A STUDY OF THE NITROGEN CYCLE IN THE WILMOT RIVER WATERSHED, PRINCE EDWARD ISLAND: INITIAL RESULTS

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ABSTRACT
Aquifers constitute the only source of freshwater on PEI. In many areas, nitrate concentrations in groundwater (GW) exceed natural levels. It is assumed that mineral fertilization for potato cropping constitutes a major source of these nitrates. However, a better understanding of the transfer dynamics of nitrates from soils to GW is required to reduce their detrimental effects. Our initial results in the Wilmot watershed indicate that 23% of the samples have $N\text{-}NO_3$ concentrations above the threshold established for human health (10 mg/L), whereas 10% have concentrations within natural ranges (<1 mg/L). Combined nitrate and water isotope results suggest that during summer and fall most nitrates in the Wilmot River are derived from GW, and that ~75% of the samples contain nitrates deriving from chemical fertilizers while the remaining ~25% contain nitrates from natural soils, manures or septic wastes.

RÉSUMÉ
Les aquifères constituent la seule source d'eau douce sur l'IPE. Dans plusieurs secteurs, les concentrations en nitrates des eaux souterraines (ES) excèdent le niveau naturel. On présume que la fertilisation minérale pour la culture de la pomme de terre constitue une source importante de ces nitrates. Toutefois, une meilleure compréhension de la dynamique de transfert des nitrates des sols aux ES est requise afin de réduire les risques reliés à la présence des nitrates. Nos résultats initiaux dans le bassin de la rivière Wilmot indiquent que 23% des échantillons ont des concentrations $N\text{-}NO_3$ au-dessus du seuil établi pour la santé humaine (10 mg/L), tandis que 10% montrent des concentrations de registres naturels (< 1 mg/L). Les isotopes des nitrates et de l'eau suggèrent que l'été et l'automne la plupart des nitrates présents dans les eaux de la rivière Wilmot proviennent des ES, et que ~75% des échantillons contiennent des nitrates dérivant d'engrais chimiques, les ~25% restant contiennent des nitrates dérivés de sols normaux ou d'excréments.

1. INTRODUCTION

1.1 Rationale

The aquifers of Prince Edward Island (PEI) constitute the only source of freshwater for its population, and supply the majority of water for industrial and agricultural uses. In many areas, nitrates concentrations in groundwater (GW) are significantly above expected background levels (Somers et al., 1998). It is assumed that mineral fertilization for potato cropping constitutes a major source of these nitrates, and that soil nitrates in excess of crop requirements leach to the water table and move with GW to the private wells and main rivers. Although this model largely attributes GW contamination to agricultural sources, the transfer dynamics of nitrates from soils to GW are not well known. A better understanding of these dynamics is required to reduce detrimental effects of nitrates on PEI (Fig. 1).

1.2 Previous Studies of the Nitrate Problem

Over the past decade, a considerable body of information on nitrate in PEI groundwater has been collected (Somers, 1992, 1998, Swain, 1995, Somers et al. 2002, Bukowski et al., 2001, Young et al., 2003).

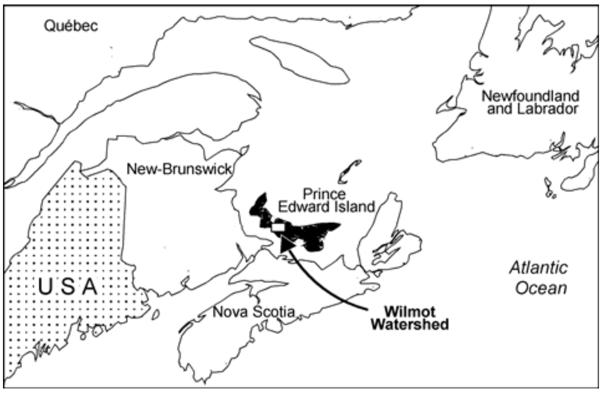


Figure 1. Location of Prince Edward Island and of the Wilmot watershed.

This work has provided a reasonable appreciation of the overall distribution of nitrate in the Province, and shed light on potential links to land use patterns and on temporal trends in observed nitrate concentrations. Elevated nitrate levels are often associated with agricultural activities and appear to be most clearly associated with extensive use of fertilizers for row crop production, rather than with livestock production (Young et al., 2003). Some of these studies also suggest that groundwater nitrate levels in many areas of the Province are increasing over time, a trend which is also seen in surface water (Somers et al., 2002, Young et al., 2003).

