ENVIRONMENTAL FATE OF NITRATE IN THE ASSINIBOINE DELTA AQUIFER

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For

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Executive Summary

The Assiniboine Delta Aquifer (ADA) is a large unconfined surface aquifer located in southwestern Manitoba covering a land area of 3,885 km^2. The majority of the aquifer lies within the boundaries of the rural municipalities of North Cypress and South Cypress. Significant portions of the municipalities of Langford, North Norfolk, South Norfolk and Victoria also lie within the aquifer's boundaries. The geological and glacial history of this region has resulted in the deposition of a classic unconfined sand aquifer which has been extensively characterized. Depth to the water table varies from 0 to more than 20 m, with an average saturated thickness of 18 m (ranging from 0 to 60 m).

The major land uses associated with the ADA region are cropland and forage (46%), grassland (27%), and forest (21%), with other land uses accounting for less that 10%. Approximately 152,000 hectares, 39% of the total land area over the aquifer, is rated either excellent or good for irrigation. However, much of the same land is also considered environmentally sensitive due to the predominance of well-drained coarse-textured surface deposits that lie above the aquifer. Approximately 26,300 hectares, 6% of the total land area above the aquifer is currently licensed for irrigation. The combination of an unconfined aquifer underlying coarse-textured material with agricultural land use creates the potential for aquifer contamination.

A review of studies of the nitrate (NO_3^-) concentration of the ADA revealed a relationship between land use and average NO_3^- concentration. In a survey samples collected from under agricultural fields utilizing irrigation had an average NO_3^- concentration of 18 mg N/L with 50% of samples exceeding the drinking water guidelines. This is compared to samples collected from under grasslands that averaged 4.5 mg N/L with only 13% of samples exceeding the drinking water guidelines. Temporal studies of groundwater NO_3^- concentrations indicated a number of wells where there is a trend of increasing NO_3^- concentration in the well with time. There were also wells where there was not obvious trend to increasing NO_3^- concentration. Studies of the distribution of NO_3^- with depth within in the groundwater suggest that NO_3^- contamination is greatest in the upper portion of the aquifer.

An estimate of the potential for NO_3^- loading to groundwater, based on speculative assumptions (which should be verified with further analysis) resulted in estimated average NO_3^- concentration of recharge water of 44 mg N/L. No single land use resulted in a dominant contribution to NO_3^- loss. The exercise emphasized the need to improve our estimates of the relative contribution of various land uses to NO_3^- loading to ground water.

A survey of the NO_3^- status of other unconfined aquifers and the behaviour of NO_3^- in subsurface environments was compiled. Unconfined shallow aquifers have long been identified as susceptible to groundwater nitrate impacts since they are often associated with coarse textured, well-drained soils. These coarse-textured soils have little capacity to retain dissolved nitrate near the root zone due to low field capacities. They also rarely

develop waterlogged or anaerobic conditions to facilitate nitrate loss by denitrification. Ironically, regions with shallow sand aquifers tend also to be highly groundwater dependent. Increased groundwater nitrate concentrations tend to occur at higher concentrations and more frequently in agricultural regions, under more permeable soils, in more shallow aquifers and/or more shallow (dug, bored) wells, and can be correlated on a regional basis with fertilizer use. Indeed, relatively severe impacts are found in regions with sandy, shallow aquifers.

The unique characteristics of the hydrology of sand aquifers is reviewed, the groundwater flow pattern in the ADA is sub-horizontal. The sub-horizontal nature of the groundwater flow complicates the linkage of NO_3^- concentration to land use.

Once it occurs in the aquifer, NO_3^- has several potential fates: sorption, mineralization/immobilization and denitrification. Of these denitrification is of greatest interest as it is the primary mechanism by which NO_3^- can be removed from groundwater sources. The factors influencing denitrification are discussed emphasizing the important role of electron donor supply in determining the denitrifying capacity of groundwater systems. In many groundwater systems inorganic electron donors may dominate.

A variety of tools to assess and monitor the NO_3^- status of the ADA and the potential for denitrification to remove NO_3^- are discussed. Assessment of the electron donor potential is a key measurement to determine the capacity of the aquifer to remove NO_3^- via denitrification.

In conclusion, the risk of nitrate contamination of the ADA as a consequence of agricultural activities is high, due to the characteristics of the aquifer and its geological setting, and to the suitability of the land for agricultural development and use. Expansion of intensive crop production, irrigation, and livestock production would further increase this risk. A clear assessment of the risk requires a field- and groundwater-based study to elucidate the potential for denitrification, including the nature and long-term supply of electron donors and their associated groundwater impacts.

A study plan is presented to allow the assessment and monitoring of NO_3^- status of the aquifer and its potential for remediation. Three stages are identified: 1) a preliminary assessment of the ADA's capacity for denitrification by a geochemistry survey of existing groundwater observation wells; 2) a retrospective study of denitrification under areas of past and ongoing agricultural production to see if denitrification is apparent; and 3) assessment of the long-term denitrification capacity of the aquifer and associated redox donors.

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1. Introduction

This review and study plan was commissioned by the Manitoba Horticultural Productivity Enhancement Centre Inc. to assess the environmental behaviour and fate of nitrate under conditions of the Assiniboine Delta Aquifer (ADA). The current condition of the Assiniboine Delta Aquifer is described with respect to land use, geology, hydrology and groundwater quality. The environmental significance of nitrate is described as well as the biogeochemical processes that influence its fate. This information is utilized to develop an understanding of the current condition of the ADA. This serves as the basis for a proposed study plan to address the major knowledge and information gaps encountered in developing this report.

The Assiniboine Delta Aquifer, located in southwestern Manitoba (Figure 1-1), is a large unconfined surface aquifer. The aquifer covers a land area of 3,885 km^2 and has been estimated to have an annual recharge capacity of 60,378 dam^3 (Render, 1987).

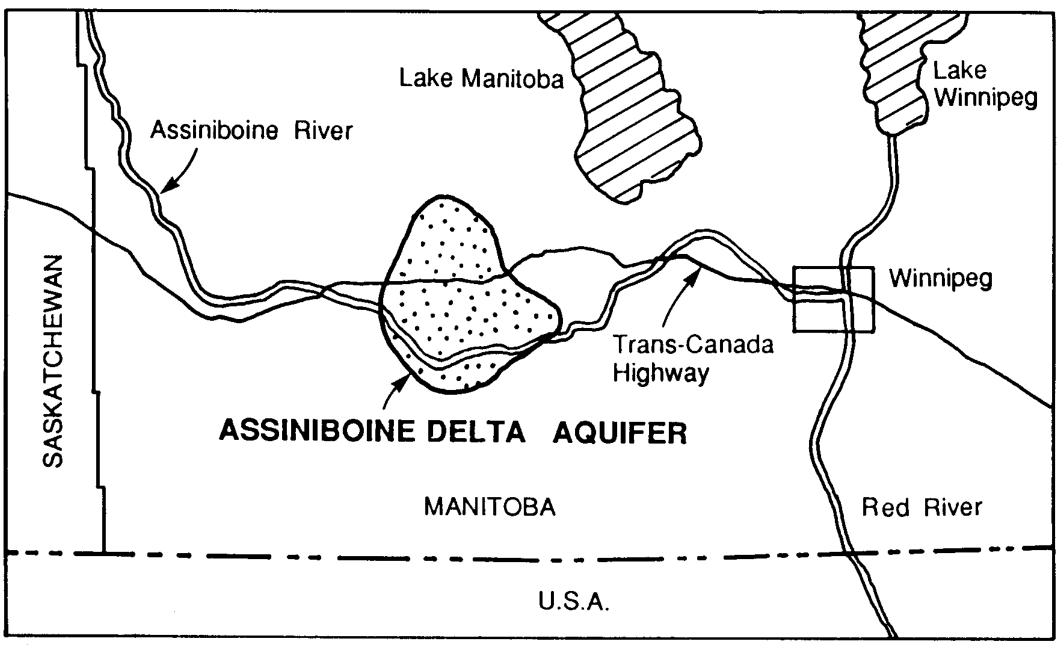


Figure 1-1: Location of the Assiniboine Delta Region, Manitoba (Kulshreshtha, 1994)

1.1 Nitrate in the environment

Nitrate (NO_3^-) is a natural substance that is ubiquitous in the environment at low concentrations. Typical 'background' or natural nitrate concentrations are less than 2 or 3 mg N/L (Mueller et al., 1995; Madison and Burnett, 1985). In some geologic settings, natural nitrate concentrations in excess of 200 mg NO_3^--N/L have been reported (e.g. Hendry et al., 1984; Rodvang et al., 1998), however these deposits tend to occur in finegrained sediment and in semi-arid to arid regions. Groundwater in unconfined late-Tertiary and Quaternary-aged aquifers like the ADA with nitrate concentrations in excess of 2 mg NO_3^--N/L are likely impacted by anthropogenic sources.

1.2 Environmental and health implications of nitrate

1.2.1 Health effects

A near-universal drinking water standard of 10 mg NO_3^--N/L is applied for drinking water supplies. In Manitoba, the nitrate standard for livestock is 20 mg NO_3^--N/L. In some countries (including the European Union), the standard is reported as 45 mg NO_3^-/L (equivalent to 10 mg NO_3^--N/L). The first North American drinking water standard for nitrate was promulgated by the U.S. Public Health Service in 1962 (Sayre, 1962). Canada followed suit in its 1968 *Canadian Drinking Water Standards and Objectives*. The nitrate standard was prompted after a pediatric resident linked cyanosis in bottle-fed infants to ingestion of nitrate-rich well water (Comly, 1945). The cyanotic condition, known as methaemoglobinaemia, occurs when iron in hemoglobin is oxidized in tandem with nitrite reduction, producing methaemoglobin (MeHb). The MeHb binds oxygen tightly, preventing its release for bodily function (Craun et al., 1981). Infants (less than 3 months of age) are particularly susceptible to the condition because the high pH of their stomachs causes nitrate to occur as nitrite. Between 1945 and 1970, more than 2000 cases of methaemoglobinaemia were reported in the world literature (Shuval and Gruener, 1972). Prevention of methaemoglobinaemia, a condition that continues to be reported (Johnson et al., 1987), simply entails the provision of low-nitrate water supplies for bottle-fed infants. A nitrate standard of 10 mg N/L was chosen because early surveys indicated methaemoglobinaemia occurred in infants ingesting well water with nitrate concentrations in excess of 20 mg N/L, and no cases were reported for concentrations less than 10 mg N/ L (Health Canada, 1992). Although the drinking water standard for nitrate has been decried as unnecessarily harsh (Lehr, 1985), there is evidence to suggest ingestion of nitrate in potable water supplies may be related to additional health issues, including gastric cancer, reproductive and developmental effects (see discussion in Health Canada, 1992).

1.2.2 Environmental effects

In addition to public and animal health concerns, nitrate in surface waters can pose eutrophication problems. Eutrophication occurs when nutrient-rich surface waters allow overgrowth of cyano-bacteria or ‘blue-green algae’ to occur. The effects on surface water include development of algal mats or ‘blooms’. These mats block out sunlight necessary for growth of periphytic organisms, consume dissolved oxygen necessary for growth of fish and other organisms, are aesthetically unappealing, and can produce toxins (Smith et al., 1999). Although nitrogen was historically believed to be responsible for eutrophication of surface water bodies, it has been widely accepted since the 1970s that phosphorus is the limiting nutrient (Schindler, 1975; Hecky and Kilhman, 1988; USGS, 1999). Nitrate is thought to be the parameter of primary importance in the eutrophication of marine waters (Hecky and Kilhma, 1988; Smith et al., 1999). In the past decade extensive hypoxic ‘dead zones’ in coast regions of the US (including the Gulf of Mexico and Chesapeake Bay) have been attributed to nutrients primarily reaching the Gulf from ground- and surface-water discharge. Coastal eutrophication is now a major issue in the

U.S. (Goosby et al., 1999), with initiatives that may have potentially significant effects on farming practices (Anon, 1999). Recent concerns over the formation of algal blooms in Lake Winnipeg likely relate to elevated nutrients, primarily of agricultural origin, in surface and groundwaters discharging into this water body (Brigham et al., 1996). There has also been recent concern over the impact of feedlot operations in Alberta on phosphorus content of surface and groundwater quality (see text box Phosphorus: The misunderstood nutrient).

Phosphorus: The misunderstood nutrient

Since Schindler's whole lake experiments on the effects of nutrient on surface water bodies in 1977, phosphorus (P) has been commonly accepted as the most limiting nutrient. Typically, surface water bodies are highly sensitive to P inputs and eutrophication can become greatly accelerated when P levels in the water are between 0.01-0.02 ppm (Howard et al., 1999). The Interim Alberta Environment surface water guideline for total phosphorus (TP) is 0.05 ppm.

Excess phosphorus stimulates increased biological growth. This in turn causes a large input of dead and dying biomass into the surface water body. The degradation of this organic material results in depleted dissolved oxygen concentrations, and the subsequent death of fish and other creatures. Some types of algae are particularly competitive and thrive in this environment, producing unsightly algal blooms and in some instances hepato- and neuro-toxin production. Additionally, eutrophication leads to increased water temperatures, impedes water flow and navigation, increased evaporitic water loss, and increased sedimentation. Highly eutrophic waters can, therefore, no longer be used as a water resource.

Currently, an ongoing study is being conducted in Southern Alberta to investigate the movement of nitrogen (N) and phosphorus (P) compounds in the subsurface and to assess the potential for the migration of P to surface water bodies. The study is funded by the Canada-Alberta Beef Industry Fund. The study area is a quarter section of irrigated, manured, cultivated field that is underlain by an unconfined, sandy aquifer. The site is bounded to the north by an engineered drainage canal that drains into the Oldman River. Groundwater flows towards the Battersea Drain and discharges into the surface water body.

Geochemical analyses confirm that the groundwater has been impacted by agricultural practices. Average TP levels are 0.24 mg/L ($\sigma = 0.55$, $n = 73$) or approximately five times the surface water guideline. Phosphate sorption and soil extraction studies have indicated that P is being stored in the aquifer; likely as sorption complexes and/or P minerals. However, in spite of the ability for the aquifer sediment to attenuate the groundwater concentrations, significant amounts of P are being discharged to the adjacent surface water body. The average concentration of TP in groundwater seeping into the canal is 0.61 mg/L ($\sigma = 1.44$, $n = 112$) or twelve times the surface water guideline. Seepage rates vary significantly with seasons, but are as high as 10 mg m^2 of seepage area. Phosphorus concentrations in the groundwater appear to be directly correlated to P concentrations in the drainage canal. Visible evidence of eutrophication is seasonally evident in the canal.

Submitted by M. Zilkey and C. Ryan.

2. Background

2.1 Delineation of the Assiniboine Delta Aquifer region

The aquifer is located in southwestern Manitoba and covers an area of approximately 388,500 hectares. There are twelve rural municipalities that lie above the Assiniboine Delta Aquifer. In a study of the economic value of groundwater resources in the ADA, Kulshreshtha (1994) considered only those rural municipalities that have a major portion of their area within the aquifer's boundaries. The majority of the aquifer lies within the boundaries of the rural municipalities of North Cypress and South Cypress. Significant portions of the municipalities of Langford, North Norfolk, South Norfolk and Victoria also lie within the aquifer's boundaries. (Figure 2-1).

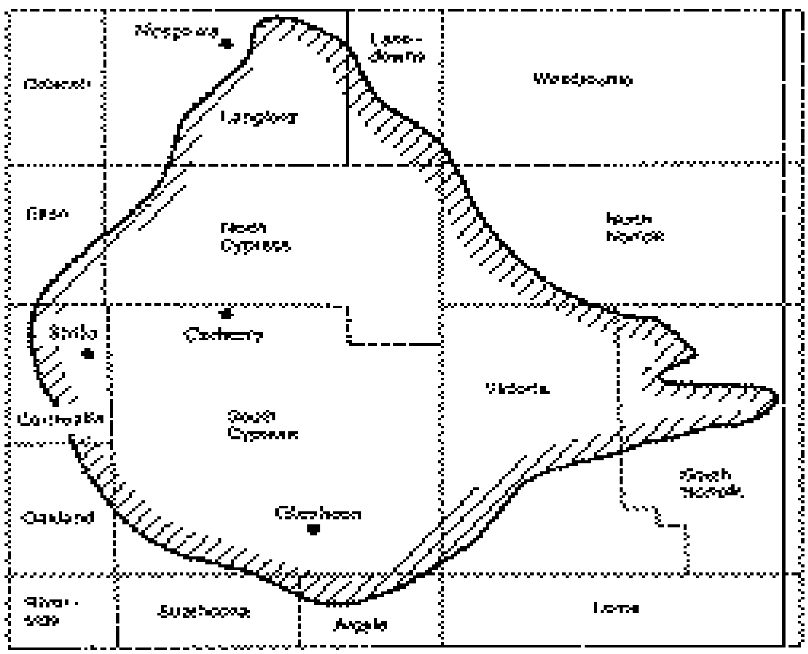


Figure 2-1: Assiniboine Delta Aquifer Region (from Kulshreshtha**,** 1994).

2.2 Physical Geology of the Assiniboine Delta Region

The Bedrock of southwestern Manitoba is composed of Mesozoic shales of the Cretaceous and Jurassic periods (Figure 2-2). Bedrock formations within the Assiniboine Delta Aquifer area include the Riding Mountain Formation, Vermilion River Formation, Favel Formation and Ashville Formation of the Upper Cretaceous, the Swan River Formation of the Lower Cretaceous, and the Sundance Formation of the Jurassic. The hard siliceous shales of the Upper Cretaceous form the cap rock of the Manitoba escarpment.

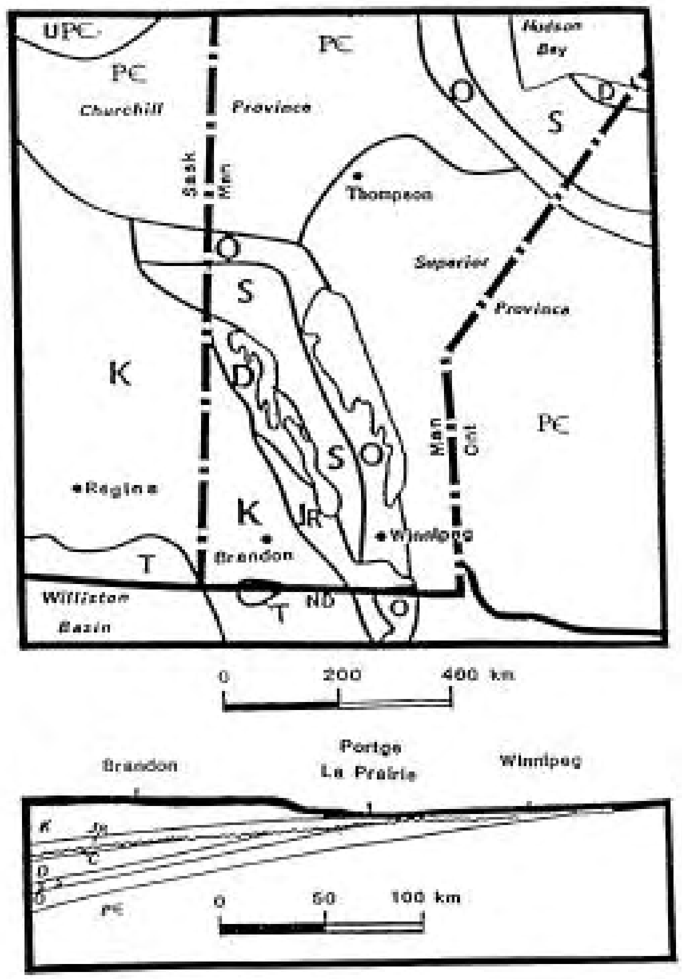


Figure 2-2: Bedrock geology of Manitoba with W-E cross section through Brandon and Winnipeg, Manitoba. K= Upper Cretaceous; Jr= Jurassic; C = Cretaceous; PE = Precambrian Shield, O = Ordovian, D = Devonian, (after Teller and Bluemle, 1983 as presented by Sun, 1993)

The elevation of the bedrock surface is lower under the Assiniboine Delta and rises to the west, northwest and south forming a broad valley or depression. The valley was eroded through the Manitoba escarpment by the waters of the pre-glacial Missouri River and extends eastward from Brandon to Carberry and Austin (Figure 2-3). A smaller bedrock valley lies along the present Souris River channel from the Pembina Spillway northward.

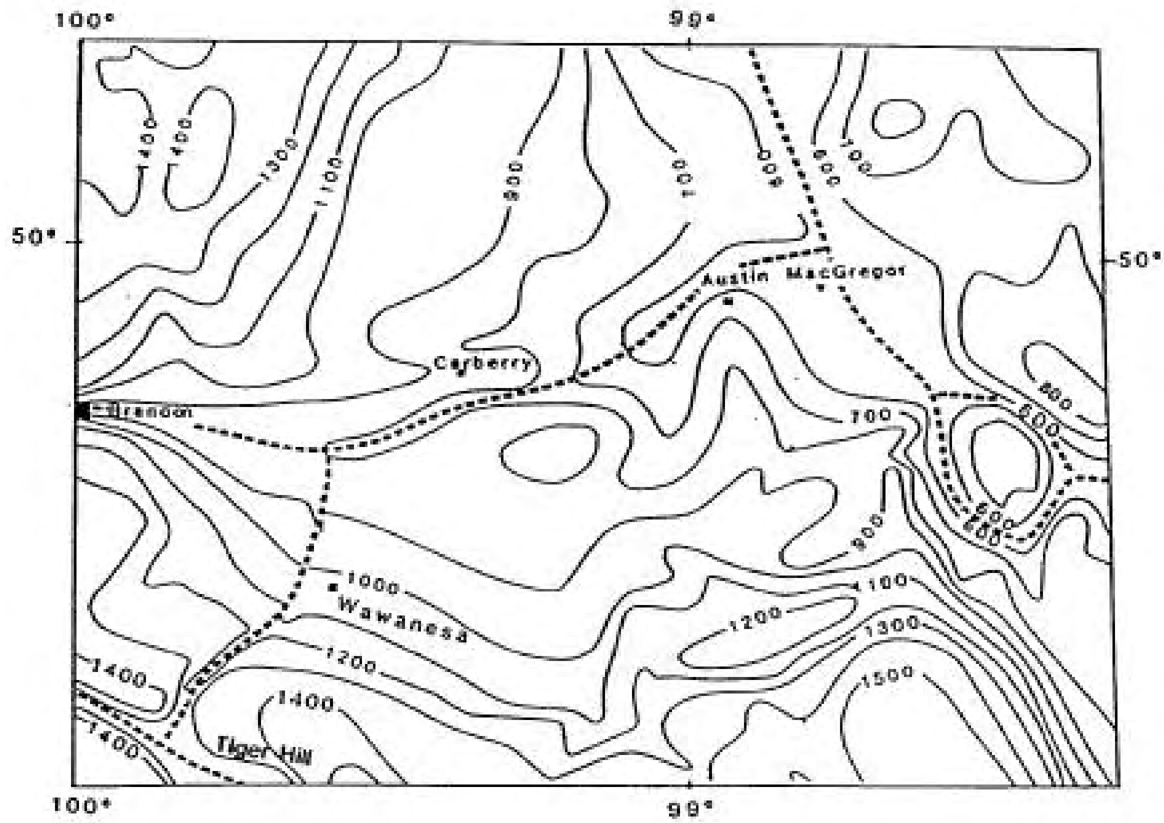


Figure 2-3: Bedrock topography of the Assiniboine Delta Aquifer. Dashed lines show the bedrock valley from Brandon to Austin and from the Tiger Hills northward to Wawanesa (after Teller, 1976). Note elevation is in feet. (Sun, 1993).

The Mesozoic shales are overlain directly by Quaternary sediments. During the Wisconsin glaciation, advancing ice sheets left a thick layer of glacial till over much of southwestern Manitoba. The deposition of the glacial till followed existing contours and the general shape of the pre-glacial features such as the Manitoba escarpment and the pre-glacial river valley near Brandon were maintained.

Glacial Lake Agassiz was formed approximately 11,500 to 12,500 years ago when the northward flowing Red River was damned by receding ice sheets. The lake existed for approximately 5000 years and at times occupied much of southern Manitoba and parts of northwestern Ontario, Saskatchewan, North Dakota, and Minnesota. The pre-glacial river valley near Brandon was also flooded and created a bay on the southwestern corner of the lake.

The Assiniboine Delta was formed during the early stages of the development of Lake Agassiz, approximately 11,000 to 11,500 years ago, when large quantities of sediment derived from the erosion of the Assiniboine and Qu'Appelle glacial spillways were deposited in the bay near Brandon (Figure 2-4). The spillways were created by meltwater from a retreating ice sheet and areas of stagnant ice to the west of the Manitoba escarpment. Coarser gravel was deposited near Brandon, but the main part of the delta was formed by the deposition of sands in a triangular area bordered by Brandon, Neepawa and Cypress River. Finer silts and clays were carried further out into Lake Agassiz.

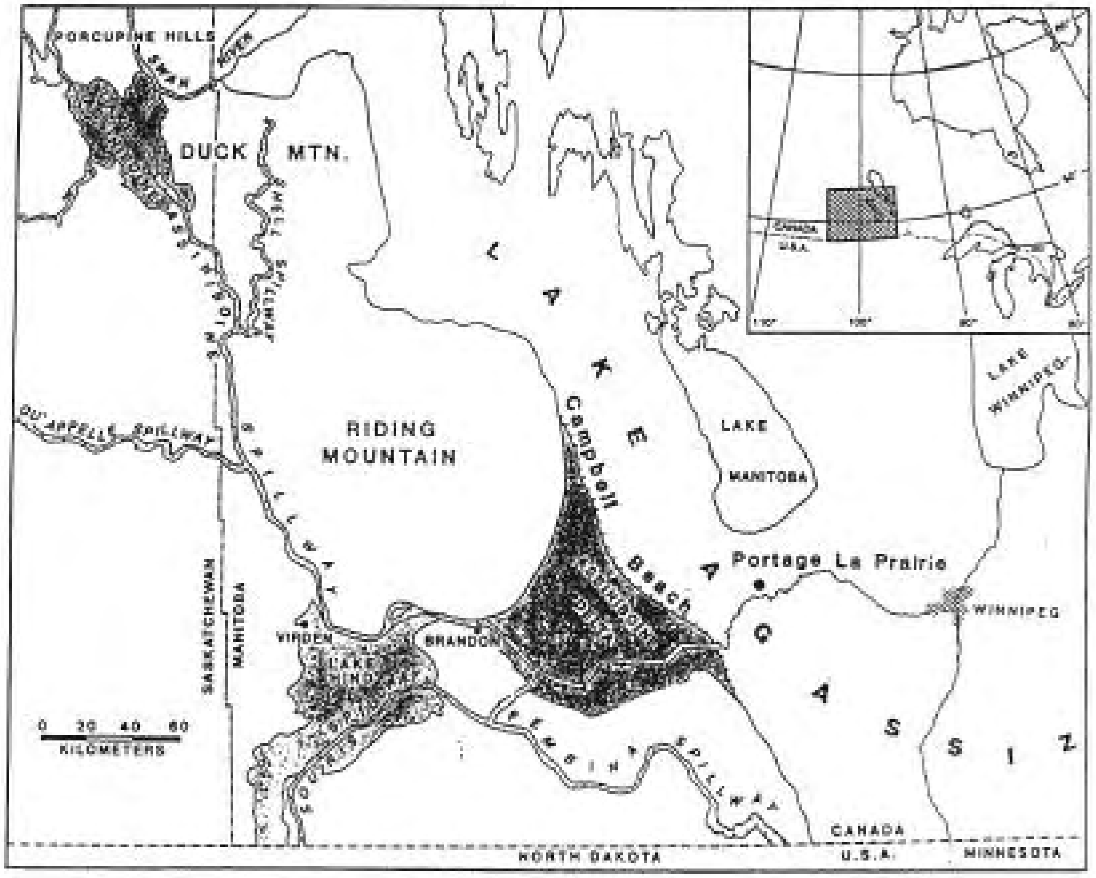


Figure 2-4: Location of the Assiniboine fan delta, showing spillways and lakes that might have contributed to the construction of the Assiniboine fan delta (from Sun, 1993).

The delta is divided into upper (older) and lower (younger) portions that are separated by the Campbell beach escarpment. The lower part of the delta is a north south belt that lies east of the Campbell escarpment and consists of a thin layer of coarse sands that overlie the clayey bottomset beds of the older delta. The coarse sands were eroded from the older delta as a result of wave action.

The sediments of the older delta to the west of the Campbell beach escarpment are thicker and contain the Assiniboine Delta Aquifer. There are five major depositional settings represented: a braided river plain, a Gilbert type delta, underflow fan deposits, subaerial debris flow deposits, and pro-delta deposits. The braided river plain deposits are located immediately to the west of Brandon and are composed of tabular cross bedded and trough cross bedded gravely sand. Gravel forset beds dominate the Gilbert delta, which is separated from the braided river plain to the west by an escarpment. The underflow fan deposits, which lie east of the forsets, make up the majority of the upper delta and are composed of massive sand and rippled sand deposits. The subaerial debris flow deposits occur in the eastern portion of the braided river plain and in the proximal fan delta near the present-day Assiniboine valley. The pro-delta deposits consist of silt and clay.

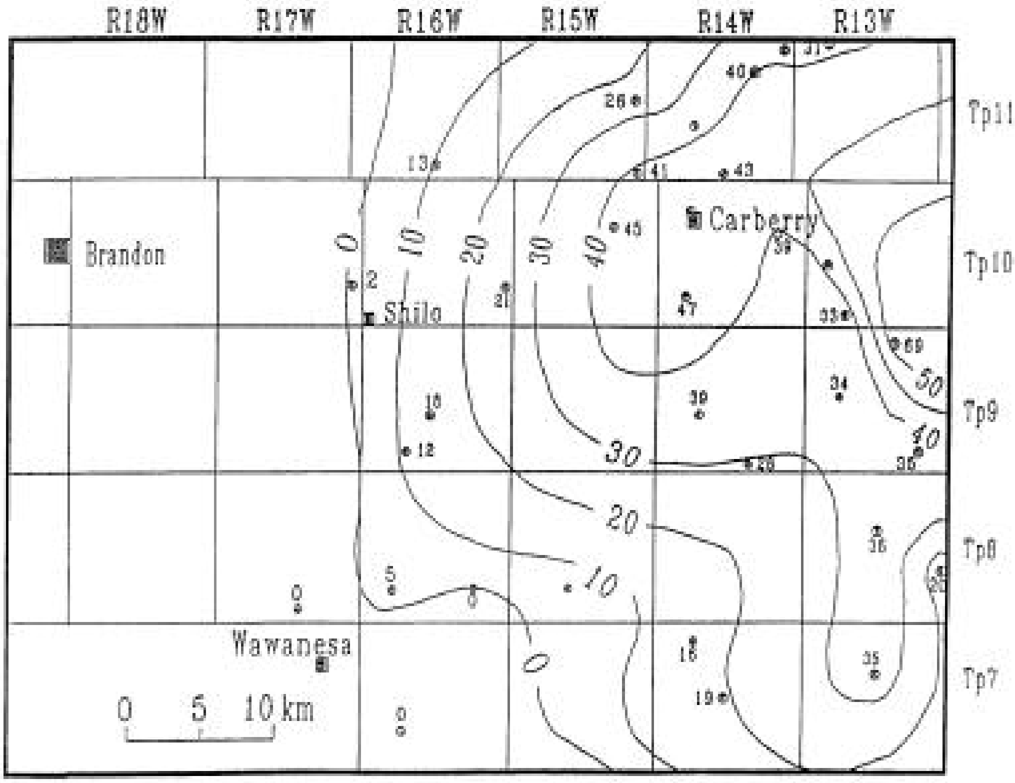


Figure 2-5: Thickness (in m) of the lacustrine clay and silt unit below the coarser fan delta deposits. This isopatch map was based on well logs, which were drilled by the Department of Mines and Energy. (Sun, 1993).

Along the western side of the upper delta the coarse-textured sands and gravel lie directly on a layer of glacial till. East of Shilo, a layer of lucustrine silt and clay is sandwiched between the sand and gravel of the delta and the glacial till that overlies the bedrock. The silt and clay unit ranges from a few meters thick near the apex of the delta to over 70 meters thick near its eastern perimeter (Figure 2-5).

The average thickness of the sand and gravel deposits in the upper delta is approximately 10 meters. The deposits are thickest in the northeastern region and thinner toward the south and southwest (Figure 2-6). The thickest part of the delta is located 10 km north and 10 km east of Carberry. The grain size of near-surface deposits of the delta varies from coarse gravel to medium sand with a mean grain diameter of 0.020 inches along the western portion of the delta to very fine sand with mean grain diameter of 0.005 inches along the eastern boundary (Figures 2-7 and 2-8). The sands consist primarily of silica.

