degree of heterogeneity of the soils/sediments and related hydraulic conductivity (Figures 4.6 and 4.7) in this area. As was discussed in Chapter 2, the “step” from the field into the riparian zone likely accumulates finer sediments that have been transported down gradient by erosion processes in the field. As a result, it is not surprising that the distribution of nitrate controls at the field edge seem to follow the topographic gradient.

5.4 Spatio-temporal Patterns in Denitrification Potential

In several locations, groundwater chemistry patterns indicated that denitrification was responsible for the observed nitrate decreases for a portion of the study period. In order to better understand the spatio-temporal distribution of denitrification potential (DEA) at the site, soil slurries amended with excess nitrate and carbon were incubated under an acetylene-helium atmosphere. Under these conditions, N2O production is considered to be directly proportional to the active population of denitrifiers in the sample (Groffman et al., 2006).

During each of the three regimes, denitrification potential (DEA) was found at all depths sampled and at all positions sampled at the field edge (1 m), transition zone (8 m) and mid riparian zone (15 m) (Table 5.1). Denitrification potential ranged from 0.5 to 240.0 *n*g N/hr/g soil. This falls within the range of denitrification potential measurements reported in other riparian zone studies. For example, Maitre et al. (2005) reported maximum DEA potential of 600 *n*g N/hr/g soil. Similarly, Clement *et al.* (2002) reported denitrification potential measurements of 210 *n*g N/hr/g soil in surface soil samples (0-25 cm depth). Furthermore, Clement *et al.* (2002) found that low denitrification rates of 0.4 *n*g N/hr/g (i.e. measured from a soil slurry incubated without nitrate and glucose additions) in deeper soils (50-75 cm depth) were still able to contribute to the reduction of groundwater nitrate along the flow path. Therefore, the denitrification potential measured at this site suggests that given the necessary redox conditions, denitrification can occur at all depths and locations at the site.

Table 5.1 Summary of DEA triplicate averages and standard deviations for each sampling location and time.

Distance from the field (m)	Depth (cm)	DEA (ng N/hr/g soil)								
		R1 (DOY 149)			R2 (DOY 255)			R3 (DOY 301)		
		Average		Stdev	Average		Stdev	Average		Stdev
1	0-30	160.0	+/-	5.9	140.0	+/-	1.0	120.0	+/-	16.0
1	30-60	54.0	+/-	2.0	69.0	+/-	7.5	91.0	+/-	19.0
1	80-110	54.0	+/-	2.0	2.1	+/-	0.1	4.9	+/-	2.0
1	130-160	6.9	+/-	1.4	2.1	+/-	0.4	----	+/-	----
8	0-30	240.0	+/-	19.0	63.0	+/-	50.0	160.0	+/-	0.7
8	30-60	31.0	+/-	4.6	59.0	+/-	12.0	12.0	+/-	2.7
8	80-110	2.1	+/-	0.6	2.4	+/-	13.0	7.9	+/-	4.2
15	0-30	190.0	+/-	4.8	140.0	+/-	24.0	130.0	+/-	26.0
15	30-60	8.4	+/-	2.3	55.0	+/-	31.0	4.8	+/-	2.5
15	80-110	8.2	+/-	0.9	5.5	+/-	1.9	0.5	+/-	0.5

Although there was a substantial amount of variability, there were no clear seasonal trends in DEA at the different sampling depths and locations (Table 5.1). This is not surprising considering the many environmental variables that could be influencing DEA during the different regimes (*i.e.* changing nitrate inputs, changes in soil moisture and temperature). Furthermore, although seasonal samples were taken in close proximity, the heterogeneity of this study site may cause of differences between soil samples at the same location, which may override any seasonal changes.

At each of the distances from the field edge, DEA averaged over all three regimes decreased with depth (Figure 5.9). A one-tailed t-test showed that the average DEA measured at 0-30 cm was significantly different than that at 30-60 cm. These results are consistent with those of Clement *et al.* (2002) who found that regardless of season or location in the topohydrosequence, shallow soils in three different riparian wetlands had significantly higher denitrification potential due to the availability of larger pools of labile carbon. Similarly, Hill and Cardaci (2004) found that denitrification potential in surface peat was four times greater than that in deeper (80-140 cm) peat.