1.3 Objectives

The «PEI N-cycle» activity (2003-2006) is a pilot investigation aimed at quantifying the annual nitrogen budget of the Wilmot river watershed where intensive potato cropping is taking place. Its long term objectives are to: (1) study the water dynamics between precipitation, GW and surface water and quantify the GW and surface water exchanges; (2) assess the source of nitrates at the watershed scale; (3) quantify the N-species contents in the N reservoirs through the annual N-cycle; and (4) assess the agricultural impacts on availability of potable GW. Our approach is to follow up the N-bearing species using their concentrations and Nitrogen and Oxygen isotopes, from soils, through the aquifer, to the discharge point at the river, and to integrate the hydrogeochemical data set with the known hydrogeological characteristics of the Wilmot watershed. In order to have a better understanding of nitrate transport, we will use Hydrogen and Oxygen isotopes.

In this paper, we report on N species concentrations ([N-NO_3^-]), nitrate N and O isotope analyses ($\delta^{15}N$, $\delta^{18}O$), and H and O isotope ratios in waters ($\delta^{2}H$, $\delta^{18}O$) obtained for summer and autumn 2003.

2. REGIONAL SETTING

2.1 Location, Topography and Land Use

The Wilmot River basin is located in west central Prince Edward Island (Fig. 1), southeast of Summerside. The watershed includes portions of the communities of New Annan, North Bedeque, Kensington and Springfield. From headwater tributaries in the Springfield region, the river drains an area of about 87 km^2 of Prince County and flows south-west to the Northumberland Strait through its estuary in the Bedeque Bay.

The topographic relief of the basin consists of gently rolling hills with slopes up to 10%. Average slopes are about 2% except near the river where they are steeper due to erosion. Elevations range from sea level, in the tidal portion of the river, to 90 m.a.s.l. in the Springfield area. The basin is approximately 17 km long and 5 km wide. The main stem of the Wilmot River is about 16 km long with two thirds of this being tidally influenced.

The Wilmot River watershed is predominantly a rural area consisting of 65% agricultural lands, 21% forests and less than 10% residential use. The largest urban centre within the watershed is the eastern part of Summerside located in the western portion of the watershed. Agricultural lands are largely used for potato cultivation, whereas the forested areas form small patches uniformly distributed on the basin surface. Theses patches generally belong to zones that are not favourable for agriculture such as swamps and steep inclines.

The Wilmot river watershed is characterized by intensive row-crop potato cultivation on a fine sandy loam soil. Potato crop occupies more than 25% of the area under cultivation. Potatoes are part of a rotational system with grains and forage crops for hay in either two- or three-year sequences. PEI soils under potato cultivation are subject to severe soil erosion during snowmelt and freeze-thaw periods which lead to sediment transport from agricultural fields to surface water.

2.2 Climate and Stream Flow

The climate of Prince Edward Island is humid-continental, with long, fairly cold winters and warm summers. Mean annual precipitation recorded at the Summerside meteorological station for the period of 1961 to 2000 was 1398 mm. Most of the precipitation falls as rain (80% or 1118 mm) and the remainder falls as snow (20% or 282 mm). The mean annual temperature is about 5.1°C and mean monthly temperatures range from –8.6°C in January to 18.4°C in July.

Streamflow data for the Wilmot River have been collected at the gauging station located above the tidally influenced portion of the river. The drainage area for this gauging station is 45.4 km^2. The mean annual discharge of the river for the period of 1972 to 1999 is 0.92 m^3/s and the mean monthly discharge ranges from 0.45 m^3/s in September to 1.88 m^3/s in April during the spring freshet.

2.3 Geological Context

Prince Edward Island is a crescent-shaped cuesta of continental red beds, Upper Pennsylvanian to Middle Permian in age, dipping to the northeast at about one to three degrees (van de Poll, 1983). The constituent mineral grains of these sedimentary rocks were carried by streams and rivers from highlands in present day New-Brunswick and Nova Scotia and deposited under oxidizing conditions in the low-lying area which is now Prince Edward Island (Prest, 1973).

The most recent and complete review of the bedrock geology of Prince Edward Island has been conducted by van de Poll (1983). The red bed units form an upward-fining series of cyclic deposits containing four «megacycles». The Wilmot basin is underlain by portions of Megacyclic Sequences III (Kildares Capes Formation) and IVa (Hillsborough River Formation-Malpeque Member) of the Lower Permian Pictou Group (Fig. 2). These sequences consist of conglomerate, sandstone and siltstone red beds. These units exhibit rapid lateral and vertical facies changes and strong cross-bedding features. The continuity of lithological units is always difficult to establish, even over short distances.

