Stable Isotopes of Nitrate Reveal the Important Role of Soil Organic Matter in Mediating Nitrogen Transfer to Groundwater with Implications for Consequences of Climate Change

George Somers
PEI Dept. of Environment, Energy and Forestry, Charlottetown, PEI, Canada
Martine M. Savard
Natural Resources Canada (GSC), Québec, QC, Canada

ABSTRACT

Stable isotopes of nitrate are used here to better understand the transfer of nitrogen (N) from soils to groundwater (GW) in two agricultural settings of Prince Edward Island (PEI). Under row crop cultivation, strong seasonal differences in the provenance of nitrate are inferred, but seem practically absent in an area of livestock production, a feature attributed to differences in the chemical behaviour of inorganic fertilizers and manures. However, in each environment, year-round nitrification of soil organic matter plays a vital transitory role in the cycling of N, with fluxes of N being especially significant during winter when there is negligible plant uptake of N. Climate change predictions for PEI suggest the probability of higher minimum soil temperatures during winter and could be expected to accelerate the rate of winter nitrification, underlining the importance of effectively managing crop residues in efforts to reduce nitrate contamination of GW.

RÉSUMÉ

Les isotopes stables du nitrate permettent ici de mieux comprendre le transfert de l'azote (N) des sols vers les eaux souterraines (ES), dans deux contextes agricoles, à l'Île-du-Prince-Edouard (IPE). Dans le contexte de la culture de pommes de terre, d'importants changements saisonniers de provenance sont mis en lumière, mais ils sont pratiquement inexistants dans le contexte de l'élevage bovin, un contraste qui s'explique par la différence de comportement chimique des fertilisants inorganiques et organiques. Cependant, dans les deux contextes, la matière organique des sols agit tel un compartiment transitoire majeur de N toute l'année durant. La nitrification de cette matière et son transfert hivernal sont importants puisque les plantes utilisent peu de N pendant cette saison. Le changement climatique à l'IPE devrait entraîner une hausse des minima de la température hivernale qui accélèrera le taux de nitrification au cours de cette saison. Cette prédiction souligne l'importance de mieux gérer les résidus de récolte dans le but de réduire la contamination des ES par le nitrate.

1 INTRODUCTION

Contamination of groundwater by nitrate represents one of the most common water quality problems in agricultural areas world wide. Land use in the Province of Prince Edward Island is dominated by agricultural activities, while at the same time the population depends entirely on a highly vulnerable aquifer for drinking water. With the Province=s small land base, competition between agricultural production and the need to protect water quality poses difficult challenges. Province-wide, 4 to 6 % of private wells have nitrate levels exceeding recommended health limits and in some more intensively cultivated watersheds, 15% or more of wells exceed guideline values. Municipal supply wells in several communities have also been affected by elevated nitrate levels, and rising GW nitrate levels are an important consideration for source water protection efforts in well field capture zones. The discharge of nitrate-rich GW (base-flow) is also a major source of nutrients in local streams and estuaries, which contributes to the growing problems of eutrophication and occurrence of anoxic events.

Numerical GW modelling, simulating the effects of current land use practices, combined with the effect of climate change, on future precipitation and recharge regimes, suggest that GW nitrate concentrations can be expected to increase in the future (De Jong *et al.*, 2007, and Vigneault *et al.*, 2007).

While considerable work has been devoted to the development of strategies to mitigate the impact of agricultural sources of nitrate, many of these efforts focus on improved fertilizer management, and there are still significant gaps in our understanding of overall dynamics of the natural processes of nitrate production and transfer to GW. Stable isotope techniques have become an important tool in investigating such processes, and are used here to highlight some important features of N cycling, that bear consideration in attempts to reduce agricultural impacts on GW quality.

Here we examine the results the isotopic characteristics of nitrate in GW and for dominant N sources in two contrasting agricultural settings, using the approach developed by Savard *et al.* (2007a), with the intent of shedding additional light on processes and timing of nitrate production and transport to underlying aquifers.