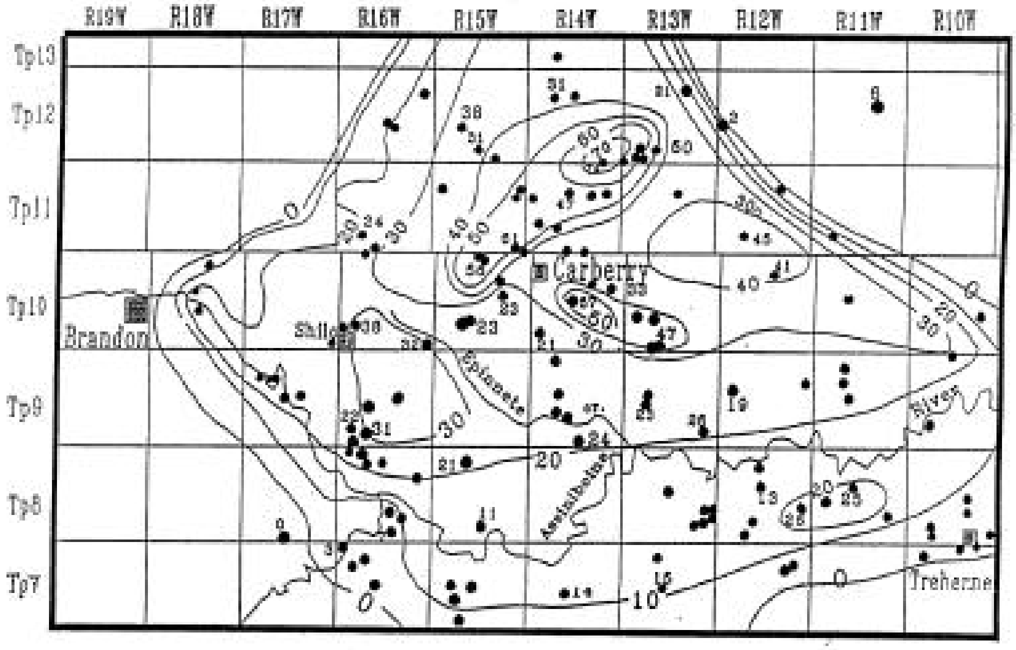


Figure 2-6: Thickness (in m) of the Assiniboine fan delta. Selected numbers used to contour the map are shown. Dots represent deep wells drilled by PFRA (1986, unpubl. report) and Manitoba Water Resources Division, Contour interval = 10 m). (Sun, 1993).

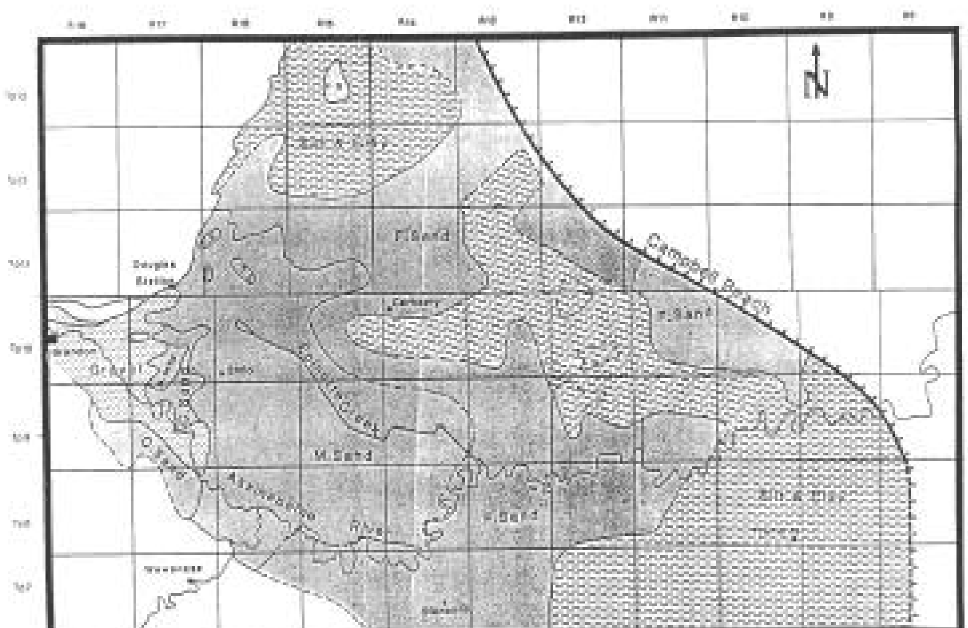


Figure 2-7: Grain size distribution of the fan delta sediments near the surface. Data used to plot this map include 400 well logs, and outcrop exposures. Only the dominant grain sizes are shown in the figure (Sun, 1993).

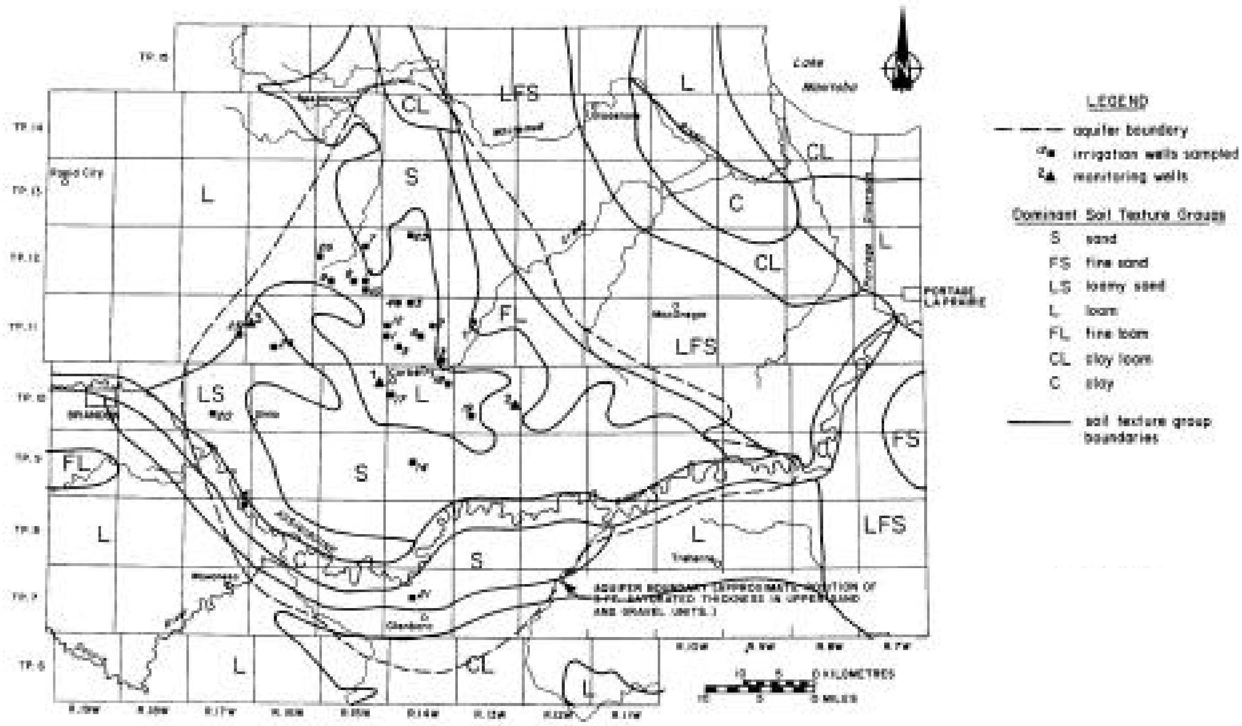


Figure 2-8: Texture of soils overlying the Assiniboine Delta Aquifer (Buth et al., 1992)

The surface expression (geomorphology) of the sand and gravel deposits in the upper delta was developed through a combination of the original deposition and subsequent water and wind erosion. Areas adjacent to the Campbell beach escarpment and major waterways have deeply incised stream beds and a dune topography (Figure 2-9).

The Assiniboine River is the most significant waterway in the study area. It originates at glacial lake Assiniboine near Kamsack, Saskatchewan, and flows south to Virden, Manitoba where it turns east towards Brandon. The river flows in a shallow and relatively straight channel from Brandon to the junction of the Souris River and then flows in a meandering deep channel to the Campbell escarpment and west towards Winnipeg. It has eroded a broad deep valley through the southern portion of the Assiniboine Delta. The Epinette Creek originates at Sewell Lake in an old distributory channel of the Assiniboine River and drains towards the southeast across the middle of the upper delta, joining the Assiniboine River north of Glenboro. After flowing north from North Dakota and turning east into the Pembina Valley near the town of Souris, the Souris River flows north from the Pembina Spillway through the town of Wawanesa before joining the Assiniboine River. Other important waterways that drain the Assiniboine delta include the Cypress River, Little Souris River, Pine Creek and Squirrel Creek.

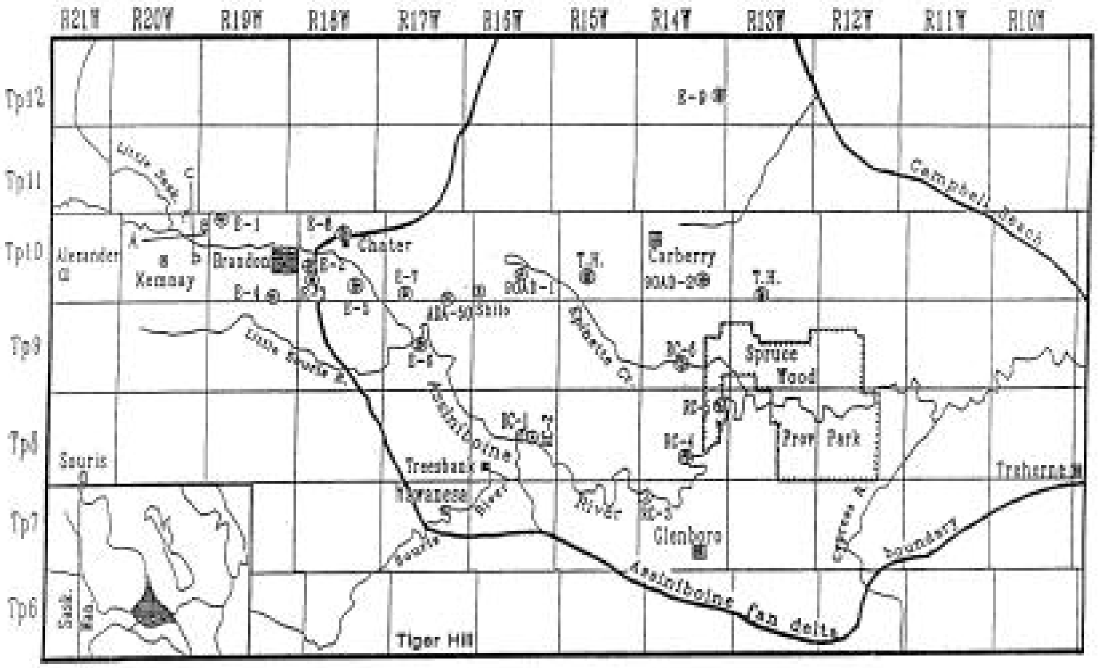


Figure 2-9: Drainage systems, and location of exposures, river cuts, and wells in the Assiniboine fan delta area. E = exposures, RC = river cuts, A-B and C-D are cross sections, ADA-50, 90AD-1, 90AD-2 and T.H. are cores. (Sun, 1993).

2.3 Hydrogeology of the ADA

Hydrogeologically, the Assiniboine Delta Aquifer is a classic unconfined sand aquifer which has been extensively characterized (Render, 1988). Depth to the water table varies from 0 to more than 20 m and the average saturated thickness is 18 m (ranging from 0 to 60 m). Aquifer transmissivity estimates range from 0.0007 to 0.03 m^2/s, and specific yield estimates range from 0.1 to 0.29. Hydraulic conductivity estimates of 10^{-3} to 10^{-4} m/s are reported for the Carberry area (Manitoba Natural Resources,1970), while hydraulic conductivities interpreted from well transmissivities and saturated thickness yield a range of 10^{-5} to 4×10^{-7} m/s (Render, 1988). Saturated thickness and aquifer transmissivities tend to decrease on the east side of the aquifer. Background aquifer water quality is excellent (Manitoba Natural Resources, 1970; Buth et al., 1992). Soils on the ADA are excessively drained, with standing water rarely observed. Render (1988) neglected overland flow in a hydrogeologic budget to arrive at a value for annual groundwater recharge of about 2.2cm in the Pine Creek sub-basin. A similar recharge estimate was obtained for the Carberry area (Manitoba Natural Resources, 1970). No other groundwater recharge estimates are available. Vertical leakage into underlying formations is not reported and the aquifer is thought to discharge exclusively to surface water. The average discharge of the Assiniboine River is 2.83 $m^3 s^{-1}$ (Assiniboine River Management Advisory Board, 1998).

The Assiniboine Delta Aquifer is divided into a number of sub-regions (Figure 2-10). These sub-regions represent variations in topography, landform or hydrology. In the monitoring of land use and its potential impact on groundwater quality these sub-regions provide a useful context. The degree and direction of flow between these sub-basins and their relationship to surface water bodies should also be defined. Render (1988) presented a diagram describing the potentiometric surface for the Assiniboine Delta Aquifer (Figure 2-11). The relationship between the potentiometric surface and the Assiniboine River should be noted.

The Assiniboine Delta Aquifer is used extensively as a source for irrigation water. The distribution of irrigation wells is presented in Figure 2-12. These wells are concentrated in the Assiniboine West, Whitemud East, Pine Creek and Pine Creek North. There are fewer well locations in the South East portion of the aquifer.

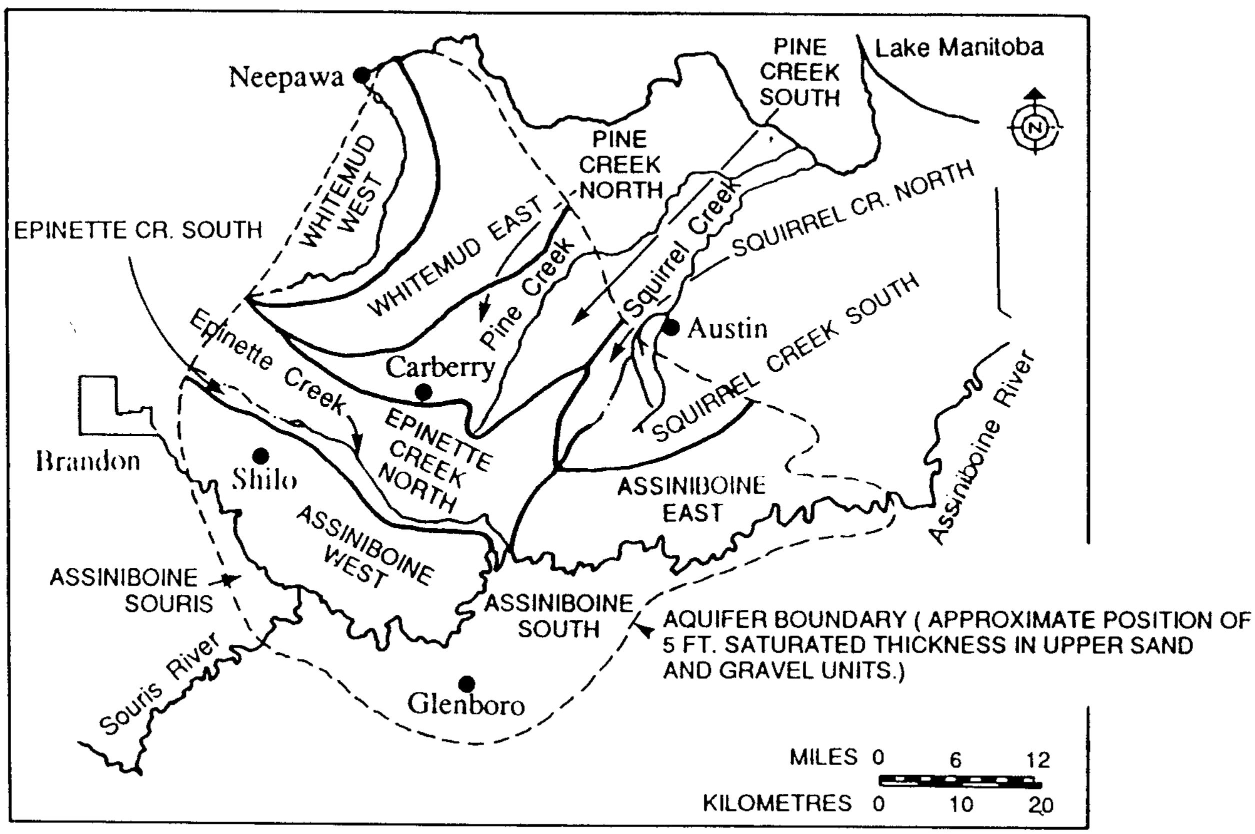


Figure 2-10: Assiniboine delta aquifer sub-regions (From Render, 1988 as presented by Kulshreshtha, 1994).

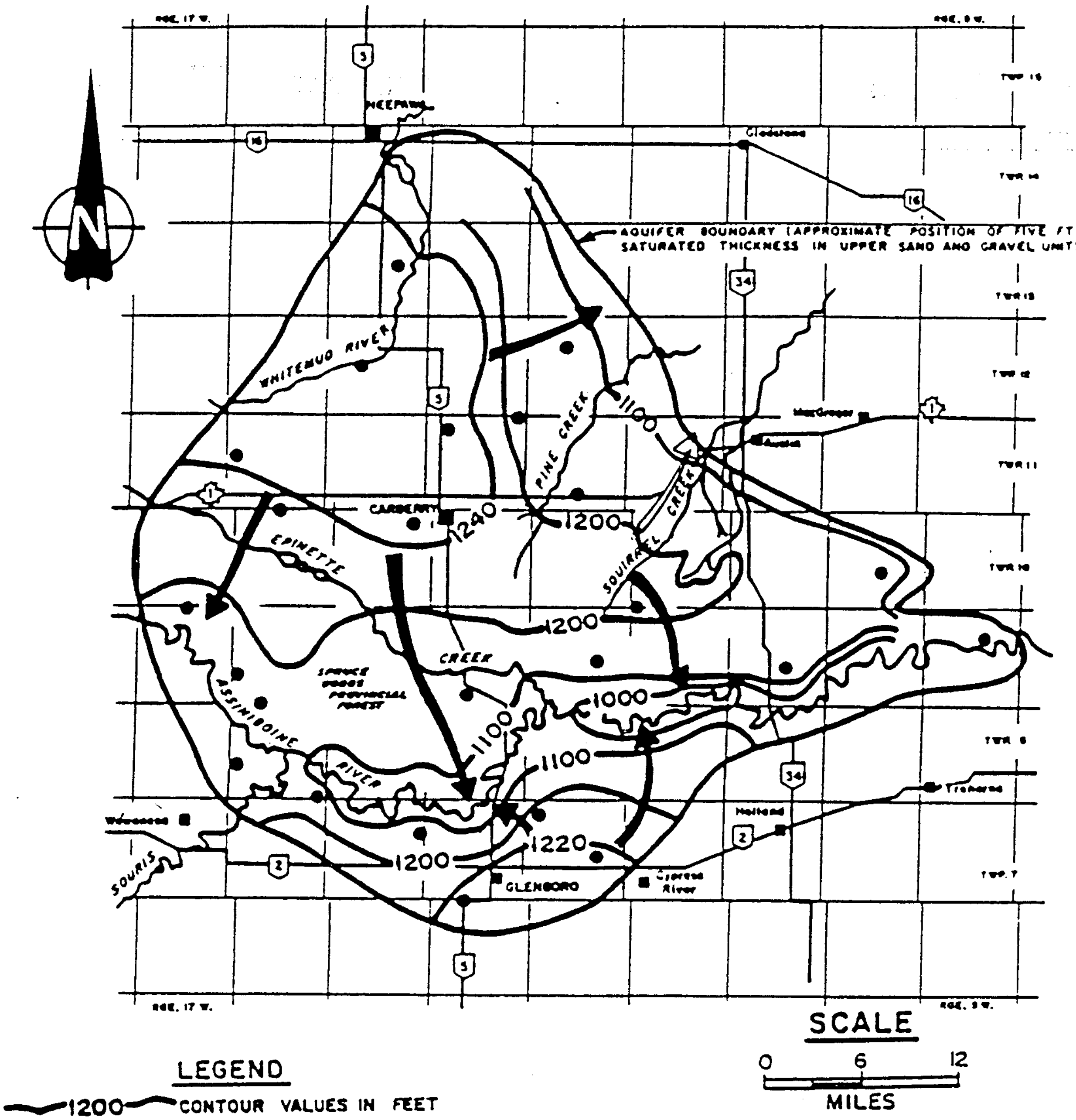


Figure 2-11: Potentiometric surface for the Assiniboine Delta Aquifer (From Render, 1988).

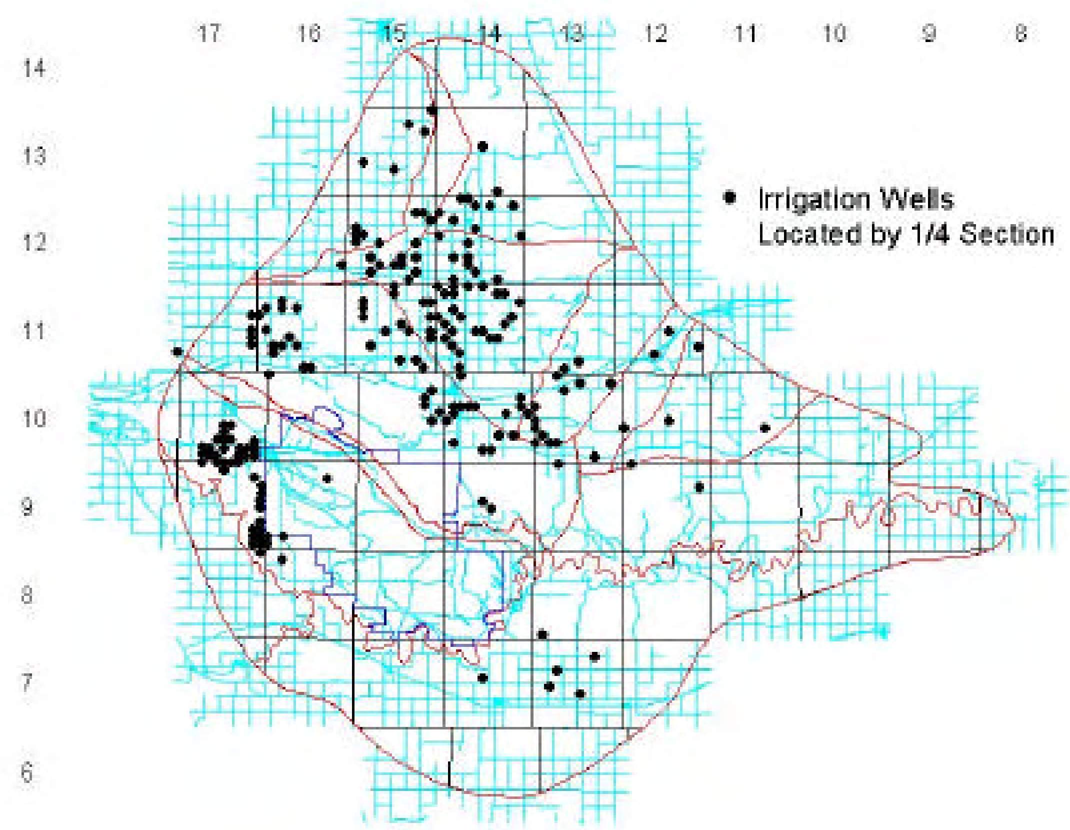


Figure 2-12: Location of irrigation wells with the Assiniboine Delta Aquifer (Source Lorry Broatch, MCDC).

2.4 Changing land use

2.4.1 Land use in Assiniboine Delta Aquifer Region

The Rural Municipality of North Cypress covers approximately 121,000 hectares. The town of Carberry (pop. 1493) is the largest population center in the municipality. Land use is predominantly agricultural in the northern and central portions of the RM. Portions of Spruce Woods Forest Reserve occur along the southern boundary of the RM. The majority of the RM lies within the aquifer area. The soils in the RM are predominately sands, coarse loams and loams.

The Rural Municipality of South Cypress covers approximately 110,00 hectares. The town of Glenboro (pop.663) is the largest population center in the municipality. Soils in the RM are predominantly well-drained medium-textured sands. Land use within the RM includes agriculture in the southern portion and recreation in Spruce Woods Provincial Park. The Spruce Woods Forest Reserve also serves as a military reserve and training area. The majority of the RM lies within the aquifer area.

The Rural Municipality of Langford covers approximately 58,000 hectares. The town of Neepawa (pop. 3301) is the largest population center. Soils in the RM include loams and medium textured sands. Land use within the RM is predominantly agriculture. Approximately 60% of the RM lies within the aquifer's area.

The Rural Municipality of Victoria covers approximately 70,000 hectares. The towns of Cypress River, Landseer and Holland are the main population centers. Soils in the RM include moderately well to well-drained sands, coarse loams, and loams. Land use within the RM is predominantly agriculture. Approximately 50% of the RM lies within the aquifer area.

The Rural Municipality of North Norfolk covers approximately 116,000 hectares. The towns of MacGregor and Austin are the largest population centers in the municipality. Soils in the RM include imperfect to well-drained sands and coarse loams. Land use in the RM of North Norfolk is primarily agricultural with small areas of woodland, urban development and recreation. Approximately 40% of the RM lies within the aquifer area.

The Rural Municipality of South Norfolk covers approximately 74,500 hectares. The towns of Treherne, Rathwell and Notre Dame de Lourdes are the largest population centers in the municipality. Soils in the RM include imperfect to well-drained sands and loams. Land use within the RM is predominantly agriculture. Approximately twenty percent of the RM lies within the aquifer area

The major land uses in the Assiniboine Delta Region (ADR) include cropping, grassland and forest cover (Figure 2-13). Other land uses collectively represent less that 10% of the total land use. The large area that is cropped reflects the fertility of soils of the ADR.

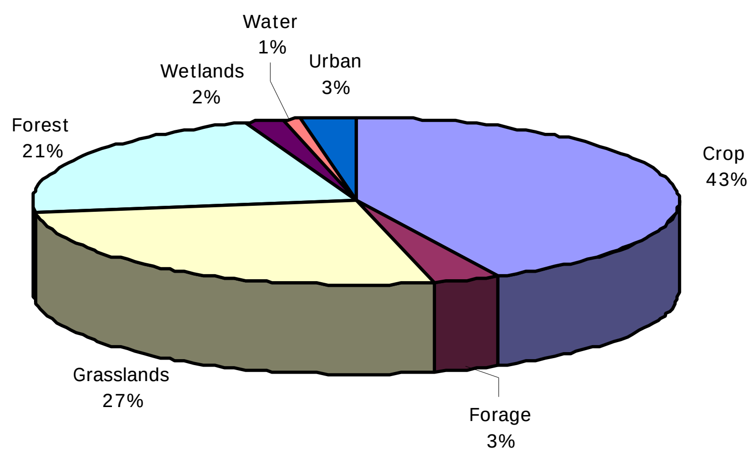


Figure 2-13: Land use in the Assiniboine Delta Region based on 1996 land use data (Statistics Canada).

2.4.2 Land clearing in the Assiniboine Delta Aquifer Region

Since 1956 there has been a steady increase in the area of cropland and improved pasture[1] in the ADA region through land clearing. There has also been a trend to an increasing percentage of the improved lands being cropped (Figure 2-14). With the increase in cultivation associated with cropping there has been an increase in the release of nitrogen from soil organic matter (Campbell et al, 1984) as well as an increase in the amount of nitrogen fertilizer applied to these lands. Together these processes increase the potential for nitrate movement to the underlying groundwater.

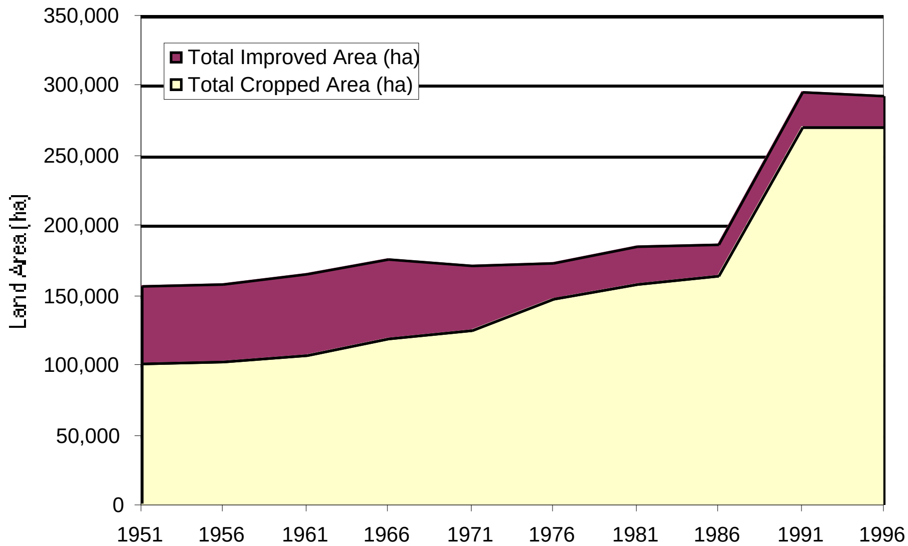


Figure 2-14: Comparison of cropped area to improved area on farms in the Carberry Aquifer Region, 1951-1996 (From Kulshreshtha, 1994 and Statistics Canada).

2.4.3 Agriculture in the Assiniboine Delta Aquifer Region

2.4.3.1 Irrigation in the Assiniboine Delta Aquifer Region

Approximately 152,000 hectares of land on the aquifer is rated either excellent or good for irrigation. However, much of the same land is also considered environmentally sensitive due to the predominance of well-drained coarse-textured surface deposits that lie above the aquifer. Approximately 26,300 hectares, 17% of the land rated highly suitable for irrigation, is currently licensed for irrigation. The 1986 Census of Agriculture indicated that 14 farmers reported using irrigation on their farms for a total irrigated area of 2,375 ha (Kulshreshtha, 1994). The difference between the licensed area and that reported to be under irrigation in a given year may reflect that most of the

[1] Statistics Canada defines "improved land for pasture" as land that has undergone some improvements such as cultivation, drainage, irrigation, fertilization, seeding or spray for bush and weed control.

irrigated land is in a two or three potato rotation with other crops. In most cases irrigation would be applied only to the potato year of the rotation.

2.4.3.2 Crop production in the Assiniboine Delta Aquifer Region

As reported in the 1996 Agricultural Statistics, wheat is the predominant crop in the ADA Region (Table 2-1). However since that time there has been increased areas of oilseeds and potato production. This information will not be reflected in the Statistics Canada data until the next Agricultural Statistics Period.

Table 2-1: Comparison of various crop areas to the total cropped area (%) in the Carberry aquifer region, 1951-1996 (after Kulshreshtha, 1994 with additional data from Statistics Canada).

Year	Wheat	Other grains	Oilseeds	Other field crops	Hay and foder
1951	30.8	52.5	8.8	0.6	7.3
1956	30.6	47.6	6.1	1.5	14.2
1961	37.5	34.3	7.0	0.4	20.8
1966	36.4	37.4	8.7	0.9	16.6
1971	23.7	45.5	13.0	1.9	15.9
1976	29.0	36.8	9.3	10.4	14.5
1981	26.9	39.5	16.6	6.3	10.7
1986	41.8	21.2	18.3	7.6	11.1
1991	41.7	21.4	14.7	10.0	12.4
1996	32.9	27.2	19.6	6.4	14.0

2.4.3.3 Livestock production in the Assiniboine Delta Aquifer Region

Regional trends in livestock production are similar to provincial trends. The numbers of cattle and poultry have shown some fluctuations, but no discernible trend. The numbers of hogs, however, have increased substantially.

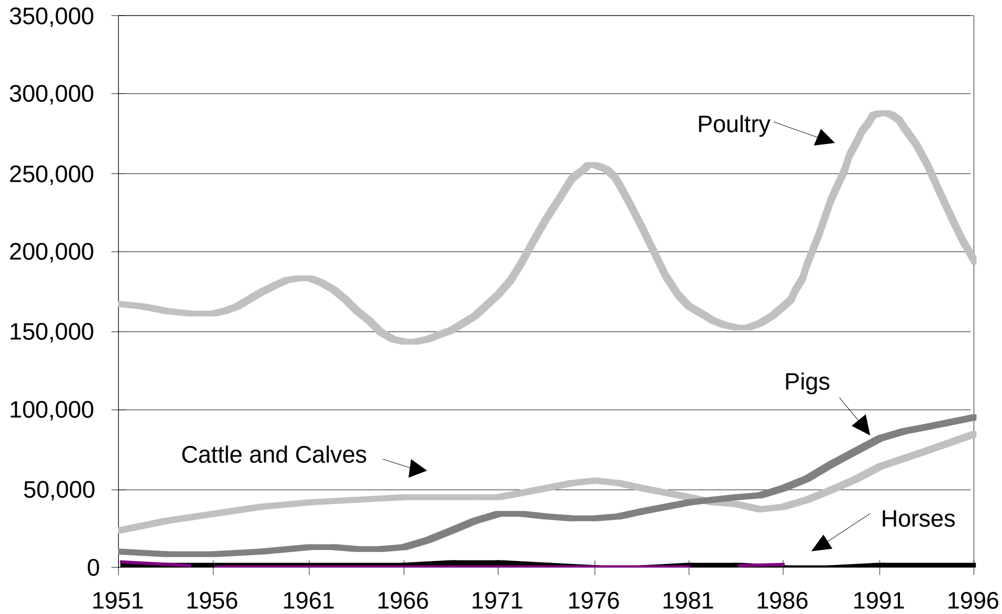


Figure 2-15: Livestock and poultry population in the Carberry aquifer region, 1951-1996 (From Kulshreshtha, 1994 and Statistics Canada).