Projects conducted outside the Wilmot basin but in the same constituting formations have indicated that the rock sequence is primarily composed of fine to medium-grained sandstone (80-85%) and mudstone (siltstone and claystone). The sandstone is highly fractured in the surface exposure with bed thickness of a few centimetres to a few meters. Vertical to sub-vertical fractures occur in addition to fractures parallel to bedding planes (Francis, 1989). More than 74% of the fractures are found in the uppermost 20 m of the sedimentary rocks.

The Permo-Pennsylvanian sequence of Prince Edward Island is almost entirely covered by a layer of unconsolidated glacial material from a few centimetres to several meters in thickness (Prest, 1973). These deposits are generally derived directly or indirectly from local rock sources and include both unsorted, ground-up rock pieces usually referred to as till, and water-worked glacio-fluvial and glacio-marine deposits. Surficial geology corresponds to ground moraine with a sand phase till for most of the Wilmot basin, and a clay-sand phase till, in some small area. The thickness of the overburden (depth to bedrock below ground surface) ranges from a few decimetres to more than 15 m, averaging about 3.6 m. Thicker overburden deposits might be expected to be found at lower elevations near the river.

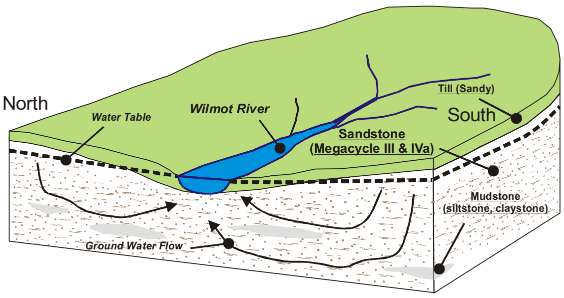


Figure 2 – Hydrostratigraphy and conceptual model of GW flow in the Wilmot watershed.

2.4 Regional Hydrogeology

2.4.1 Hydraulic Conductivity

Although field-derived hydraulic conductivities are not available for the Wilmot Valley, hydraulic conductivity estimates based on grain-size analyses and slug tests are available for the Winter River basin, located north of Charlottetown, not far from the Wilmot study area. Hydraulic conductivity estimates for tills in the Winter River basin range from 6.7×10^{-8} to 1.3×10^{-5} m/s as based on grain size, and from 10^{-7} to 10^{-5} m/s based on slug tests. Given the high degree of geological similarity throughout the island, it can be assumed that hydraulic conductivities in the Wilmot basin are of the same magnitude as those determined for the Winter River basin.

Separation of the relative contribution to hydraulic conductivity of fractures and matrix pores was also conducted by Francis (1989) through field measurements of *in situ* hydraulic conductivity and laboratory measurements of inter-granular permeability. The field profiles of hydraulic conductivity obtained using constant head injection tests isolated by pneumatic packer assembly shows a range from 10^{-7} to 10^{-3} m/s. An overall trend of decreasing hydraulic conductivity with depth is generally observed. Results of the laboratory measurements of inter-granular conductivity indicate that each rock type exhibits a narrow range of hydraulic conductivities both perpendicular and parallel to the core axis. Sandstone values ranged from 10^{-8} to 5×10^{-7} m/s, whereas siltstone and shale permeability was less than 5×10^{-10} m/s (Francis, 1989). The ratio of horizontal to vertical permeability in sandstone samples ranged from 1.5 to 18.5. It has been concluded that the decrease in hydraulic conductivity with depth is the result of decreases in fracture frequency and fracture aperture with depth. Results of laboratory measurements of porosity on fine-grained sandstone cores indicate an average of 16% (n=9). These observations can be extrapolated to the Wilmot basin given the presence of the same lithological units in both basins.

The principal aquifer in the Wilmot watershed is located in the porous and fractured rock formations of the Permian sequence (Fig. 2). Fractures represent the main groundwater flow path, and matrix pores act as reservoirs. Based on work in the Winter river basin by Francis (1989), horizontal bedding-plane fractures in the same lithological units as those found in the Wilmot basin form 82% of all fractures, and sub-vertical fractures were infrequent below 35 m. The average spacing of the horizontal bedding-plane fractures decreases from 0.1 m in the upper 35 m, to 0.5 m below. The vertical set has an average spacing of 0.6 m in the upper 35 m, and 4.9 m below. The mean fracture aperture in the upper aquifer zone above 35 m is about 0.19 mm and about 0.11 mm below this zone. This is a very important reduction considering that the GW flow through a fracture is proportional to the cube of the aperture (Snow, 1969).

