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Dynamics of nitrate transfer from agricultural soils to aquifers inferred from stable isotopes

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Abstract

Contamination of groundwater (GW) by nitrate from agricultural sources is of particular importance in Prince Edward Island (Canada), where agricultural lands dominate the landscape and GW is the sole source of potable water. In this region and in many others, the transfer of N compounds from agricultural soils to aquifers is a key process, and it is important to assess if values coming from residual soil nitrate estimations, and associated estimates of N loading to aquifers match estimations based on GW concentrations measured at the top of aquifer. The nitrate "dual isotope" characterization is gaining popularity in the field of hydrogeochemistry, and such study promises to shed important insights into the processes involved in the transport of nitrogen from agricultural soils to GW. The current watershed scale sampling program indicates that nitrate concentrations in the region are relatively stable throughout the year, as are the water isotope characteristics (δ^2H and $\delta^{18}O$) in both surface water (SW) and GW. In contrast $\delta^{18}O$ values in dissolved nitrate in both GW and SW display distinct seasonal characteristics. The differing behavior of the water and nitrate oxygen isotopes can be resolved by invoking mixtures of recent recharge water (soil leachate) characterized by high nitrate concentrations and seasonally distinct isotopic characteristics, with deeper and older multi-year GW having lower nitrate concentrations and practically uniform isotopic characteristics. Mixing 25% or less of seasonal recharge with older, less impacted GW accounts for the observed characteristics of GW from domestic wells, implying that the greatest proportion of N flux in GW is at this time restricted to relatively shallow portions of the aquifer. This same rationale also helps explain why currently observed nitrate concentrations in well water in the watershed are below those that would otherwise be expected based on calculated estimates of nitrate loading to the aquifer.

Introduction

Prince Edward Island (PEI) residents are 100% dependent on GW for potable uses and for the vast majority of industrial and commercial water use (Natural Resources Canada, 2005; Piggott *et al*., 2001). Agricultural activities dominate both the landscape and the economy of the province, and contamination of GW by nitrate from agricultural sources is a significant concern. The distribution of nitrate in GW in the province has been well studied for decades, and linkages have been drawn between the intensity of agricultural activity and average nitrate levels, with the closest association being between row crop production and elevated nitrate levels, rather than livestock production.

The traditional understanding of the key sources and behavior of nitrogen in the local environment had been mostly limited to the interpretation of field scale agricultural experiments for individual crops. More recently the fate of nitrate has been examined in the province at a watershed scale, combining stable isotope techniques with a program of seasonal sampling of GW, SW and precipitation (Savard *et al*., 2007 a, b).

Nitrate concentrations measured in GW from individual wells, and for the watershed as a whole show only limited seasonal variation. Similarly, δ^2H and $\delta^{18}O$ results for GW and SW in the study area are relatively consistent throughout the year. In marked contrast, $\delta^{18}O$ values in the nitrate ion show distinct seasonal changes (Savard *et al.*, 2007b). An examination of the combined phenomena of nearly constant nitrate concentrations and $\delta^{18}O$ ratios in water and distinct seasonal $\delta^{18}O$ ratios in the nitrate ion, provides interesting clues to the nature of the local GW flow regime and the behavior of nitrate in this environment. Overall, our approach in this paper is to focus primarily on reconciling the difference in seasonal $\delta^{18}O$ ratios in GW and the nitrate ion, using both hydraulic and geochemical arguments. Following from this same line of reasoning, we go on to discuss how these findings bear on the apparent discrepancy between measured nitrate concentrations in the GW and expected concentrations based on calculated N inputs to the aquifer

Study Setting

The Province of PEI is situated in the Gulf of St. Lawrence in eastern Canada, with a total land mass of only 5684km^2, and a population of just under 140,000. The province has a coastline of 805km, indented by frequent estuaries and bays. Topography is gently undulating to flat, with a maximum elevation of 152 m above sea level. The province has numerous short river systems, with the estuarine portion of these rivers comprising a significant portion of their overall length. The climate of PEI is humid-continental, with long, fairly cold winters and warm summers. Mean annual precipitation, at the Summerside meteorological Station in the central portion of the island is 1078mm, most of which falls as rain (approximately 75%), the remainder falling as snow. The mean annual temperature is about 5.1 C and means for monthly temperature range from minus 8.6 C in January, to 18.4 C in July.