2.4.3.4 Hog production (Manitoba)

Manitoba is Canada's third largest hog-producing province, after Quebec and Ontario, with 18.9% of national production in 1998. Manitoba hog production has increased steadily over the past 40 years from approximately 400,000 commercial marketings in 1956 to approximately 3,000,000 commercial marketings in 1996 (Figure 2-16).

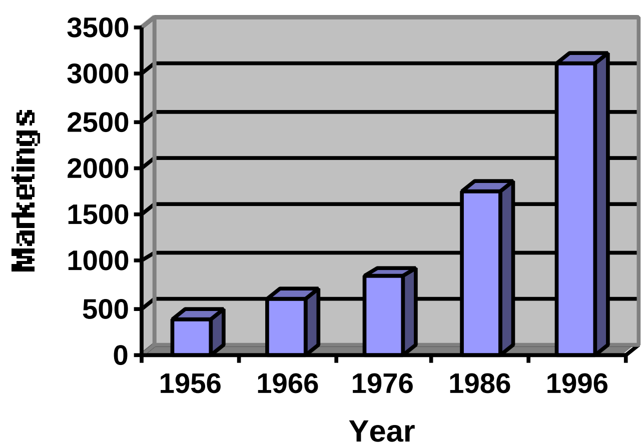


Figure 2-16: Hog production in Manitoba (1956-1996)

While the majority of these hogs are not produced in the Assiniboine Delta Region, the number of hogs per Rural Municipality in 1996 ranged from 5,000-19,000 to 20,000-49,999 (Figure 2-17).
With the recent expansion of the three existing processing plants in Manitoba and the completion of the new Maple Leaf plant in Brandon, the provincial demand for hogs is expected to increase a minimum of 82,000 hogs a week or 4,000,000 hogs a year.

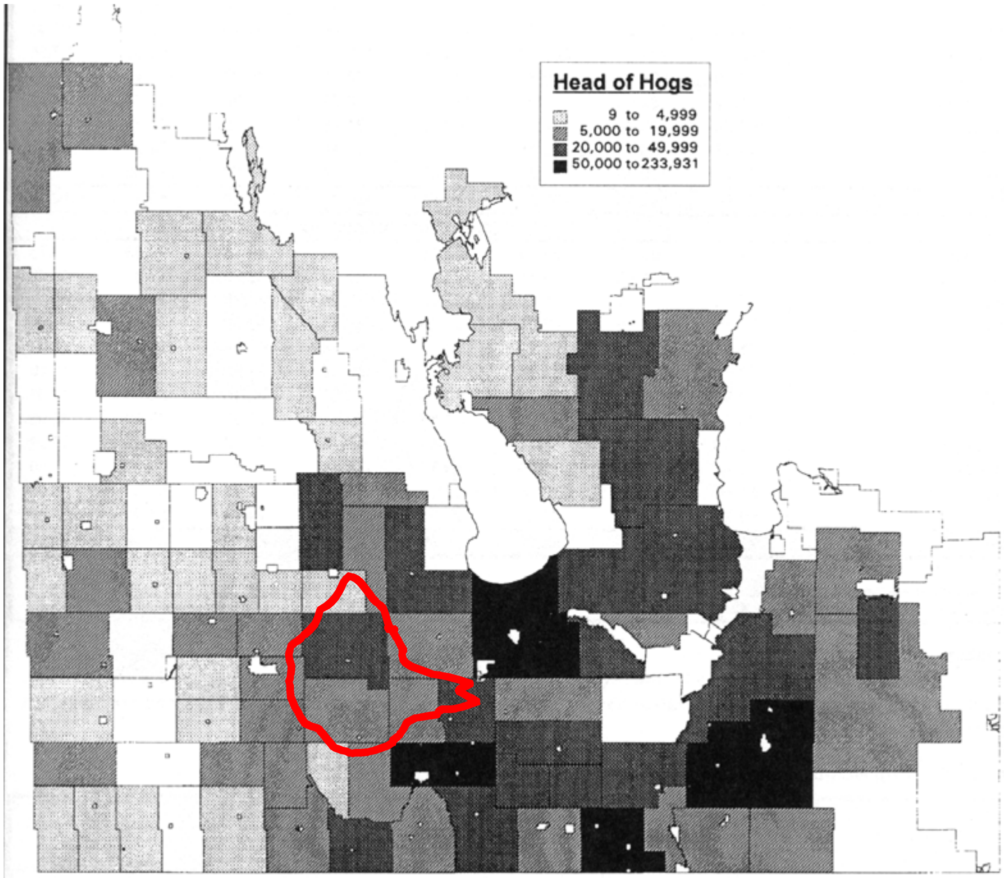


Figure 2-17: Total hog production in Manitoba in 1996 by Rural Municiplaity (Manitoba Agriculture, 1998).

2.4.3.5 Potato production (Manitoba)

Manitoba's commercial potato industry is the second largest in Canada and, involves the production of potatoes for the fresh, processed and seed markets. Commercial production is concentrated south and west of Winnipeg in the Portage la Prairie, Winkler, Morden, Treherne, Holland and Carberry areas. Manitoba potato production has increased steadily over the past 40 years from approximately 100,000 tonnes in 1956 to approximately 600,000 tonnes in 1996.

With large areas of land suitable for irrigated potato production and the potential for an expanding processing industry, Manitoba could become the largest potato producer in Canada.

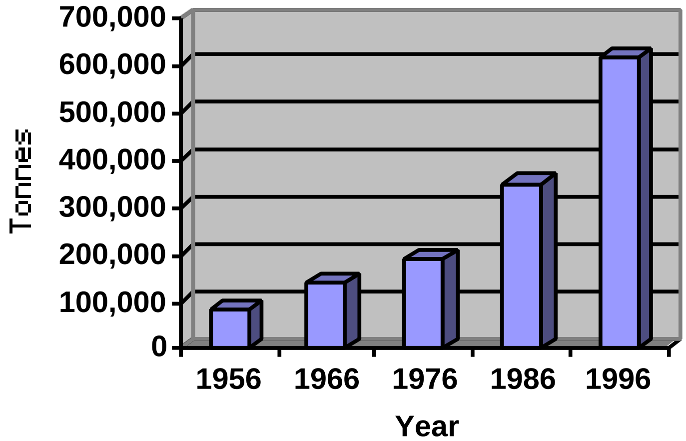


Figure 2-18: Potato production in Manitoba (1956-1996)

Medium to coarse-textured soils and the proximity of a large source of water for irrigation, make the Assiniboine Delta Aquifer Region an ideal location for potato production. The potato production in the ADR is associated with three Rural Municipalities: North Cypress, Victoria and North Norfolk. All three R.M.s had an increase in the area devoted to potato production from 1991 to 1996.

Table 2-2: Potato production in the Rural Municipalities of the Assiniboine Delta Region as reported by Statistics Canada.

	1991		1996		
	Farms Reporting	Hectares	Farms Reporting	Hectares	% change
Manitoba	227	20,023	272	28,354	+ 42%
South Cypress	3		4		
North Cypress	39	4,274	52	7,798	+ 82%
Langford	3		0		
Victoria	7	883	8	1,282	+ 45%
South Norfolk	2		2		
North Norfolk	14	2,270	14	2,961	+ 30%
ADA (% of total)	68	7,427 (37%)	80	12,041 (42%)	+ 30%

The increase intensive cropping (potato) and animal production (hogs) on the ADA increases the potential for NO_3^- impacts on the aquifer. Care must be taken to ensure the potential for environmental impact is considered in land use decisions and the development of agronomic practices. To understand this process we must consider the soil and groundwater properties that impact upon the movement of NO_3^- to groundwater and the fate of NO_3^- in groundwater.

3. Processes contributing to nitrate movement to groundwater

3.1 Sources of groundwater nitrate

Nitrate in groundwater may be derived from a number of industrial, municipal, residential and agricultural sources. There are few cases where the relative contribution of each of these sources has been adequately evaluated. In the following section we examine the primary sources of NO_3^- in the Assiniboine Delta based on studies of nitrate leaching in other areas of the world and land management practices in the Assiniboine Delta region.

3.1.1 Role of intensive agriculture

The loss of nitrate from the root zone to the groundwater occurs in all ecosystems to a greater or lesser degree; it is not unique to agricultural systems. Agriculture has exacerbated NO_3^- loss to groundwater through the disruption of natural nutrient cycling processes. High rates of nitrogen mineralization, induced as a result of the breaking of prairie soils, supported prairie grain production for several decades. Campbell et al. (1984) has estimated that over the past 100 years approximately 20% of the soil organic N present at the time of sod breaking has been leached to groundwater.

Over the past century we have increased the yields of our agricultural crops through the use of improved plant varieties, improved pest management practices and by reducing nutrient limitation through the application of inorganic fertilizers, animal manures and the growth of legume crops. For example, the total amount of N fertilizer used in agriculture in Manitoba has increased from approximately 20,000 tonnes in 1965 to 220,000 tonnes in 1989 (Figure 3-1). In the past two decades the rate of N additions has risen to a level roughly equivalent to the amount N removed in the grain. More recent premiums for high protein wheat have resulted in higher N fertilizer applications to produce higher protein content. The residual NO_3^- remaining in the profile in the fall increases the risk of nitrate leaching. The increase in the land area devoted to high value, nitrogen-demanding crops such as potato and vegetable production has resulted in increase N fertilizer inputs.

A recent increase in the number of intensive livestock operations (ILOs) has also resulted in the addition of nutrients to Manitoba soils. The degree to which the rates of manure nutrient application are offset by crop nutrient removal determines the net loading of nutrients to the system. To date, relatively few of these ILOs have been located on the Assiniboine Delta Aquifer.

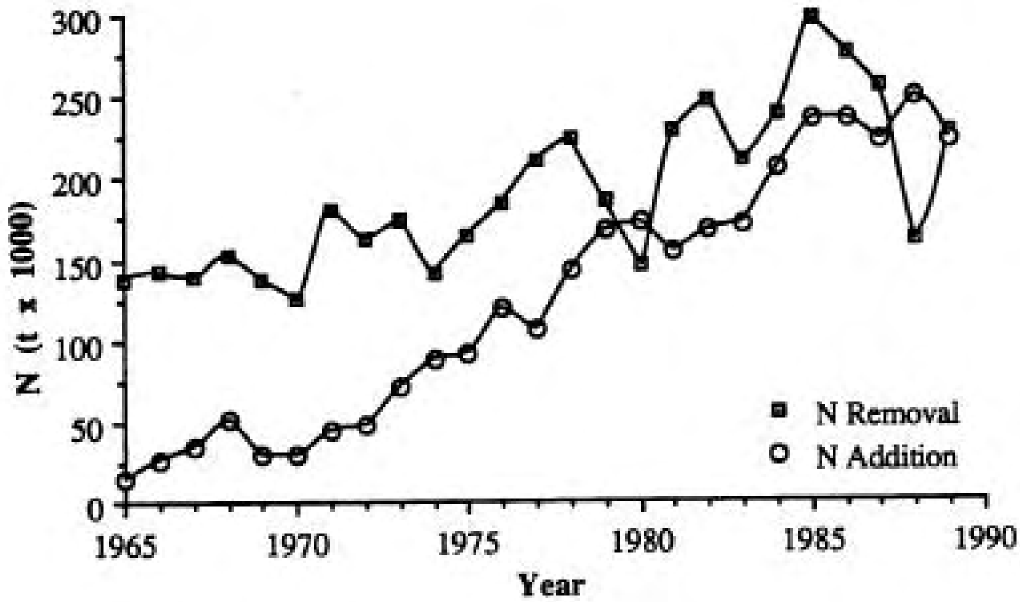


Figure 3-1: Crop removal and fertilizer replacement of N in Manitoba from 1965 to 1989. Note that this data is calculated based on the assumption that N is removed by seed only and straw is returned to the soil. Data from Statistics Canada (1974, 1981, 1989), Spearin and O'Connor (1991) and Western Canada Fertilizer Association (from Doyle and Cowell, 1993).

3.2 Where and under what conditions is nitrate leaching a problem?

The amounts of nitrate accumulating in the soil, and thus available to be leached from it, is dependent upon the net effect of several processes in the nitrogen cycle (Figure 3-2). The transformations affecting nitrate occur simultaneously with the transport through the profile. The extent to which the various biochemical processes impact on NO_3^- concentration will vary throughout the soil profile as a result of changes in the soil/plant environment and the resulting impact on microbial activity. Thus evaluation of the extent of nitrate movement must consider the simultaneous occurrence of transport and transformation. The net effect of these processes, and thus the potential for nitrate movement from the root zone to groundwater, depends on climate, soil type and land use.

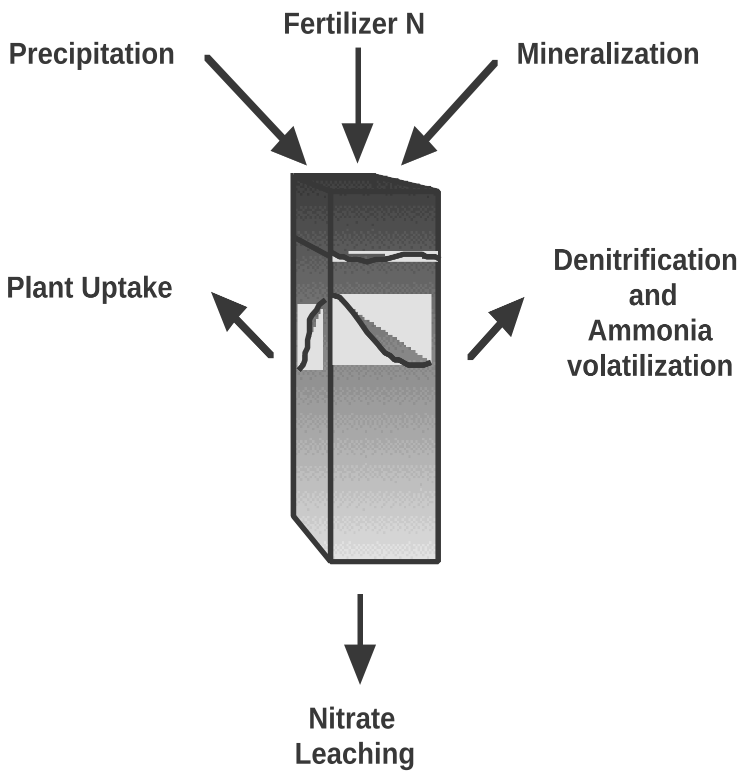


Figure 3-2: Sources and sinks for nitrate in the soil profile.

Climate - Nitrate movement below the root zone only occurs when there is net drainage. This occurs when precipitation exceeds the evapotranspiration and runoff. The extent and timing of periods of drainage depend upon the climate. Under the climate conditions of the ADA region, precipitation exceeds evapotranspiration during the spring and fall and thus there is often net drainage of water from the root zone during this period. On average it has been estimated that the total net drainage of 2.2 cm/year[2] would occur in the ADA. Due to annual variation in climate, the extent to which potential nitrate loss will be realized will vary. Management strategies that minimize nitrate accumulation during high leaching risk periods will, in the long-term, reduce nitrate loss to the groundwater.

Soil type - Soil texture impacts on biological activity and the rate at which solutes are transported through the soil profile. Nitrate found in soil originates from N fertilizers, atmospheric deposition of N and from the mineralization of crop residues, animal manure and soil organic matter. Nitrate that accumulates in soil may either remain in the soil, be taken up by the plant, be denitrified or be leached from the profile (Figure 3-2). These processes are influenced by the rate at which water moves NO_3^- through the soil. The

[2] Based on data presented by Render (1988), the average total net drainage of the soils overlying the ADA is be estimated to be 2.2 cm/year as calculated from the difference between precipitation (pptn = 43.28 cm/year; 17.04"/year) and evapotranspiration (ET = 41.07 cm/year; 16.17"/year). (Render, 1988)

more rapidly NO_3^- is transported the less opportunity for reactions that operate as a sink for NO_3^- (plant uptake, denitrification) to remove it from the soil solution. Texture has a strong influence on soil hydraulic properties. Fine-textured soils have a low water infiltration rate, and thus, processes that occur at the surface (runoff) or in the upper profile (plant uptake or denitrification) have greater opportunity to occur due to the time required for water to pass through the profile. In coarse-textured soils the rate of percolation is much higher, and when sufficient rainfall occurs, the leaching of nitrate through the profile may be very rapid. The soils of the ADA are predominantly coarse-textured (Figure 2-9) with high rates of hydraulic conductivity. Approximately three quarters of the soils in this region are considered to be well to rapidly drained (Manitoba Land Resource Unit, 1996-7)

Soil aeration influences soil biological activity. Maximal aerobic biological activity occurs at approximately 60% of water-filled pore space (Fig. 3.3). At water-filled porosities above this level anaerobic processes predominate. Texture influences this relationship. Coarse-textured soils have a high percentage of large air-filled pores and as a result aerobic processes predominate. Denitrification is a process associated with anoxic zones in the soil and reduces nitrate to nitrous oxide (N_2O) and nitrogen gas (N_2). The aerobic nature of coarse-textured soils reduces the potential for denitrification loss and by reducing this sink for NO_3^- increases the potential for NO_3^- contamination of groundwater. The low water-holding capacity of these soils may cause water availability to limit microbial activity and reduce N mineralization.

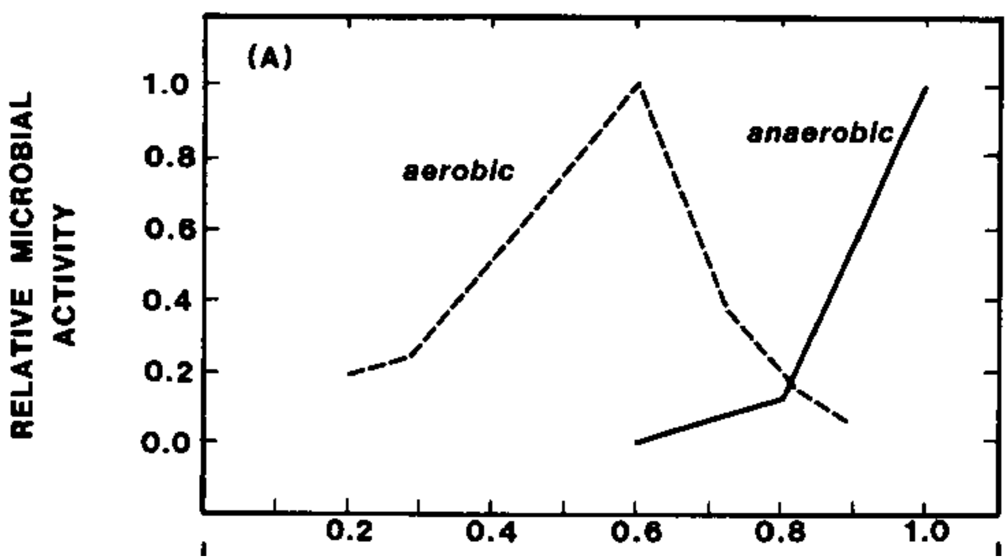


Figure 3-3: Influence of percent water-filled pore space on soil biological activity.

Preferential Water Flow

Under some circumstances, significant amounts of water may flow through large soil pores (macro-pores) even though they make up only a small percentage of total pores. This type of water flow is called preferential flow (Figure 3-4), and may account for water and contaminant movement through finer textured soils once thought to be relatively impermeable. In this respect, fine and medium textured soils with frequent worm holes, cracks, or other vertical channels have the potential to allow nitrate movement deep into the soil beyond the rooting zone.

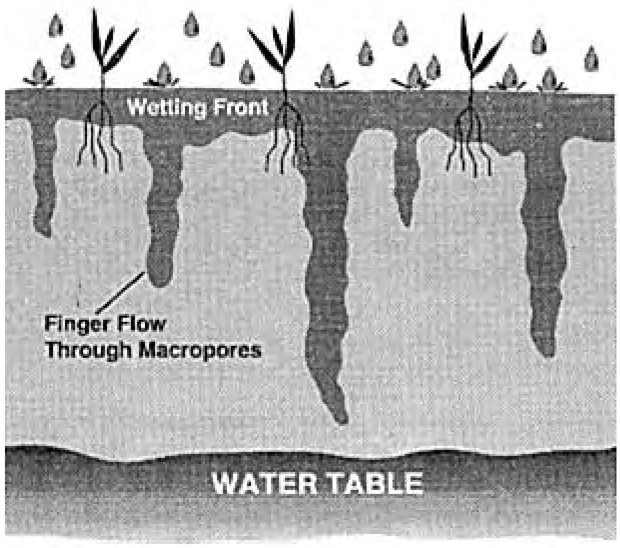


Figure 3-4 Illustration of water movement by preferential flow through a soil profile.

Preferential flow through soil depends on a continuous connection between macropores at the soil surface and those that occur much deeper in the soil. If preferential flow is significant in some soils, management techniques such as tillage that break the connection between surficial and deeper macropores would be important to groundwater protection.

Source: http://www.ext.nodak.edu/extpubs/plantsci/soilfert/eb64w.htm#Presence

In coarse-textured soils similar patterns of preferential flow have been observed. In these systems the preferential channels are thought to be a pedogenic phenomena and not necessarily a function of the formation of biopores.

Management system - The accumulation of nitrate in the soil increases the risk of nitrate loss to groundwater. Management strategies that limit the amount of nitrate in the soil will reduce the potential for loss. Choice of the rate, timing and formulation of fertilizer N application has an important impact on nitrate accumulation in soil. Previous crop also influences the amount of residual soil NO_3^- remaining in the soil (Table 3-1). Residual soil NO_3^- will be particularly high following drought years where adverse plant growing conditions limit nitrogen uptake by the crop.

Table 3-1: Residual soil NO_3^--N levels in Manitoba as affected by previous crop and growing conditions.

Previous crop	Soil nitrate-N lb./ac in 0-24 in. depth	
	Drought years (1988-89)	1990-1998
Wheat	102	50
Barley	76	43
Canola	79	38
Flax	88	39
Corn	107	64
Potatoes	94	71

* Data from AGVISE Laboratories.
(Source: www.gov.mb.ca/agriculture/soilwater/soilfert/)

Manitoba Agriculture recommends nitrogen fertilizer application rates for a range of crops based on soil NO_3^- testing and agronomic N response trials (Table 3-2). Adherence to these recommended rates of nitrogen application and annual soil testing will help to reduce over-application of nitrogen fertilizer. Note that the determination of the rate of fertilizer N application depends upon the expected yield goal for the crop. The use of unrealistically high yield goals will result in excessively high rates of fertilizer N, increasing the risk of nitrate contamination of groundwater, and reducing the profitability of the enterprise.

Table 3-2: Nitrogen recommendations for hard red spring wheat (based on spring broadcast application)

		Nitrogen Recommendation (lb/ac)								
Soil Moisture Category		Ideal			Moist			Dry		
		Target Yield (bu/ac)								
Fall Soil NO_3^--N lb/ac in 0-24 in	Rating	50	45	40	45	40	35	40	35	30
20	VL	120	90	65	110	70	45	100	55	30
30	L	100	70	45	85	45	25	80	30	10
40	M	80	50	25	65	30	5	60	10	0
50	M	60	30	5	50	10	0	40	0	0
60	H	40	10	0	25	0	0	20	0	0
70	H	20	0	0	0	0	0	0	0	0
90	VH	0	0	0	0	0	0	0	0	0
90	VH	0	0	0	0	0	0	0	0	0
100	VH+	0	0	0	0	0	0	0	0	0

Source: http://www.gov.mb.ca/agriculture/soilwater/soilfert/

It is important that other nitrogen sources, such as previous legume crops or animal manure applications, should be considered in estimating fertilizer N requirements. Failure to account for the N contributed by these sources results in excessive rates of N application and increases the potential for NO_3^- loss from the root zone. Manitoba Agriculture can assist the producer in estimating the nitrogen-supplying capacity of these sources. This issue may be of particular importance in estimating potential NO_3^- impacts on the ADA. Conversations with various government and industry personnel have indicated that for these N sources, particularly animal manures, the nutrient content is often either discounted or negated altogether in making fertilizer N recommendations. Continuing research, education and extension relating to the effective inclusion of these alternate N sources in an efficient N management strategy is necessary to protect groundwater.

The application of fertilizers containing a high percentage of ammoniacal or ammoniacal producing forms of nitrogen (Urea, UAN, anhydrous ammonia) delays the formation of nitrate and thus reduces the potential for loss during this period. Similarly the use of nitrification inhibitors in combination with ammoniacal N sources delays nitrification (the conversion of ammonium to nitrate) and reduces the potential for nitrate loss. Banding of urea and ammonium-based fertilizers also delays nitrification and reduces the potential for nitrate loss. It has long been recognized that delaying nitrogen fertilizer application results in increased availability to the plant and reduced potential for NO_3^- leaching (Appleton and Helms, 1925). Split applications of N fertilizer are also a commonly used approach to increase fertilizer use efficiency. Racz et al. (1994) examined influenced the influence rates fertilization of the preceding potato crop on fall residual soil nitrogen content. The use of split applications of N, controlled release nitrogen products or nitrification inhibitors all decreased the amount of nitrate remaining in the soil during the fall period (Figure 3-5).

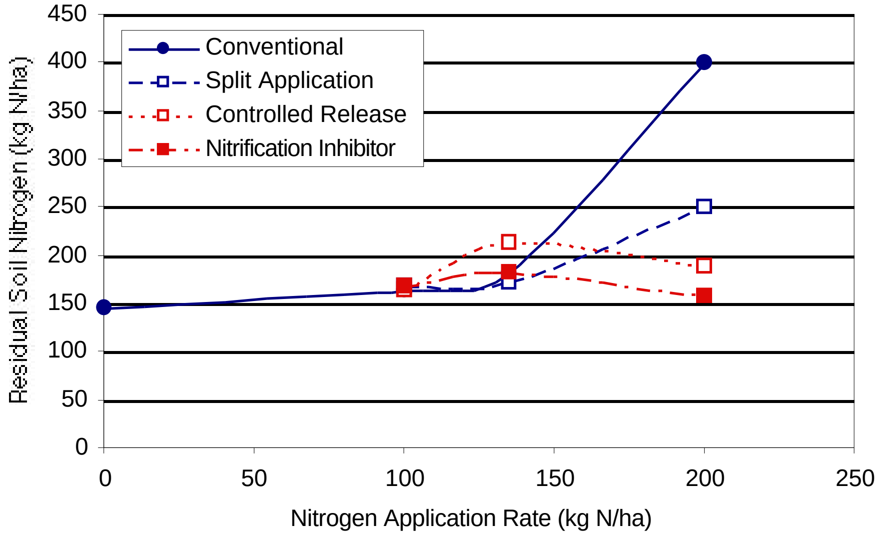


Figure 3-5: Influence of nitrogen delivery technologies on the relationship between rate of nitrogen fertilizer addition and residual soil NO_3^- in the fall. Data presented by Racz et al. (1994).

The disproportionately large increase in residual soil nitrate observed for the highest rate of N in the conventional treatment (225 kg N/ha residual soil N increase as a result of an increase of N application rate of 40 kg N/ha) may reflect the high degree of variability in these data and/or a disproportionate influence of rates of N application in excess of crop N requirements.

Tillage affects the potential for nitrate leaching by altering the rate of residue breakdown and by disrupting soil macropores. Crop residues left on the soil surface reflect light and insulate soil, reducing soil temperature and loss of water through evaporation (Bond and Willis, 1969). This creates a favorable environment for microbial activity in soils that normally tend to be warm and dry (Power et al., 1986). Crop residues also serve as a carbon and nitrogen substrate, which is decomposed through microbial activity. In an undisturbed system, most N released during oxidation of organic matter is immobilized in the cells of microorganisms, taken up by plants, or conserved as surface litter (Doran and Smith, 1987). Tillage alters this steady state by increasing soil aeration, removing the insulating effect on evaporation and temperature, and distributing the organic substrate throughout the plow layer (Van Veen and Paul, 1981). This increases the accessibility of the organic substrate to decomposition by soil microorganisms, and thus increases mineralization (Elliott, 1986). The incorporation of residues in the soil associated with conventional tillage practices increases the rate of breakdown relative to conservation tillage practices where residues accumulate on the soil surface. Rapid decomposition results in the mineralization of nitrogen, increasing nitrate availability to the plant and the potential for nitrate loss from the profile. If crop residue breakdown occurs when there is no actively growing crop, nitrate will accumulate in the soil and may be leached from the profile. Thus, by retaining nitrogen in crop residues, conservation tillage practices may reduce leaching of nitrate over the fall to spring period following the incorporation of crop residues under conventional tillage. In addition to incorporating crop residues, tillage disrupts the continuous pores and channels which form as a result of plant root growth and earthworm activity. In fine-textured soils these channels may be the major pathways of water percolation (Edwards et al., 1989). Disruption of the continuous channels will slow water movement through the soil and increase the availability of N to the processes occurring at or near the surface (runoff, plant uptake, denitrification). Thus tillage may decrease the rate of water movement through fine-textured soils.

Long-term comparisons of tillage have indicated that, with adequate applications of N fertilizer, greater or equal corn yields can be achieved under no-tillage than conventional tillage. Yields of corn under no-tillage systems are generally lower when small amounts of fertilizer N are added, but approximately equal when amounts in excess of 100 kg N/ha are added (Doran and Power, 1983; Meisinger et al., 1985; Thomas and Frye, 1984). This has been attributed to greater immobilization of fertilizer N and less mineralization of soil N in non-tilled soils (Kitur et al., 1984; Rice and Smith, 1982). Immobilization is a storage process, not a loss, so that over the long-term, yield response of non-tilled crops may be comparable to those of conventionally tilled crops at low rates of N fertilizer application. The placement of fertilizer N below the surface layer of non-tilled soils, where biomass levels and concentration of high C:N ratio substrates are lower, can increase immediate N availability, N uptake and crop yields (Doran and Smith, 1987; Mengel et al., 1982).

<u>Cover Crops</u> - Crop rotation and the use of cover or 'catch' crops have also been shown to reduce the amount of N available for leaching (Varvel and Peterson, 1990). Brandi-Dohrn et al. (1997) demonstrate the ability of a winter cover crop to reduce soil solution NO_3^--N levels to below the water quality objective level of 10 mg N/L (Figure 3-6).

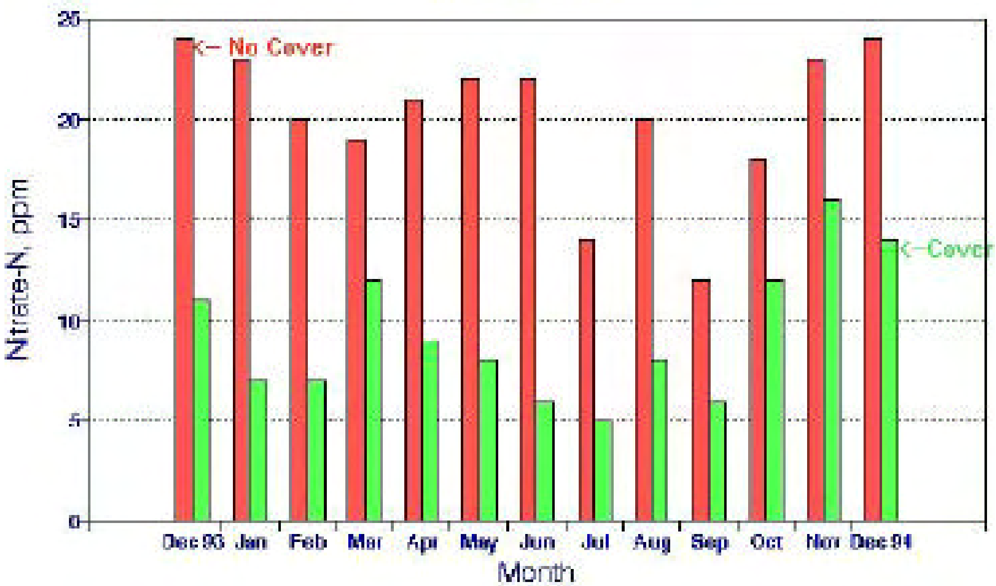


Figure 3-6: Influence of a winter cover crop of cereal rye on flow-weighted mean concentration of soil solution nitrate-N collected at a 4 foot depth under a sweet corn crop fertilized with 225 kg N/ha. Mean data presented are monthly means. (Data taken from Brandi-Dohrn et al., 1997)

Thomsen and Christensen (1999) observed that a ryegrass catch crop reduced nitrate leaching by 50% over a 5-year period. The authors noted that cropping systems must be adjusted to exploit the additional nitrogen released when N is mineralized following incorporation of the ryegrass catch crop.

Irrigation - The following extension article from North Dakota State describes the influence of irrigation on nitrate leaching:

> Irrigation - Irrigation creates conditions that can carry a higher risk of groundwater contamination compared to dryland farming. Irrigation generally occurs on coarse-textured soils that have good drainage and are prone to leaching. Irrigation often occurs over shallow aquifers. Because irrigation increases yield potential, increased nitrogen levels are required to meet that potential. Excessive inputs of either nitrogen or water, particularly on irrigated coarse-textured soils, substantially increase the potential for nitrogen leaching.
>
> Sprinkler systems, especially center pivots, allow good water control and less leaching risk. Careful scheduling can provide adequate water for daily crop needs at soil water storage levels much less than field capacity (Lundstrom and Stegman, 1988). Furrow and flood irrigation systems are the poorest in terms of water application efficiency.
>
> Under irrigation, profitable crop production and groundwater protection have been demonstrated when existing guidelines for nitrogen application and water management are followed. Montgomery et al. (1990) found that high corn yields could be produced with carefully managed irrigation and nitrogen fertilizer inputs in North Dakota. Lower irrigation inputs with well managed scheduling resulted in significant reductions in nitrate leaching (Table 3-3).
>
> Table 3-3. Nitrogen and irrigation amounts applied to lysimeters and the resulting nitrate-nitrogen losses and final grain yields averaged over three years (Montgomery et al., 1990).