2.4.2 Water Table Position

The Wilmot aquifer is unconfined and a map of its phreatic surface is drawn from water level measurements in domestic private wells (Fig. 3). This map provides a general picture of groundwater flow in the horizontal plane. Topography is the major factor determining hydraulic head distribution as shown by the strong correspondence between surface water and groundwater divides. The general pattern of groundwater flow is from the highest elevations to the lowest elevations at the river and estuary zone. The river functions as a GW discharge zone except during high tide periods, when the groundwater flow direction may be reversed from the estuary to the aquifer.

At higher elevations the water table is well below the overburden-rock contact. Moving down-gradient toward the river, the overburden is somewhat thicker, and the water table approaches the overburden-rock contact, until it meets ground surface at the river. The aquifer is a water table aquifer except in small zones where less permeable mudstone beds alternate with sandstone to form semi confined aquifers. At the regional scale, the conceptual model of the aquifer can be represented by a permeable unit of sedimentary rocks with mixed porosity (fractures and matrix pores), covered by permeable till of variable thickness (Fig. 2).

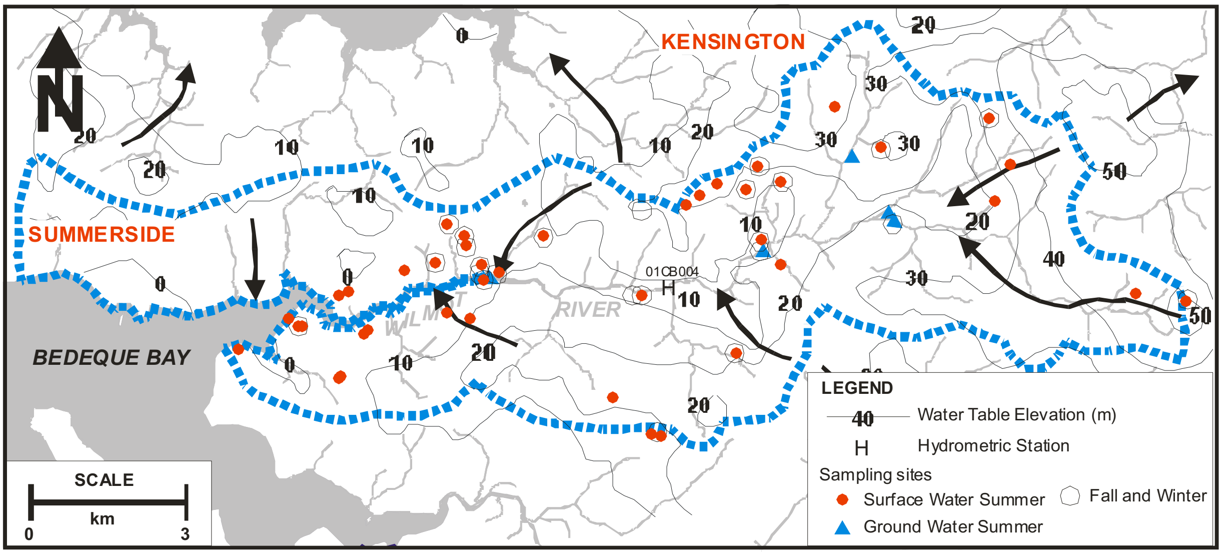


Figure 3. Map of the water table levels also showing the delineation of the Wilmot watershed (and aquifer) and the location of the sampling sites. The contour intervals for the water table levels are of 10 m.

2.4.3 Ground Water Level Fluctuations

The fluctuations of the water level in a monitoring well in Kensington demonstrate the seasonal response to climate typical for the region. The response includes a major spring recharge event followed by a summer decline of the water table, a moderate autumn recharge event and finally, a decline in the water table through the winter punctuated by moderate recharge events, prior to the next spring recharge event (Fig. 4). Recharge events during the December-March period are common, a result of winter thaws, rain and snowmelt. Depending on the frost conditions in the soil, these recharge events can be very significant. For example, the well-hydrograph separation for 1972 analysed as in Meinzer (1923) shows that about 40% of the recharge has occurred during winter, another 40% during spring melt, and 20% during fall (Fig. 4). Total recharge based on this technique with 8% effective rock porosity (half the total porosity) was estimated for 1972 at 335 mm.