These DEA results suggest that the maintenance of higher water tables in the riparian zone can promote higher denitrification rates because they indicate larger active denitrifier populations are present in shallow soils.

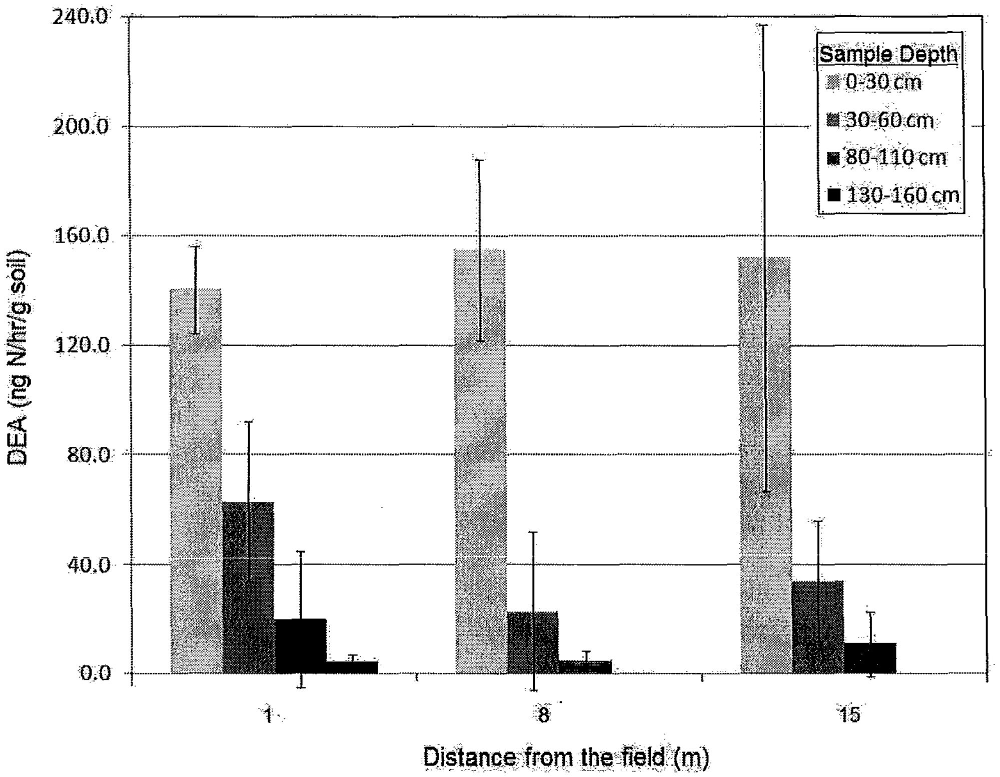

Figure 5.9 Average denitrification potential (over all three hydrologic regimes) and standard deviation at each of the different sampling depths and distances into the riparian zone.

Discussion

5.5 Nitrate Inputs to the Riparian Zone

Nitrate concentration data showed that there were always elevated nitrate concentrations within 10 m from the field. The groundwater chemistry patterns at the site suggest that there are at least two distinct groundwater sources supplying nitrate to this riparian zone: 1) shallow subsurface groundwater inputs from the adjacent field, and 2) deeper flow paths up-welling in the riparian zone (recall that some of the deeper flow paths discharging <11 m from the field edge had nitrate concentrations over 20 mg/L, whereas those >11 m had average nitrate concentrations < 2 mg/L). The spatial extent of these inputs changed over the study period. Nitrate inputs from the field dominated during regime R1, when field-to-riparian hydraulic gradients were greatest. Nitrate inputs from the deeper flow paths dominated during the regime the R2 flow reversal, when field inputs were limited. Both Clement *et al.* (2003) and Molenat *et al.* (2008) found similar patterns in their studies; when upland water tables dropped, inputs from deeper flow paths became more dominant in the riparian zone.