Nitrogen Rating	Nitrogen Fertilizer	Relative Irrigation Amount	Irrigation Amount	Nitrate Leaching Losses	Final Grain Yield
	lb/ac		in.	lb/ac	bu/ac
Low	83	Low	7.6	17.6	200
Low	83	High	10.0	30.2	195
High	127	Low	7.6	19.7	215
High	127	High	10.0	30.1	215

Source: http://www.ext.nodak.edu/extpubs/plantsci/soilfert/eb64w.htm#Presence

Irrigation has not always been associated with elevated NO_3^- levels. Data collected in Alberta for the recovery of deep banded urea by barley indicates that N recovery in irrigated systems was at least as good as under dryland conditions (Figure 3-7).

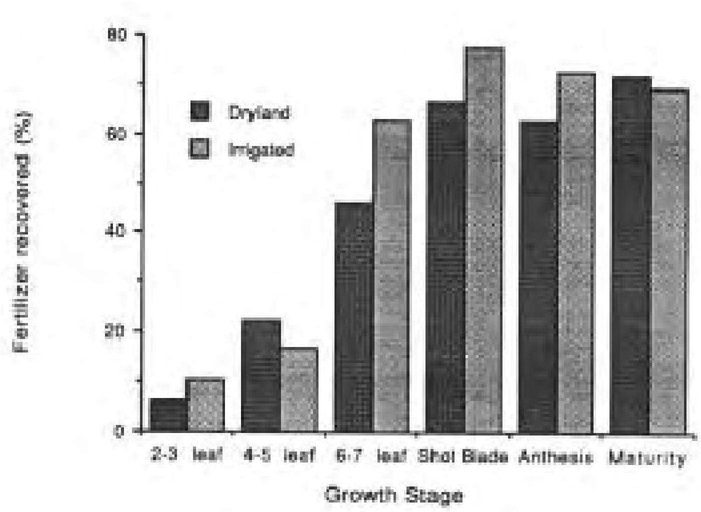


Figure 3-7: Recovery of deep banded ^{15}N-labelled fertilizer at various growth stages of barley (from Hartman and Nyborg, 1989)

3.2.1 Assessment of deep-leached nitrate

One approach to assessing the nitrate loss from particular management systems is the measurement of NO_3^- accumulation in the soil profile below the normal rooting zone. Manitoba Agriculture has conducted a survey of 'deep-leached' nitrate in the early '90s (Table 3-4; Ewanek, 1995). Nitrate concentrations of greater than 150 lbs N/acre (168 kg N/ha) in the top four feet of soil were considered to be in excess of acceptable concentrations.

The results of this survey indicate that a number of the cropping systems studied had high frequencies (approaching 50%) of NO_3^- accumulation in the subsurface in excess of acceptable concentrations. The data also indicate the ability of some cropping systems (grass, alfalfa) to reduce nitrate accumulations. Campbell et al. (1994) found that, although deep-rooted forage crops such as alfalfa remove NO_3^- and water at depth, the increased N-supplying power of the soil resulting from legume growth provided the opportunity for considerable NO_3^- leaching. It is clear from the data presented in Table 3-4 that, in some of the management systems, steps should be taken to reduce NO_3^- loss from the root zone. These systems should be the focus of efforts to improve nutrient management and the utilization of nutrient delivery systems that result in improved nutrient use efficiency.

Table 3-4: Summary of data collected in Manitoba from 1992-94 on the number of survey sites which have NO_3^- concentration in excess of 150 lbs. N/acre found in the subsurface in soils under various cropping systems. (From Ewanek, 1995).

System	Number of fields Sampled	Number of fields having a NO_3^--N level > 150 lbs/acre top 4 feet	Number of fields with NO_3^- below 4 feet
Grass	9	0	0
Zero Till	7	4	2
Vegetables	6	5	6
Fertilized Alfalfa	5	0	1
Potatoes	41	27	15
Fertilized Annual Crops	41	18	14
Manure applied to Annual Crops	84	46	26
Manured Alfalfa	12	1	2
Corn	22	15	16

3.3 Nutrient management planning

Effective nutrient management represents the primary means of controlling nitrate leaching. Increasing the efficiency of nutrient supply and avoiding nitrate accumulations during periods of groundwater recharge will result in decreased loading of nitrate to groundwater. The first step in this process is an overall assessment of the magnitude of nutrient cycling in the management system. Construction of whole farm nutrient budgets has been used as a tool to examine the efficiency of nutrient use and the potential for environmental impact. Nutrient management planning exercises are quickly becoming a required component of intensive agricultural production. Ontario, through the Ontario Farm Management Coalition, has established a Nutrient Management Working Group with an aim to developing nutrient management plans.

4. Current assessment of Assiniboine Delta Aquifer

Assessment of the current status of the ADA can be achieved by direct measurement of water quality or by examining land use in the context of what is known about the hydrology of this aquifer. Both approaches have their merits. The strength of indicators based on direct monitoring is that they provide an unequivocal assessment of the NO_3^- status of the aquifer. One weakness of this approach is that spatial and temporal variation in the aquifer complicates the interpretation of measurements. A second short-coming is that this approach provides information on the impacts of historical land use and does not provide a direct assessment of the impacts of current land use and the future status of the water body – that is to say it is a reactive indicator. Assessment of the potential impacts of land management does not provide a clear, quantitative and unequivocal estimate of NO_3^- impact but does help in assessing the potential impacts of current and future land uses on water quality. Together these tools provide important insight into the current status of the aquifer and provide some insight on how land use decisions and land management will impact on the future quality of the aquifer.

4.1 Current water quality information

There is little doubt that over the past 50 years the NO_3^- concentration of drinking water samples collected from wells located in ADA have been tested on numerous occasions. We were unable to locate any databases listing the results of these well water tests or any effort to compile such a database. Manitoba Conservation has undertaken a rather extensive survey of well water quality but at a scale such that there are relatively few points being measured on the ADA. The compilation of the results of past and future well water tests would provide useful information on the quality of water being consumed in this area. This data would be somewhat challenging to interpret in terms of the quality of the aquifer in general, but none-the-less would provide an important first step in assessing the quality of drinking water drawn from the ADA.

While there is not an extensive amount of information available on groundwater quality there have been a number of key studies undertaken in this area.

4.1.1 Keystone Vegetable Producers Association/PFRA/Agriculture Canada/Manitoba Agriculture Study 1992

This study examines the water quality in 26 irrigation wells and three monitoring wells located on the ADA (Buth et al., 1992). The depths of the irrigation wells were not specified in the report. The monitoring wells had 0.76 m of screening beginning from 5.0 to 7.1 m from the surface. Irrigation well samples were collected between August 27 and September 5, 1991. Monitoring wells were sampled on March 16, 1992. The analytes examined included nitrate, atrazine, bromoxynil, carbofuran, dicamba, diclofop-methyl, fenoxaprop-ethyl, fonofos, MCPA, methoxychlor, metribuzin, picloram, sethoxydim, thifensulfuron and 2,4-D. The distribution of wells sampled is shown in Figure 4-1. Soil samples were collected to a depth of 5.5 m from sites immediately adjacent to monitoring well sites 1 and 2.

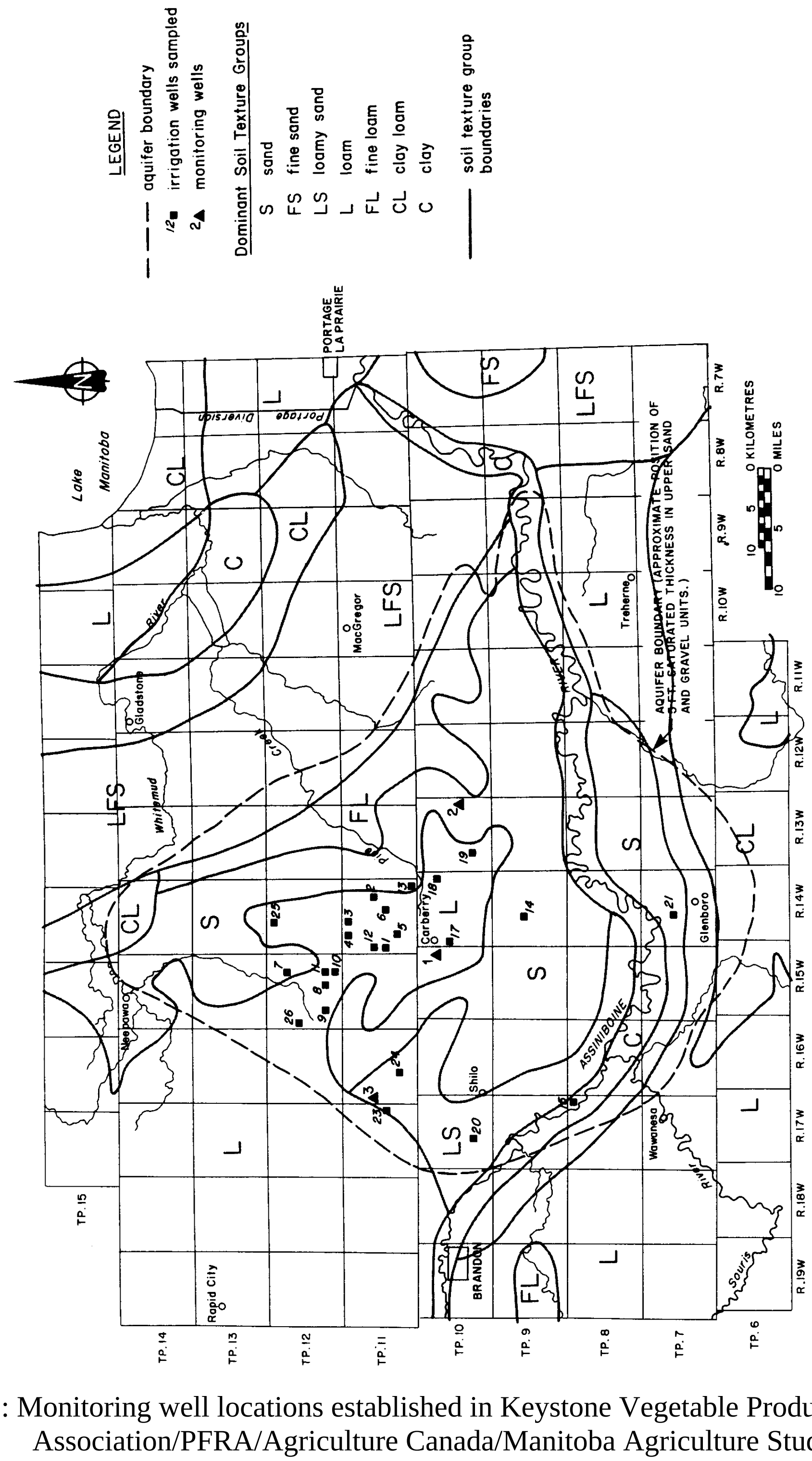


Figure 4-1: Monitoring well locations established in Keystone Vegetable Producers Association/PFRA/Agriculture Canada/Manitoba Agriculture Study 1992 (Buth et al., 1992).

Nitrate nitrogen levels in irrigation wells ranged from <0.4 to 7.8 mg N/L. The nitrate nitrogen concentration of monitoring wells ranged from <0.2 to 16.4 mg N/L. The highest nitrate concentrations in both irrigation wells and monitoring wells occurred on the loamy sands occurring north and west of Carberry. Only in MW-1 was the nitrate concentration above the drinking water standard of 10 mg NO_3^--N L^{-1}. Soil samples collected at MW-1, the monitoring well with the highest nitrate concentration, reflect nitrate accumulation in the soil profile (Figure 4-2). Note that current soil nitrate guidelines stipulated in the Manitoba Manure Livestock Regulation indicate that in coarse-textured soils cropped to annual crops the soil nitrate concentration should not exceed 101 kg N/ha in the top 60 cm (90 lbs N/ ac in the to 2 feet). Assuming a soil bulk density 1.3 Mg/m^3, this translates into an average soil nitrate concentration of 12.9 µg N/g soil in the 0-60 cm zone.

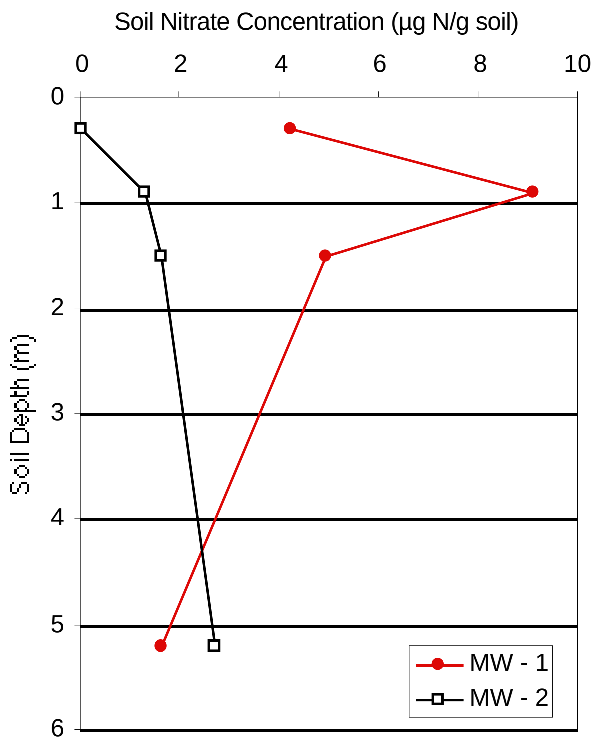


Figure 4-2: Distribution of soil nitrate with depth as reported in Buth et al., 1992.

4.1.2 Carberry Aquifer Monitoring Project

This project was initiated in 1994 under the Canada-Manitoba Agreement on Agricultural Sustainability (CMAAS) and continued as a result of the support of other funding agencies. The project is under the coordination of the Manitoba Crop Diversification Centre (MCDC). The main objective of the project was to establish baseline conditions at the MCDC site with respect to pesticide and NO_3^- concentrations of groundwater. It is an ongoing project, monitoring pesticide and nutrient concentrations in the ADA, both on and off the MCDC site.

Monitoring wells include a series of wells (MW1-5) located on the MCDC Research Site. Data from the first several years of monitoring of NO_3^- concentration in these wells indicate wells MW1 and MW4 have concentrations in excess of the 10 mg N/L drinking water guideline through out the majority of the monitoring period (Figure 4-3). Monitoring wells MW 5 and to a lesser extent MW5, MW3A, and MW3B are low at the beginning of the monitoring period and have increased rapidly in concentration over the past 2-3 years.

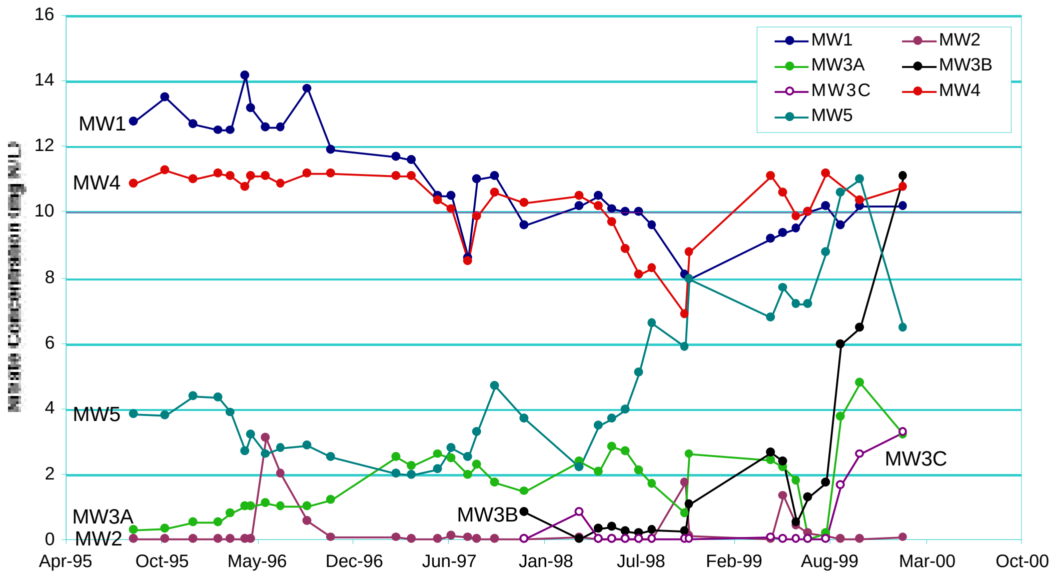


Figure 4-3: Nitrate concentrations in groundwater samples collected from monitoring wells located on the MCDC site.

Regional wells distributed through out the ADA have also been included in this project (Figure 4-4). Nitrate concentrations in these wells show trends of little or no impact (MW-A, MW-B, MW-C, MW-E, and MW-G), wells with moderate impact and an increasing NO_3^- concentrations (MW-D, MW-F1 and MW-F*), and wells with severe impact (MW-H). While there is significant variability in this data and a number of sites with no evidence of impact, there are a sufficient number of wells with high NO_3^- concentration or a trend of increasing NO_3^- concentration to serve as a warning of potential impact on the aquifer.

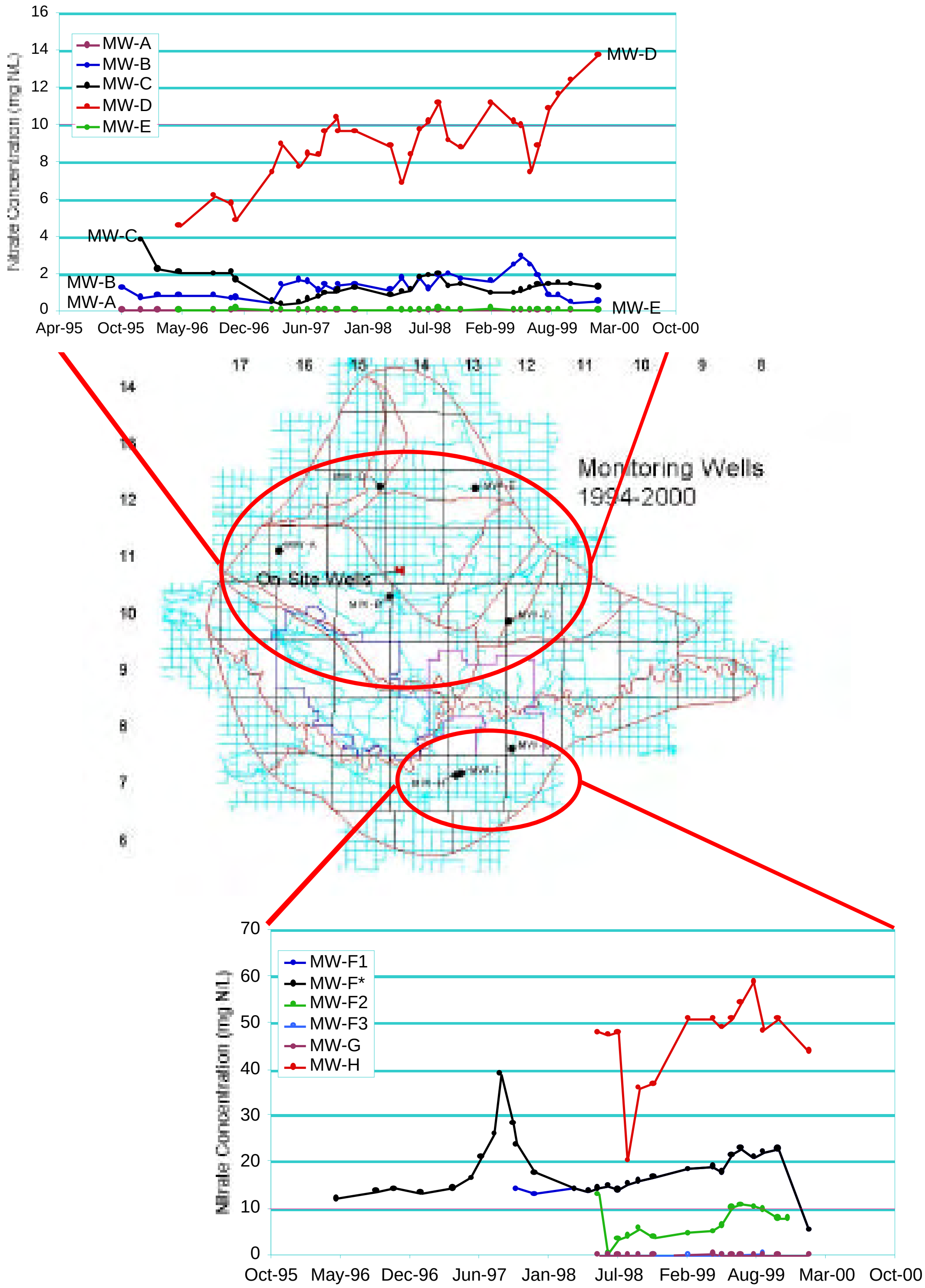


Figure 4-4: Location of monitoring wells in the Carberry Aquifer Monitoring Project and the nitrate concentrations of samples collected from off-site wells from the spring of 1996 to the fall of 1999.

Additional study wells have being added to this project to focus on areas of high agricultural activity (Pine Creek North and Assiniboine River South) and to increase the number of monitoring stations (Figure 4-5). These additional sites and continued monitoring of existing sites will provide a larger data set to better evaluate the trends in water quality in the ADA.

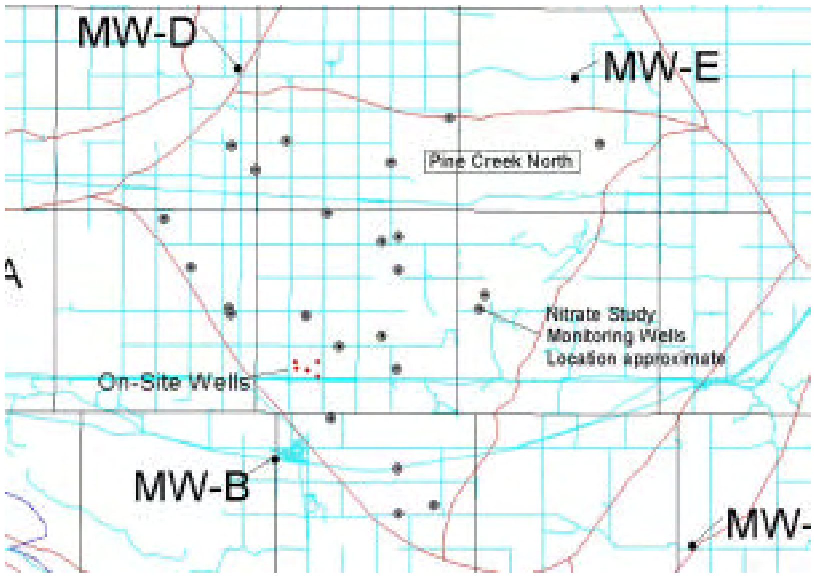


Figure 4-5: Location of additional monitoring wells established in the Pine Creek North sub-basin.

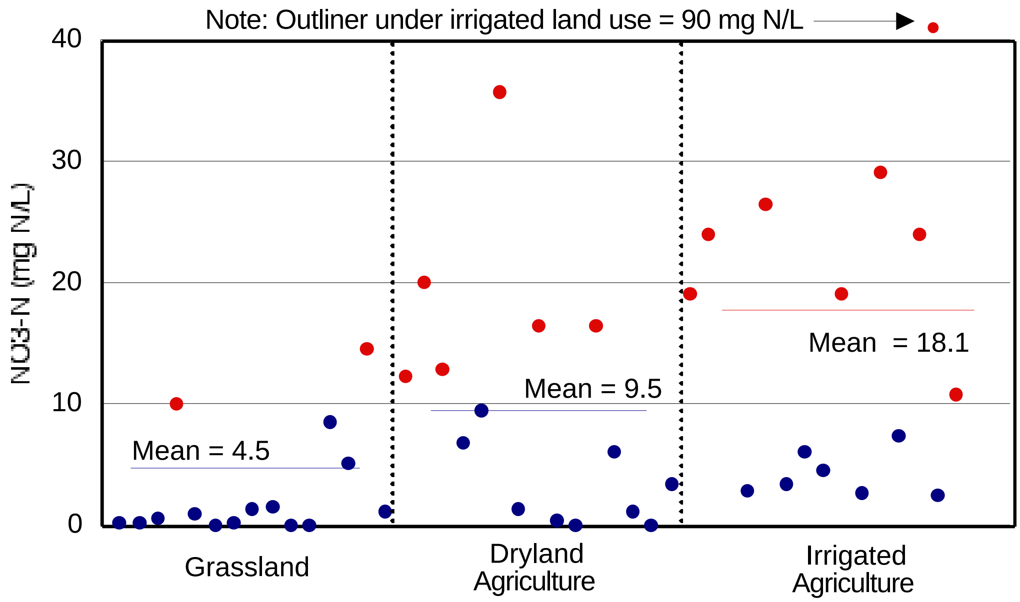


Figure 4-6: Nitrate concentrations observed in samples collected from wells established in the Pine Creek North and Assiniboine River South sub-basins as influenced by land use. Points represent individual observations, lines indicate mean concentration for each management type.

4.1.3 Manitoba Conservation Groundwater Quality Study

Bob Betcher (Manitoba Conservation) has established a research site located within the Assiniboine Delta Aquifer to study the potential impacts of intensive animal production on groundwater quality. Numerous groundwater monitoring wells were installed on the site in the fall of 1999. Wells were installed with the screens sampling the top of the aquifer (top 2 m), intermediate depths (2-3 m) and the deeper portions of the aquifer (3-6 m). Samples were collected from these wells in October of 1999. The data collected to date are considered to be pre-manure impact (i.e. impacts due to commercial fertilizers that have been in historic use). Manure application on the fields has occurred, and these data will be compared with post-manure impact data to determine the net impact of the use of manure as a fertilizer.

The data collected in this to date are consistent with our understanding of agricultural impacts on groundwater in shallow sand aquifers (see earlier section). Nitrate concentrations are highest in the shallow wells, and decrease with depth (Figure 4-7). Particularly interesting to the current question are $\delta^{15}N$ analyses which suggest that denitrification is occurring in the aquifer (Figure 5-7). The association of enriched values of $\delta^{15}N$ with relatively low nitrate concentrations is indicative of denitrification (Clarke and Fritz, 1997).

While denitrification is apparently occurring in the aquifer, it is not clear what the electron donors are. Drilling cores taken during piezometer installation showed a characteristic colour change from brown to grey (Personal communication, Bob Betcher). This is indicative of a redoxcline going from oxidized (the brown colour) to reduced (the grey colour). It is likely that denitrification, if it is occurring, occurs in the lower, reduced zone. Ongoing work is aimed at investigating the geochemical conditions in the aquifer, and to assessing aquifer sulfide and organic carbon as long-term supplies of electron donors to facilitate denitrification.

4.2 National Agri-Environmental Indicator Series

In an effort to develop a standardized national series of indicators to assess the sustainability of agriculture in Canada, Agriculture and Agri-Food Canada initiated the Agri-Environmental Indicator Project in 1993. A description of the development process and the suite of indicators that have been proposed can be found on Agriculture and Agri-Food Canada's website (http://www.agr.ca/policy/environment). The two water quality indicators proposed are of particular relevance to this report.

Risk of Water Contamination by Nitrogen - this indicator utilizes the Residual Nitrogen Indicator and an estimate of excess water (30-year average precipitation - potential evapotranspiration). Figure 4-8 illustrates the Residual Nitrogen Indicator for Prairie Canada. In the ADA region residual soil nitrogen is in the range of 41-60 kg N/ha.

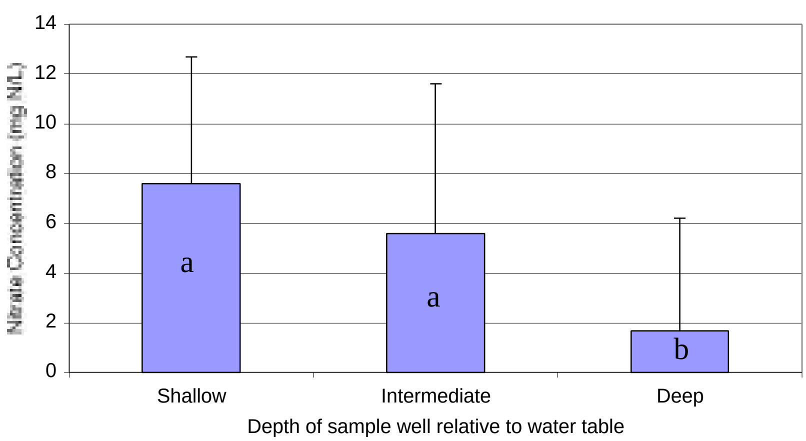


Figure 4-7: Analysis of average nitrate concentration (mg N/L) of samples as a function of depth of the observation wells. Shallow wells refer to wells installed 2 m from the top of the water table, deep wells indicated wells installed 3 m below the water table and the intermediate wells are intermediate between shallow and deep wells. Bars with different letters are significantly different at the $p \leq 0.05$ level. Data obtained from Bob Betcher, Manitoba Conservation.

One of the shortcomings of this indicator is that it relies on annual data. Thus the indicator cannot be calculated for regions where the annual potential evapotranspiration exceeds annual precipitation such as most of the prairie region. The indicator is unable to assess seasonal water recharge. If the estimated Residual Nitrogen (41- 60 kg N/ha) is applied to the estimated annual recharge to the aquifer (2.5 cm/year) the concentration of nitrogen in recharge water[3] is 160 mg N/L. In more humid regions of the country, the majority of residual fall nitrogen is leached or denitrified from the soil. In the prairie region, a significant percentage of fall soil nitrate will be carried over the winter period and is available in the next cropping year. A more accurate estimate of NO_3^- loading based on land use can be acquired by considering nutrient budgets for the major land uses found in the ADA.

[3] 40 kg N/ha year x 1ha/10^4m^2 x 1m^2/10^4cm^2 x 1 year/2.5cm x 10^3cm^3/L x 10^6mg N/kg N = 160 mg N/L

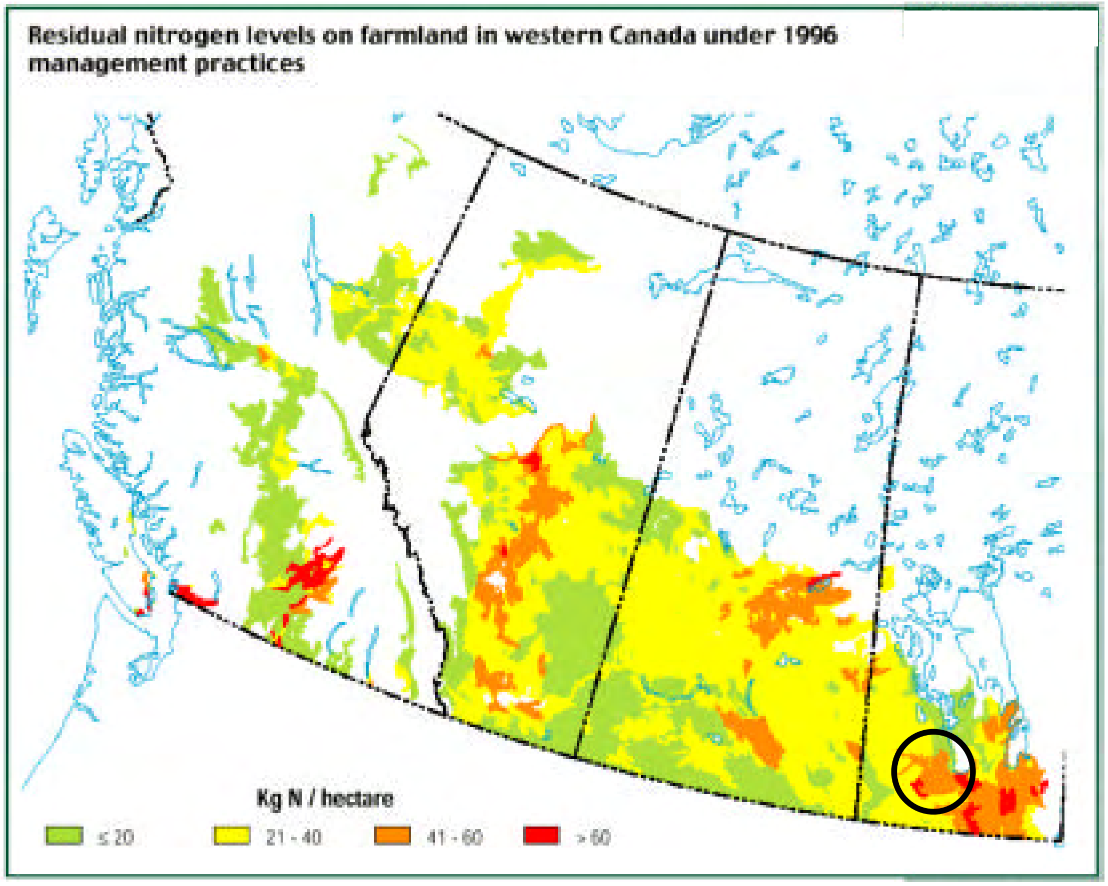


Figure 4-8: Estimated soil residual soil nitrogen as calculated by the national agri-environmental indicator for residual soil nitrogen (www.agr.ca/policy/environment/).