2.4.4 Hydrologic budget

The relatively high hydraulic conductivity of the overburden and the rock formations in the Wilmot basin results in a very direct relationship between the water table position, amount of precipitations and stream discharge (Fig. 4). The short time lag (~ 5 days) between precipitation events and the water table response (see winter events on Fig. 4) is an indication of the high hydraulic conductivity of the overburden and rock formations. Moreover, the presence of small seeps along the river and significant flow in the river and its tributaries even several weeks after precipitation events or snowmelt, are an indication of the importance of groundwater discharge to the Wilmot streamflow Fig. 4).

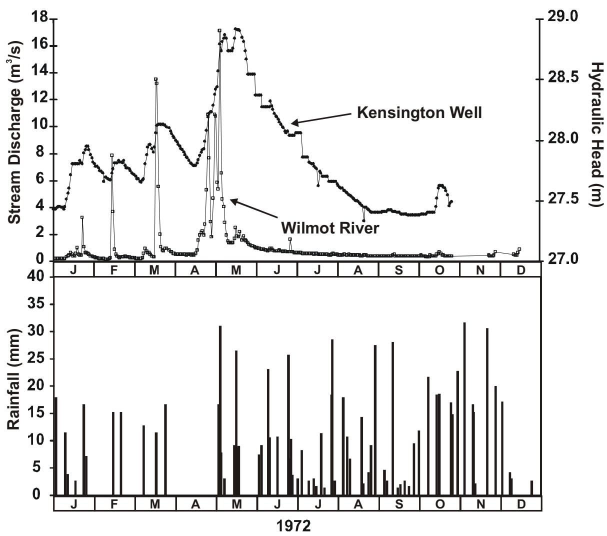


Figure 4 – Hydrograhs of the Kensington well and Wilmot River for 1972 which are representative for the Wilmot watershed flow system (top graphs). The hydrographs are compared to the precipitation amounts for 1972.

The presence of small seeps along the river and significant flow in the river and its tributaries even several weeks after precipitation events or snowmelt, are an indication of the importance of groundwater discharge to the Wilmot streamflow.

A quantitative evaluation by Francis (1989) of the annual hydrologic budget for the Wilmot basin indicates that 39% of the annual precipitation is lost by evapotranspiration. Whereas runoff and baseflow account for 21% and 40% of precipitation, respectively. However, baseflow may be the only source of water to the river during summer period when the precipitation is all intercepted by vegetation and subject to evapotranspiration. The annual recharge rate for the Wilmot aquifer based on the water budget technique (Freeze and Cherry, 1979) is 446 mm for the 1972-1988 period.

3. SAMPLING AND ANALYTHICAL METHODS

3.1 Water Sampling

At this stage we have analysed 61 GW samples (41 summer, 20 autumn) from private wells, 10 samples from the Wilmot River (6 summer, 4 autumn) and 6 rain samples (3 summer and 3 autumn) at various locations in the watershed (Fig. 3). Water level measurements were obtained at 10 sites in summer, 6 sites in autumn. In most cases, untreated groundwater samples were obtained from outdoor taps. Prior to sampling, the wells were purged of 2-3 well volumes until stabilization of temperature, pH, and conductivity values were observed. Dissolved oxygen levels were also measured *in situ*. Unfiltered samples were obtained for water isotopes (δ^2H and δ^{18}O in H_2O), N and P ions, and dissolved N_2O. Samples obtained for major ion and isotope analyses (δ^{15}N and δ^{18}O in nitrate) were filtered using a 0.45 micron filter to remove particulate matter. Major ion sample bottles, 1 mL of $HN0_3$ 0.2 % was added to each 125 mL bottle to inhibit bacterial growth. All samples were refrigerated during transport and storage. Water samples for N isotope analyses that could be processed in the field within 24 hours of collection were filtered through cation resins to isolate nitrate for isotopic analysis (ion exchange resin method modified from Chang et al., 1999, and Silva et al., 2000). Samples that could not be processed within 24 hours were frozen and shipped to the lab for processing.

Stream samples were obtained from the edge of the stream at least 10 cm below the water surface, at portions of the stream where water flow was swift. Stagnant areas were avoided. The initial stream sampling was completed during a dry period of minimal rain, during which time the majority of water in the Wilmot River was supplied by stream baseflow.

Precipitation samples for δ^{18}O and δ^2H analyses were obtained from 30.5 cm diameter collectors. Two collectors were located in open crop areas, whereas a third was located in a forested woodlot. To reduce the possibility of evaporation, a minimum 2.5 cm layer of oil was added to the bottom of the collector and the collectors were fitted with funnels that matched the diameter of the collector at the top and narrowed to a couple of centimetres at the bottom.