The geology of PEI is dominated by an essentially flat lying sequence of continental red beds, Upper Pennsylvanian to Middle Permian in age. These sequences consist of conglomerate, sandstone and siltstone red beds, exhibiting rapid lateral and vertical facies changes. Bedrock 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 dominantly unsorted tills with rare water-worked glacio-fluvial and glacio-marine deposits. With few exceptions these surface deposits are not saturated, and as a consequence the underlying bedrock formations are the only significant aquifers. The aquifers are characterized as dual porosity in nature, with fractures controlling GW flow, and matrix porosity determining storage characteristics. In most parts of the Island the aquifer is unconfined but because of the dominance of sub-horizontal fractures and delayed drainage, the response under shorter term pump tests resembles that of a confined aquifer. The geometry of individual GW flow systems is generally controlled by topography and the boundaries of these systems generally mimic local surface watershed boundaries. Groundwater and SW resources are closely linked with GW discharge (base flow) accounting for two thirds of annual stream flow, and during dry periods, nearly all stream flow represents this base flow.

Groundwaters are typically of a Ca-HCO_3 or Ca-Mg-HCO_3 type, depending on the dominant cementing agent in the matrix, although natural ion exchange processes result in Na-HCO_3 type waters in deeper portions of some longer flow systems. Na-Cl type waters occur locally in some coastal areas, but are generally limited to a few 100's of meters from the coast. Fresh SW quality generally mimics GW quality, except for those periods of the year where it is diluted by direct overland runoff.

The current study area comprises the Wilmot watershed, located in the west-central portion of the Province. The watershed was selected for study because of the history of intense row crop production, the availability of data from previous studies and surveys, and a history of elevated nitrate concentrations in both GW and SW. The Wilmot River drains an area of about 87km^2 and flows south-westerly to Bedeque Bay on Northumberland Straight. The basin is approximately 17km in length and 5km wide, with nearly half of the river tidally influenced. Maximum elevations in the watershed (90m above sea level) are found at the headwaters in the eastern extent of the watershed.

The watershed is predominantly rural in character, with the population residing in dispersed homes and farmsteads, and a few small hamlets. Agricultural activities cover 76% of the watershed, the remaining land occupied by forest (11%,) residential development (9%,) and wetland areas. Potato production dominates agricultural activity in the watershed, accounting for 80% percent of agricultural land use, and 60% percent of total land use in the watershed. Typical potato production systems are maintained as two or three year rotations (ie , potato followed by hay, or potato, followed by a cereal crop, followed by hay).

The geology and hydrogeology of the watershed is characteristic of other areas of the Province, with sandstone, dominating the sequence tapped by domestic or commercial wells, with locally variable amounts of inter-bedded siltstones and mudstones. Hydraulic conductivities determined from packer tests of discrete intervals (Paradis *et al*., 2007) show significant decreases with depth, a phemomenon also recognized by Francis (1989) in work in the nearby Winter River Basin. The aquifer displays significant vertical horizontal anisotropy, with K_h being several orders of magnitude higher than K_v (Francis, 1989; Jiang *et al.*, 2007). This is generally attributed to the dominant role that sub-horizontal fractures play in determining GW flow, a feature that becomes less significant with depth in the aquifer.

Sampling and Analytic Methods

Samples were collected on a seasonal basis from domestic wells over the period between summer 2003 and spring 2005, and supplemented by samples collected from dedicated piezometer installations, the Wilmot River and temporary rain collectors. Domestic well sampling locations were distributed across the watershed, and all wells are of open hole construction, completed in bedrock. The wells have an average depth of 18m and are generally cased down to the overburden-rock contact. The water level is generally below the casing, in the rock formations. The locations of domestic wells sampled during the program are shown on Figure 1.

Groundwater samples were obtained using outdoor taps from water systems devoid of treatment. Prior to sampling, the systems were purged until temperature, pH and conductivity stabilized. The samples were filtered using a 0.45 micron filter to remove particulate matter and then analyzed by spectrophotometer to estimate the concentrations of NO_3^- and other ions in order to determine how much GW would subsequently be needed for ion resin exchange extraction. Samples were collected once every season during the 2003-2005 period.