2 STUDY AREAS

The two subject areas of this study are the Wilmot River watershed and the Earnscliffe Peninsula, situated approximately 60 km apart, in central PEI (see Figure 1). The Wilmot River watershed is located west of the Provincial Capital of Charlottetown, and drains an area of 87 km^2, with elevations ranging from sea level to 90 m.a.s.l. The Earnscliffe Peninsula is located to the east of Charlottetown and covers an area of approximately 22 km^2 and has a maximum elevation of 34 m.a.s.l.

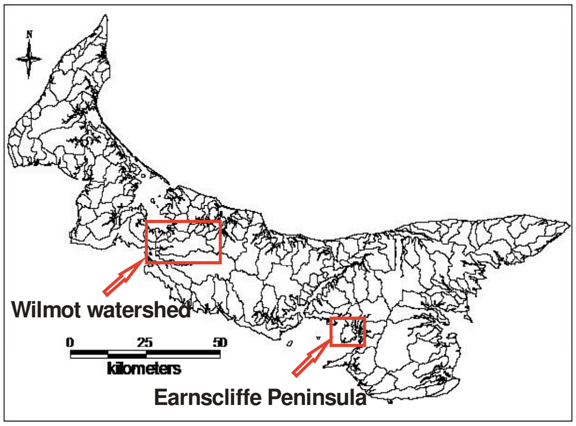

Figure 1 Study area locations: Wilmot watershed and Earnscliffe Peninsula

Land use in both study areas is dominated by agricultural activities, with intensive row crop production (potato rotation systems) characterizing activity in the Wilmot River watershed (Atlantic Agritech, 2006), and livestock production, and associated cereal and forage crop production, being most significant in the Earnscliffe region (Atlantic Agritech, 2008). In both regions, key N inputs include atmospheric deposition, inorganic fertilizers and manures. Inorganic fertilizers constitute the principle anthropogenic N input in the Wilmot watershed, while manures are the most significant N source in the Earnscliffe region (Jacques Whitford Environment Ltd, 2001) see Table 1.

Table 1. Selected land use characteristics of the Wilmot and Earnscliffe study areas

Land use characteristics	Wilmot	Earnscliffe
Agricultural land as percent of total land area	78	72.7
Annual area of potato production as percent of total land area	26	7.3
Annual fertilizer application (kg/ha)	73.2	29.4
Annual manure application (kg/ha)	24.7	96.8

The climate of PEI is humid-continental, with long, fairly cold winters and warm summers. Mean annual precipitation averages 1153mm, with 73% falling as rain and the remainder falling as snow. The mean annual temperature is 5.3°C with mean monthly temperatures ranging from –7.9°C in January to +18.5°C in July.

Groundwater resources across the Province are essentially limited to a sequence of “red bed” sediments of Upper Carboniferous to Lower Permian age, overlain by a thin veneer of generally sandy glacial till, and the main geological and hydrogeological features of both study areas are essentially the same. The lithology of the red bed sequences is dominated by sandstone with variable amounts of inter-bedded basal conglomerates, siltstone and clay-stone (van de Poll, 1983). These strata are essentially undisturbed and flat lying, with dips commonly to the northeast at about one to three degrees. The formation can be characterized as a fractured porous semi-confined aquifer with near horizontal bedding plane fractures dominating the fracture network. Groundwater flow is dominantly lateral, with the uppermost portions of the aquifer being the most active and responsive to seasonal recharge (Jiang and Somers, 2008). The principle difference in GW flow regimes in the two study areas lies in the geometry of the respective regions. Whereas in the Wilmot watershed, numerical modelling indicates dominant GW flow directions are from the up-land basin margins toward the Wilmot River (Paradis *et al.*, 2007, Jiang and Somers 2007), on the Earnscliffe Peninsula, shallow groundwater flow directions are assumed to radiate from local topographic high points in the centre of the peninsula toward the coast line (Somers and Savard, 2008).