3.2 Analyses of Nitrate Concentrations and Isotopes

All water analyses of N species concentrations were performed at the AAFC water quality laboratory (Ste-Foy). Nitrate concentrations were determined by Flow Injection Analysis (FIA) colorimetric method (LACHAT) for which the detection limit was 1.53 mg/L NO_3^- (0.04 N-NO_3^-) and the precision was 0.4 mg/L NO_3^- (0.09 N-NO_3^-).

An important aspect of the first year of the PEI N-cycle activity was to provide protocols for sampling and analyses of stable isotopes of nitrates dissolved in GW. We therefore developed guidelines for sample treatment including a protocol for NO_3^- purification, concentration on ion exchange resin, and a subsequent nitrate extraction using the procedure previously used by USGS (Chang et al., 1999, Silva et al., 2000). We have also developed the analytical routines for δ^{15}N and δ^{18}O analyses of nitrates with an online combustion system (EA-CF-IRMS), and online pyrolysis system (TC/EA-IRMS), for N and O isotopes respectively.

After field filtering, a spectrophotometer was used to estimate the concentrations of SO_4^{2-}, and NO_3^- in order to determine how many resin cups would be needed for the ion resin exchange protocol. The anion resin cups were were subjected to Silver nitrate precipitation and N and O isotope analyses at the GSC Delta-Lab.

3.3 Analysis of Water Isotopes

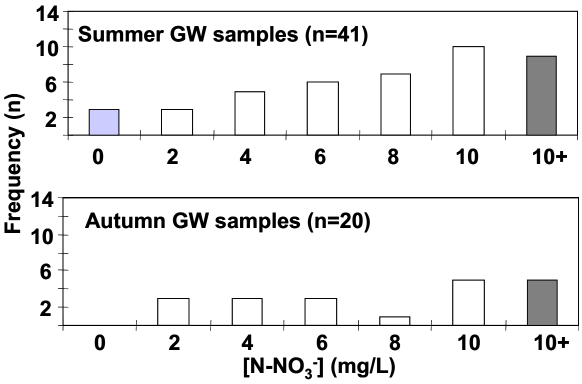
Two water aliquots around 0.5 ml were analysed respectively for their δ^2H and δ^{18}O ratios using an on-line IRMS water equilibration system (Gas Bench-Delta Plus^{XL}) at the Delta-Lab of the GSC. Precisions on the δ^2H and δ^{18}O ratios were 0.8 and 0.07‰, respectively.

4. RESULTS AND INTERPRETATIONS

4.1 Concentrations of Nitrates in Waters

As expected, groundwater sampled during summer and autumn shows a broad range of nitrate concentrations (<1 to 14.6 mg/L). Overall, 23% of the summer and autumn GW samples have N-NO_3 concentrations above the threshold of 10 mg/L established for human health (Health Canada, 2003), whereas 10% have concentrations within the natural range (<1 mg/L). The majority of the samples, i.e. 72%, are likely influenced by anthropogenic activities producing nitrates (Fig. 5).

Moreover, the 10 river samples have concentrations ranging between 5.22 and 7.67 mg/L. Therefore all river samples have concentrations above the natural range.



[Figure 5](#). Histogram of the concentration of N-NO_3^- for summer and autumn groundwater samples.

4.2 Nitrogen Isotope Ratios and Nitrate Concentration

The combination of δ^{15}N values and NO_3^- concentrations is commonly used to help understand which processes produced existing levels of nitrates in GW (Kendall and Aravena, 2000). In this type of graph, the Wilmot results for GW and river samples show a flat trend in which the nitrate concentration varies widely whereas the δ^{15}N values cluster around 3.0 ‰ (Fig. 6).

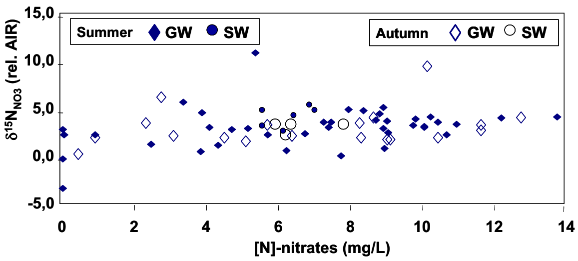


Figure 6. δ^{15}N values relative to concentrations of N- NO_3^- in GW and surface water (SW) samples.