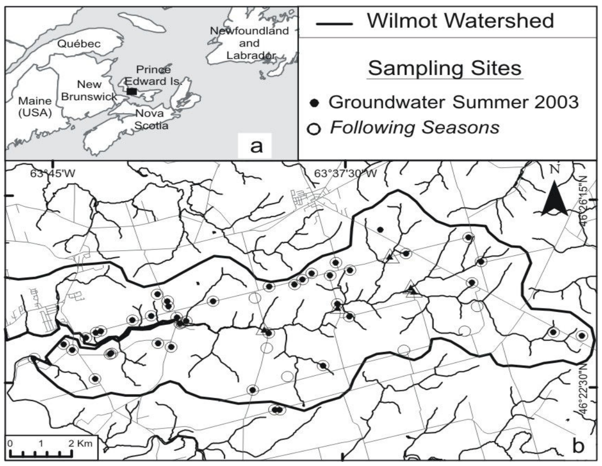

Figure 1. Location of domestic well sampling sites (modified from Savard *et al.*, 2007a).

Surface water samples were collected from the river's edge at least 10cm below the water surface and at portions of the stream where flow was swift. None of the sampling trips coincided with any major precipitation events and samples are considered to be representative of base flow from the aquifer. Precipitation samples were collected for analysis of δ^2H and $\delta^{18}O$ ratios, and were obtained from 30.5cm diameter plastic collectors 45cm in height. Collectors were fitted with a funnel, 30.5cm in diameter at the top, narrowing to 3cm in diameter at the lower end, to reduce exposure to air. To further minimize evaporation, a layer of vegetable oil 2.5cm thick was added to the bottom of the collector. Each collector was left for a one-month period (or longer), during which time a composite precipitation sample, representing all precipitation that fell during the month, was collected. A 60 mL plastic syringe was used to obtain water samples from below the layer of oil.

For snow, samples were obtained by inserting a plastic cylinder, 1m long with a 3.8cm inner diameter, into the snow pack vertically, transferring the snow to a plastic bag and repeating until sufficient snow had been collected for a sample representative of the snow pack. The samples were allowed to melt at room temperature over several hours, then homogenized and transferred into 60mL HDPE bottles.

All isotope analyses were performed at the Delta-Lab of the Geological Survey of Canada (Québec). Nitrate was extracted using modified cation and anion-exchange resins and silver-nitrate precipitation protocols proposed by the USGS (Chang *et al.*, 1999;

Silva *et al*., 2000). The extraction is followed by analyses of the $\delta^{15}N$ and $\delta^{18}O$ ratios, using on-line combustion and pyrolysis-IRMS systems, respectively. Average precision obtained on sample duplicates (n=86, 161) is 0.1‰ for $\delta^{15}N$ and 0.2‰ for $\delta^{18}O$. Analysis of nitrate concentrations was conducted at the AAFC-Québec laboratory by Flow Injection Analysis (FIA) colorimetric method (LACHAT) for which the detection limit was 0.04 mg/L N-NO_3^- (1.53 mg/L NO_3^-) and the precision was 0.09 N-NO_3^- mg/L (0.4 mg/L NO_3^-).

Results

Groundwater samples exhibited a broad range of nitrate concentrations, from site to site (<1 to 14.6mg/L N-NO_3^-), but were relatively consistent at individual sites throughout the 8 sampling periods, averaging 6.9mg/L. Seasonal mean values for individual sampling campaigns ranged from 5.5 to 8.1mg/L, Overall, 22% of the summer GW samples have N-NO_3^- concentrations above the 10mg/L drinking water guideline recommended by Health Canada (2004), whereas 7% of summer GW samples have concentrations of less than 1mg/L, expected for areas devoid of human impacts.

Samples from the Wilmot River exhibited a narrower range of values, falling between 5.1 and 7.7mg/L, assumed to represent base-flow conditions, essentially an integration of shallow GW discharges throughout the watershed. On average, nitrate concentrations in SW are very similar to those for GW, with an average of annual value of 6.2mg/L(N-NO_3^-), and limited seasonal variation with average concentrations of 6.6, 6.5, 6.2 and 5.4mg/L (N-NO_3^-) for summer, autumn, winter and spring samples, respectively.

Oxygen isotope ratios for GW samples showed only very limited seasonal variation, averaging -11.1‰ and ranging from -11.2 to – 10.5$^0/_{00}$. Surface water values displayed an essentially identical pattern averaging -11.1‰ and ranging from -12.5 to -9.6‰. Figure 2. presents δ^2H and $\delta^{18}O$ results for both GW and SW, which cluster on or near the local meteoric water line (MWL). The results have been interpreted by Liao *et al.*, 2005 to indicate that GW is derived from local precipitation and SW samples are likely derived primarily from local GW discharge.