The recharge rate of the red bed aquifers are high, in the range of 30-35% of annual precipitation or on average 400 mm/y. Groundwater discharge (base-flow) comprises a highly significant component (55-60%) of total stream flow in PEI, and except immediately following rainfall events, during low-flow summer and early fall periods almost all fresh water flow is derived from base-flow (Jiang and Somers 2008). Jiang and Somers (2008) estimated that approximately 80% of this base-flow is derived from shallow depths of the aquifer, consistent with the dominantly lateral flow regime in the red bed aquifers of PEI. This feature has particular importance in the role that GW contamination by nitrate plays in nutrient loading of the Province’s streams and estuaries.

Major element chemistry of PEI GW is determined primarily by cementing agents in the red bed sequences and waters are typically well oxygenated, moderately hard to hard Ca-Mg-HCO3 type, with saltwater intrusion having only a limited effect in selected coastal regions of the Province. High nitrate contents and more locally, high chloride concentrations related to road salting (Somers *et al.* 1999) are the principle anthropogenic impacts on GW quality. Average GW nitrate concentrations and the frequency of occurrence of wells with nitrate levels exceeding recommended health limits have increased progressively in many areas of the province over the past 30 years and historical samples representing base-flow conditions from many areas of the Province also reflect the same trend toward increasing nitrate contents noted for GW (Somers *et al.*, 1999).

3 METHODS

The methods used in this study follow the approach initially proposed by Savard *et al*. (2007a) with the aim of estimating, in a semi-quantitative manner, the relative seasonal contribution of discrete N sources to overall nitrate flux to GW, as well as shedding light on the processes, timing and fate of nitrate in agricultural soils. The approach combines a program of seasonal sampling and examination of the isotopic characteristics of oxygen and hydrogen in water (precipitation and GW) and oxygen and nitrogen in nitrate (GW and potential N sources) A constant input from atmospheric deposition of approximately 5% is imposed as based on mass balance considerations. A discussion of model assumptions used to estimate N source proportions for the Wilmot watershed can be found in Savard *et al*. (2007a) and, where different, the rationale for the selection of specific N source isotopic characteristics used for the contribution of N sources in Earnscliffe is discussed in Section 5 of the present report.

Sampling included collection of precipitation, GW and SW samples (Wilmot only) as well as a limited number of fertilizer, soil and manure samples. Precipitation samples were captured in 30.5cm diameter collectors located in the Wilmot watershed (2003-2005) and Charlottetown area approximately 16Km west of the Earnscliffe Peninsula (2007-2008). Groundwater samples were collected over an 8 season period from a suite of 15 domestic wells in the Wilmot area (2003-2005) and over a 6 season period from10 wells on the Earnscliffe Peninsula (2007-2009). All domestic wells sampled were of open hole construction with average well depths of 18m in the Wilmot watershed and 26 m in the Earnscliffe Peninsula. In each case, wells are generally cased to a depth slightly below the overburden-rock contact. Domestic wells were sampled using outdoor taps from systems devoid of treatment devices and piezometers were sampled using a Waterra sampling system using dedicated pumps. Prior to sampling the systems were purged until stabilization of temperature, pH and conductivity values. Dissolved oxygen levels were also measured in situ. Unfiltered samples obtained for analyses of water isotopes were refrigerated during transport and storage.

Representative fertilizer and manure samples were supplied for analysis by the PEI Department of Agriculture and Agriculture Agri-food Canada in Charlottetown, and subsequently frozen prior to shipping to the Delta-Lab of NRCan. In addition, a suite of soil and tile drain water samples from Agriculture and Agrifood Canada's Harrington Experimental Farm (just north of Charlottetown) were collected, as well as GW samples from domestic wells in the Murray River Watershed, where watershed conditions are essentially pristine.

All water analyses for nitrate concentrations were conducted by the PEI Analytical Laboratories. Nitrate concentrations are determined by quantitatively reducing to nitrate to nitrite by passage of the sample through a copper cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl ethylenediamine dihydrochloride (NED). The resulting water soluble dye is measured by colorimetry at 520 nm, using a Quickchem 8000 Flow Injection Analyzer. Precision for nitrate analysis is 7%.