Only two samples do not follow the flat trend. This trend departs significantly from the curve expected to result from microbial denitrification and corresponds better to natural attenuation due to dilution of nitrate-rich waters with water devoid of nitrates (Kendall and Aravena, 2000).

Note that the river water samples which are not shown on Figure 6 fall right in the middle of the δ^{15}N-[NO_3^-] ranges, suggesting that the river water nitrate load represents a mixture of what is transported in GW.

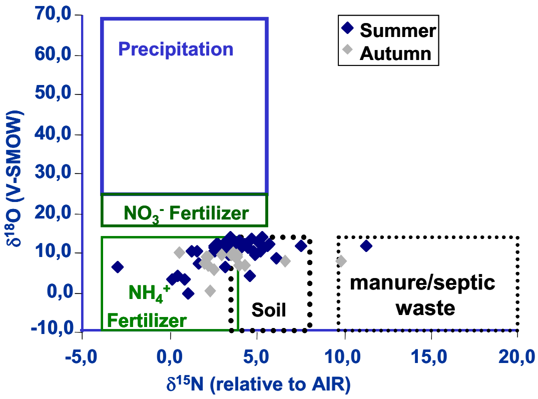
4.3 Nitrate Isotopes - δ^{18}O and δ^{15}N values

The δ^{18}O ratios of the nitrates in the Wilmot aquifer vary between -0.1 and +13.9‰, and the δ^{15}N ratios vary between –3.0 and +11.3‰. The analysis of the co-variation of these isotopic tracers can be used when trying to understand the processes involved during transport of nitrates and to fingerprint their sources.

The Wilmot GW sampled during summer and autumn yielded results clustering broadly within the same range. For sampling sites where analyses were performed for both seasons, autumn results are only slightly lower than the summer ones. These observations suggest that the same sources were generating nitrates during both seasons and that the same processes were uniformly effective.

We have not yet determined the isotopic characteristics of the potential regional sources of nitrates. So here the δ^{15}N and δ^{18}O ratios are compared with the isotopic domains generally obtained for various nitrate sources and compiled from the literature (Fig. 7).

This type of comparison should be made with caution because important variations of isotopic ratios that do not reflect local conditions can be incorporated when outlining theoretical domains. Here the comparison of the Wilmot results with the theoretical domains is informative as apparently transformations taking place in soils (and reducing environment) did not significantly alter the isotopic ratios, which would have obscured the source signatures. The combination of the two tracers suggests that approximately 75% of the samples share characteristics with nitrates known to be derived from chemical fertilizers, the remaining ~25% would be derived from natural soils and organic residues. Note that the group of GW samples that have isotopic values of natural soil affinities could also be produced by mixing nitrates derived from manures and ammonium-fertilizers These results highlight the need to characterize the sources themselves (manures, mineral fertilizers and soil leachates).



[Figure 7](#). δ^{18}O values of nitrate dissolved in GW relative to their δ^{15}N values. Theoretical fields are modified from Kendall and Aravena (2000).

The results can be interpreted as isotope mixing curves of nitrates derived from 3 end-members: ammonium and ammonium-nitrate fertilizers and manures, with a contribution that could originate from natural soil and perhaps mix with the other sources (Fig. 7). The results within the δ^{15}N-δ^{18}O space supports the interpretation advocated in the former section that microbial denitrifiers do not affect these nitrates. Indeed, the general trend observed here does not satisfy the bacterial denitrification curve for which the magnitude of $^{18}O/^{16}O$ fractionation is half of that of $^{15}N/^{14}N$ due to inherent properties of each isotopic system (slope of 1:2).

The GW nitrates with $\delta^{15}N$ values roughly between +4.0 and +8.0‰ share characteristics with nitrates known to derive from natural soils. During nitrification in soils, if soil water has the same $\delta^{18}O$ value as GW (average -11.0‰), the nitrate product is expected to have a $\delta^{18}O$ value of 0.0 to 1.0‰ = [(2/3 x –11.0‰ soil water) + (1/3 x +23.0‰ in air)]. Here we find $\delta^{18}O$ values between +2.0 and +14.0‰ in the N-soil domain, and of 0.0 and +14.0‰ in the fertilizer domain. If soil water was coming from summer rain (-6.0‰), the nitrate product would have $\delta^{18}O$ of +3.0‰. Evaporation of waters in discrete portions in the vadose zone could have produced a high $\delta^{18}O$ value later incorporated in nitrate during plant organic matter mineralization. Briefly, summer rain and evaporated vadose water likely represent the sources of oxygen involved in soil nitrification.