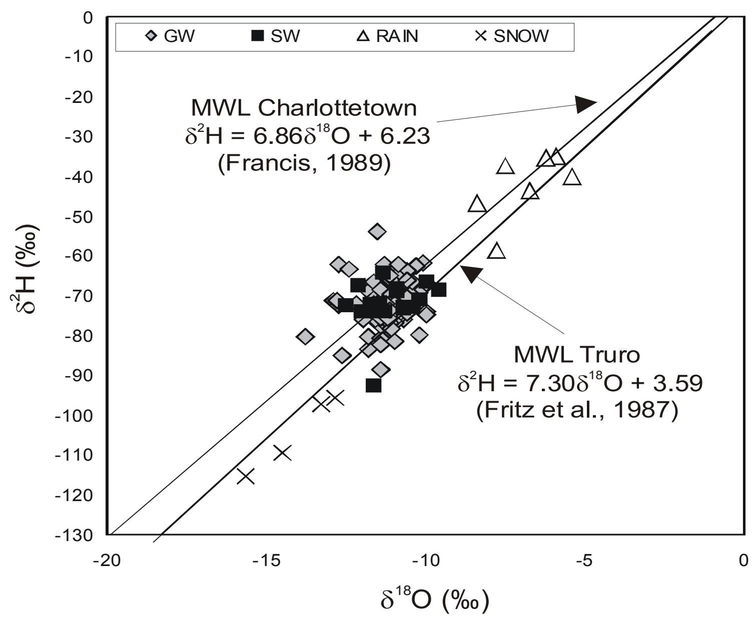

Figure 2. Groundwater and surface water samples in relation to local meteoric water lines (Liao *et al.*, 2005).

Analysis of extracts of dissolved nitrate for $\delta^{15}N$ showed moderate seasonal variation with mean values ranging from 3.4 to 4.9‰, over the 8 sampling campaigns. In marked contrast, mean seasonal $\delta^{18}O$ ratios ranged from a high of +10.5‰ in the summer of 2003 to a low of -2‰ the following spring. A similar, though less dramatic downshift in $\delta^{18}O$ ratios is observed during the following year. Table 1 summarizes mean seasonal results for NO_3-N and $\delta^{18}O$ in GW and $\delta^{18}O$ in the nitrate ion, and Figure 3 illustrates graphically the results for the 1st year of sampling.

Table 1. Average characteristics of groundwater and nitrate dissolved in groundwater measured seasonally in domestic wells.

Season	Summer 2003	Autumn 2003	Winter 2004	Spring 2004	Summer 2004	Autumn 2004	Winter 2005	Spring 2005
NO_3^--N (mg/L)	7.2	6.5	6.4	5.5	8.1	6.9	7.1	7.4
Water δ18O (‰)	-11.1	-11.2	-11.0	-11.2	-11.1	-11.1	-10.5	-11.2
Nitrate $\delta^{18}O$ (‰)	10.5	8.1	-1.2	-0.2	2.3	2.1	-0.2	2.0