Groundwater chemistry data also show that rain events could be important in transporting nitrate from the field into the riparian zone. For example, the rain event that coincided with the second in-bank flood (DR-2) caused the field edge location, T3-3, to be reconnected to upland inputs. Also, the large rain event on DOY 279, caused high DO and nitrate-rich water from the field to be transported to G23-6. This corresponds with the spikes in field-to-riparian specific discharge rates that followed rain events (Figure 4.10 in Chapter 4). Higher resolution temporal water chemistry and hydrology data are needed to fully understand the impact of rain on nitrate inputs; however the results described in this chapter show that rain events could have a significant impact on field nitrate fluxes to the riparian zone. Cirmo and McDonnell (1997) emphasize the importance of rainfall-runoff on nitrogen transport and transformations in the riparian zone.

5.6 Role of the Riparian Zone in Protecting the Stream from Upland Nitrate Inputs

At distances greater than 11 m from the field edge, groundwater discharging in the mid riparian zone had nitrate concentrations less than 2.0 mg/L throughout the study period. This is well below the 44.0 mg /L Ontario drinking water standard.

In this study, we hypothesized that the elevated near stream water tables caused by the influent stream would disrupt the field-to-stream transport of nitrate rich groundwater from the uplands. The above analysis suggests that this may not be the case at this site, where groundwater discharging in the mid riparian zone (low nitrate >11 m from the field) already acts as a barrier to field-to-stream nitrate transport. However, at other sites where the groundwater discharging in the floodplain has high nitrate concentrations or where a shallow confining layer inhibits fluxes from depth, managing stream water levels to artificially create an influent stream could become an important strategy in protecting surface water from upland nitrate inputs.

5.7 *Groundwater Nitrate Removal*

5.7.1 Heterotrophic Denitrification in the Riparian Zone

Although the majority of the spatio-temporal nitrate decreases observed in the riparian zone were the result of shifting sources and flow paths, evidence of denitrification was seen between 5 m and 8 m from the field. This zone of denitrification was sensitive to the changing regimes. For example, denitrification appeared to stop at the G23-8 (100 cm) when field inputs where replaced with those from the mid riparian zone. In fact, evidence of denitrification was only seen with field origin water. This may be due to differences in labile carbon between these two hydrologic sources. At this site, dissolved organic carbon (DOC) concentrations were not significantly different between the field edge and mid riparian zone (DeSimone, 2009); however, differences in the quality of DOC (no data available) could still be significant between the different sources. For example, Hill and Cardaci (2004) found that the quantity and quality of carbon played a significant role in riparian zone denitrification. This apparent impact of hydrologic source on denitrification could also be related to differences in specific discharge rates between the field edge and mid riparian zone. For example, at 100 cm depth, G23-6 and G23-10 both received nitrate inputs and both had DO concentrations <2 mg/L but evidence of denitrification was only seen at G23-6. Saturated hydraulic conductivity was 9.9 x 10^{-7} cm/s and 2.4 x 10^{-3} cm/s at G23-6 and G23-10, respectively. Ocampo (2006) found that in locations where flow rates exceed reaction rates, nitrate transport will dominate over attenuation. Thus, perhaps the high saturated hydraulic conductivity at G23-10 supports flow rates that are too fast to support denitrification at this location.

The results also suggested that rain events could be an important control governing denitrification at the site. The 41.6 mm rain event (DOY 279), which marked the beginning of regime R3, transported DO rich field inputs to G23-6, where DO concentrations had previously remained below 2 mg/L. Thus, the frequency and size of rain events could impact spatio-temporal denitrification patterns of this site. More research is needed to understand denitrification at this site but these results are consistent with the concepts of denitrification hot spots and hot moments presented by McClain *et al.* (2003).

The size of a nitrate sink is dependent on both riparian zone denitrification rates and the nitrate in groundwater fluxes to the riparian zone (Cey *et al.,* 1999). This study did not measure *in-situ* denitrification rates; however, the low field-to-riparian specific discharge rates (Table 4.3 in Chapter 4) indicate that nitrate removal rates are likely limited by the low nitrate fluxes from the field, so this riparian zone is not a significant nitrate sink in this landscape.