Isotope analyses are produced at the Delta-Lab of the Geological Survey of Canada (Québec). Groundwater samples are filtered (0.45μm) within 24 hours of sample collection and stored frozen until further processing. Prior to extraction, concentrations of ions are determined to calculate sample volumes necessary for the ion-resin exchange extraction. The extraction of NO_3-N for $\delta^{15}N$ and $\delta^{18}O$ analyses is performed following the protocols of ion exchange resin extraction and silver nitrate precipitation as described in Savard *et al.* (2007b). The $\delta^{15}N$ values isotopic analyses combustion of $AgNO_3$ is performed in silver capsules (Silva et al., 2000) are determined using an Elemental Analyzer connected to a Isotope Ratio Mass Spectrometer (IRMS), whereas the $\delta^{18}O$ analysis uses a pyrolysis system connected to an IRMS (*Savard et al.,* 2008). Average precisions obtained on sample duplicates are 0.1‰ for $\delta^{15}N$, and 0.2‰ for $\delta^{18}O$ values.

4 RESULTS

Nitrate concentrations in both study regions exhibit significant variation between wells during each sampling event, and at some individual sampling sites, significant variations in nitrate concentrations are observed between sampling events. However mean nitrate concentrations, either in the Wilmot or Earnscliffe areas remain relatively constant throughout all sampling periods, with an average mean value of 6.6 mg/L (range of 6.04 to 7.15 mg/L) and 7.05 mg/L (range of 5.6 to 8.1 mg/L) for the Earnscliffe and Wilmot regions respectively.

Nitrogen isotopes ($\delta^{15}N$) in dissolved nitrate (Figure 2) display a relative large range of values in each of the two study locations, with the range of values varying only slightly in either location on a seasonal basis. In contrast, a significant seasonal shift between summer and winter $\delta^{18}O$ ratios is observed for data from the Wilmot watershed, while $\delta^{18}O$ ratios for all seasons for the Earnscliffe show little variation.

Isotopic analyses of fertilizer and manure samples, provided by the PEI Department of Agriculture and Agriculture Agri-food Canada in Charlottetown show distinct characteristics with respect to $\delta^{15}N$, with inorganic fertilizer values of approximately 0 $^{0}/_{00}$, (-1.9 to 1.1$^{0}/_{00,}$ and solid and liquid manure $\delta^{15}N$ ratios of 14.5 and 20.0 $^{0}/_{00}$ respectively. Some constraints can also be placed on $\delta^{15}N$ characteristics of representative soils in the region. Samples from a check plot (ie no fertilizer or manure application) at the Harrington Experimental Farm display δ^{15}N ratios of $4.0^{0}/_{00}$ (3.7 to $4.3^{0}/_{00}$ for total N in soils, and $4.85^{0}/_{00}$ (3.5 to 5.7$_{)}$ in nitrate of tile drain water. Groundwater samples from a essentially forested watershed, essentially devoid of agricultural activity (Murray River) in eastern PEI have average δ^{15}N ratios of 4.35 $^{0}/_{00.}$

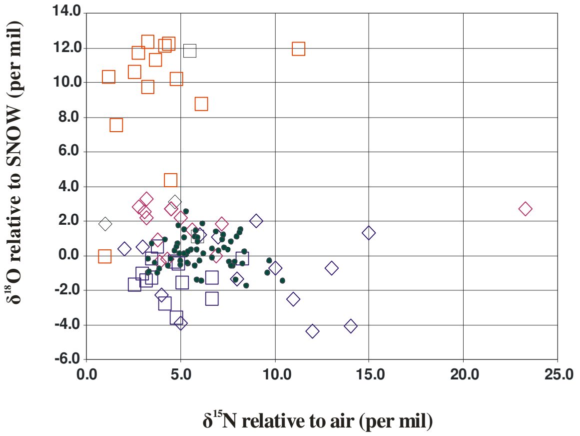

Figure 2. Nitrate istotope distributions for Wilmot and Earnnscliffe study areas. Wilmot: summer 2003 in red open squares, winter 2004 in blue open squares, summer 2004 in red open diamonds, winter 2005 in blue open diamonds. Earnscliffe data all as black filled diamonds.