4.3 Estimating the nitrogen loading of the ADA based on land use

The scientific assessment of the nutrient cycling and fate in various agricultural production systems has been an area of intense interest over the past 50-100 years. Despite this intense interest, there are surprisingly few systems where the major processes of nutrient transformation have been well-documented. These efforts are often carried out in conjunction with long-term cropping system research. A Manitoba example of a project of this nature is the Long-term Cropping Systems Study being conducted at the Glenlea Research Station (Entz et al., 1997).

The development of nitrogen budgets for the major land uses on the ADA would permit an assessment of the overall nitrogen loading. Local soil resource characteristics, climate and land management practices are important determinants of rates of nitrogen loss. As a result, estimates of nitrogen loading should be based on studies conducted in the Assiniboine Delta region. Few of this nature have been conducted in this region. Nitrogen budgets conducted on agroecosystems from other areas of the world are a useful first approximation of nutrient loading. The development of nutrient budgets from local data would further refine these estimates. We have generally based this exercise on rates of fertilizer use and manure application as recommended by Manitoba Agriculture. Where actual rates of application exceed these rates the impact on groundwater would be expected to be far greater. As a result this exercise is likely a conservative estimate of total loading. The results of this exercise should only be used to guide future investigations aimed at providing local data to either support or refute the estimates obtained here.

Wheat production - Table 4-1 presents a typical nutrient budget for dryland wheat production in Central Kansas where precipitation limits yield potential. The rates of nitrogen fertilizer application are somewhat lower than would be observed in a wheat crop over the ADA. Note that nitrate leaching from this system is relatively small.

Table 4-1: Simplified annual N Balance for a wheat crop in Kansas.

Inputs			**Outputs**		
	N	P		N	P
	(kg ha^{-1} $year^{-1}$)			(kg ha^{-1} $year^{-1}$)	
Inorganic Fertilizer	34	13	*Grain*	36	7
Manure			Denitrification	5	
PPT + Dry deposition	6	0.1	NO_3^- Leaching	4	
N_2 fixation	*t*		NH_3 Volatilization	*t*	
			Runoff	1	3
Sum	***40***	***13***		***45***	***10***

In addition data provided AGVISE Laboratories suggests that from the period of 1990-1998 the residual soil NO_3^- level following wheat averaged 50 kg N/ha (Table 3-1). While it is unlikely that all of this NO_3^- would be lost via leaching, over winter leaching loss rates of 25% are not unreasonable.

Assumption for NO_3^- Loading Calculation:

- ***For grain crops it was assumed that annual NO_3^- loss is equivalent to 10% of the maximum recommended rate of nitrogen fertilizer.***
- ***The maximum recommended fertilization rates of nitrogen fertilizer application for this region is 100 kg N ha^{-1} (Manitoba Agriculture).***
- ***Therefore, for a recommended range of 100 kg N/ha, the estimated annual NO_3^- loss would be 10 kg N/ha***

Potato production - Potato production on the ADA is largely irrigated. In eastern North America rainfall is sufficient that potato production can occur under rain-fed conditions. The only example of a system for which an exhaustive nitrogen budget had been constructed was rain-fed potato production in Maine (Table 4-2). The coarse-textured nature of the soils and high rainfall characteristic of this region result in a significant leaching of nitrate to groundwater with relatively less denitrification.

Table 4-2: Simplified annual N Balance for a potato crop in Maine.

Inputs			**Outputs**		
	N	P		N	P
		($kg\ ha^{-1}\ year^{-1}$)			
Inorganic Fertilizer	168	101	*Potatoes*	80	10
Manure	0		Denitrification	15	
PPT + Dry deposition	6	0.1	NO_3^- Leaching	64	
N_2 fixation	*t*		NH_3 Volatilization	*t*	
			Runoff	15	5
Sum	***174***	***101***		***174***	***15***

In a survey of potato production in New Brunswick and Prince Edward Island, Milburn and MacLeod observed the nitrate concentration of tile-drainage water from irrigated potato fields to be in the range of 15-20 mg N/L (see text box).

In a study of the nitrogen fertility of potatoes in Manitoba, Racz et al., 1994 observed the amount of NO_3^- accumulating in the soil was a function of the rate of nitrogen fertilizer application. Optimum economic rates of nitrogen fertilizer application were from 284 to 362 kg N/ha, depending on variety. The amount of residual soil NO_3^- remaining in the top three meters increased linearly with application rate for application rates greater that 160 kg N/ha (Figure 4-9).

Nitrate leaching in Prince Edward Island potato production
P.H. Milburn, AAFC, Fredericton, N.B. and J.A. MacLeod, AAFC, Charlottetown, P.E.I.

Optimum potato production requires high rates of nitrogen fertilization and the use of sandy soils that are prone to nitrate leaching. As a result, tile-drainage water leaving potato fields often contains substantially higher levels of nitrate than water draining from fields planted to other crops. The nitrate levels in tile-drainage water from potato fields often exceeds the safe limit for nitrate-nitrogen in drinking water of 10 milligrams per litre.

Table 4-3: Nitrate-nitrogen level in tile-drainage water

Crop	Location	Nitrate-nitrogen Concentration (milligrams per litre)
Potatoes	New Brunswick and P.E.I.	15-20
Pasture	New Brunswick	1-3
Corn silage	New Brunswick	5
Grass	New Brunswick	5

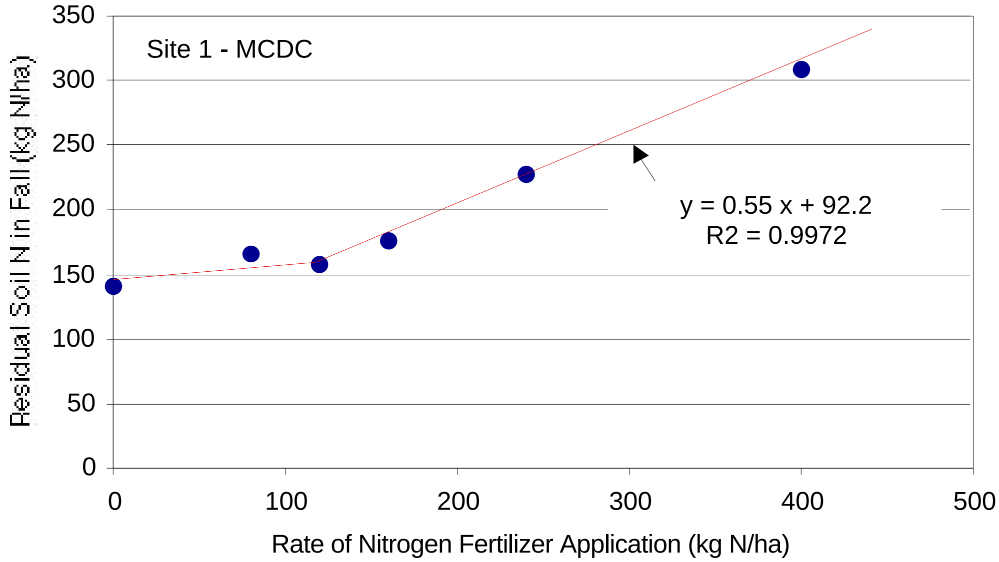
Potatoes are the primary cash crop in Prince Edward Island, generating about $100 million in revenues annually and occupying about 48% of the improved cropland (not all this land is seeded to potatoes every year). Because this province relies on groundwater for 100% of its drinking water, potential contamination of groundwater by nitrate from potato production is of great concern.

http://res.agr.ca/CANSIS/PUBLICATIONS/HEALTH/c10-7.html

The slope of the relationship at the MCDC Site suggests that 55% of the amount of N added in excess of 160 kg N/ha remained in the soil at the October sampling date. The single rate above the 160 kg N/ha level at Site 2 supports this conclusion, with dramatically increased residual fall soil NO_3^- levels.

It is also interesting to note the high NO_3^- content of the soil profile even in systems that have not received fertilizer in the current year of production. This may reflect previous land use (previous fertilizer addition) or may reflect NO_3^- accumulation associated with the mineralization of soil organic N associated with tillage (Campbell et al., 1984). No matter the source, this NO_3^- has the potential to move to groundwater and represents a significant potential impact. Deep sampling of this nature would be an effective tool to assess potential future impacts that may be associated with previous land use practices.

From this data the NO_3^- concentration of soil pore water can be estimated (Figure 4-10). This exercise indicates that at the lower rates of N application (< 160 kg N/ha) porewater NO_3^- is approximately at the drinking water health standard of 10 mg N/L. At higher rates of N fertilization, the porewater NO_3^- concentration exceeds this value by a significant amount.



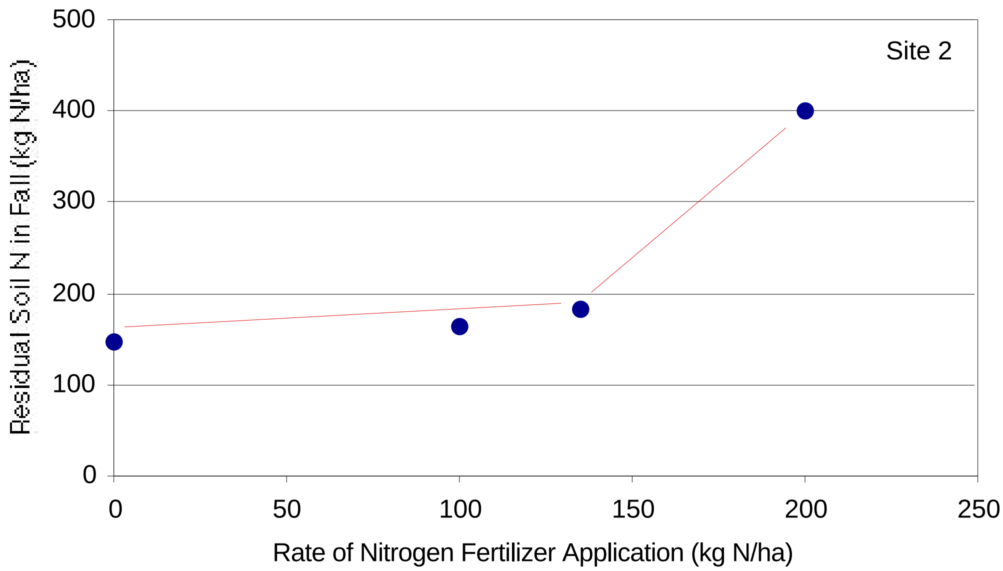


Figure 4-9: Relationship between rate of nitrogen fertilizer application rate (kg N/ha) and amount of NO_3^- remaining in the soil (kg N/ha) to a depth of 3 metres in October at two sites located on the ADA as calculated from data presented by Racz et al. (1994).

Clearly the application of nitrogen fertilizer in excess of 150-160 kg N/ha resulted in far greater amounts of NO_3^- remaining in the soil profile in the fall and therefore being potentially lost to groundwater. The recommended rate of N fertilizer for potatoes in Manitoba of 146 kg N/ha is approaching the threshold value. We are unaware of statistics reporting the actual rates of N fertilizer use in this area.

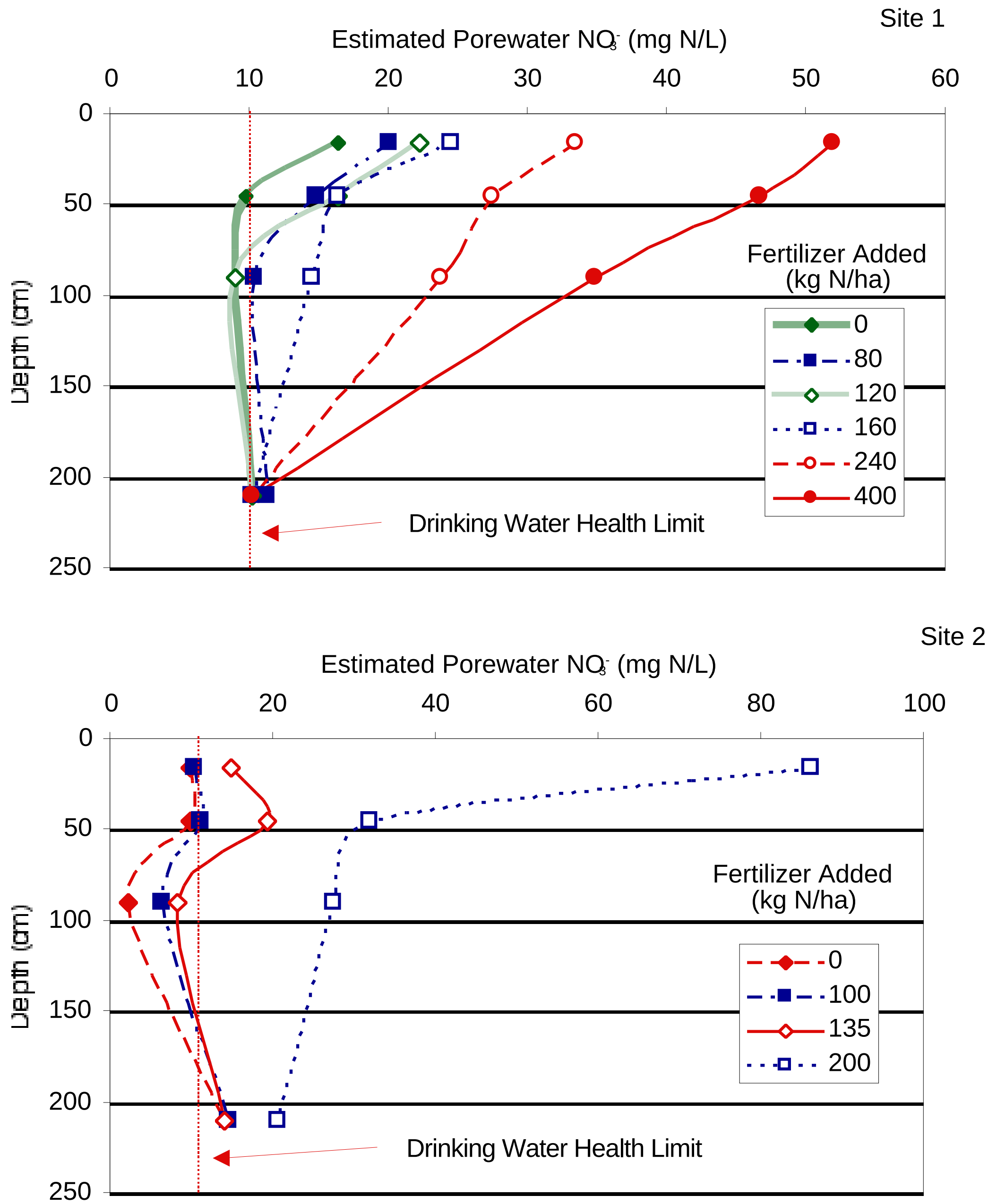


Figure 4-10: Estimated porewater nitrate concentration in October as influenced by rate of nitrogen fertilizer application to the preceding potato crop. Porewater NO_3^- was calculated assuming a soil bulk density of 1.5 Mg/m^3 and a gravimetric water content of 30%.

Assumption for NO_3^- Loading Calculation:

- ***For potatoes it was assumed that annual NO_3^- loss is equivalent to 30% of the maximum recommended rate of nitrogen fertilizer.***
- ***The maximum recommended fertilization rate was 146 kg N/ha (Manitoba Agriculture).***
- ***Therefore, for a recommended rate of 146 kg N/ha, the estimated annual NO_3^- loss would be 44 kg N/ha.***

NO_3^- leaching from legume crops - Evaluating the nitrate leaching potential of legume crops is complex. Since these systems have the capacity to fix atmospheric nitrogen, they seldom receive significant inputs of supplemental inorganic nitrogen. Further, many legumes such as alfalfa are known to be effective nitrogen scavengers. The key to understanding the potential of these crops to contribute to NO_3^- loss from the root zone is the management of the nitrogen rich plant residues. Campbell et al. (1994) observed that that an additional 50 kg N/ha was found in the profile following a legume green manure. The potential for leaching of this NO_3^- increased if plow-down was followed by a fallow period. It seems unlikely that this scenario would be a common practice under the conditions of the ADA. Nonetheless, the nitrogen released following legume plow-downs should be included in the nitrogen recommendation for the crop that follows. Adams and Jan (1999) found that the timing of the plow-down of a clover crop and re-establishment of the next crop were an important determinants in the extent of NO_3^- leaching. The magnitude of leaching losses in this Welsh study ranged from 10-240 kg N /ha yr. Delayed fall plowdown or immediate re-establishment of a crop were conditions that reduced leaching losses.

Assumption for NO_3^- Loading Calculation:

- ***Nitrate leaching losses from growing alfalfa stands were assumed to be zero.***
- ***Alfalfa plowdown was assumed to have NO_3^- leaching losses of 50 kg N/ha and 1/4 of the total area in alfalfa would be plowed down each year.***
- ***Therefore the area in alfalfa was assumed to have an annual NO_3^- loss rate of 12.5 kg N/ha.***

Intensive Livestock Operations - Intensive livestock production results in the production of significant quantities of manure. In Manitoba animal manures are primarily utilized on cropland. While manure is rich in nutrients, in many cases the economics of intensive animal production favour the application of manure at the maximum allowable rate of application. The maximum allowable rate of application is based on a theoretical assessment of the effect of soil texture and land use and should not exceed the nitrogen requirement of the crop (Manitoba Agriculture[4]). These values are theoretical in that they

[4] details available at Manitoba Agriculture's web site (http://www.gov.mb.ca/agriculture)

are based on generalized estimates of crop nutrient requirements and not on actual measurements of nitrate loss. The rates of water transport on sandy soils creates a high potential for nitrogen loss.

In a study of nitrate loss from manure amended systems conducted in Southern Ontario (Table 4.4), the magnitude of nitrate loss was influenced by nitrogen source and rate of nitrogen application (Burton et al., 1994). In general NO_3^- leaching from animal manure was less than that from NH_4NO_3. However traditionally producers have considered animal manure a waste product and have applied it at rates in excess of those that would be recommended on an agronomic basis. Durieux et al., 1995 found that nitrogen application rates based on soil nitrogen testing resulted in reduced nitrate leaching. Application rates in excess of those recommended to supply plant growth can result in significant accumulations of NO_3^- in the root zone..

Table 4-4: Nitrate loss from the root zone calculated from estimated monthly net water surplus/deficit and average soil solution NO_3^- -N concentration. Values are the sum of monthly estimates.

	1992 NO_3^- Loss (kg N ha^{-1})	1993 NO_3^- Loss (kg N ha^{-1})
N Source		
NH_4NO_3	168 c[§]	52 b
Liquid Dairy Cattle Manure	126 b	48 b
Solid Beef Manure	75 a	33 a
`		
Time of Application		
Spring Application	102 a	38 a
Fall Application	144 b	51 b
Rate of Application		
50% of Recommended Rate	108 a	33 a
100% of Recommended Rate	120 b	42 b
150% of Recommended Rate	142 c	59 b
Control	44	21
Analysis of Variance		
N Source	***[†]	***
Time of Application	***	***
N Rate	**	**
Source x Time	**	NS
Source x Rate	***	NS
Time x Rate	NS	NS
Source x Time x Rate	NS	NS

[§] Means with in groupings followed by different letters are significantly different at $p \leq 0.05$. Means comparisons performed using Duncan's Multiple Range procedure.

† *, **, *** indicate significance at probability levels of 0.10, 0.05 and 0.01, respectively. NS indicates no significant treatment effect.

In a study conducted in Southern Alberta, Chang and Entz (1996) found that under non-irrigated conditions, manure applied at one to three times the recommended rate resulted in a significant accumulation of NO_3^- in the root zone (Figure 4-11). However, minimal leaching loss was observed below 1.5 m except for years with unusually high precipitation. Under irrigation NO_3^- contamination of groundwater was significant for manure application rates greater than the recommended rate of 60 Mg/ha of manure. Annual losses ranged from 93 to 341 kg N/ha. With higher NO_3^- loss observed for the sites that received manure at three times the recommended rate on an annual basis.

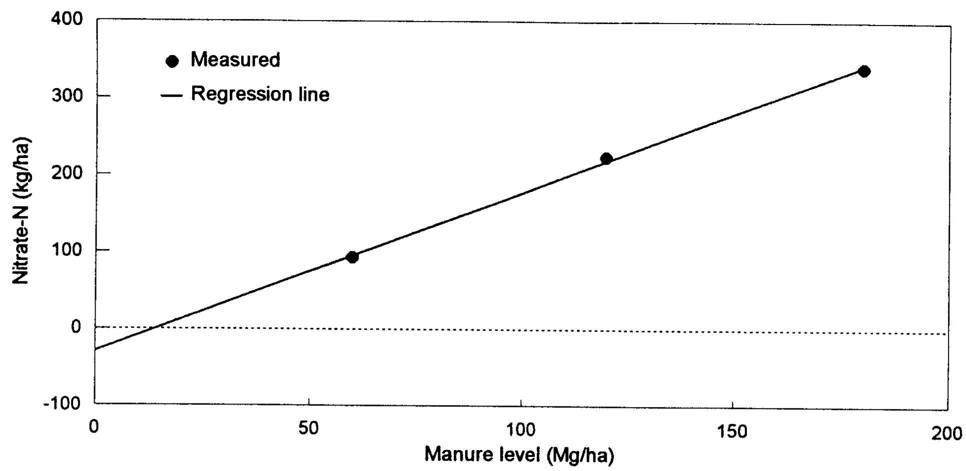


Figure 4-11: Relationship between the rate of annual manure addition and NO_3^- leaching (from Chang and Entz, 1966).

Adams et al., 1994 found that the addition of 20 Mg/ha of poultry litter or poultry manure to pastures resulted in NO_3^- concentrations in average soil porewater NO_3^- concentration at 120 cm of 24 and 37 mg N/L, respectively. Application of 10 Mg/ha of poultry litter did not result in NO_3^- porewater concentrations above the drinking water standard.

Assumption for NO_3^- Loading Calculation:

- ***For the purposes of this calculation NO_3^- leaching from intensive livestock operations where manure is primarily collected and distributed a few times during the year we assumed 25% of the total N in the manure would be leached to groundwater.***
- ***For more extensive operations where the animals spend at least a portion of the time grazing in pastures total loss to groundwater was assumed to be 10% of total estimated manure production.***

Pasture – The primary source of nitrogen in pastures is animal manure. Animal numbers were used to estimate total manure production independent of whether these animals are pastured. Therefore NO_3^- leaching losses associated with animals in pasture are covered off in the animal-based estimates of NO_3^- loading.

Summer Fallow - Campbell et al., 1984 estimated annual NO_3^- leaching from fallow land to be as great as 123 kg N/ha y and to average 43 kg N/ha y over a 96-year period. This value is likely to decline as the period over which fallow is practiced increases. Greater clarification is needed to determine whether the area that Statistics Canada lists as fallow is in fact true summerfallow.

Assumption for NO_3^- Loading Calculation:

- ***It is assumed that the area that Statistics Canada reports as fallow is indeed summerfallow.***
- ***A conservative estimate of 25 kg N/ha was used as the annual estimate of NO_3^- loading to groundwater for land under summerfallow.***

Clearly these estimates require further refinement. However, from these approximations, we can estimate the annual NO_3^- loading of the aquifer. Based on this analysis the total loading of nitrate to the aquifer underlying the Assiniboine Delta region is 4,130 tonnes of NO_3^-N/year.

Assumption for NO_3^- Loading Calculation:

- ***For the purposes of this calculation an average annual recharge rate of 2.2 cm/year was used.***

Conclusion - Based on annual recharge rate of 2.2 cm/year, the concentration of nitrate in the recharge water[5] would average 44 mg N/L. The contribution of various land uses is depicted in Figure 4-12.

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[5] 4,130t N/yr x 10^9 mg N/1t N x 1 yr/2.2cm x 1/3,885km^2 x 1km^2/10^{10}cm^2 x 10^3cm^3/L = 44mg N/L

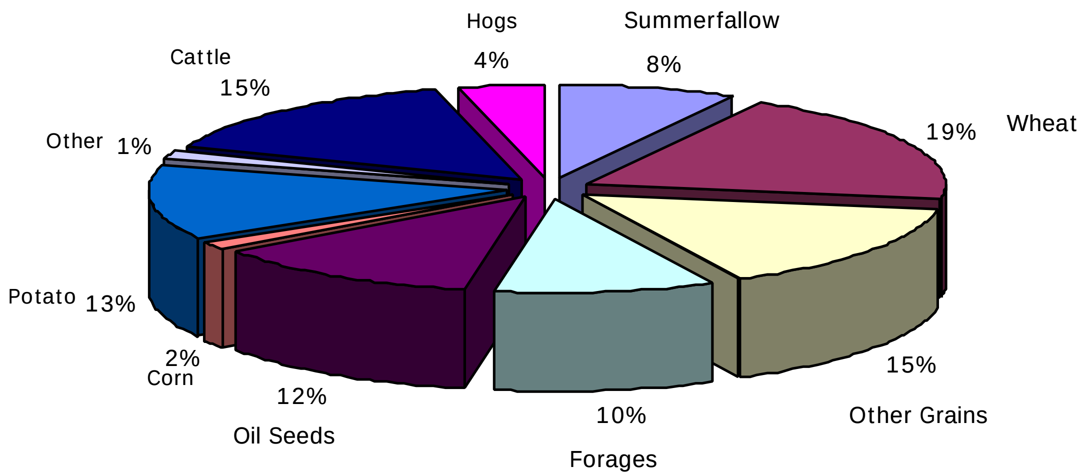


Figure 4-12: Relative contribution of various land uses to nitrate loading of the Assiniboine Delta Aquifer. Estimates are based on land use as reported in the 1996 Statistics Canada Agricultural Census and typical rates of nitrogen use and nitrate leaching as reported in literature sources.

Note that this estimate is only for land area under agricultural production. Contributions such as rural septic systems or other municipal or industrial sources would increase the NO_3^- loading to the aquifer. The 4,130 tonnes of NO_3^--N leached per year represents a rate of NO_3^--N leaching of 9.5 kg NO_3^-N/ha when averaged over the area of the aquifer under agricultural production (435,000). This value translates into a relatively high concentration in groundwater when considered in terms of the relatively limited amount of recharge estimated for this aquifer (2.2 cm/year).

This limited recharge capacity represents both a constraint and an opportunity. It is a constraint in that there is relatively limited opportunity for recharge water to dilute the estimated NO_3^- loss. It is an opportunity in that, depending on timing of recharge, there is much greater opportunity retain fall NO_3^- to be utilized by subsequent crops than is true in more humid climates. The National Indicator series did not calculate a Risk of Water Contamination by Nitrogen indicator because the difficulty in estimating the amount of fall residual fall NO_3^- that can be leached in a particular year. The relatively conservative estimates of potential NO_3^- loss from the various crops combined with the high residual fall NO_3^- levels reported in Figure 4-7 point to the need for soil NO_3^- testing as a basis for determining nitrogen application rates.

The 44 mg N/L estimated here points to the high potential for loss and is cause for concern. Relatively conservative estimates were used in this exercise. High rates of nitrogen fertilization of vegetable crops, high protein wheat or the use of high rates of animal manure could significantly increase this estimate. Improved N budgets for the major crops grown in the region coupled with actual measures of leaching loss is needed to assess the validity of this estimate. Research of this nature could also assess the potential for soil N management to reduce this number.

5. Assessment of the fate of nitrate in unconfined aquifers

Surveys of nitrate in well water supplies have been conducted since the public health aspects of groundwater nitrate were first reported (e.g. George and Hastings, 1951; Johnston, 1955). Unconfined shallow aquifers have long been identified as susceptible to groundwater nitrate impacts since they are often associated with coarse textured, well-drained soils. Sandy soils have little capacity to retain dissolved nitrate near the root zone due to low field capacities. They also rarely develop waterlogged or anaerobic conditions to facilitate nitrate loss by denitrification. Unfortunately, coarse textured soils are particularly suitable for a number of row crops that require high rates of fertilizer N application (e.g. corn and potatoes) and are also shallow-rooted (requiring irrigation if significant water deficits occur, and cannot uptake nitrate that has moved below the shallow root zone). Regions with coarse textured soils have been some of the earliest areas to be cultivated. In addition to their suitability for cash crops, well-drained soils are preferentially cultivated for their longer growing seasons. In regions with cold winters the fields are workable earlier in the season than finer textured soils (which tend to be waterlogged later into the spring, preventing farm machinery from getting onto the fields early in the season). Ironically, regions with shallow sand aquifers tend also to be highly groundwater dependent.

The US Environmental Protection Agency (EPA) conducted their National Pesticide Survey (NPS) between 1988 and 1990 which sampled 1300 water supplies. The survey concluded that 1.2% of community water supply wells and 2.4% of rural domestic wells had nitrate concentrations greater than the drinking water standard of 10 mg N/L (U.S. EPA, 1992). Although no national survey has been conducted in Canada, similar work has been conducted on a provincial basis in Ontario and Alberta. In Ontario, 14% of 1292 water wells sampled contained nitrate concentrations greater than 10 mg N/L (Goss et al., 1998). Of 813 farmstead water wells and dugouts selected in Alberta, 6% had nitrate concentrations greater than 10 mg N/L. (Fitzgerald et al., 1997). Numerous regional water well surveys like these consistently provide basic information about groundwater nitrate. Increased groundwater nitrate concentrations tend to occur at higher concentrations and more frequently in agricultural regions, under more permeable soils, in more shallow aquifers and/or more shallow (dug, bored) wells, and can be correlated on a regional basis with fertilizer use (Nolan et al., 1997; see discussion in Goss et al., 1998).

Although relatively few wells are contaminated on a national or provincial basis, a different picture emerges when well water surveys are specifically conducted in regions with sandy shallow aquifers. Indeed, relatively severe impacts are found in regions with sandy, shallow aquifers when well water survey data are analysed in the context of groundwater regions (e.g. Hamilton and Helsel, 1995; Gosselin et al., 1997). The following paragraphs chronologically review well water surveys and field scale research studies conducted in regions with sandy or coarse-textured shallow aquifers.

- A 1950-1954 survey conducted in Ontario reported 19% of dug wells (which tend to be shallow) had nitrate concentrations in excess of 10 mg N/L, compared to 6% of drilled wells (Johnston, 1955). Analyses were conducted on well water samples submitted to the Ontario Agricultural College's Bacteriology Department, forming a more or less random sampling methodology.
- Hill (1983) found nitrate concentrations greater than 10 mg N/L in 41% of 164 water wells sampled in an irrigated and predominantly potato-growing region of Ontario. The flat-lying sand plain aquifer was about 88 km^2 in area, about 10 m thick, with a 3-6m thick unsaturated zone. Elevated nitrate concentrations tended to occur in more shallow wells and were correlated with fertilizer use, and low nitrate concentrations occurred under uncultivated areas.
- Extensive shallow sand aquifers in Minnesota were surveyed in the mid-1980's. Nitrate concentrations exceeded the drinking water standard in about 20% of the wells sampled regionally (Ruhl, 1987). The fraction of wells with nitrate concentrations greater than 10 mg NO_3^--N/L increased to 50% in a second survey that targeted water wells located in heavily farmed areas in the central part of the state (Anderson, 1989).
- Fifteen percent of 180 Ontario farm wells surveyed in 1986 had nitrate concentrations greater than 10 mg N/L. "All of the contaminated wells were either surface sand point wells or shallow dug wells under 10 m deep…. Most of the [contaminated wells] were on sandy loam soils on farms located in the corn-soybean growing areas of southwestern Ontario".
- In New Brunswick 47 private wells were monitored in three intensive potato-producing regions. In the most intensive agricultural regions, 39% of the wells exceeded 10 mg N/L (Richards et al., 1990).
- A survey of 301 rural wells in Huron County, Ontario conducted in 1991 found nitrate concentrations greater than the drinking water objective in 30% of the dug or bored wells sampled compared to 4% of drilled wells (Fleming, 1992). Huron County contains sand plains of significant areal extent (Chapman and Putnam, 1984). Many of the shallow wells would likely have been located in shallow sand aquifers.
- About 30% of 850 groundwater samples taken between 1990 and 1993 in the Lower Umatilla Basin in northeastern Oregon were contaminated with nitrate concentrations greater than 10 mg N/L. The area, which receives 250 mm of precipitation annually, has predominantly sandy soils and shallow, unconfined aquifers (Mitchell and Harding, 1996).
- A 205 km^2 area of the South Platte River alluvial aquifer system near Greely, Colorado consists of unconsolidated Quaternary sands and gravels. Saturated aquifer thickness is about 10-20 m, and precipitation is 400 m y^{-1}. The region is intensively cultivated to corn, alfalfa, sugar beets and vegetables, with a substantial amount of intensive livestock operation. Groundwater under the terrace deposits has an average nitrate concentration of 25 mg N/L (McMahon and Bölke, 1996).
- Water wells in areas of heavy corn production that were well constructed and maintained, and less than 10m in depth, were selected for a groundwater monitoring program in southwestern Ontario (Lampman, 1995). The wells are reported as 'positive' for nitrate if concentrations exceed 5 mg N/L. In 1985, 79% of 266 wells

tested positive for nitrate. In subsequent years 64% of 21 wells tested positive for nitrate in 1986, 87.5% of 20 wells in 1987, and 90% of 12 wells in 1988.