5.7.2 Autotrophic Denitrification in the Up-gradient Aquifer

Groundwater chemistry patterns in the mid riparian zone indicated that autotrophic denitrification may be occurring in the up-gradient surficial aquifer. The importance of autotrophic denitrification in aquifers has been discussed in several other papers (Miotlinksi, 2008; Bohlke, 2002; Puckett, 2002). More research is required to confirm that this is indeed a significant process influencing groundwater (and ultimately surface water) nitrate pollution at this site. However, if autotrophic denitrification is indeed responsible for the low nitrate concentrations discharging in the mid riparian zone, then the up-gradient aquifer may be a much more important nitrate sink than the riparian zone itself.

5.8 Conceptual Model Evaluation: Nitrate Removal

As described in Chapter 1, Vidon and Hill (2004c) built on their hydrologic conceptual model (Figure 4.11) to create one that uses landscape features to predict riparian zone nitrate removal characteristics (Figure 5.9). In this nitrate model, depth of permeable sediment in the riparian zone and grain size was used to predict flow paths and residence times through the riparian zone. As with the hydrologic model, this study site fell in the top left-hand portion of the conceptual model diagram (Figure 5.9) which corresponds to the following characterization:

- Nitrate input is a continuous small to medium flux.
- Because this site is not dominated by coarse sand and gravel, 90% of nitrate removal occurs in less than 20 m
- The riparian zone will be a small to medium nitrate sink.

Again, the analysis the results within the context of this model, reveals several significant deviations from the characteristics described there. First, the model entirely ignores the possibility of vertical inputs in the mid riparian zone and does not address the possibility of the convergence of different flow paths in the floodplain. As was discussed in Chapter 4, this model can not accurately predict nitrate-rich groundwater fluxes from the field because it assumes that field inputs dominate riparian hydrology and therefore does not account for other important hydrologic inputs to the site, such as, stream-inputs and the mid riparian discharge zone. Furthermore, the model could not account for the fact that a portion of the groundwater fluxes from the adjacent field are likely diverted downward instead of moving through the riparian zone. This omission would result in the model over estimating nitrate fluxes to the riparian zone.