Oxygen isotopes for the same sources are somewhat less distinct, and for some sources, will vary, reflecting seasonal changes in precipitation involved in nitrification. Measured δ^{18}O values for ammonia nitrate fertilizers are in the range of $30^{0}/_{00}$, compared with values of 15.3 and 19.0 $^{0}/_{00}$, for solid and liquid hog manures respectively. GW samples from a watershed devoid of agricultural activity (Murray River) and from tile drain water from a check plot (no application of fertilizer or manure) suggest average soil nitrate δ^{18}O in the range of -6.8 $^{o}/_{oo)}$ to -2.5 $^{o}/_{oo}$ respectively.

5 DISCUSSION AND INTERPRETATION

Results of Hydrogen and Oxygen isotopes of water (δ^{2}H and δ^{18}O) have been used previously to demonstrate the link between recent local precipitation and GW in each study area (Liao *et al.,*2005, Somers and Savard, 2008a,b). For the Wilmot watershed, these data also demonstrate a close link between GW discharge (baseflow) and SW. As there are no major watercourses on the Earnscliffe Peninsula, the measurement of base-flow quality is not possible. Furthermore, we have demonstrated that the process of denitrification does not play a significant role in the attenuation of the flux of N from agricultural soils to GW or SW (Savard *et al.,* 2007b). Given these factors, we can assume that local precipitation, GW recharge, and subsequent discharge to SW play the dominant role in cycling of N throughout these environments.

Mean nitrate concentrations in each watershed are 4 to 5 times higher than expected regional background, and based on land use characteristics (see Table 1), can be attributed to agricultural influences. While mean nitrate contents across both study areas are relatively consistent, the fact that nitrate concentrations from at least some individual sampling sites vary by up to 40% between sampling seasons (Somers and Savard 2008), suggests that both aquifers are responding rapidly to recharge events and are sensitive to significant seasonal changes in the flux of N from soils to the aquifer system.

Savard *et al.* (2007b) have used stable isotopes and mass transfer calculations to demonstrate important seasonal differences in the influence of major N sources on the overall flux of N to the Wilmot aquifer. Furthermore, Somers and Savard (2008b) used isotopic mixing calculations and the vertical distribution of hydraulic properties of the aquifer, to conclude that GW sampled from the domestic wells represents a mixture of a small amount (10-25%) of nitrate rich “seasonal” leachate, and a larger portion of “multi-season”, lower nitrate GW, with the leachate dominating the nitrate characteristics of the water by virtue of its high concentration relative to deeper GW.

While specific loads of nitrate leached from the soil layer on a seasonal basis are difficult to quantify on a watershed basis, if we assume that nitrate concentrations in domestic well samples are dominated by the impact of recent leaching to the water table as suggested above, we can use this crude relationship, to make a first order estimate of the relative proportion of nitrate leached to the water table during the growing season (summer and fall) and non-growing seasons (winter and spring).

Estimates of seasonal recharge are made using the approach by Healy and Cook (2002) using observation well data from several sites in central PEI, for the two periods of interest (2003-2005 and 2007-2009). Seasonal recharge estimates were first calculated over the time between sampling events, and subsequently normalized to a daily recharge rate for the period, and then recalculated for 90 day periods representing seasonal recharge amounts. Mean seasonal nitrate concentrations for the individual sampling events are used to represent the concentrations of nitrate in recharging GW over these periods. It is recognized that the use of mean GW concentrations rather than actual leachate concentrations will under-estimate the actual seasonal loading to the aquifer, however here we are only attempting to estimate the relative seasonal (not absolute) N loading to the aquifer (Figure 3.) In each case, the results suggest that while the majority of N applied to agricultural lands occurs during the summer, and in-spite of the fact that each aquifer responds rapidly to seasonal recharge and N loading, the largest portion of N transfer to the aquifer is occurring during the non-growing season. It is suggested this is at least in part a result of the fact that there is negligible plant uptake of N during these periods, whereas during the growing season, available N is rapidly taken up by plant growth.