- Thirteen percent of 137 water wells sampled in Kings County, Nova Scotia had NO_3^- concentrations greater than 10 mg N/L (Briggins and Moerman, 1995). Kings County is the most intensive farming area in the province, includes potato and corn crops, and has coarse-textured soils overlying surficial and bedrock aquifers. The area is 90% groundwater dependent.
- A state survey of well water in the Port Edwards Groundwater Priority Watershed in Wisconsin reported that more than 22% of the wells in the sandy unconfined aquifer were above 10 mg NO_3^--N/L, with local exceedences of 50 to 70% (Kraft et al., 1999).
- The MAC for nitrate was exceeded in more than 25% of 368 groundwater samples taken from the Sumas aquifer (which straddles the border between Washington State and British Colombia; Cox and Kahle, 1999). A mass balance approach was used to conclude that about 87% of the groundwater nitrate was derived from an agricultural practices. The authors also estimated that 18% of soil zone nitrogen was leached to groundwater.

The Abbotsford aquifer

The Abbotsford aquifer case study is particularly relevant to the current task of defining the groundwater nitrate risk to the ADA by intensified agriculture. It has been well studied, and has long-term groundwater nitrate monitoring records. It is similar to the ADA insofar as it is a regionally extensive unconfined aquifer where manure application to fields has increased with a growing intensive livestock industry (in particular poultry). Located in the Fraser Valley in southwestern British Colombia, the Abbotsford aquifer is comprised of extensive sand and gravel deposits. The aquifer's area is 200 km^2 and its thickness varies, ranging from 5 to 30m thick. Estimates of groundwater flow velocities range from 4 to 450 m yr^{-1}. The primary difference between the Assiniboine Delta and Abbotsford Aquifers is the annual recharge rate. Annual precipitation in the Abbotsford area is 1500 mm, of which an estimated 37 to 81% is groundwater recharge. This is very high compared to 480 mm of precipitation in the ADA, of which a relatively small fraction is thought to contribute to groundwater recharge.

Land use in the Abbotsford Aquifer region is primarily agricultural, with intensive raspberry and poultry production. Nitrate concentrations in some monitoring wells have been steadily increasing since measurements began in 1955 (Liebscher et al., 1992). Nitrate concentrations in 63% of 73 groundwater samples were above 10 mg N/L in a 1989 Environment Canada survey (Liebscher et al., 1992). In a survey of 117 domestic and municipal water wells and research piezometers in 1993, nitrate concentrations were above 10 mg N/L in 53% of the water samples (Wassenaar, 1995). Stable isotope ratios of N and O in NO_3^- indicated that much of the groundwater NO_3^- was derived from manure, and that groundwater nitrate concentrations were not being significantly ameliorated by bacterial denitrification. The aquifer continues to be studied for nitrate, and for pesticides. The major contributor to groundwater nitrate concentrations is manure. Environment Canada is currently funding manure export by trucking from the

Abbotsford aquifer region to less intensively cultivated regions lower down in the Fraser delta.

5.1 Temporal changes in groundwater nitrate in municipal water supplies

Water quality analyses are not required for privately owned domestic water supply wells, but they are usually required for municipal groundwater supplies. The set of water quality analyses required of water purveyors typically includes drinking water parameters, including nitrate. Although these analyses are not often published in the scientific literature, anecdotal information and some data are summarized here:

- Nebraska's Panhandle is located on the Platte River. Soils in the 13 km^2 area are well drained sandy loams which overlie a shallow sand and gravel aquifer. Groundwater from the aquifer is used for domestic, municipal and irrigation purposes. Nitrate concentrations in municipal and domestic wells in two towns located on the Panhandle (Oshkosh and Sidney) have increased with time to above the drinking water standard in a number of wells. Nitrate concentrations in eight municipal wells in Sidney increased steadily between 1966 and 1987. The average nitrate concentrations in thirteen domestic wells near Oshkosh were more than twice the drinking water standard in 1988 and 1989 (Exner and Spalding, 1994)
- Intensive agriculture in the U.K. has caused an increase in nitrate in water supplies from shallow aquifers. Nitrate levels in 1970 in 60 public groundwater supply sources in England and Wales intermittently exceeded the drinking water standard. This number increased to about 90 in 1980, and 142 in 1987 (House of Lords, 1989, in Hiscock et al., 1991).
- In an intensive potato-growing region in New Brunswick, 39% of 18 water supply wells had nitrate concentrations greater than 10 mg N/L (and only 6.3% of the wells had NO_3^--N concentrations less than 5 mg N/L). The degree of groundwater nitrate impact was correlated with relative intensity of agricultural production in several regions, and the authors concluded that the nitrate source was predominantly agricultural N (Richards et al., 1990).
- The Village of Hensall, Ontario is located about 65 km north of the City of London on a aquifer that is about 8 m deep and 7 m thick. In the early 1980s, nitrate concentrations above 10 mg N/L were found in the Village's main 'King Street' well. A new well subsequently brought on line began to exhibit increasing nitrate concentrations (4-8 mg N/L), necessitating the drilling of a deeper well in 1984 (Giraldez and Fox, 1995).
- Strathroy, Ontario is located on the edge of the Caradoc Sand Plain in Southern Ontario. The town relies on shallow sand points and water wells for municipal water supply. Increasing nitrate concentrations in the groundwater supply has caused them to take a number of water supply wells out of service (Corporation of the Town of Strathroy, 1989). In some instances water supply wells exhibited elevated concentrations during the initial testing period (Wilson Associates, Ltd, 1988). Groundwater nitrate concentrations are an ongoing concern for the Town, which has recently put out a Request for Proposals to evaluate the town's groundwater supply.
- The Regional Municipality of Waterloo is located in a predominantly agricultural area. Much of the population in the Region is contained within three cities (Kitchener, Waterloo, and Cambridge). Until the late 1980s, the urban population's

water came from well fields in and around the cities. At this time the Region was the largest population in Canada that was completely groundwater dependent. Increasing nitrate concentrations in a number of water wells necessitated the blending of high and low nitrate concentration wells to keep nitrate concentrations below 10 mg N/L. In the late 1980s, the water supply system was augmented with a surface water supply. In the past few years, their Baden well field was abandoned due to high nitrate concentrations (Hodgins, 2000).

- In the state of California, which is home to both intensive agricultural and industrial activities, more public water supplies have been closed due to violation of the nitrate-N drinking water standards than from any other contaminant (Spath, 1990, in Franco and Cady, 1997).

5.2 Subsurface NO_3^- behaviour

5.2.1 Flow related fate

5.2.1.1 Groundwater flow in sandy water table aquifers

Groundwater flow in water table aquifers in flat-lying sand plains in temperate regions is usually near horizontal. Vertical migration distances of less than one meter are typically associated with the first 100 m of horizontal travel (Novakovic and Farvolden, 1974; Kimmel and Braids, 1980; MacFarlane et al., 1983; LeBlanc et al., 1991; Postma et al., 1991; Wassenaar, 1995). The classic representation of flow in a sandy water table aquifer (Figure 5-1) has a flow divide on the upgradient side, with groundwater flowing out of the domain on the downgradient side. The bottom is typically bounded by a relatively impermeable unit (e.g. Hubbert, 1940). This classic cross section is used both conceptually (e.g. Steinheimer et al., 1998; Postma et al., 1990) and mathematically (Frind et al., 1990) in groundwater nitrate investigations in sandy water table aquifers. The vertical exaggeration in vertical cross-sections of regional groundwater flow is significant. For example, a representative cross-section drawn for the ADA (Figure 5-2) has a saturated vertical thickness of about 20m and a total horizontal distance of about 45 km, or a vertical exaggeration of about 2000 times. If this type of vertical exaggeration were applied to the previous cross-section (Figure 5-1), predominantly sub-horizontal flow lines would result.

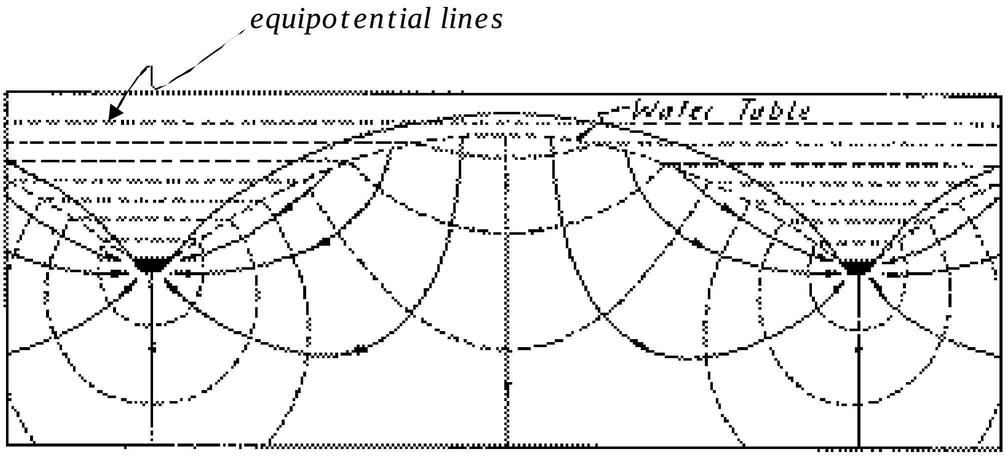


Figure 5-1: Classic representation of groundwater flow in an unconfined aquifer (Hubbert, 1940)

A second method of characterizing the groundwater flow regime is by rudimentary estimations of vertical and horizontal components of groundwater flow. An estimated hydraulic conductivity of 5 x 10^{-4} m/s (Manitoba Natural Resources, 1970), regional hydraulic gradient of 0.0005 (Render, 1988), and porosity of 0.3 (Fetter, 1994) yield an average linear groundwater flow estimate of 25 m/yr in the horizontal direction. (Average linear groundwater velocity, $v = -Ki/n$, where K is hydraulic conductivity, i is hydraulic gradient, and n is porosity). An estimate for the vertical component of groundwater flow of 7 cm/yr is based on an estimated annual recharge rate of 2.2 cm a^{-1} (Render, 1988), and a saturated porosity estimate of 0.3. Hence, flow in the ADA is sub-horizontal. The above estimates for horizontal and vertical groundwater velocities suggest flowpaths have an angle of about 0.2^{o} from the horizontal.

The latter method of estimating groundwater flow is clearly an oversimplification. In particular, it does not account for near-vertical groundwater flow near groundwater divides (Figure 5-1), and increasingly horizontal flow and discharge along the flow direction (Vogel, 1967). Although over-simplistic, it is a useful approximation on which a field-scale conceptual model is discussed in the following section.

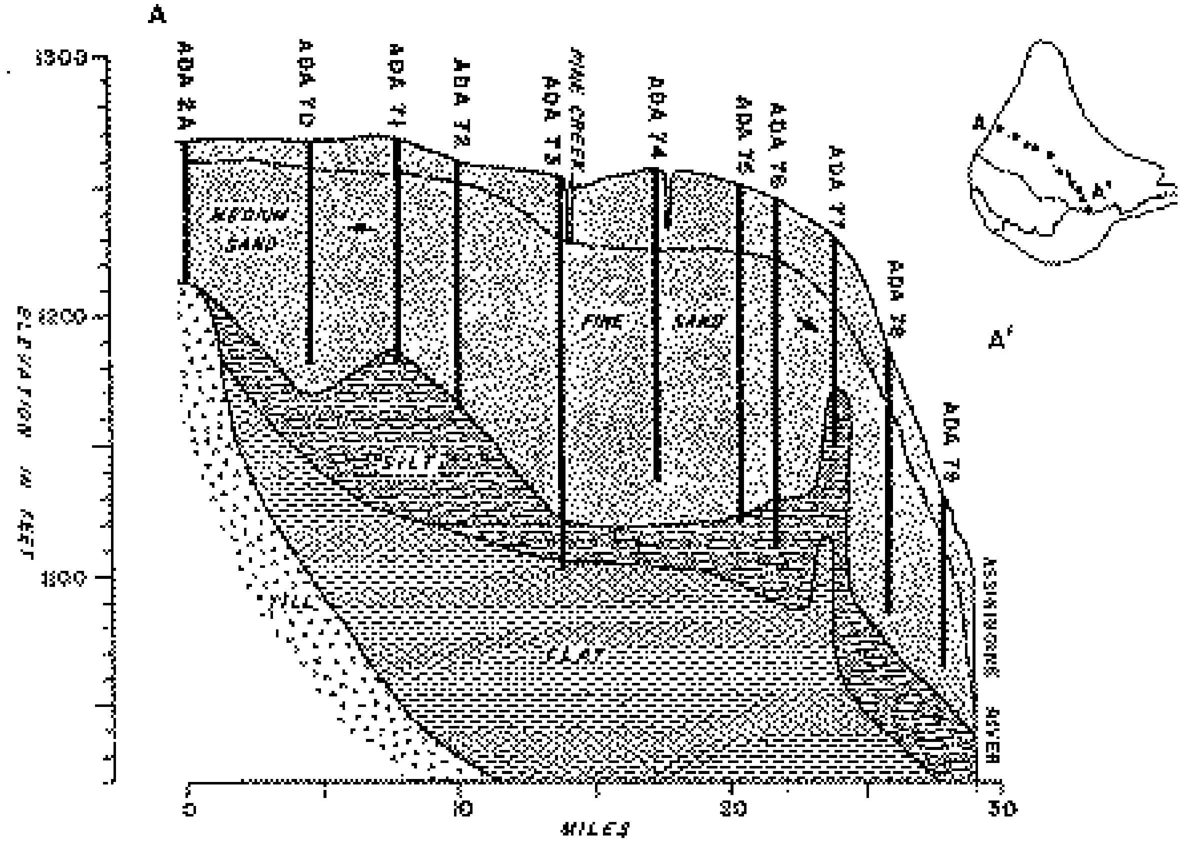


Figure 5-2: Representative cross-section of Assiniboine Delta Aquifer (Manitoba Natural Resources, 1970, in Render, 1987).

5.2.1.2 Field-scale groundwater nitrate impacts in shallow sand aquifers

A robust conceptual model of groundwater flowpaths is a prerequisite to a field-scale understanding of groundwater nitrate impacts from agriculture. We will first develop a conceptual model for an idealized groundwater flow system without dispersion and subsequently discuss the effects of dispersion and other processes. Figure 5-3 is a field-scale representation of flowpaths in a vertical cross-section including several farm fields. The diagram is not to scale since significant vertical exaggeration is inherent in illustration of sub-horizontal groundwater flowlines.

Groundwater in the unsaturated zone is assumed to travel more or less vertically (subject to preferential flow) in the unsaturated zone, and assumes a sub-horizontal flowpath once it enters the groundwater zone. Groundwater at increasing depths below the water table has been recharged at increasing distances upgradient. Flowlines emanating from the boundaries between fields are drawn as solid lines in Figure 5-3. In the saturated zone, the solid flowlines boundaries occur between groundwater infiltrated under the different farm fields. In cross-section, groundwater infiltrated from an individual field is contained within a sub-horizontal parallelepiped of the aquifer (Figure 5-3). For the ADA's groundwater velocity estimates described above, and a field about 800m long, the parallelepiped would have a vertical thickness of 2.8m in groundwater under the downgradient edge of the field. Groundwater sampled at the upgradient edge of the field, or from more than a few metres depth in the middle of the field, would sample at least some groundwater infiltrated under adjacent fields. If different masses of nitrate were leached under different management practices on each field, groundwater nitrate concentrations would vary in each parallelepiped. Note that, although dispersion is neglected in Figure 5-3, it is a relatively weak process in directions perpendicular to flow (Fetter, 1999). Thus, the boundaries between fields could remain distinct even after significant flow distances.

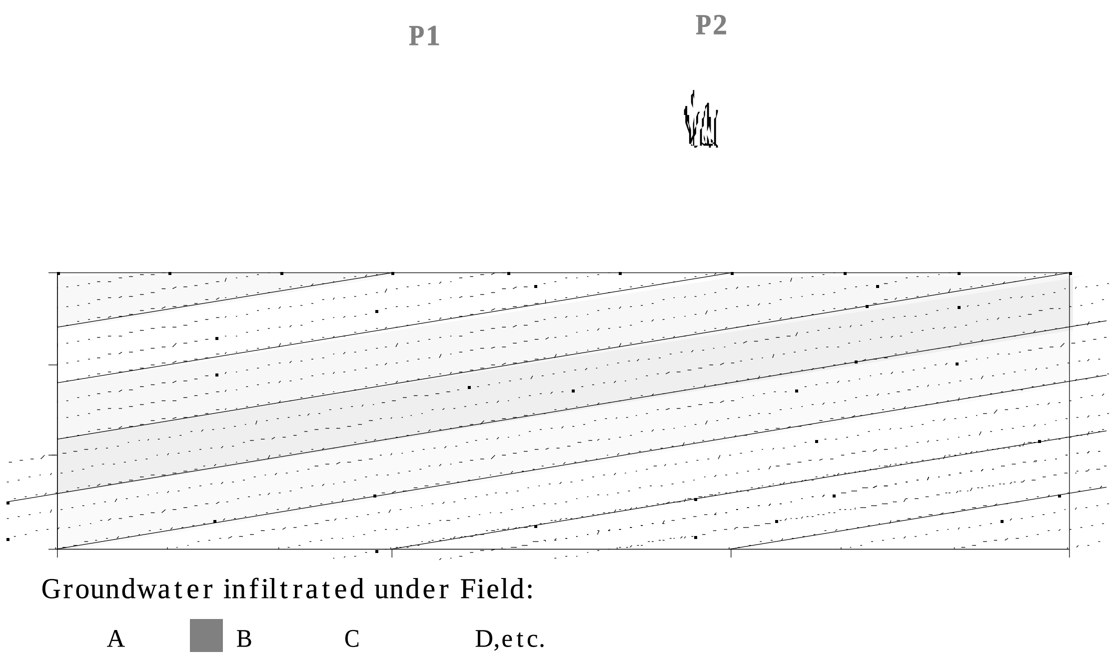


Figure 5-3: Conceptual view of groundwater flow in a shallow sand aquifer below three fields. Figure is a vertical cross-section oriented parallel to groundwater flow direction. Groundwater flow is sub-horizontal. Solid flow lines are boundaries between groundwater infiltrated under different fields. P1 would sample groundwater infiltrated under Fields B and C. Despite the fact that P2 is located on Field B, it would sample groundwater infiltrated under Field C.

This conceptual model has been particularly apparent in field scale research when upgradient land use includes forest or grassland, which leach very low nitrate concentrations (Postma et al., 1991; Komor and Anderson, 1994).

If annual isochrons are included, it can be seen that groundwater recharged under an individual field during a single year is contained within smaller, horizontal parallelepipeds in the aquifer. The boundaries on the 'annual parallelepipeds' are isochrons on the top and bottom, and flowlines emanating from the up- and down-gradient field boundaries on the sides. These parallelepipeds would have a vertical thickness equal to the annual vertical migration distance, or 7 cm in the ADA. If annual crop rotations with significantly different nitrate fluxes are used, nitrate concentrations could fluctuate significantly between years.

5.2.1.3 Spatial and temporal variability of source function of nitrate to water table of sandy shallow aquifers

When detailed groundwater nitrate monitoring is conducted in shallow sandy aquifers, significant temporal and spatial variations are usually observed. (Postma et al., 1991; Bjerg and Christensen, 1992; Clay et al., 1996; Kelly, 1996; Steinheimer et al., 1998). Where it occurs, denitrification can increase this variability (Montgomery et al., 1997). Soil and vadose zone processes that impart spatial and temporal variability to groundwater nitrate are discussed here. The recharge of nitrate-rich water to the water table requires that a) nitrate be available for leaching as the water moves through the soil zone, and b) infiltration is significant enough to permit nitrate-laden water to be leached below the root zone and/or permit recharge to occur.

The amount of nitrate available for leaching from the soil zone can vary significantly over very short time periods. On an annual basis, the rate of fertilizer N application can vary due to crop rotation, and where conducted, soil N test results. Whereas commercial fertilizer is typically applied during the spring, manure fertilizer application can occur in spring or fall, and does not necessarily occur on an annual basis. The fraction of fertilizer N available for leaching is further a function of the form of fertilizer N (e.g. ammonium nitrate, urea ammonium nitrate, anhydrous ammonium, manure N, etc) since soil zone N transformations must occur for non-nitrate N forms to be nitrified and available for leaching. The dependence of these transformations on soil temperature and moisture status impart a further source of temporal variability. During the growing season, the amount of fertilizer N available for leaching typically decreases as crop uptake occurs. The amount of nitrate available for leaching from the fall season plow-down (or kill-down in no-till cropping) of forages is not well known and could be an additional source of soil zone N available for nitrification.

Whether or not sufficient water moves through the soil zone to permit groundwater recharge depends on precipitation, evapotranspiration, and the timing and nature of spring thaw. Relatively little infiltration occurs during the growing season due to significant evapotranspiration losses. In regions with cold winters, frozen ground often prevents significant infiltration from occurring. Spring thaw is often the most significant leaching event in regions with cold winters (as indicated by significant water table rises during this period; Fetter, 1994; Render, 1988). Infiltration may also occur during seasons with significant precipitation and minimal evapotranspiration (i.e., immediately before and immediately after the growing season; Reardon et al., 1980).

In the 'piston displacement' flow model for water movement through the vadose zone (Reardon et al., 1980), water moves out of the bottom of the vadose zone profile when infiltration adds water to the top of the profile in a 'conveyor belt' fashion. During infiltration events, water from the bottom of the profile that is recharged to the groundwater could have passed through the soil zone at a significantly earlier time, with soil zone nitrate concentrations that have no relation to those present when infiltration occurs. Thus the nitrate leached to the water table during "spring thaw" could actually have been leached from the soil zone during the subsequent "fall rains".

Although the piston flow model is useful conceptually, there is considerable evidence indicating that flow through the vadose zone is subject to preferential flow (Komor and Emerson, 1994). Proposed mechanisms for preferential flow include fingering (Hillel and Baker, 1988), ‘bypass’ flow through macropores (Beven and Germann, 1982), and subsurface heterogeneity (Kung 1990a and b). The effect of preferential flow is to decrease vadose zone residence times and increase spatial variability in groundwater solute concentrations. In one field study, a dyed tracer was evenly applied to ground surface overlying a sandy shallow aquifer and allowed to infiltrate into the vadose zone under dryland/irrigation conditions. The vadose zone was subsequently excavated to observe the tracer pathways. The investigators concluded that solute transport was occurring in less than 1% of the aquifer at the bottom of a 7m unsaturated zone (Kung et al., 1990a). In effect, recharge was occurring at discrete locations of the water table located at the bottom of the preferential flow paths. Preferential flow was also observed in the vadose zone over another sandy shallow aquifer (van Wesenbeeck et al., 1994). At this site, preferential flow occurred in tongues of the B horizon that extended into the C horizon. A thin, relatively impermeable B_t horizon at the interface effectively channeled water into the B horizon tongues which were located a few metres apart.

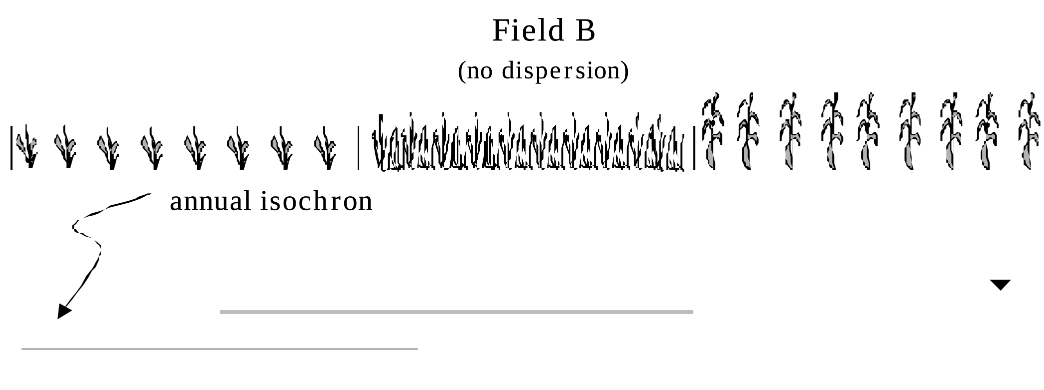
Another process that causes variability in nitrate leached to groundwater from agricultural fields in regions with cold winters is soil-ice depression focussed recharge. Depression focussed recharge (DFR) is a well-known phenomenon in regions with fine-textured surface sediments (Keller et al., 1988; Logan and Rudolph, 1997). In fine textured soils, infiltration is limited by relatively low hydraulic soil conductivity. Significant overland transport of water can occur during precipitation events. Water subject to overland flow tends to pool in topographic depressions that act as reservoirs for infiltration. In these settings, significantly more infiltration occurs under the topographic depressions. The effect is strong enough that even 'micro-topographic depressions' (on the order of cm deep) can result in focussed recharge.

Coarse-grained soils overlying shallow sandy aquifers are 'freely' and sometimes 'excessively' drained and standing water is not normally observed even during major precipitation events. This is the case with the Assiniboine Delta Aquifer (Render, 1988). In regions with cold winters, however, continuous soil ice layers can develop which are relatively impermeable and areally extensive (Derby and Knighton, 1995 a and b; Burton et al., 1994; Solomon et al., 1995; Delin and Landon, 1996). When spring thaw is initiated, thawing occurs from the surface downwards. During early spring thaw, meltwater tends to be transported along the top of the impermeable soil ice towards depressions, where spring meltwater pools can form. These meltwater pools can be rapidly infiltrated through the first breach in the impermeable soil ice layer, resulting in depression focused recharge.

5.2.1.4 Effect of dispersion on groundwater nitrate concentrations

Dispersion is a process that causes solutes to 'spread out' as they are transported along with groundwater flow (Fetter, 1999). The effect of dispersion is to 'smooth out' concentration changes with flow distance. It is a relatively strong process in a direction parallel to groundwater flow (known as longitudinal dispersion), but a relatively weak process in a direction perpendicular to flow (known as transverse dispersion). In the conceptual view of groundwater flow in a shallow sand aquifer, longitudinal dispersion occurs in sub-horizontal flow direction (Figure 5-4).

Figure 5-4 illustrates conceptually the effect of dispersion on annually fluctuating groundwater nitrate concentrations. In the absence of dispersion, the annual parallelepipeds (Figure 5-4) would alternate between grey (representing relatively high nitrate concentrations) and white (representing relatively low nitrate concentrations) colours (illustrated in Figure 5-4 in groundwater recharged from Field B). The effect of longitudinal dispersion (illustrated In Figure 5-4 in groundwater recharged from Field C) is to increasingly smooth out colour changes along the groundwater flow direction. At some depth, the annual fluctuations would be masked and the groundwater nitrate concentrations would be constant along the direction of flow.



In our conceptual view of groundwater in a shallow sand aquifer under farm fields, transverse dispersion acts to mix groundwater solutes within and between fields (Figure 5-4). Since this is a relatively weak process, concentration changes across boundary lines between groundwater infiltrated under different fields can be expected to be maintained for significant transport distances. Although field data of this nature are not available for agricultural nitrate, narrow (e.g. 10 m) and discrete plumes emanating from septic systems have been well-mapped, in some instances for kilometers (e.g. Le Blanc, 1984; Robertson et al., 1991; van der Kamp et al., 1994).

5.3 Biogeochemical fate

5.3.1 Sorption

Nitrate adsorption has been reported in tropical volcanic ash soils (Kinjo and Pratt, 1971). Clay minerals formed from the weathering of these andisol soils include amorphous aluminosilicates such as allophane and non-amorphous aluminosilicates such as halloysite and allophane (Wada, 1989). Allophane has a high anion exchange capacity, due mostly to its small particle size, high surface area, and the presence of surface Al-OH-Al groups and defect sites in the mineral structure (Theng et al, 1982). Nitrate sorption in shallow sand aquifers has not been reported.

5.3.2 Minineralization & Immobilization of Nitrogen

The contribution of mineralization and immobilization of nitrogen both in surface soils and in groundwater is particularly difficult to estimate as it involves the measurement of small changes in relatively large pool sizes. Long-term studies are necessary to estimate the net effect of theses process. Campbell et al., 1984 estimated that 20% of the soil organic N initially present in prairie soils has been leached to groundwater over the past 100 years. Few long-term studies assessing the role of mineralization and immobilization in groundwater and its influence on nitrate content have been conducted. Immobilization would be limited by the supply of sufficient electron donors to support growth. It seems unlikely that immobilization would be a significant long-term sink for groundwater nitrate. Mineralization of organic nitrogen sources leached from the root zone is more probable and could be estimated from measurements of the soluble organic nitrogen content of soil pore water below the root zone. This is not a parameter that is commonly measured in groundwater or vadose zone samples.

5.3.3 Denitrification

Denitrification is respiratory process which results in the sequential reduction of NO_3^-, NO_2^-, NO, N_2O to N_2, involving the transfer of electrons from an electron donor. The reaction involves successive paired electron transfers. This is characteristic of respiratory systems. In the course of catabolism organisms accumulate a considerable amount of reducing power. Respiration recycles this reducing power and releases the energy it contains in the form of ATP. Normally oxygen is used as the terminal electron acceptor. It is the preferred electron acceptor as it has the highest oxidation potential and thus provides the greatest energy yield. In the absence of oxygen some organisms are able use inorganic terminal electron acceptors such as NO_3^- or SO_4^- as terminal electron acceptors in what is known as anaerobic respiration. This should not be confused with fermentation, the process by which anaerobes generate energy through the reduction of organic compounds.

Denitrifiers are taxonomically diverse with few of the major groups not having a denitrifying member. The majority of denitrifiers are gram negative although Bacillus, a gram positive organism, is among the most common species of denitrifiers. Among the gram negative species, *Pseudomaonas* and *Paracoccus* dominate.

5.3.3.1 Distal and proximal regulators on denitrification in sub-surface environments

The concept of distal and proximal regulators introduced by Robertson (1989), reflects the importance of understanding scale when considering the control of biological processes in natural environments. Proximal regulators reflect the factors influencing the process at the scale of the organism. Distal regulators consider how these proximal regulators are expressed at various scales of integration in the natural environment. As an example, Robertson (1989) presented the proximal and distal regulators of denitrification in surface soils.

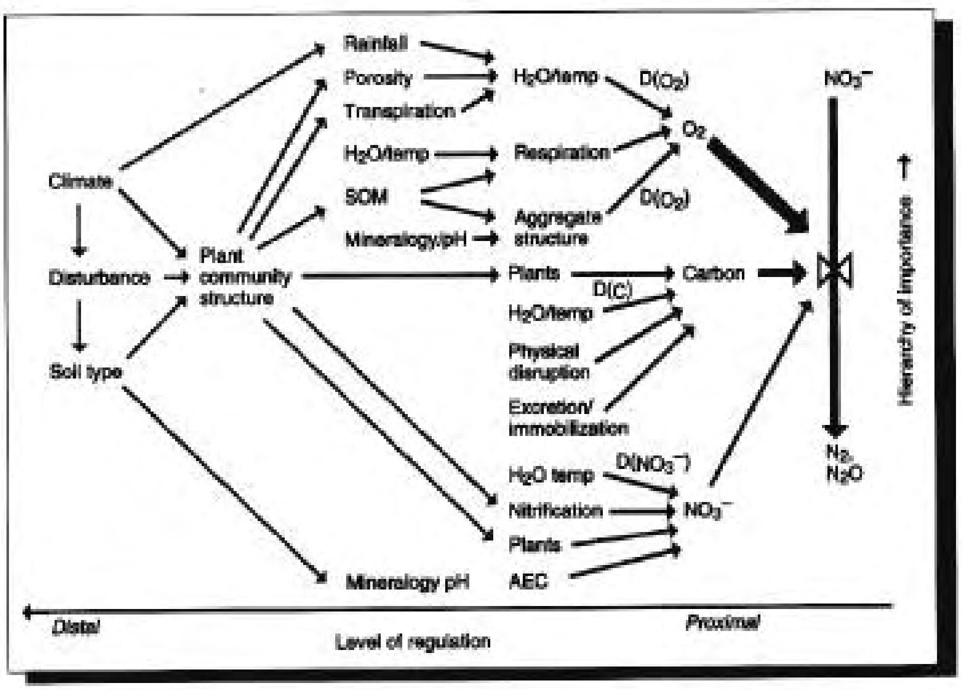


Figure 5-5: Proximal and distal regulators of the denitrification in surface soils (Robertson, 1989).

Oxygen, microbial substrate (carbon) and nitrate are the proximal regulators of denitrification. Characterizing these parameters at more extensive scales (aggregate, horizon, or field) is best achieved by the measurement of the factors that control the intensity of these parameters. For example at the scale of the aggregate, air filled porosity, biological oxygen consumption and aggregate structure are the primary regulators of soil oxygen content. Note that the absence of denitrifying organisms is not thought to be a factor limiting denitrification in surface soils.

In groundwater systems the proximal regulators of denitrification are similar to those in surface soils, but the distal regulators are somewhat different. The proximal regulators, electron donor and electron acceptor are the same but the relative importance of specific electron donors and acceptors differs. The distance from the soil surface, lower microbial activity and lower temperatures change the dynamics of these systems. Localized zones of oxygen depletion associated with aggregate structure, key to understanding the dynamics of denitrification in surface soils, become less important in controlling oxygen concentration. These anaerobic zones are very sporadic and short-lived in most surface environments. In the sub-surface, the spatial extent and duration of anaerobic zones can be greater due to the distance from the atmosphere, the major source of O_2.