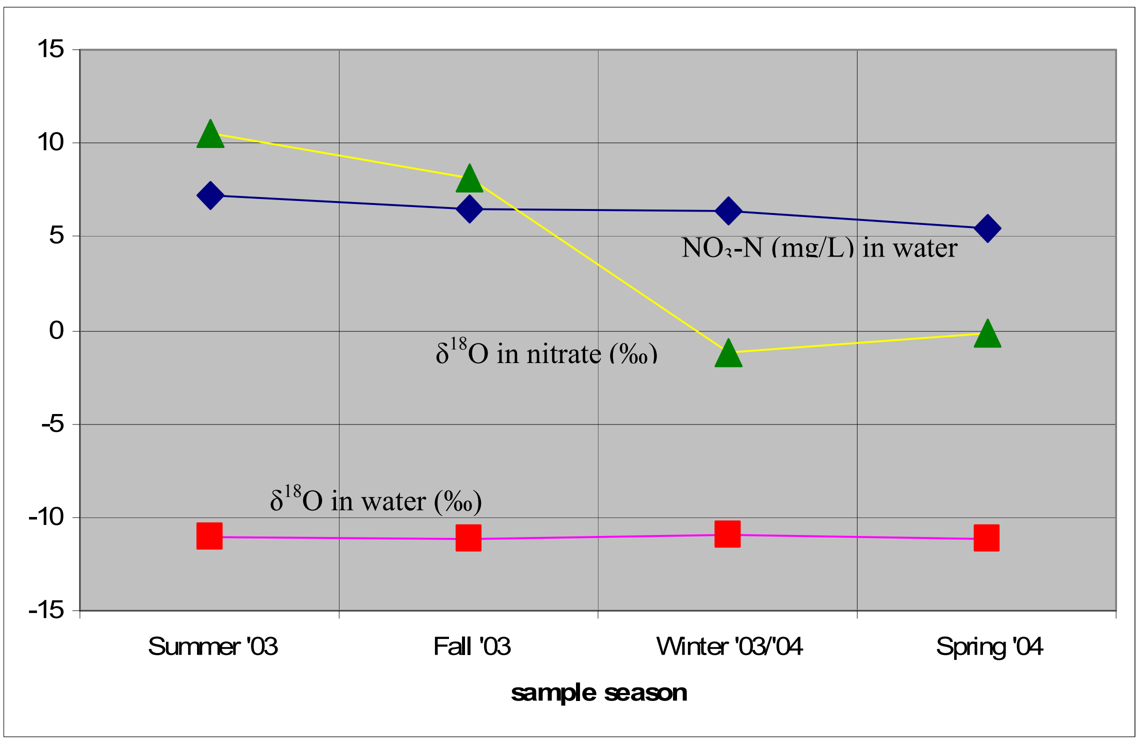

Figure 3. Seasonal results for 1st year of sampling program, NO_3^--N and $\delta^{18}O$ ratios in groundwater, and $\delta^{18}O$ ratios in nitrate dissolved in groundwater.

Interpretation and Discussion

The results described above have a number of implications regarding the behavior of nitrate in the local GW flow regime, as well as for an understanding of the relative importance of different N sources during different seasons (described in detail by Savard et al. (2007a, b). Briefly, Savard *et al*. (2007b) attribute the distinct decrease in $\delta^{18}O$ ratios in the nitrate ion during cold periods to active nitrification even during the winter and spring periods of the year, a phenomenon not well recognized in the literature for temperate climatic regimes. Essentially, as nitrification proceeds, the incorporation of 2/

3rds of the oxygen in the nitrate ion from soil water, carries a seasonally distinct isotopic ratio providing clues on the timing of nitrification. This characteristic, in conjunction with $\delta^{15}N$ ratios in the nitrate ion, assists in quantifying the relative importance of individual N sources at different times of the year (Savard *et al*., 2007a; Somers *et al*., 2007). Here, to explain the difference in seasonal characteristics of $\delta^{18}O$ in H_2O as compared with $\delta^{18}O$ in NO_3^- we propose a conceptual model involving the mixing of shallow, nitrate rich soil leachate, bearing the seasonal $\delta^{18}O_{(NO3)}$ characteristics resulting from incorporation of seasonal precipitation, with deeper, multi-season or multi-year GW with lower nitrate concentrations and uniform isotopic characteristics. The plausibility of this model is first evaluated from a hydraulic perspective, and subsequently by a series of geochemical mixing calculations.

It has already been noted that the local aquifer is characterized by declining hydraulic conductivity with depth, and by corollary, it can be assumed that the greatest contribution of water to a well penetrating the aquifer will be from the highest part of the well bore, with progressively decreasing contributions with depth. Given a reasonable estimate of the specific yield (Sy) of the aquifer, and of the flux of recharging water at any particular time, it is possible to estimate the vertical extent of the aquifer (or well bore) influenced by recent recharge events, in contrast to deeper portions of the well receiving older water accumulated over a number of seasons or years.

While direct measurement of Sy is difficult, reasonable estimates can be made based on lithology, and by interpretation of numerical GW modeling results. Driscoll (1986) suggests typical Sy values for sandstones ranging from 5 to 15%, and Francis (1989) estimated a value in the range of 10% for sandstones of the same geological formation in the nearby Winter River basin. Interpretation of modeling simulations using MODFLOW (Jiang and Somers, 2007), and FEFLOW (Paradis *et al*, 2007) produced estimates of Sy of 5% to 10% and 10% respectively. Given our interest here in the characteristics of the very top of the aquifer where fracturing is most significant, it is likely that a value near the upper end of this range is most appropriate. In addition, it can be expected that under pumping stress the hydraulic gradient toward a well will be greatest in the upper portions of the well bore (*i.e.* within the cone of depression), emphasizing the relative contribution of the upper most portion of the well. Therefore Sy values in the range of 10 to 15% are suggested for the uppermost portion of the aquifer.