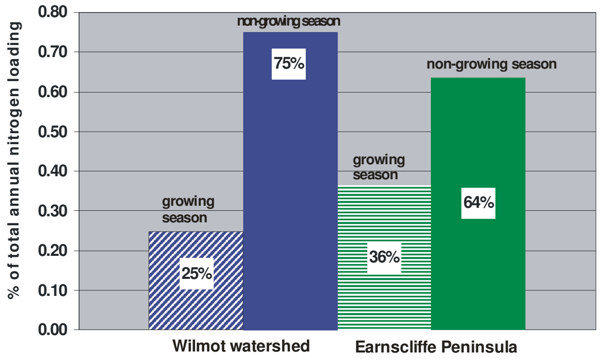

Figure 3. Estimated proportions of growing and non-growing season N fluxes, for Wilmot and Earnslicffe study areas.

Using the approach proposed by Savard *et al.* (2007a), the mean isotopic characteristics of nitrate in GW and principle N sources (Figure 4) are used to estimate the relative contributions of key N sources to the underlying aquifers.

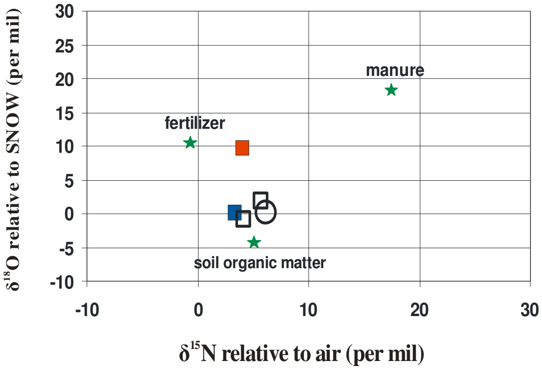

Figure 4. Mean δ^{15}N and δ^{18}O values: Wilmot: summer 2003 as open red square, winter 2004 as open blue square, summer 2004 open red diamond, winter 2005 open blue diamond. Earnscliffe, all seasons green open circle. Green stars represent source end member characteristics for Earnscilffe source apportionment (see Savard et al., 2007 for Wilmot model conditions).

Principle N sources include atmospheric deposition (wet and dry), inorganic fertilizers, manures (including domestic sewage) and soil organic matter. This latter source is somewhat more complex than the former three. In one sense it can be considered as a source, with respect to N fixed by leguminous plants,and the products of nitrification of soil organic matter (assumed to be derived chiefly from crop residues). At the same time it acts as a temporary "sink" for anthropogenicaly derived fertilizer and manure sources with subsequent release during mineralization and nitrification from the overall soil organic matter pool.

It is recognized that the rapid assimilation and cycling of applied N from fertilizers (or manure), within the broader soil N pool will have a tendency to obscure some of the initial isotopic features of these sources (Kendal *et al.*, 2007). Nonetheless, in either setting (Wilmot or Earnscliffe), the dominant anthropogenic source of N is not in question. Indeed, the two study areas were selected specifically to highlight the behaviour of N in these two contrasting agricultural settings (see Table 1). Thus the primary purpose of the current study is not to identify the key sources of N in the respective regions, but to shed light on the behaviour of N in these two contrasting environments. Furthermore, by virtue of analyses of local N sources, we are able to constrain to some degree, the isotopic composition of these end-members.

As a consequence, while we do not purport that the relative proportions of discrete N sources will duplicated the exact proportions of anthropogenic inputs, we do believe such an assessment highlights the importance of specific processes effecting the cycling of N in these two environments. The resulting estimate of relative source proportions is assessed by assuming a constant contribution for the atmosphere (5%) and solving a system of 3 equations with 3 unknowns for the remaining 3 sources.

In the case of the Wilmot watershed, where marked seasonal changes in the isotopic characteristics of nitrate are observed, both winter and summer contributions are considered. In the case of the Earnscliffe region, the very limited seasonal variation in nitrate isotopes does not justify the calculation of seasonally distinct source contributions, and in this case the mean of all GW values of nitrate isotopes are used in the estimation of the relative contribution of discrete N sources. In each setting, the isotopic characteristics of the N source members used in the calculation represent the results of analysis of fertilizer and manure samples, or where necessary, values drawn from the literature (Kendall and Aravena, 2000). A more detailed discussion of source end-member isotopic characteristics for the Wilmot is included in Savard *et al.*, 2007a). Model conditions and key assumptions for the Earnscliffe calculations are generally similar to those initially used in the Wilmot watershed, however the isotopic values of some parameters have been slightly modified to reflect local conditions.