In surface environments, due to intensive biological activity associated with photosynthesis and the subsequent utilization of the reduced carbon that it produces, carbon is the predominant electron donor. In the subsurface, isolation from the intensive biological activity associated with the surface electron donors tend to be more varied and in general are in shorter supply. The use of alternate electron donors such as sulfide ($S^{=}$) and ferrous iron (Fe^{+2}) result in lower energy yield. The availability of these electron donors is largely dependent upon the origin/mineralogy of the geologic deposits and rate of weathering of those materials in the environment of the aquifer. This complicates the estimation of the demand for electron acceptors.

The separation of the groundwater system from a source of oxygen such as the atmosphere results in more uniform oxygen status. The availability of substrate (carbon) becomes a much more dominant regulator of denitrification with the majority of carbon being transported from surface horizons with percolating water.

5.3.3.2 Groundwater Denitrification: Tools for identification and shallow sand aquifer case studies

Much of our understanding about denitrification is derived from soil zone studies that have been conducted over the past century (Paul and Clarke, 1989). Groundwater denitrification is a more recent concern. Hiscock et al. (1991) and Korom (1992) have prepared groundwater denitrification reviews. The four basic requirements for denitrification are the presence of nitrate (or other N oxides), the presence of bacteria to facilitate the process, suitable electron donors, and suboxic conditions (<2 mg/L).

A diverse bacterial flora facilitate denitrification (Knowles, 1982). A lack of appropriate bacteria is not usually a factor limiting groundwater denitrification. Many of the bacteria are facultative anaerobes - they will preferentially reduce O_2 if present, and then ‘switch over’ to nitrate as an electron acceptor as O_2 becomes depleted (hence the requirement of suboxic conditions for denitrification). In catalyzing the electron transfer from the electron donor (which is oxidized) to nitrate (which is reduced and gains electrons) during denitrification, the bacteria obtain thermodynamic energy.

In general, groundwaters evolve to increasingly reducing redox conditions as bacteria catalyze redox reactions and progressively use up electron donors and acceptors (Champ et al., 1979). The order in which bacteria use electron donors and acceptors is specifically related to the amount of thermodynamic energy they receive for facilitation of the electron transfer (Stumm and Morgan, 1996), and the presence or absence of each species in the groundwater flow system. For example, if an electron donor is present in unlimited concentrations (e.g. dissolved organic carbon (DOC) in Figure 5-6a), the preferred order of use of electron acceptors would be O_2, NO_3^-, Fe^{3+}, and SO_4^{2-}. The O_2 would be used preferentially, followed by the use of NO_3^- until the O_2 supply is exhausted, subsequently followed by the use of Fe^{3+}, and so on.

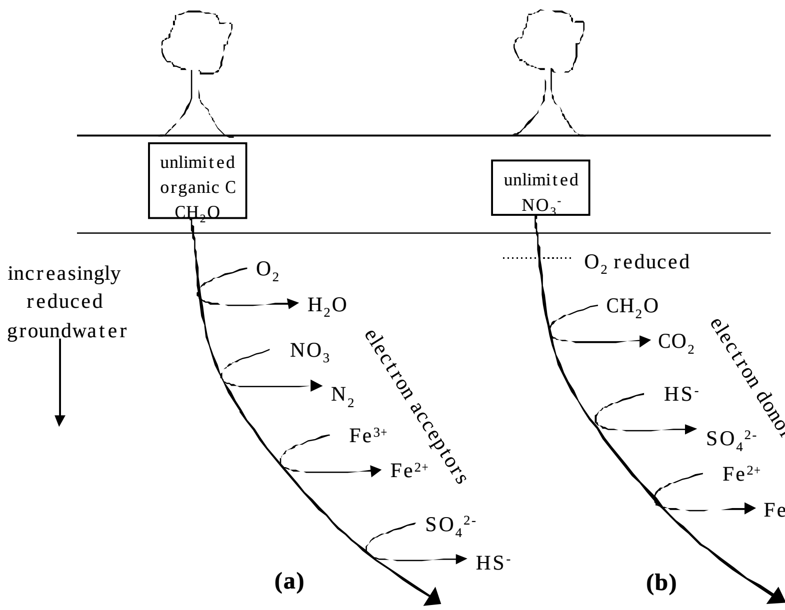


Figure 5-6: Redox processes that would occur depending on availability of electron acceptor (a) and electron donors (b) for a groundwater system with (a) unlimited organic carbon available for oxidation (CH_2O -> CO_2), and b) unlimited nitrate available for denitrification (NO_3^- -> N_2). Adapted from Korom (1992).

Conversely, if there is a significant amount of nitrate in a groundwater flow system, the denitrification half reaction ($2\ NO_3^- + 12\ H^+ + 10\ e- \rightarrow N_2 + 6\ H_2O$) would proceed preferentially with the reduction of organic carbon (CH_2O), followed by the reduction of sulfide (HS^-), and then iron (Fe^{2+}). Although there are other electron donors that are oxidized during denitrification (e.g. Mn^{2+}; Apello and Postma, 1993), the three species included in Figure 5-6b are the most commonly observed (Korom, 1992).

Chemical formulae for denitrification with the three most commonly occuring electron donors are included here, and more detailed case studies with examples of each follow. The chemical equation for denitrification coupled with the oxidation of organic carbon varies according to the form in which organic carbon is expressed. A commonly used form of organic C (CH_2O) is included in the reaction shown below (Appelo and Postma, 1993).

$5\ CH_2O + 4\ NO_3^- \rightarrow 2N_2 + 4\ HCO_3^- + CO_2 + 3\ H_2O$ ………………(1)

Since the bacteria use organic carbon source as their energy source, reaction is often referred to as heterotrophic denitrification. As a first approximation, the amount of nitrate that can be denitrified by organic carbon is approximately a 1:1 ratio in mg C or N per L^{-1} (Korom, 1992). Since most groundwaters in shallow sand aquifers would be expected to have only low concentrations of DOC (e.g. 1-2 mg/L; Thurman, 1985), sand aquifers typically have an intrinsically low capacity for heterotrophic denitrification. Potential carbon sources can infiltrate with nitrate from the surface (e.g. high DOC's are associated with recharged wastewater, and presumably manure-impacted groundwater), or be associated with solid organic C deposited contemporaneously with aquifer sediments (Starr and Gillham, 1993).

The nature of organic carbon probably determines the rate of heterotrophic denitrification. Different forms of organic carbon have widely varying lability or 'degradability' (Burford and Bremner, 1975). As will be seen in the case studies of groundwater denitrification presented below, organic carbon sources in aquifers are often not easily degradable. In these cases, while reaction (1) may be thermodynamically favourable (i.e. the microorganisms gain energy by facilitating the reaction), it can be kinetically limited. In the latter case, the bacteria need a substantial amount of time to degrade the organic carbon and obtain the necessary electrons with which to reduce nitrate-N, and the rate of denitrification is relatively low. In some cases, denitrification with sulfide oxidation is the dominant process, despite the presence of significant concentrations of dissolved organic carbon (Komor, 1992; Apello and Postma, 1993; Wassenaar, 1995). In essence, the thermodynamic sequence is reversed.

Denitrification coupled with sulfide oxidation is represented by the following chemical formula.

$5\ FeS_2 + 14\ NO_3^- + 4\ H^+ \rightarrow 7\ N_2 + 5\ Fe^{2+} + 10\ SO_4^{2-} + 2\ H_2O$ ………………(2)

Sulfide minerals are the usual reported form of reduced sulfur. Pyrite (FeS_2) is also often the source of reduced iron. The reaction written with dissolved Fe^{2+} is

$10\ Fe^{2+} + 2\ NO_3^- + 14\ H_2O \rightarrow 10\ FeOOH + N_2 + 18\ H^+$ ………………(3)

5.3.3.2 Dissimilatory nitrate reduction

It should be noted that bacterial reduction of nitrate to ammonium (known as dissimilatory nitrate reduction or DNR) has also been observed in sewage-contaminated aquifers (Smith and Duff, 1988; Bulgur et al, 1990; Smith et al., 1991). DNR is a less desirable nitrate fate than denitrification since it doesn't remove nitrate-N from the subsurface N cycle (i.e., the ammonium can be nitrified to nitrate). In general, DNR is thought to occur in electron-rich environments (i.e., environments with a high ratio of potential electron donors to nitrate; Tiedje et al., 1982; deCatanzaro et al., 1987). Its occurrence in soil and groundwater environments is not well defined (Paul and Clarke, 1989). Much of the groundwater nitrate work conducted on shallow sand aquifers to date has been focussed on fertilizer nitrate. It is possible that DNR will be a more important process in manure-impacted aquifers where relatively high concentrations of organic carbon are associated with the manure-N (as in the sewage-impacted aquifers cited above).

5.4 Tools to identify denitrification in groundwater

In the past decade, a number of tools and approaches have been elucidated to investigate whether or not denitrification is occurring in groundwater. These tools can be divided into two categories: those that provide circumstantial evidence (i.e., that denitrification would occur if nitrate was present) and direct evidence (i.e., that denitrification has occurred). Since subsurface environments can be complex both geochemically and physically, it is usual to employ as many tools as possible to elucidate the presence and extent of denitrification.

i) The *geochemical and thermodynamic approach* to the identification of denitrification entails the following:

a) <u>Evaluation of the redox potential using Eh and dissolved oxygen</u>. Denitrification usually requires dissolved oxygen concentrations less than 2 mg/L, and an Eh less than 0.28 volts (Spalding and Parrot, 1994; Gillham, 1991).
b) <u>The presence or absence of electron donors and their redox or oxidized forms</u> (which would be produced by denitrification). During denitrification, an electron donor (e.g. dissolved organic carbon, sulfide, or reduced iron (Fe^{2+})) is oxidized. Geochemical investigations into denitrification frequently measure these parameters to assess if electron donors are present, and observe evidence that they have been oxidized concurrent with nitrate reduction (i.e. denitrification). In some instances only one half of the redox pair is measured since low solubility of the other means it is not present in significant concentrations in usual groundwater conditions.

   For example, for the sulfate/sulfide pair, only SO_4^{2-} is typically measured since S^{2-} is expected to occur mainly in solid phase if present in the system. Since Fe^{3+} has limited solubility, total Fe is often considered to be a surrogate parameter for Fe^{2+} (which is relatively soluble). The redox pair for dissolved organic carbon is inorganic carbon (e.g. HCO_3^-). The participation of inorganic carbon in a variety of pH-sensitive inorganic carbon reactions can make interpretation of this parameter somewhat problematic (Appelo and Postma, 1993). Dissolved organic carbon is frequently measured for this redox couple.

c) Interpretation of geochemistry along a flowpath. In denitrification investigations, it is ideal to instrument the groundwater flow system along a flowpath in order to observe geochemical changes with time and/or distance. The observation of congruent redox and geochemical data can provide convincing evidence that denitrification is occurring. This is particularly true when the loss of nitrate-N can be stochiometrically correlated with the increase in the oxidized forms of the electron donors.

Groundwater flow systems often include sharp horizontal redox boundaries, with nitrate-rich groundwater above the redoxcline, and nitrate-poor groundwater (where denitrification has apparently occurred) below the redoxcline (Postma et al., 1991; Starr and Gillham, 1993; Robertson et al., 1993; Spalding and Parrott, 1994). A common approach is to identify the denitrification reaction by means of geochemical changes, and then conduct a mass balance on the reactants above the redoxcline compared to the products below the redoxcline. In addition to nitrate and the electron donors, there is also a change in pH, dissolved oxygen, Eh, etc.

d) Groundwater age dating. Modern groundwater age dating techniques can sometimes determine the groundwater age to within a few years. When historic rates of fertilizer use are known, groundwater age dating can be a valuable tool. If denitrification is occurring, it is reflected in a decreased ratio of the historic rate of fertilizer-N application (used as a surrogate of the amount of nitrate leached to the groundwater) to nitrate concentrations in groundwater of the appropriate age (e.g. Böhlke and Denver, 1995; Johnston et al., 1998).

e) Field or laboratory denitrification experiments. Some investigators have conducted laboratory and/or *in situ* field experiments where nitrate is introduced into aquifer sediments to evaluate whether or not denitrification proceeds (e.g. Trudell, 1986; Starr and Gillham, 1993). This type of investigation provides circumstantial information. (it does not demonstrate outright that denitrification has occurred, rather that it *would* occur if nitrate was present in the aquifer). Techniques employed to measure the occurrence and rate of denitrification include the acetylene-block method (acetylene inhibits the final stage of denitrification and causes N_2O to accumulate), ^{15}N tracer methods, and measurement of the amount of N_2 produced (Seitzinger et al., 1993).

f) Stable ^{15}N and ^{18}O isotopes in nitrate. Microbially mediated processes like denitrification typically cause significant shifts in the stable isotope compositions of elements. An increase in the heavier N and O isotope (i.e., ^{15}N and ^{18}O) occurs during the denitrification process (Clarke and Fritz, 1997). Thus, stable isotope ratios of ^{15}N and ^{18}O in nitrate provide a tool that can be used in concert with other geochemical indicators (in particular nitrate concentrations). In addition to nitrate isotopes, ^{34}S and ^{18}O in SO_4^{2-} can yield insight into whether or not sulfide oxidation is occurring during denitrification. In addition to confirming the presence and extent of denitrification, ^{15}N and ^{18}O isotopes can also yield insight into the nitrate sources (Komor and Anderson, 1993).

g) Excess N_2/N_2O gas. One of the most recent techniques employed to evaluate whether groundwater denitrification is occurring is the measurement of nitrogen gases. Since there are not any other usual groundwater sources of these gases, their presence in concentrations significantly above those expected in equilibrium with the atmosphere provide convincing and direct evidence of denitrification (Vogel et al., 1981; Blicher-Mathiesen et al., 1998).

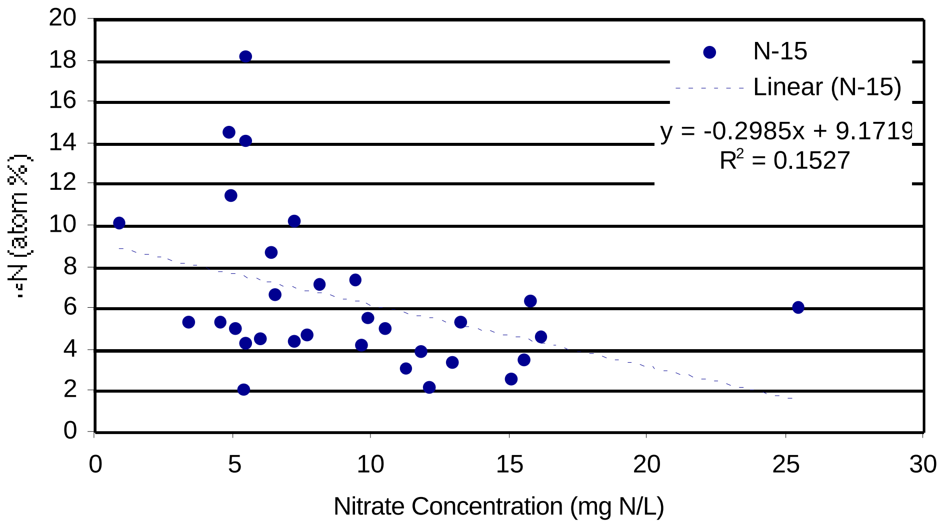


Figure 5-7: The change in ^{15}N abundance (delta ^{15}N (‰) as a function of initial groundwater nitrate concentration. Data from Bob Betcher, Manitoba Conservation.

5.4.1 Case studies of denitrification in shallow sandy aquifers

Denitrification has been observed in a number of shallow sand aquifers. Examples with details about associated geochemical conditions and electron donors are summarized here. Significant denitrification is only conclusively demonstrated in aquifers with sulfide present as electron donors in these case studies. Heterotrophic and iron electron donors in denitrification are minor relative to sulfide.

Rabis aquifer, Denmark Although the nature of the sediments is not clear, denitrification coupled with organic carbon oxidation is inferred from vertical profiles of groundwater geochemistry in a shallow aquifer in Germany (Apello and Postma, 1993). From the water table to deeper groundwater (11 m below the water table), dissolved oxygen initially decreases to about 2 mg/L while nitrate decreases from about 25 to 10 mg N/L. The nitrate decrease is accompanied by increases in HCO_3- and pH. On a mass balance basis, heterotrophic denitrification could account for 60% of the nitrate loss (investigation of sulfide and iron as electron donors was not conducted). The relatively slow rate of denitrification is gradual (inferred by NO_3^- concentrations gradually decreasing over almost 10 m of aquifer depth, rather than a discrete or abrupt boundary) is attributed to low reactivity of organic matter. The possibility of sulfide and/or iron acting as electron donors was apparently not evaluated.

Alliston and Rodney aquifers, Ontario Varying water depths was the reason invoked for varying degrees of denitrifying conditions observed in two shallow, sand aquifers in Southern Ontario (Starr and Gillham, 1993). Dissolved oxygen and nitrate persisted in the Alliston aquifer with a water table depth of 4 m, while low oxygen and nitrate concentrations were measured in the Rodney aquifer, which had a water table depth of 1m. In situ denitrification experiments confirmed that *in situ* electron donors were present to facilitate denitrification in the Rodney aquifer if nitrate were present (Trudell et al., 1986), but not in the Alliston aquifer (Starr and Gillham, 1993). The authors hypothesized that dissolved organic carbon was being transported through the relatively shallow unsaturated zone at Rodney, but was oxidized before it reached the water table at Alliston. The possible contribution of sulfide and/or iron to the electron donor supply was not evaluated.

Abbotsford aquifer, B.C. The evidence for heterotrophic denitrification in the two aquifers described above is circumstantial, and the possibility that sulfide and/or iron was acting as electron donors were not rigorously evaluated. No studies that conclusively demonstrate extensive heterotrophic denitrification in shallow sand aquifers were found in this literature review. Although denitrification with organic carbon oxidation has been observed in other shallow sand aquifers, it is a minor process compared to denitrification by sulfide oxidation even when significant concentrations of organic carbon are present (see following section). For example, the possibility for heterotrophic denitrification presumably exists in the Abbotsford aquifer since most of the nitrate is derived from poultry manure (Liebscher, 2000) which is rich in organic carbon. A stable isotope investigation conclusively indicated, however, that significant denitrification was not occurring in the aquifer (Wassenaar, 1995).

Thus, despite the fact that heterotrophic denitrification is usually considered to be the most favourable for microorganisms (Figure 5-6), literature on field-based research suggests it does not extensively occur. It is not clear if the apparent absence of heterotrophic denitrification in sand aquifers is because an inappropriate carbon form is assumed in thermodynamic calculations for heterotrophic denitrification (i.e. that it is not thermodynamically favourable to sulfide oxidation), or because the process is kinetically limited (i.e., it is thermodynamically favourable, but occurs at very low rates). As will be seen in the subsequent section, the occurrence of denitrification with sulfide oxidation is apparently more common in shallow sand aquifers.

In general, only low levels of dissolved organic carbon (1 to 3 mg L^{-1}) are found in groundwater (Thurman, 1985). In large part this is because labile organic carbon is oxidized to CO_2 as it moves through the unsaturated zone (Starr and Gillham, 1993;

deSimone and Howes, 1998). Although solid aquifer carbon (also known as aquifer 'kerogen' can often be present in aquifers, there is no literature evidence that it can act as a significant electron donor in denitrification due to its low availability.

5.4.1.1 Denitrification with sulfide oxidation

Fuhrberg aquifer, Germany The Fuhrberg aquifer in northern Germany is well studied (e.g. Frind et al., 1990; Bottcher et al., 1990) because it provides 20 million m^3 y^{-1} of water supply to the city of Hannover. The aquifer is areally expansive, has an average saturated thickness of about 20m, a hydraulic conductivity ranging from 4.6×10^{-4} to 1.7×10^{-3} m/s, and a hydraulic gradient on the order of 0.001. The aquifer is comprised of Quaternary sandy sediments with lignitic pebbles that impart a significant fraction of organic matter (up to 1%) and pyrite. The presence of these reduced constituents makes the aquifer almost anoxic, with low levels of oxygen only observed near the water table.

Significant agriculturally derived nitrate that is recharged to the aquifer is denitrified within 8m of the water table. A commensurate increase in sulfate indicates that sulfide is the primary electron donor. Organic carbon is present in the denitrifying zone, but bacteria apparently prefer to use the sulfide. The increasingly reduced environment in the Fuhrberg aquifer with depth causes the sulfate to be subsequently re-reduced in tandem with the oxidation of organic carbon at depths of 8 to 16 m below the water table. Decreasing sulfate concentrations that correlate with increasing HCO_3^- concentrations are consistent with the reaction

$$SO_4^{2-} + 2\ C_{org} + 2\ H_2O \rightarrow 2HCO_3^- + H_2S$$

Sulfate reduction begins in the aquifer when nitrate concentrations are decreased to less than 1 mg N/L due to denitrification. The sulfide product is subsequently precipitated.

In terms of water quality, high sulfate concentrations in the middle aquifer depths exceed the drinking water standard of 250 mg/L. Although the subsequent sulfate reduction ameliorates this issue, municipal water supplies are nonetheless significantly affected (Kölle et al., 1985) as discussed in a later section. An accurate estimate of the mass of sulfide present in the aquifer has not been obtained because its content is spatially variable (Frind et al., 1990). If all or part of the sulfide is eventually oxidized, the aquifer's protective capacity will be depleted and nitrate will break through to the water wells.

Central Platte Valley aquifer, Nebraska Although the electron donor species was not identified, reduced sediments were also correlated to denitrification in the Central Platte valley in Nebraska (Spalding and Parrott, 1994). A low level of correlation between nitrate concentrations and depth in the aquifer, in contrast to a high level of correlation between nitrate and redox conditions (Eh) in the aquifer, led the authors to conclude the redoxcline location was laterally variable. The authors suggest the location of municipal supply wells at depth (i.e., below the redoxcline where reduced sediments or electron donors occur) in the aquifer could afford long term groundwater protection from nitrate.

Atlantic Coastal Plain aquifer, *USA* An insightful example of the effect of reduced sediments on an aquifer's denitrification capacity is provided by field studies into two adjacent agricultural watersheds in the Atlantic Coastal plain (Böhlke and Denver, 1995). The Morgan Creek and Chesterfield Branch watersheds have sub-parallel streams, similar narrow riparian zones and recharge areas, and similar agricultural activities. Despite these similarities, nitrate concentrations in Morgan Creek (2-3 mg N/L) are consistently lower than in Chesterfield Branch (9-10 mg N/L). The main difference between the watersheds is in their subsurface sediments. Chesterfield Branch is underlain by a shallow sand aquifer comprised of sediments from two oxidized formations known as the Aquia formation. Reducing marine sediments underlie the Aquia formation. The base of the oxidized aquifer is sloping (Figure 5-8). As a result, the Aquia formation is much thinner under the Morgan Creek watershed and much of the groundwater passes through the underlying reduced formation.

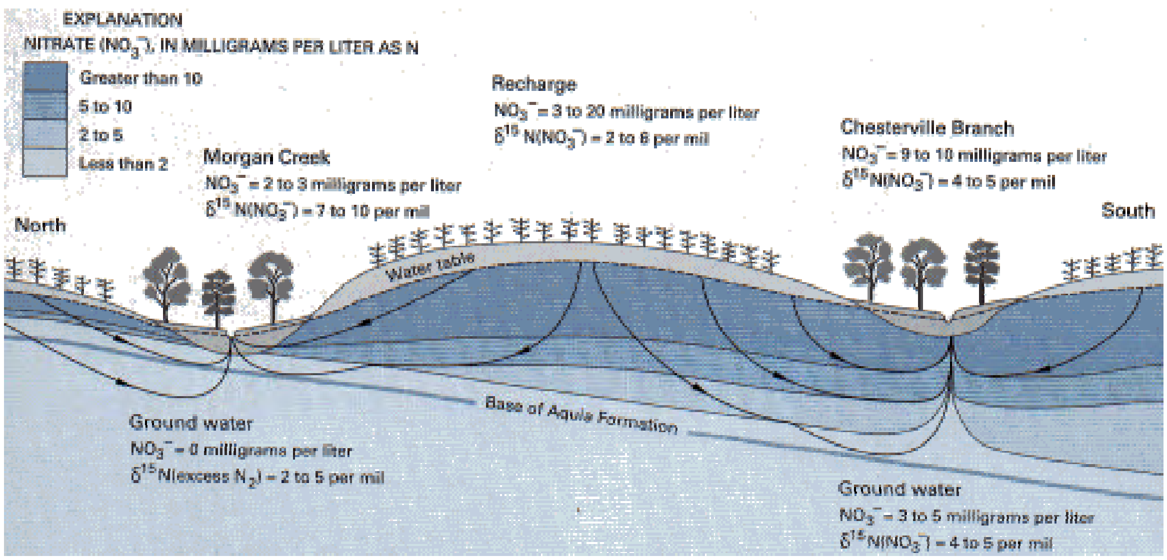


Figure 5-8: Denitrification had a greater effect on ground water discharging to Morgan Creek that the Chesterfield Branch (Locust Grove) because a larger fraction of the groundwater penetrated the reduced sediments at or near the bottom of the Aquia formation. (Modified from Winter et al., 1998 and Böhlke and Denver, 1997)

An integrated approach to comparing the two watersheds included geochemical characterization and age dating of the groundwater, measurement of nitrogen gas, the use of stable isotopes in nitrate and sulfate, and historic N loading. The authors determined that the lower nitrate concentrations in Morgan Creek were due to groundwater denitrification in the reduced formation underlying the Aquia formation. Since groundwater flowpaths in Morgan Creek intersected more of the reduced formation, denitrification was more extensive, and nitrate concentrations in water discharging to the creek were lower.

Rabis aquifer, Denmark Denitrification with sulfide oxidation was observed in a shallow sand aquifer in the Rabis aquifer in Denmark (Postma et al., 1991). As in the Fuhrberg aquifer, the presence of denitrification was controlled by reduced pyrite-sulfide in the aquifer. The aquifer had a 15m deep water table, average horizontal groundwater velocity of 40-60 m/yr, and a saturated thickness greater than 90m. The aquifer has a sharp redoxcline located 10-15 m below the water table which separates an upper oxic zone and a lower, anoxic zone. The redoxcline coincides with the appearance of reduced sulfur and carbon in the aquifer sediments. Significant nitrate leaching occurs under agricultural fields, and nitrate persists through the 10-15 m oxic zone until it reaches the redoxcline. Increased sulfate, iron, and inorganic carbon concentrations are associated with the disappearance of nitrate below the redoxcline. Mass balances across the redoxcline indicate that sulfide is the dominant electron donor, despite the fact that organic carbon is present at high concentrations. The authors fitted a geochemical model to historic data to conclude that the elevated concentrations of groundwater nitrate were causing the pyrite oxidation to be accelerated by a factor of five. The relatively slow rate of downward progression on the redoxcline (a few centimetres per year) suggests the aquifer can provide nitrate mitigation for centuries.

5.4.1.2 Denitrification with iron oxidation

Detailed lab studies have shown that iron can act as an electron donor in denitrification (Till et al., 1998). When reduced iron and sulfate are both available in an aquifer, sulfide is the dominant electron acceptor, as expected (Figure 5-6; Frind et al., 1990; Postma et al., 1991). In both case studies, geochemical data show that minor amounts of iron are oxidized during denitrification. In the Rabis aquifer, iron oxidation occurred after substantial sulfur oxidation. Although geochemical evidence indicates that iron oxidation (and organic carbon oxidation) occurred during denitrification, their contribution was relatively minor.

In summary, significant denitrification in shallow sand aquifers appears to be significant only in cases where significant sulfide is available for oxidation. Although organic carbon has historically thought to be an important electron donor in groundwater denitrification, this has not been borne out in field studies. This is also apparently true in septic system plumes. A very careful mass balance was conducted over the initial three years of development of a plume of waste water contaminated groundwater in Cape Cod, Massasschusetts (DeSimone and Howes, 1998). The plume water was anoxic (<0.05 mg L^{-1} dissolved oxygen), and nitrate was the dominant form of nitrogen. Denitrification was not a signficant process despite the presence of dissolved organic carbon. The authors concluded that the low rates of denitrification (less than 0.01 mg N L-1 day-1) were due to the lack of labile organic carbon in the aquifer.

5.4.2 Availability of sulfide in shallow sand aquifers for denitrification

In all instances when an electron donor was identified in shallow sand aquifers where significant denitrification was observed, the electron donor was sulfide (Frind et al., 1990; Postma et al., 1991; Böhlke and Denver, 1995). The sulfide is presumably allochthanous (i.e. deposited contemporaneously with the sand and gravel in the aquifer). Reduced sulfur in the form of pyrite is reported to be found in many aquifers in Denmark at a level of 1-2% in association with lignite (Pedersen et al., 1991). In the Rabis aquifer, pyrite-sulfide was found throughout the aquifer at concentrations in the reduced part of the aquifer ranging from 0.02 to 0.18 % by weight (with up to order of magnitude variations in concentration; Postma et al., 1991). Pyrite-sulfide concentrations were also variable in the Fuhrberg aquifer (Frind et al., 1990), where pyrite was associated with lignite and also present as micro-crystalline particles. Kölle et al. (1985) point out that the availability of pyrite-sulfur for oxidation depends on its micro-crystalline structure. They recommend a lab assessment of the pyrite's reactivity or 'sulfate formation capacity'.

5.4.2.1 Typical rates of denitrification in the vadose zone

Yeomans and Bremner (1992) observed that denitrification in Iowa subsoils (3 m depth) were primarily limited by substrate (electron donor) availability. The denitrification capacity[6] in the four soils considered was in the range 0.1 – 6.0 µg N denitrified per g of soil in a 24 hour incubation. The assay was conducted in a 1:2.5 soil:water ratio. The rate of NO_3^- removal when expressed on a solution basis becomes 40-2400 µg N/L over a one day period. It must be emphasized that this is a denitrification potential where all conditions other than carbon availability were optimal.

5.4.2.2 Typical rates of denitrification in the saturated zone

Korom (1992) summarizes denitrification rates for both laboratory samples from aquifers and field studies in a review paper. Rates included for more than 20 laboratory studies range from zero to 1.16 mg N kg^{-1} dry sediment per day. Denitrification rates for about seven agriculturally-related sites ranged from zero to 3.1 mg N L^{-1} per day, with an approximate average of 0.8 mg N L^{-1} per day. Denitrification rates at a Cape Cod septic system were less than 0.01 mg N L^{-1} per day (DeSimone and Howes, 1998).

5.4.3 Addition of substrate

Numerous studies have examined the use various substrates to stimulate denitrification either above or near ground surface, or as an aqueous supplement in the groundwater zone.

- Soares, M.I.M. and Abeliovich, A. 1998. Wheat straw as substrate for water denitrification. Water Res. 32, 3790-3794.
- Volokita, M., Abeliovich, A. and Soares, M.I.M. 1996. Denitrification of groundwater using cotton as energy source. Water quality international '96 selected proceedings of the 18th Biennial Conference of the International Association on Water Quality, held in Singapore, 23-28 June 1996 / International Association on Water Quality Conference. p. 379-385.
- Kohler-Staub, D., Frank, S., Leisinger, T. 1995. Dichloromethane as the sole carbon source for Hyphomicrobium sp. strain DM2 under denitrification conditions. Biodegradation 6, 229-235.
- Laurino, C.N. and Sineriz, F. 1991. Denitrification by thermophilic soil bacteria with ethanol as substrate in a USB reactor. Biotechnol. Letters 13, 299-304.

[6] Denitrification Capacity was defined as the rate of denitrification in laboratory incubations of soil to which 300 µg NO_3^--N was added per gram of soil and incubated under an anaerobic atmosphere.

- Manoharan, R., Liptak,, S., Parkinson, P., Mavinic, D. and Randall,-C.W. 1988. A comparison of glucose and methanol as carbon sources for denitrification in biological treatment of leachate. Proc. Ind. Waste Conf. Purdue Univ. Chelsea, Mich., Lewis Publishers. 1988. (43rd) p. 195-202.
- Paul, J.W. and Beauchamp, E.G. 1989. Effect of carbon constituents in manure on denitrification in soil. Can. J. Soil Sci. 69, 49-61.
- Sommer, K. and Ottow, J.C.G. 1985. Denitrification with cellulose as a single energy source (hydrogen donator). J. Basic Microbiol. 25, 77-80.
- Skrinde, J.R. and Bhagat, S.K. 1982. Industrial wastes as carbon sources in biological denitrification Addition of maize silage derivative, whey, yeast for the stimulation of the activity of heterotrophic bacteria. J. Water Pollut. Control Fed. 1982. (54) p. 370-377.

5.5 Environmental issues related to denitrification

Although only reactants and products have been identified in the reactions above, denitrification occurs in a series of successive reductions ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). Although an assumption is commonly made that denitrification predominantly proceeds to the terminal electron acceptor N_2 (e.g. Apello and Postma, 1993), there is little published information to indicate whether this is truly the case. When N_2O (a gas of significant global warming concern) is looked for in groundwater, it is sometimes found in significant concentrations (Ronen et al., 1988; Spalding and Parrot, 1994). Certainly N_2O production can be a significant soil zone process (Pathak, 1999).