Typical estimates for annual recharge, based both on base-flow separation and interpretation of numerical simulation results are in the vicinity of 400mm/year. While the magnitude of individual recharge events will vary from year to year, typically in PEI major recharge events are restricted to the spring and fall, with the spring event in most years being more significant because of the combined influence of recent precipitation and melting of the winter snow pack. Because of the variability of both the total amount of annual recharge, and the relative proportions for the spring and fall periods, it is assumed here that recharge is split equally between these two periods. With values of Sy in the range of 10 to 15%, it is apparent that the influence of seasonal recharge (recent soil water leachate) is limited to approximately the top 1 to 2m of the aquifer.

To assess the contribution of this shallow portion of the aquifer relative to contributions from deeper portions of the aquifer, we can use the vertical distribution of hydraulic conductivity values to construct a hypothetic profile depicting the flow to the well bore at different depths. Table 2 presents the measured hydraulic conductivity (K) for discreet intervals in one of the piezometers installed near the centre of the basin (Paradis *et al.*, 2007), as well as the calculated unit flow and fraction of total flow per interval. In the last column, the results for the very top of the aquifer, intermediate depths and the deepest portion of a hypothetical well bore are presented.

Table 2. Relative flow proportions for shallow, intermediate and deep zones of hypothetical domestic well bore (Wilmot aquifer).

Interval:	thickness (m)	K (m/s)	unit flow	fraction of flow	flow/interval
shallow seasonal water	1.3	4.50E-04	5.85E-04	0.13	0.1
multi-season impacted water	4.7	4.50E-04	2.12E-03	0.48	0.8
	6.0	9.13E-05	5.48E-04	0.12	
	6.0	8.50E-05	5.10E-04	0.12	
	6.0	4.43E-05	2.66E-04	0.06	
deep "pre-impact" water	6.0	6.75E-05	4.05E-04	0.09	0.1
total unit flow			4.43E-03	1.00	

The results of this calculation suggest that recent (seasonal) recharge would account for approximately 10% of the total flow to the well from the aquifer. It must be stressed that these figures should be taken as a broad generalization only, and exact proportions of flow may vary significantly depending on specific characteristics of each actual well, and the relative magnitude of recharge during any particular season. In spite of these limitations, theses calculations should be sufficiently representative of actual field conditions to place some constraints on the results of the geochemical mixing calculations that follow.

The second approach to estimating the GW characteristics involves calculating the isotopic ratios expected in water and in nitrate as a result of mixing various proportions of soil water leachate with deeper GW using the classical fluid mixing equation (Faure, 1986). Individual $\delta^{18}O$ values are calculated for water and nitrate for a series of hypothetical mixtures using the nitrate content in each of the two components to weight the appropriate seasonal $\delta^{18}O$ characteristics of each end member in the mixture. For the purpose of calculation, it is assumed that the nitrate concentrations for seasonally produced soil leachate and deep GW were 30 and 3 mg/L, respectively (Chapters 2 and 3 of Savard *et al.*, 2007a). The calculations consider a constant $\delta^{18}O$ ratio in deep GW of -11‰, and in soil leachate of -6, -9, -15 and -6‰ for summer, fall, winter and spring respectively. In the same manner, it is assumed that the $\delta^{18}O$ ratio in nitrate of deep GW is constant throughout the seasons at -4.5 ‰, while $\delta^{18}O$ ratios in NO_3-N in leachates are set at 18, 9.6, 0.9 and 5.9 ‰ for summer, fall, winter and spring, respectively. Figure 4. illustrates the results of calculations for $\delta^{18}O$ in nitrate and $\delta^{18}O$ in water, as well as the range of observed $\delta^{18}O$ ratios in samples from domestic wells for the 2003-2004 seasons.