For manure, both δ^{15}N and δ^{18}O have been modified to reflect the dominant use of solid (vs. liquid) manures in this setting. For soil organic matter, δ^{15}N has been increased slightly for the Earnscliffe setting, to reflect the fact that δ^{15}N in areas with a long history of manure application are likely to be somewhat higher than those where inorganic sources have predominated (Kendall and Aravena, 2000), and to coincide better with values observed in GW elsewhere in other locations in PEI, where there is limited, or no inorganic N input.

Oxygen isotope values of -5.9 and $5.0^{0}/_{00}$ are used for soil organic matter and fertilizers, justified by the observation that year round, $\delta^{18}O$ values observed in all Earnscliffe GW samples are consistently low, and must reflect the products of nitrification involving "cold season" (i.e. snow melt and winter/spring) precipitation. This interpretation implies that the majority of the products of nitrification during warmer periods of the year in the Earnscliffe region are rapidly incorporated into crops or the broader soil organic matter pool, and are not leached in substantial quantities to underlying GW.

Mean $\delta^{15}N$ and $\delta^{18}O$ values for GW for the Wilmot and Earnscliffe regions are shown on Figure 4. For the Wilmot watershed we suggest that the summer nitrate flux is marginally dominated by inorganic fertilizer sources, followed in diminishing order by manure inputs and finally by nitrate derived from nitrification of soil organic matter. In winter, the pattern is reversed, with nitrate from soil organic matter clearly dominating the N flux, followed again in diminishing order by inorganic fertilizer and manure sources. In the Earnscliffe setting the contribution of soil organic matter clearly dominates all other sources, followed by manures and a negligible input attributed to inorganic fertilizers.

The strong seasonal differences seen for the Wilmot are inferred to reflect the influence of rapidly available N from inorganic fertilizers, applied in excess of crop needs during the growing season with the incorporation of "warm", summer soil water oxygen during nitrification of ammonia fertilizer components, and the subsequent incorporation of remaining excess N into the soil organic matter pool, and its later release as a result of mineralization and nitrification of soil organic material and during the remaining portions of the year. In contrast, for the Earnscliffe livestock/forage crop setting, there are only slight seasonal differences in nitrate isotopes values in GW, and on annual basis, the contribution from soil organic matter clearly dominates the flux of N to the aquifer year round, with only minor direct evidence of manures inputs, and still less influence of fertilizer inputs. It should be noted that in the case of manure inputs, these calculations only reflect the influence of highly labile components, and some portion of N derived from manures can be attributed to either un-digested plant material (from animal feed) or manure bedding pack in which case the direct contribution of manures to total N loading may be somewhat underestimated.

These differences in seasonal behaviour can be attributed in part to differences in the behaviour of the dominant N source in each case, with N from inorganic fertilizer being rapidly available, whereas the release of N from manures, particularly solid manures, occurs more gradually. In addition, whereas inorganic fertilizers are applied only in the summer, the majority at the time of planting, manure is applied in large amounts from storage in the spring and fall, as well as directly to the land by pastured animals during spring, summer and fall.

Perhaps most importantly, in-spite of marked differences in the seasonal behaviour of N in these two contrasting agricultural settings, it is apparent that regardless of initial N sources, soil organic matter plays a vital role in mediating the cycling of N between agricultural soils and GW, especially during the winter and spring non-growing seasons. When combined with the importance of winter and spring N fluxes (Figure 3), we can suggest nitrification of soil organic matter during the non-growing season mediates the flux of between ½ (Wilmot row crop environment) and ¾ (Earnscliffe livestock environment) of the total annual N flux. It is clear in either case that careful management of this important transitory N pool is necessary in the development of effective measures for the mitigation of nitrate contamination of GW.