4.4 Water Isotopes - δ^2H and $\delta^{18}O$ values

Hydrogen and Oxygen isotope values for the entire sample set (precipitation, surface water and GW) all fall on or near the meteoric water line of Charlottetown (MWLC; Fritz et al., 1987). Interestingly, the position of the rain values for the Wilmot basin on the MWLC indicates that the MWLC effectively represent the water isotope results of the Wilmot region (Fig. 8). Note that the GW and river water isotope values do not present excursions from the MWLC. Particularly, the apparent absence of surface (river) water excursions from the MWLC indicates that the river is not undergoing significant evaporation during the time of year when evaporation is expected to be highest. This is likely the result of continual recharge from groundwater, and a short residence time of water in the river channel (Fig. 8).

There is a certain spread in GW isotope results which could be partly a function of the variation in well depths sampled. Moreover, the position of the water data in the δ^2H-$\delta^{18}O$ space relative to the position of rain ratios indicates that the isotopic ratios of GW and surface water are weighted towards the depleted winter values (snowmelt). It will be necessary to see a complete yearly cycle of GW, surface water and precipitation in order to confirm this. Finally, results obtained for river water appear within the GW cluster, indicating that the surface waters, and incidentally their nitrates, were mostly derived from local GW during the sampling period of summer and autumn 2003. The $\delta^{15}N$-[N-NO_3^-] of river water relative to GW data (Fig. 6), and the overlap of the GW and surface water clusters in the δ^2H-$\delta^{18}O$ space (Fig. 8), both suggest that most nitrates present in the Wilmot river are derived from water transiting in the rock aquifer.

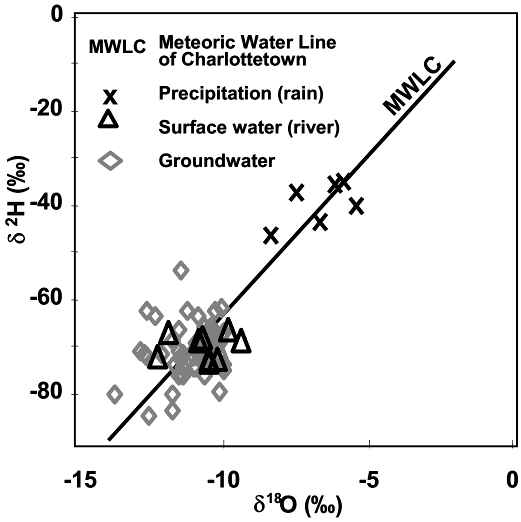


Figure 8. Water isotopes for summer and autumn samples of 2003. The meteoric water line is extracted from Fritz et al., 1987.

5. DISCUSSION

The preliminary appraisal of the sources of nitrates suggested that around 75 % of nitrates in GW are derived from fertilizers. As mentioned in section 2.1, small forest patches equally distributed represent about 20 % of the total surface in the Wilmot watershed. These forested areas are likely the site of the natural production of soil nitrates alone. But note that a part of the nitrate samples falling in the natural soil isotope range could derive from a mixture of ammonium-nitrate fertilizer and manure nitrates. Characterizing the potential sources, such as the fertilizers and manures, as well as the water directly collected under the root zone for various land uses will help finalize the assessment of the nitrate sources in the Wilmot watershed.

In terms of processes involved in the determination of the nitrate load in the Wilmot watershed, if denitrification takes place, it does so only locally. This process perhaps occurs during the slow migration through swamps or in some primary pores in the sedimentary rocks. Indeed, mixed porosity in the aquifer includes a large proportion of primary pores that are not necessarily efficient (dead end pores); denitrification can occur in these pores. Therefore, nitrate concentration in these pores would be lower than in the nearby more porous flowpaths where water travels more rapidly. Molecular diffusion from the flowpath waters to the isolated pores potentially makes the latter ones true sinks of nitrate (storage). Note that in the aquifer portions of faster flow rate, the oxygen level in GW is always higher than the required level for anaerobic microbial denitrification.

All the interpretations presented in this proceeding are preliminary and the set of samples and analysis of samples from the second year will allow for confirmation of initial interpretations, as plans for summer 2004 sampling include characterizing GW of the vadose zone and potential local sources of nitrates, and seasonal monitoring of GW and dissolved nitrate characteristics in selected wells. The PEI N-cycle activity which will include a phase of modelling during its third year should provide a better understanding of the N transfer dynamics in the Wilmot watershed.

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