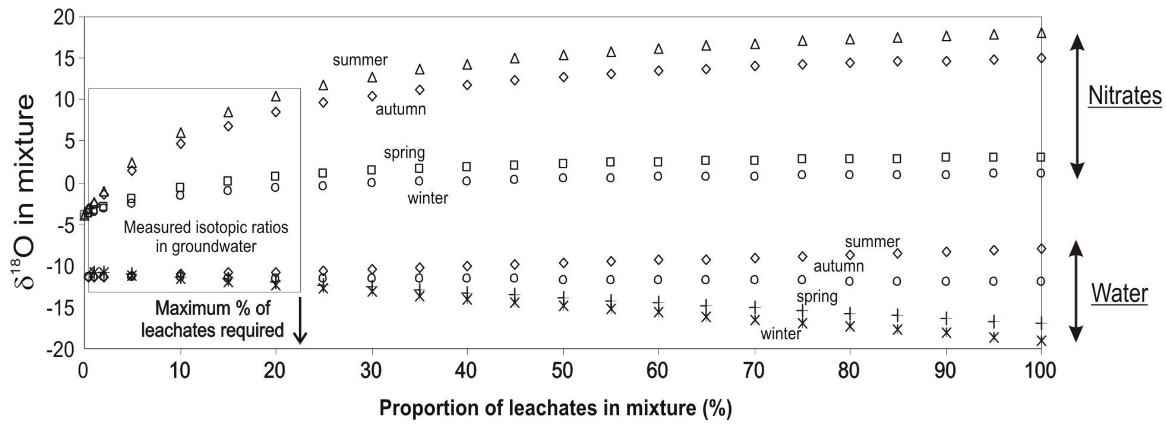

Figure 4. Hypothetical δ^{18}O ratios in water and NO_3^- as a function of proportion of seasonally produced soil leachate in groundwater mixtures.

The mixing calculations suggest that a mixture of roughly 10 to 20% of seasonally distinct leachate with deep GW can explain the essentially constant δ^{18}O ratios in water, and variable δ^{18}O ratios in the nitrate ion. Alternate assumptions for the nitrate concentrations in leachate and deep GW will of course yield somewhat varying results, and it is stressed that these calculations are not intended to match exact field conditions, nor can they be expected to represent the degree of variability likely to be present in a natural system. Indeed, even for a single well, the relative influence of each stratigraphic zone will depend on prevailing recharge conditions, and variability in well construction and local geological conditions. As a consequence, both the hydraulic and geochemical observations drawn here should only be considered in a conceptual sense.

In addition to reconciling the discrepancies between water and nitrate ion isotopic characteristics, this mixing model also provides an explanation for the apparent difference between observed nitrate concentration in the watershed and the concentrations that might be expected, based on assessments of nitrate loading to the aquifer. Several estimates of nitrogen loading and subsequent N leaching losses have been made for the Wilmot watershed in attempts to link the impact of agricultural practices to observed nitrate levels in GW (van Bochove *et al.*, 2007, Somers *et al.,* 2007, Jiang and Somers, 2007). All of these estimates are in reasonable agreement, with an average estimated leaching loss of 33.8 kg N/ha/yr. Assuming an average annual rate of recharge to the aquifer of 400mm per year, this loading rate should correlate with a GW nitrate concentration of approximately 8.4 mg/L. Nonetheless, the mean value of observed mean nitrate levels in the watershed is only 6.9mg/L. This difference between these two GW nitrate values (observed vs. predicted) implies that either some nitrate is being lost prior to, or during transfer to the aquifer, or that current GW nitrate concentrations do not reflect the full impact of the agricultural practices in the area.

The most commonly invoked explanation for a loss of nitrate from soils prior to or during transfer to the aquifer is denitrification, yet GW in PEI is typically well oxygenated (Savard *et al*., 2007b), and indeed dissolved oxygen levels measured at the time of sampling averaged 8.8 mg/L, a concentration which does not allow denitrification. Furthermore, in the δ^{18}O and δ^{15}N graphic space (see Figure 5), the process of denitrification should result in a progressive shift in values in dissolved nitrate toward heavier values for both isotopes (Kendall and Arevena, 2000), however the only significant shift in values involves a drop in $\delta^{18}O$ ratios associated with colder seasons.