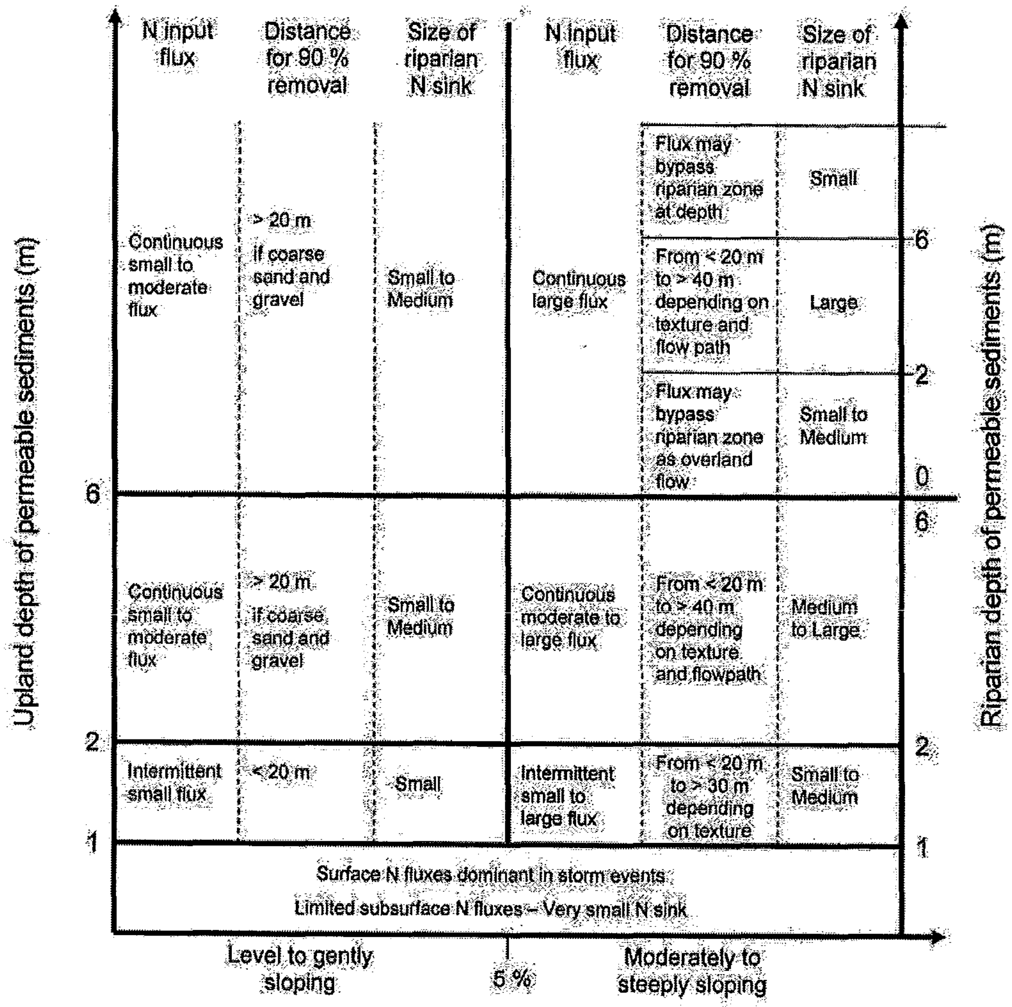

Figure 5.10 Conceptual model linking the upland depth of permeable sediments (m), the riparian depth of permeable sediments (m), and topography to nitrate removal in riparian zones (Vidon and Hill, 2004c).

In addition, the model cannot account for the second, non-field, nitrate source upwelling in the mid riparian zone. This exclusion would result in the underestimation of nitrate fluxes entering the riparian zone. This underestimation could be particularly significant at this site, where specific discharge rates of the second source were orders of magnitude higher than those at the field edge, indicating that the nitrate fluxes from the non-field source may be substantially higher than those from the field.

These shortcomings build on the discussion in Chapter 4 to further exemplify how this model could be improved by including other significant hydrologic controls in the landscape.

6 Conclusions

The results of this study showed that the upstream dam had a significant impact on riparian zone hydrology and shallow groundwater nitrate patterns. This riparian zone acted primarily as a physical barrier to upland nitrate inputs to the stream, so these impacts did not affect its ability to protect the stream from upland nitrate inputs. However, these findings indicate that dam management practices should be set with consideration of how they will impact the nitrate buffering function of downstream riparian zones. Future research should examine the impact of an upstream dam on riparian zone nitrate removal in a variety of hydrogeologic settings.

Furthermore, the results demonstrated the utility of using multiple geochemical indicators to identify dominant controls on nitrate concentrations patterns in shallow groundwater. The understanding of shifting hydrologic flow paths and sources, as well as biological removal mechanisms influencing nitrate patterns at the site relied on the combined use of chloride, nitrate, sulphate and DO concentration data. The omission of any one of these variables from the data set could have led to the misinterpretation of the nitrate patterns at the site.

Finally, this study demonstrated the importance of understanding the limitations of conceptual models linking landscape features to the hydrologic and nitrate removal function of riparian zones. Vidon and Hill's models have been shown to be applicable to a variety of different hydrogeologic settings (Vidon and Hill, 2006) but are based on relatively simple hydrologic controls and are therefore not relevant for more complex hydrogeologic settings. The hydrogeologic setting in this study was complicated by the upstream dam, the upstream marsh, the convergence of multiple hydrologic sources in the floodplain and the degree of spatial heterogeneity in the hydraulic properties of the riparian zone sediments. Perhaps future research could investigate how these types of hydrogeologic features might be used as indicators to help guide the correct application of models across different landscapes.

6.1 Significance

These results are significant because they show that an upstream dam influences riparian hydrology in a relatively predictable way (*e.g.* elevated near stream water table levels, stream inputs to the riparian zone). They can facilitate the incorporation of upstream dams as components in models such as those developed by Vidon and Hill (2004). Therefore, the results of this study can contribute to the enhancement of these models by providing information about an important hydrologic control on riparian zone hydrology and nitrate removal capacity.

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