Although nitrate reduction by denitrification can successfully ameliorate groundwater nitrate contamination on a regional scale, the products of the coupled oxidation reaction are deleterious to water quality to varying degrees. Production of inorganic carbon during oxidation of organic matter increases water hardness and iron oxidation can cause iron staining in domestic water supplies. These two issues are of aesthetic concern, however, and don't threaten groundwater potability. Sulfate production during denitrification can render groundwater undrinkable, however. In the Fuhrberg aquifer, for instance, denitrification is successfully ameliorating agricultural nitrate impacts in the municipal aquifer, the associated sulfide oxidation is causing increasing sulfate concentration in the municipal well water supply. Sulfate concentrations in two wells increased steadily between 1965 and 1985, and have exceeded the drinking water standard of 250 mg/L in one of the wells (Kölle et al., 1985). The same well waters are also affected by the oxidation of iron and organic carbon during denitrification. Decreased well performance due to precipitation of oxidized iron has incurred expensive cleaning costs (Kölle et al., 1985).

In one instance, an increase in arsenic concentration has been associated with denitrification coupled with pyrite oxidation (Van Beek et al., 1989, in Appelo and Postma, 1993). The authors conclude that pyrite oxidation is releasing trace arsenic that had substituted for iron in the pyrite mineral lattice. Groundwater arsenic concentrations in this instance were well above the WHO drinking water limit of 0.05 mg/L.

Hypoxia in the Gulf of Mexico

In the United States the nutrient loading of the Mississippi Drainage Basin and its impacts upon the eutrophication of the Gulf of Mexico have received considerable attention.

5.5.1 Groundwater quality considerations related to the use of manure fertilizer

While the scientific literature on groundwater nitrate contamination is extensive, groundwater impacts associated with the use of manure as a fertilizer is a much less well studied topic (the Abbotsford aquifer being a notable exception). For example, it is not clear whether commercial fertilizer has a higher or lower propensity to leach nitrate to groundwater compared to manure fertilizer. Also, manure may have a higher component of reduced N (i.e. organic and NH_4^+). An inverse relationship between NH_4^+ and NO_3^- observed in a regional well water study in the midcontinental U.S. (Kolpin et al., 1993) was unexpected since conventional wisdom holds that NH_4^+ is not transported to water table aquifers due to sorption (Korom, 1992). Apparently NO_3^- is present in oxic, and NH_4^+ in anoxic, shallow sand aquifers. Since few water well surveys analyse for NH_4^+, it is difficult to know how widespread the groundwater NH_4^+ issue is.

In addition to nitrate, phosphorus impacts on groundwater is an issue if discharge to surface water is a possibility. As management practices evolve to minimize overland P transport, there is concern that the mass flux will be shifted to the groundwater zone (Litke, 1999).

Although there is a lack of field-scale studies on manure impacts on groundwater in shallow sand aquifers, there is a considerable body of literature on septic system impacts on groundwater. While the characteristics of domestic effluent and manure are probably different, and the former passes through a septic tank and tile field, it is worthwhile to briefly outline septic system impacts on shallow sand aquifers as an analogy to potential impacts of manure. Septic systems located over sandy unconfined aquifers develop long, narrow, and sub-horizontal plumes that can be kilometers long with nitrate concentrations frequently in excess of 10 mg N/L (Robertson et al., 1991; Le Blanc, 1993; van der Kamp et al., 1994). Although phosphorus transport is retarded by sorption and precipitation of low solubility P-bearing minerals, substantial PO_4^{2-} plume sizes develop with elevated concentrations (e.g. 750 m long, 1.5 mg P/L; Stollenwerk, 1996). While sorption slows the rate of P transport, it also stores P in the subsurface. If aqueous concentrations decrease, the sorbed P will de-sorb, resulting in a long term source of additional P. In addition to nitrate and phosphorous issues, pathogens in groundwater are of concern in septic systems (DeBorde et al., 1998)

5.5.2 Riparian zone attenuation of groundwater nitrate

The riparian or buffer zone is the strip of land between the stream channel and hillslope and forms an important transition zone between land and freshwater systems (Hill, 1996). Because of their location, stream riparian zones have the potential to regulate and attenuate movement of nutrients in surface runoff and groundwater flowing from uplands to the stream. They are complex environments characterized by spatial heterogeneities in hydrology, sediment characteristics, and biogeochemical processes in both the horizontal and vertical directions requiring an interdisciplinary approach to their study (Hill, 1996). Recent research has focussed on determining: (a) the potential for NO_3^- removal via denitrification and other microbial processes, and plant assimilation (Peterjohn and Correll, 1984; Lowrance, 1992; McMahon and Bohlke, 1996; Jacinthe et al., 1998; Cey et al., 1999) and (b) the relative effectiveness of vegetation type on NO_3^- removal (Martin et al, 1999).

Although riparian zones are promulgated as being effective at removing NO_3^- from subsurface water, there remains some uncertainty of the relative importance of the attenuation mechanisms (Hill, 1996). Generally, denitrification, and plant uptake are credited as the most important mechanisms, however other microbial processes such as immobilization (Jacinthe, 1998) have also been suggested. Although microbial immobilization in riparian zones is known to occur, the effects of immobilization on the overall attenuation of NO_3^- are minimal. Plant uptake of NO_3^- has been identified in riparian zones with shallow water tables (Peterjohn and Correll, 1984), but it is generally not thought to be a dominant process in most areas (Hill, 1996).

Nitrate removal by denitrification in riparian zones has been inferred by denitrification enzyme assays (Lowrance, 1992), and declines in NO_3^-/Cl^- or NO_3^-/Br^- ratios (Simmons et al., 1992; Nelson et al., 1995; Martin et al., 1999). Isotopic ratios of ^{15}N in NO_3^- and N_2 and ^{18}O in NO_3^- have been used to ascertain the importance of denitrification in riparian zones of Colorado (McMahon and Bohlke, 1996) and southern Ontario (Cey et al., 1999). The results are summarized below.

1. South Platte River, Colorado: The effects of denitrification and surface-groundwater mixing on NO_3^- loading in an unconsolidated, sand and gravel aquifer were investigated between 1992 and 1994 (McMahon and Bohlke, 1996). Median concentrations of NO_3^- in the terrace, floodplain, and riverbed sediments and the South Platte River were 26, 6.6, 6.5, and 4.5mg N/L, respectively. $\delta^{15}N$ values of NO_3^- and N_2 in groundwater indicated that denitrification accounted for 15-30% of the difference in NO_3^- concentrations between the deposits. Mixing between river and groundwater in the floodplain deposits accounted for the remainder.

· Kintore Creek watershed, southern Ontario: Groundwater flow and geochemistry in the riparian zone of a small agricultural watershed was studied in the spring of 1996 (Cey et al., 1999). The study area is underlain by approximately 45 m of calcareous sand-silt till and is bounded to the east and south by a drainage canal; the Logan Drain. Nitrate concentrations range from 61.7 (March), 130 (April) , 57.2 mg-N/L (May) beneath the field, to below detection limit (< 0.1 mg-N/L) within 10 m of the field riparian zone boundary. Lateral decreases in NO_3^- are thought to be due to groundwater flow patterns. Vertical decreases possibly result from longer residence times in a lower-permeability unit as the groundwater is forced downward beneath the riparian zone. Denitrification, as the cause for NO_3^- attenuation, is suggested by decreasing DO and Eh with depth. Elevated values of $\delta^{15}N$ and an increasing linear relationship between $\delta^{15}N$ and $\delta^{18}O$ further support this theory.

Vegetation type is the most easily manipulated characteristic of riparian zones (Martin et al., 1999). Comparative studies of the effectiveness of various types of ground cover could, therefore, lead to the establishment of useful design criteria. In general, forested riparian zones have a greater and more consistent capacity for NO_3^- retention than grasslands (94 % and 83% respectively; Hill, 1996). In a study of the riparian zone of Carroll Creek, Ontario, NO_3^- concentrations were depleted more quickly over a shorter distance under woody riparian zones than under the adjacent grassy riparian zone (Martin et al., 1999). This observation was inferred to mean that a greater portion of the woody zone is 'unused' and they may be more appropriate as long term buffers than grassy riparian zones.

On a larger scale, the overall efficacy of riparian zone attenuation of groundwater nitrate before it enters surface water bodies is questioned by the consistent increases in surface waters in agricultural areas that have been measured on decadal scale (Smith et al., 1987; Mueller et al., 1995; Goolsby et al., 1999). In light of the long-term increase in nitrate observed in streams and rivers in agricultural areas, it seems unlikely that nitrate attenuation by riparian zone denitrification can be relied upon to mitigate potential groundwater nitrate impacts in the ADA.

6. Is the ADA at risk of widespread elevated nitrate concentrations?

While there has been a great deal of research effort directed at elucidating management practices to select those that minimize nitrate leaching, many of these studies have been conducted in the soil zone. While they are useful insofar as they indicate relative groundwater impacts, the extrapolation of these studies into the groundwater zone to predict groundwater impacts is problematic at best. While some management practices have some promise to mitigate groundwater nitrate impacts (e.g. soil-test based N application rates; fertigation), there is an absence of field-scale groundwater study to evaluate whether they can maintain groundwater nitrate concentrations below the drinking water objective.

There are no field-based groundwater studies to indicated that economically viable, usual agricultural activities can occur over shallow sand aquifers without significant nitrate leaching to groundwater. In virtually all groundwater studies, signficant groundwater nitrate impacts are observed, at least in the shallow groundwater. In some aquifers (presumably aerobic where denitrification does not occur), these groundwater nitrate impacts often threaten municipal and domestic water supplies.

There is good evidence that denitrification is an active process mitigating nitrate contamination on a field and even regional scale in a number of shallow sand aquifers around the world. The long term sustainability of the denitrification process relies on a supply of electron donors (e.g. reduced sulfide, organic carbon, or iron) to facilitate the process. In each field study where these supplies were identified in shallow sand aquifer denitrification, aquifer sulfide was the main source of electron donors. It thus appears that the likelihood of denitrification as a long term mechanism to prevent widespread nitrate contamination of the Assiniboine Delta Aquifer relies on the question of whether or not there is a significant supply of sulfide minerals in the aquifer that is available to facilitate denitrification. Preliminary evidence collected by Bob Betcher (Manitoba Conservation) suggests that denitrification is occurring in the aquifer. The observation of a redoxcline in the aquifer (indicated by sediment colour change from brown to grey), suggests reducing conditions occur in the lower aquifer. More direct evidence is provided by means of stable isotope work.

While denitrification amelieorates nitrate contamination of groundwater, it can unfortunately have deleterious side effects. In particular, facilitation of denitrification by sulfide oxidation produces sulfate, which has a drinking water objective in Canada of 250 mg L^{-1}. The mass of sulfate produced is a function of the mass of sulfide oxidized during denitrification. In at least one instance (the Fuhrberg aquifer), sulfate concentrations produced during denitrification are high enough to present water quality problems in a municipal water supply.

The risk of nitrate contamination of the ADA as a consequence of agricultural activities is high, due to the characteristics of the aquifer and its geological setting, and to the suitability of the land for agricultural development and use. Expansion of intensive crop production, irrigation, and livestock production would further increase this risk. A clear assessment of the risk requires a field- and groundwater-based study to elucidate the potential for denitrification, including the nature and long-term supply of electron donors and their associated groundwater impacts.

7. Management options

7.1 Land use change and land use regulation

The soils overlying the ADA have been identified as soils with a high sensitivity to groundwater impacts (Manitoba Land Resource Unit, 1996-7). Clearly land use decisions in this region must be based both on economic considerations as well as the long-term sustainability of soil and water resources. The assessment of impact of current land use on groundwater conducted in section 4, estimated that the current NO_3^- loading to groundwater was 4,130 tonnes of NO_3^--N/year and when diluted in the average annual volume of recharge water represented a NO_3^- concentration of 44 mg N/L. While this calculation is based on numerous approximations it points to the importance of obtaining an accurate estimate of the NO_3^- impact of current land use practices on the aquifer. In particular high impact land uses should be targeted and their suitability assessed.

Current land use practices can also be modified to improve the nitrogen use efficiency and reduce NO_3^- leaching. Numerous examples of this have been provided throughout the report. These include:

- Durieux et al. (1995) and Campbell et al. (1994) found that nitrogen application rates based on soil nitrogen testing resulted in reduced nitrate leaching.
- Racz et al (1994) found the use of split applications of nitrogen, controlled release fertilizers and nitrification inhibitors to reduce the amount of NO_3^- accumulating in the soil during the fall.
- Sexton et al. (1996), in a study of NO_3^- leaching from irrigated corn fields, found that reducing nitrogen fertilizer application rate to 95% of that required from maximum crop yield resulted in a 35% decline in NO_3^- leaching.

Management changes of this nature offer promise in reducing the groundwater NO_3^- impacts of existing land use practices. Other more sophisticated tools need to be considered to improve our understanding of the nature and extent of NO_3^- impact on the ADA.

7.2 Groundwater Models

7.2.1 Groundwater flow and transport modelling

More than a decade ago, the use of flow and transport modelling to assess groundwater contamination was described as being “in its infancy” (Bogardi et al., 1988), and relatively little progress has occurred since. Groundwater modelling has been almost entirely conducted with point source contamination examples (Anderson and Woessner, 1992; Fetter, 1999).

The Fuhrberg aquifer in Germany, described above, is one of the most significant agricultural nitrate in groundwater case studies that has been mathematically modeled (Frind et al., 1990). The authors used a finite element-based numerical model to represent a non-linear transport problem involving multi-component species. In addition to reproducing historical distributions of sulfate and nitrate, the model was also used in a predictive sense.

In the Rabis aquifer, Postma et al. (1991) assume a 1-D vertical flow system to conduct geochemical modelling of denitrification using PHREEQM, which combines equilibrium speciation with a one-dimensional mixing model. As in the Fuhrberg aquifer, historic data was available for model calibration, and the model was used in a predictive sense.

7.2.2 Unsaturated zone leaching models

A significant number of unsaturated zone leaching models are available with widely varying complexity and general applicability to field situations (Vachaud et al., 1988). Many of these models rely on regional scale estimations (i.e. 'distributed parameter' estimations) of relevant parameters like depth to water table, physical characteristics of aquifer sediments. The concluding remarks of the 1988 review (emphasized by underlining in the paper) as whether the scientific community should continue to "develop more and more sophisticated …. models or should it put an emphasis on field experiments?". This question is remarkably similar to a comment on a specialized conference on "The application of GIS, Remote Sensing, Geostatistics, and Solute Transport Modeling to the Assessment of Non-point Source Pollutants in the Vadose Zone" held a decade later: "Perhaps the most controversial thought-provoking presentation was a keynote paper [that] stabbed directly at the heart of distributed parameter modeling and thereby the use of GIS as a viable approach for assessing NPS pollutants…. Scientists may be studying NPS pollution at a level of understanding and detail dictated by measurement instruments rather than at a level dictated by the appropriate conceptual framework" (Anonymous, 1998).

Two well water nitrate surveys used DRASTIC to compared their results with the model assessment of vulnerability. At a county level, median well water nitrate concentrations and DRASTIC scores had a correlation coefficient (r^2) of 1.7%. Correlation between mean nitrate concentrations and DRASTIC scores was slightly higher, with r^2=30.2%. The authors conducted regressions on a variety of concentration measures (e.g. 25th and 75th percentiles, percentages exceeding drinking water standard, etc) and concluded that DRASTIC could not be used with any confidence. A co-operative domestic well water survey in Iowa, had slightly better success with DRASTIC correlation to mean nitrate concentration (r^2=0.55 ; Baker, 1990). One other study used A GIS-linked model for the assessment of nitrate contamination in groundwater in a 20 km^2 catchment (Lasserre et al., 1999). The authors reported good agreement with results of parallel groundwater flow and transport modelling (using MT3D-MODFLOW).

7.3 Artificial Groundwater nitrate remediation

Nitrate remediation investigations have primarily employed denitrification, but also include ion exchange and precipitation. The rate and occurrence of denitrification depends on several variables including; concentration of dissolved oxygen, redox conditions, and availability of an organic carbon source. Lab and field studies have investigated methods of artificially enhancing the natural denitrification process. Lab experiments have considered the feasibility of using alternate carbon sources (Abu-Ghararah, 1996; Volokita et al., 1996; Hunter et al., 1997) and ion exchange columns (Fritsche, 1993; Lin and Wu, 1997) to remove nitrate from solution. Field experiments considered above-ground and in-situ remediation techniques (Hiscock et al., 1991; Schipper et al., 1998). Varying degrees of success have been found in all methods.

Nitrate remediation by biologic denitrification typically employs organic carbon as an electron donor or energy source. Alternate carbon sources suggested in the literature including methanol, ethanol, acetic acid, cellulose and vegetable oils. Key results of these studies are summarized below.

- A series of experiments in anoxic upflow packed bed reactors found biologic denitrification to be effective at removing NO_3^- from amended (up to 115 mg N l^{-1}) tap water (Abu-Ghararah, 1996). Methanol was most efficient for NO_3^- removal (97%) at nitrate loading rates of 0.45 kg N m^{-3}. However, NO_2^- tended to accumulate in the effluent. Acetic acid had very low efficiencies for NO_3^- removal (23-37%), however, NO_2^- levels were substantially reduced. Ethanol was overall the most effective for both NO_3^- (88-92% efficiency) and NO_2^- removal.
- Cellulose is a convenient and cost effective C source (Volokita et al., 1996). Nitrate (45 mg N l^{-1}) amended tap water was pumped through upflow reactors with cotton as the sole physical and chemical substrate. Treated water had no NO_3^-, very low DOC, no detectable color or odor, and bacterial colonies forming units on the order of 10^5 ml^{-1}. Post treatment by sand filtration and chlorination would be required to attain drinking water standards. Denitrification rates increased steadily with time, even when only 60% of the cellulose substrate remained. Colonization of the substrate may be the rate-limiting factor. Increased NO_3^- loading (high flow rates) improved the efficiency of denitrification until a threshold velocity of 1.23 m $d^{-1}$was reached. Denitrification rates were higher at higher temperatures (doubled with temperature increase from 14º C to 30º C). Clogging by N_2 bubbles was not a problem as it has been in sand columns and formations (Volokita et al., 1996; Hiscock et al., 1991). Cotton was entirely consumed in the reaction thereby alleviating the need for post-treatment waste disposal.
- Ion exchange columns have been used to remediate NO_3^- contaminated waters (Lin & Wu, 1997; Fritsche, 1993). Problems associated with their use include; large volumes of waste brine production, and resin regeneration processes. In one experiment (Dowex-SAR resin), pH and temperature had little to no effect on the rate of denitrification (Lin & Wu, 1997). The effectiveness of the column appears to be solely dependent on initial NO_3^- concentration with higher concentrations tending to enhance the ion exchange process for both NO_3^- and NO_2^- removal. Slight degradation of the column efficiency was noted after column regeneration, likely due to small amounts of NO_3^- and NO_2^- remaining in the resin. In a separate instance (Fritsche, 1993), yellow bismuth hydroxide was 93% efficient at removing NO_3^- from amended (15 mg N l^{-1}) tap water by precipitation.
- Vegetable oil has been postulated as a unique source of organic C (Hunter et al., 1997). In theory, an emulsion of water and oil will produce small droplets that will become trapped in sediment pore spaces providing a bio-reactive zone rich in organic C. In static water trials, conducted in closed sand-filled serum bottles, both corn and

soybean oil were able to promote denitrification (C_o: 180 mg NO_3-N l^{-1}) within 24 to 48 h under anoxic conditions. The rate of denitrification was comparable to that obtained using glucose as the carbon source. Denitrification ceased when the C supply was exhausted. Denitrification rates were stable over the range of oil concentrations tested (0-120 g l^{-1}), but NO_3^- was the limiting reagent at higher concentrations. Flowing water experiments used aquifer materials for both the solid and liquid phases. As little as 9 mg of soybean oil was capable of initiating denitrification processes, although larger amounts were required to sustain the effect. Injected oil was largely confined to the first 5 cm of the column and no oil was ever detected in the effluent.

Field experiments have considered both above ground and in-situ techniques for NO_3^- and NO_2^- remediation (Hiscock et al., 1991; Schipper et al., 1998). Compared with ion exchange methods above-ground treatment does not generate large amounts of waste, but is more difficult to automate (Hiscock et al., 1991) and can be cost- and site-prohibitive. In-situ treatment enables both denitrification and secondary treatment to be conducted *in situ* in the aquifer. Clogging of aquifer pore spaces with gaseous products and dead biologic materials remains an issue. The results of these studies are summarized below.

- Three above-ground treatment methods were investigated: (1) packed column units with gravel as bacterial support medium; (2) suspended growth units containing a floc blanket of denitrifying bacteria; and (3) fluidized sand bed containing bacterial growths as thin films coating each sand grain (Hiscock et al., 1991). The latter produced the highest denitrification rates (1.57 kg N m^{-3} h^{-1}), and afforded the greatest ease in removing excess biomass. All above-ground treatment methods shared the following characteristics: raw water composition had little effect on the rate and extent of denitrification, no temperature problems were associated with the technology, and little waste is produced. Treated water contains low DO, increased suspended solids, requiring that the water be re-aerated and filtered.
- Two other methods of in-situ treatment have been suggested: injection well and pumping well systems (Hiscock et al., 1991), and a denitrification wall amended with sawdust (Schipper et al., 1998). The "Daisy" well configuration (see description in Hiscock et al., 1991) produced the highest denitrification rate (3.64 kg N h^{-1}) using the "Nitredox" method in a gravel aquifer. In general, in-situ treatment results in lower NO_3^- removal rates (< 0.3 g N h^{-1}) than above ground treatment (~ 1.54 kg N h^{-1}). The sawdust amended denitrification wall produced a maximum rate of removal of NO_3^- of 3.6 g N m^{-3} d^{-1} (Schipper et al., 1998). Although there was no significant decrease in total C, the availability of the remaining C declined over time.

We are not aware of any instance where artificial remediation efforts are being conducted on a field scale (in a non-research sense) to mitigate groundwater nitrate concentrations. We thus draw the conclusion that artificial remediation of groundwater nitrate is not an economically feasible alternative at the present time.

8. Study Plan

The development of a study plan should be based on what information we currently have, what knowledge and information gaps have been identified and on other initiatives are ongoing in related areas. This study plan is framed within the context of the need to maintain water quality and the anticipated changes that may occur in the prairie ecozone.

8.1 Proposed Groundwater Study Plan to assess the ADA's capacity for denitrification

This section assumes that field scale groundwater nitrate remediation is not a viable option, and has, as its goal, the prevention of extensive groundwater nitrate impact. Since the only natural remediation strategy available to mitigate widespread groundwater nitrate is denitrification, our recommendation is to assess the potential for aquifer denitrification.

The following groundwater study plan is a staged study that begins by conducting a preliminary assessment. At any stage, if the outlook for significant denitrification is not positive, the study can be disbanded. The final stage is a retrospective study on groundwater under a long-term manured field to assess the extent of denitrification, the nature and long-term supply of electron donors, and their associated impacts. Because of the typical time period required for changes in agricultural management to be reflected in groundwater quality (even in shallow sand aquifers like the ADA, this can be 3 to 5 years), a retrospective study (i.e. a study of the impacts of past agricultural practices) is recommended.

Stage One: A *preliminary assessment* of the ADA's capacity for denitrification by a geochemical survey of existing groundwater observation wells.

Evidence for both a low redox aquifer zone at depth and associated denitrification have been collected by Bob Betcher (Manitoba Conservation) at one site on the ADA. A preliminary assessment could be easily conducted on a more regional basis by field and laboratory measurement of redox-sensitive parameters. This preliminary assessment would provide at least circumstantial evidence of the aquifer's potential for denitrification. This survey should include all available groundwater monitoring wells and the following parameters:

1. Field measurement (either downhole, or in a flow through cell which minimizes atmospheric contact and temperature change of sampled groundwater) of dissolved oxygen and redox potential (Eh). If values are not sufficiently low (i.e. < 2 mg/L dissolved oxygen, and Eh < 0.28 V), it can be concluded that the aquifer has a very low capacity for denitrification.
2. Samples should be taken for laboratory measurement of major ions. The ions should be assessed as indicators of redox conditions (e.g. presence of Fe, NH_4^+ and/or organic N, and absence of SO_4^{2-} and NO_3^-would indicate of reducing conditions). Although a relatively small number of ions are redox sensitive, all major ions should

be analysed in order to conduct an ion balance. These data should be inspected in particular to look for changes with depth that might indicate increasingly reduced conditions with depth.

Costing: Estimate 40 (?) wells available for sampling. Time commitment = 2 weeks for field hydrogeologist. Major ions on forty samples.

Stage Two: A retrospective study of denitrification under areas of past and ongoing agricultural production to see if denitrification is apparent.

If the preliminary assessment indicates reduced groundwater is present at depth in the ADA (i.e. that denitrification could proceed if nitrate were to reach these depths), a retrospective study should be conducted at at least two sites. In this stage, direct and more convincing evidence (as opposed to circumstantial) can be collected. This investigation should logically link with ongoing work being conducted at one site by Bob Betcher of Manitoba Conservation.

The objectives of this stage are to characterize one or two sites physically and geochemically to see if denitrification is occurring based on geochemical changes along a flowpath (e.g. decrease in nitrate concurrent with the oxidized couple of an electron donor like sulfate or bicarbonate). Stable isotopes are used to aid in identification of the denitrification process and the electron donor which is facilitating the denitrification.

Site selection for the retrospective study should include:

1. Consideration of existing and past agricultural activity. Ideally the site should have been under long-term use of manure as fertilizer with irrigation.
2. Hydrogeologically representative of ADA in terms of depth to groundwater, hydraulic properties of aquifer, etc.
3. Co-operation of producer/farmer to have groundwater piezometers installed in fields, provision of historic and ongoing fertilizer records, crop yields etc.
4. The final stage of the site selection process requires the installation of at least three groundwater monitoring wells on the property in order to assess the hydraulic conductivity, and groundwater velocity and flow direction prior to its selection as a study site.

Groundwater instrumentation at the site. The goal of the groundwater instrumentation will be to provide an opportunity to assess denitrification with flowpath distance as a surrogate for time (i.e. sampling increasingly older groundwater to observe geochemical changes with time). Given the horizontal nature of groundwater flow in environments like the ADA, the instrumentation will be ideally located along a flow path. Given the low cohesion associated with high hydraulic conductivity sediments in the ADA, multi-level samplers (where sampling tubes of varying depths are clustered around a single centre-stalk) could be used, providing a cost effective means of looking at changes in nitrate concentrations with depth. The centre stalk is used to monitor water levels. Thus, geochemical changes will be observed in relation to distance along a flow path and depth (and in particular depth in the context of the redoxcline).

Multi-level samplers (MLSs) will be installed by drilling at six locations arranged in a transect parallel to groundwater flow. Each of the six locations will consist of a multi-level sampler, with screened sampling ports located at 25-100 cm depth intervals below the water table depending on the saturated thickness of the sediments. Geology of the site(s) and in particular, the redoxcline (as evidence by colour change) should be described in detail during drilling. Water-table wells will be installed at a minimum of the six MLS locations and the additional three groundwater wells installed in the early part of the site selection. Hydraulic conductivity (K), which is a measure of the permeability of sediments, will be measured by conducting slug tests on all water-table wells. Hydraulic gradient (*i*), which is a measure of the change in water level with distance, will be determined by surveying the elevation of each water table well and associated water level. These field measurements will permit a further estimation of groundwater flow direction and velocity.

Physical hydrogeology of the site In addition to the subsurface characterization of the site described above, levels in the water-table wells should be monitored on an ongoing basis. In addition, tipping rain gauges should be installed to monitor precipitation and irrigation amounts. A water balance for the site(s) will be determined using the following equation: Q_{wb} = SO - SI - P + E, where each parameter is defined and measured as follows.

- Q_{wb} = groundwater discharge according to the water balance equation.
- SI and SO are surface inflow and surface outflow, respectively. They will be measured by monthly stream gauging immediately up stream and down stream of the site, respectively. If the incremental difference between SO and SI across the site is too small to measure accurately, stream-gauging stations will located further apart up- and down-stream of the site, and it will be assumed that groundwater discharge between the two points is uniformly distributed between fields. Where no adjacent surface water body is available, surface inflow and outflow will constitute overland runoff, measured by installation of a collection trench.
- A tipping-bucket rain gauge with an automated recorder will be installed on the site to determine total daily precipitation and irrigation (P).
- Evaporation (ET) will be estimated from literature values for the ADA and/or similar regions.

Groundwater flow modeling will be conducted for the selected site(s) using a flow simulation program such as MODFLOW. The drilling information and field measurements will be used to discretize a two-dimensional groundwater flow model (MODFLOW) along the instrumented flowpath. Sensitivity analyses will be conducted for hydraulic conductivity and recharge estimates. Groundwater age dates (see below) will be measured to validate model parameters.

Groundwater Geochemistry will be evaluated by analysis for the following suite of chemicals:

Nutrients: nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), dissolved organic carbon (DOC), orthophosphate (PO_4^{3-}), dissolved phosphorus (DP), and total phosphorus (TP)
Anions: sulfate (SO_4^{2-}), chloride (Cl^-), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-),
Major cations: (Ca, Mg, Fe, and Na).

Groundwater age dating Groundwater age dating by means of sampling for chloroflourocarbons (CFCs) should be conducted in the centrestalks of the six water-table wells. CFC analysis provides a fairly well constrained age date (± 2 or 3 years). This will provide some constraint on the expectation of whether or not nitrate is 'expected' to occur in the groundwater based on its age (i.e. did the groundwater recharge during a time period when significant rates of fertilizer were being used?). The age dating will also provide a means by which the goodness of the mathematical model can be assessed.

Stable isotope analysis
^{15}N and ^{18}O in nitrate (for the assessment of denitrification);
^{34}S and ^{18}O in sulfate (to assess whether sulfide oxidation is occurring); and
^{13}C in dissolved inorganic carbon (DIC) (to assess whether organic carbon oxidation is occurring concurrently with denitrification).

Dissolved gas analysis would be additionally useful to determine if the groundwater contains "excess air" due to the production of N_2, NO_2, and N_2O gases during denitrification.

Costs: Estimates should include: 1) instrumentation supplies (PVC pipe and screens, copper pipe for CFC center stalks, spaghetti tubing and nytex screen for sampling points); 2) drill rig, mobilization costs, and drilling crew for two days; 3) field technician for sampling event(s) and drill supervision; 4) geochemical analysis for suite of chemicals, isotopes, CFCs, and gases; 5) transportation costs for field technician monitoring and drilling; 6) lease on land; 7) sampling bottles. Professional time for data collation, mathematical modeling and geochemical/isotopic interpretation.

Stage Three: Assessment of the long term denitrification capacity of the aquifer and associated redox donors. If the potential for aquifer denitrification is confirmed, the aquifer's total reducing capacity should be assessed. This should include an assessment of the mass and geochemical availability of electron donors including sulfide, organic carbon, and iron. The aquifer should be carefully cored above and below the redoxcline, and sub-samples of increasing depth taken from the cores with minimal exposure to atmospheric oxygen. At a minimum, reduced carbon, sulfide and iron should be measured on the sub-samples (e.g. Postma et al, 1991). A method for estimation of the 'total reducing capacity' of sediment (hot digestion in potassium dichromate) has been published (Pedersen et al., 1991), but not extensively used. Kölle et al (1985) assessed the geochemical availability of sulfide for oxidation by assessing sediment's 'sulfate formation capacity'. They simply exposed aquifer sediment to a nitrate solution, and measured geochemical parameters to see if denitrification proceeded.

Once the reducing capacity of aquifer sediments has been established, it should be compared with the mass flux of nitrate through the hydrogeologic system to evaluate i) the potential for long term facilitation of denitrification, and ii) the possibility of water quality impact by increased sulfate concentrations.

Costs: 1) drill rig, mobilization costs, and drilling crew for two days; 2) field technician for drill supervision and sampling; 3) geochemical analysis for sulfide, iron, and carbon. Professional time for data collation and interpretation.

8.2 Improved watershed loading estimates: Land use inventory and NMP

One of the short comings of relying solely on monitoring-based approaches is that they detect problems after they have occurred. Regional scale nutrient management planning provides the opportunity to assess potential impacts prior to their occurrence and provides valuable input into region land use decisions.

One of the concerns we encountered was the reliability of current land use information compiled by Statistics Canada. Statistics Canada is tasked with compiling a national census of land use. The constraints placed on this exercise as a result of its national scope can, in some cases, limit the validity of this information on a regional or local scale. For example it seems unlikely that 13,272 ha of land in the Assiniboine Delta region are actually in summerfallow. It is more likely that the term summerfallow has been applied to other land uses. A more regionally accurate land use data set is required to provide accurate estimates of nutrient loading to the aquifer.

The use of nutrient budget information taken from other ecological regions can be questioned. Assessment of rates of nitrogen loss from the major land use classes and land uses which have been deemed to have the potential of high impact should be conducted within the Assiniboine Delta region to ensure local resource, climate and land use practices are accurately reflected in these estimates.

8.3 Alternate manure management – composting, export

Based 1996 census data, animal manures were estimated to account for 34% of the nitrogen loading to the aquifer. The potential for significant growth in the hog industry in Manitoba has been highlighted in recent years. The suitability of land in the Assiniboine Delta region for extensive hog operations needs to be assessed in light of the potential nitrogen loading to groundwater. In this report we have used a relatively conservative estimate of nitrate leaching for these systems (10% of manure N applied). Improved estimates of nitrate leaching from manure amended soils in this region and the assessment of alternatives to land application (composting, export) is recommended.

9. References

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