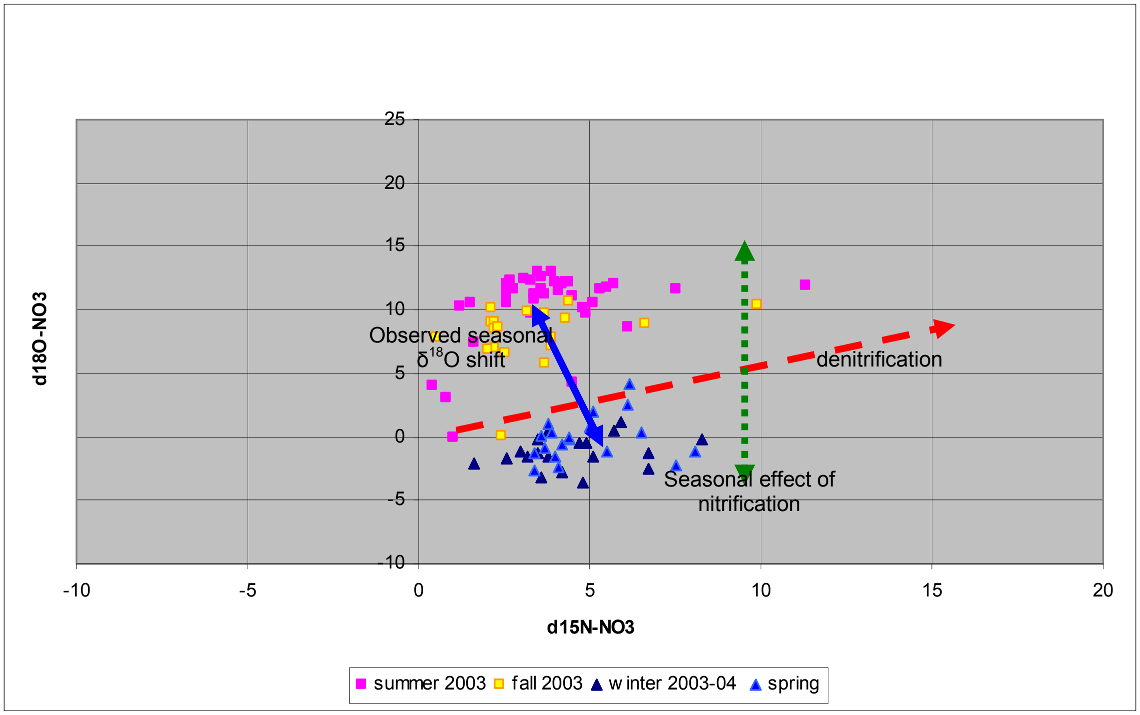

Figure 5. The groundwater nitrate $\delta^{18}O$ values as a function of $\delta^{15}N$ ratios (modified from Savard *et al*., 2007b).

An alternate and more plausible explanation is provided by consideration of the mixing model presented above, whereby the principle flux of nitrate is via transport from soil to shallow groundwater, and followed by discharge via base-flow to the river. It is noted that the same strong seasonal $\delta^{18}O$ signal seen in nitrate of soil leachate is also observed in nitrate in surface waters, implying rapid transfer of nitrate from shallow portions of the aquifer to surface water. Thus while sample results clearly show that deeper groundwater has been impacted by nitrate leaching, a very significant portion of nitrate is cyclingi through shallow portions of the groundwater/surface water flow system, and the full impact of current nitrate loading rates has not affected deeper portions of the aquifer to the same extent. This explanation is supported by predictions made by numerical GW transport simulations conducted by both Jiang and Somers (2007), and Paradis *et al.* (2007). In both cases it is suggested that nitrate levels will continue to climb even under current N loading rates, and that the impact of any reduction in N-loading will be most profoundly and rapidly observed in shallow groundwater and base-flow to the river.

Conclusions

Both the hydraulic and geochemical arguments described here support the basic premise that contributions from the shallowest depths are dominating the nitrate characteristics of water withdrawn from the aquifer by typical domestic wells. Hypothetical calculations based on the vertical hydraulic conductivity profile of the aquifer, as well as recharge and storage characteristics of the aquifer suggest that water quality in the top one or two meters of the aquifer should be dominated by recent, seasonal recharge, whereas deeper waters would represent the averaged characteristics of water recharged over several seasons or years. These observations are consistent with independent assessments of local GW flow conditions, with flow being dominantly horizontal throughout much of the GW flow systems. Our geochemical mixing model using the observed NO_3-N and $\delta^{18}O$ characteristics of soil leachate and deeper indicates that mixing of 25% or less of seasonal recharge with older, less impacted GW can account for the observed isotopic characteristics, again implying that the greatest proportion of N flux in GW is at this time confined to relatively shallow portions of the aquifer, controlled by a dominantly horizontal GW flow regime.

One of the important implications of these findings is that the most impacted portions of the aquifer respond rapidly to changes in N fluxes, and any reduction in N loading may be expected to have a relatively immediate impact on shallow GW quality. In addition, the work presented here highlights the importance of considering the detailed characteristics of the local GW flow regime, including seasonal recharge characteristics, in the interpretation of hydrogeochemical data.

Acknowledgements
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