The insight provided above regarding the behaviour of N in agricultural settings is based on the assumption of current climatic conditions. Numerous predictions have been made regarding future climatic conditions, and indeed numerical modelling, coupling future climate scenarios (Qiang and De Jong, 2007) with current land use practices (De Jong *et al.*, 2007, Vigneault *et al.*, 2007) at the a province-wide scale suggest increases in future GW nitrate concentrations. In the absence of any change to agricultural practices, these increases are primarily attributable to decreased precipitation in the future, not to increases in N inputs.

Many investigators have commented on the relationship between soil temperatures and the rate of nitrification (*e.g.* Campbell *et al.,* 1970, de Haan and Zwerman 1978,Lepistö *et al*, 2008), with increased soil temperatures correlating with increased rates of mineralization and nitrification. If one considers the importance of the nitrification of soil organic matter in the overall cycling of N in these environments, particularly in winter, and the sensitivity of the rate of mineralization and nitrification to soil temperatures, it would be reasonable to expect that an increase in winter temperatures would accelerate the rate of winter nitrification of soil organic material.

Qiang and De Jong (2007) have estimated generally increasing temperature over the next 50 years, based on scaling down results from a series of more regional global climate change models (GCM). Using CGM2 and HadCM3, with greenhouse gas scenarios IPCC SRES A2 and B2, they concluded the most notable effect of climate change in PEI to be increased temperatures, with more modest, and less certain changes in precipitation regimes. They suggest that minimum temperatures are likely to increase more than maximum temperatures, with the greatest impact occurring during winter. Predicted increases in January mean daily minimum temperatures range from +1.5°C (HadCM3 B2) to +4.6 °C (CGCM2 A2). Assuming that these increases in non-growing season temperatures also are reflected by increases in soil temperatures, then it would seem reasonable that the period of active mineralization and nitrification in soils would be expanded, and the rate of these processes would be accelerated. If such is the case, and as we suggest here, winter nitrification of soil organic material is among the most important processes in annual cycling of N between agricultural soils and aquifers, it becomes even more important to manage soil organic matter wisely. In particular, it will be important in the development of future agricultural practices to delay as much as possible the release of winter derived N until the time of more active plant uptake or crop needs. Such strategies might include delaying of ploughing from fall to spring or the timing of manure application, and a corresponding reduction of N fertilizer inputs at the time of planting.

6 CONCLUSIONS

Using a dual isotope technique, combined with a regime of seasonal sampling, we have described the general behaviour of nitrate in two strongly contrasting agricultural settings, one dominated by row crop production and intensive fertilizer use, and the other characterized by livestock and forage crop production and extensive use of manures. In each case, cycling of N is complex, and cannot be fully understood simply in terms of N inputs and outputs.

Significant differences in the behaviour of nitrate in the two settings are documented, with important seasonal changes in N sources being associated with row crop production, while N sources in the livestock setting are more evenly distributed throughout the year. This contrasting behaviour can be explained in part by differences in the nature of the N sources in the two settings, as well in differences in agricultural practices, highlighting the unique characteristics of N cycling in individual environments. Regardless of these differences in N behaviour, two important common elements are demonstrated: (1) the importance of soil organic matter as a crucial transitory pool of N, mediating the rate and timing of N release to GW; and (2) the significance of nitrate production and transfer to the aquifer during the non-growing periods of the year.

Current management of water resources, including measures designed to protect water quality, are generally based on historical conditions and practices. At the same time, the reality of changing climatic conditions is now well accepted, and long range strategies for the protection of water resources need to consider the impact of future climatic conditions on the processes that will influence water quality. The likelihood of increased winter temperatures can also be reasonably expected to have an influence on soil temperatures, and consequently on the rate and importance of mineralization and nitrification of soil organic matter. While beyond our ability to quantify these factors at this point, given the importance of non-growing season N-fluxes to GW, and the vital role that nitrification of soil organic matter plays in mediating these fluxes, it is vital that these considerations be accounted for in the development of appropriate mitigating strategies.

The reduction of agricultural impacts on GW quality represents a significant challenge, which can only be realized by aggressive actions, guided by a comprehensive understanding of the combined influence of agricultural practices and natural soil processes. Toward this end, stable isotope studies, such as that presented here, can make a valuable contribution.

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