Numerical modelling and isotopes underline climate impacts on groundwater nitrate in temperate agricultural settings

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Abstract

The nitrogen (N) cycle is highly modified by human activities in agricultural settings, with significant impacts on water quality when nitrate in excess of crop needs contaminates freshwater. Will this nitrate problem be counteracted or exacerbated by climate change? To address this question, we have: (1) evaluated how climate change (CC) and associated adaptation of agricultural practices could impact groundwater (GW) nitrate concentrations in the Canadian Province of Prince Edward Island (PEI); and (2) examined the seasonal transfer of nitrate from agricultural soils to GW in a selected intensively cultivated watershed where various N sources are involved, to gain further insight into the potential effects of CC.

Groundwater is the only source of drinking water on PEI, where nearly 5% of domestic wells have nitrate concentrations exceeding the drinking water guideline, and where regions of intense potato cropping have as many as 20% of wells exceeding the guideline. A three-dimensional numerical GW flow and transport model was used to estimate future GW nitrate concentrations under existing land-use conditions and under CC. Without any influence of CC, average GW concentrations are predicted to increase by 11% by 2050. When the effects of CC are considered, nitrate levels are expected to increase by another 6%, and when the adaptation of agricultural practices (APC) are also considered, nitrate levels are predicted to increase by a total of 32%. At these forecasted concentrations, the proportion of domestic wells with GW nitrate in excess of the health guideline would be substantially higher than seen currently, especially in heavily cultivated regions of PEI.

Given the potential for substantially increased GW nitrate concentrations, we examined the main sources and processes involved in N transfer from agricultural lands to aquifers. Groundwater, surface water (SW) and key N sources from the intensively cultivated Wilmot watershed were collected and analyzed for water (δ^2H and $\delta^{18}O$) and nitrate ($\delta^{15}N$ and $\delta^{18}O$) isotope ratios. Sampling was conducted seasonally over two years to capture the behaviour of nitrate. Nitrate isotopes indicate that winter nitrate production is highly significant. The main sources of nitrate are chemical fertilizers during summer (~40% of total load) and, residual crop material (soil organic matter) during winter (~75%). Our study shows that CC and APC are expected to modify the N cycle and to exacerbate the nitrate problem of PEI. Warmer temperatures have the potential to increase the rate of nitrification of soil organic material and the frequency of winter thaws which could in turn enhance the winter transfer of crop-derived N to GW.

Introduction

Given the potential impacts of climate change on water availability, it is becoming increasingly important to evaluate the variations in hydrologic conditions that may occur in light of potentially different climatic conditions. Global warming could affect future nitrate concentrations in GW because it is expected to change the hydrological cycle (Gleick, 1986) as well as the agricultural practices (Olesen and Bindi, 2002; McGinn and Shepherd, 2003). The overall impact will depend on both the magnitude of the change induced by CC on the hydrologic cycle, and how agriculture adapts to different climatic conditions. Recent studies addressing the issue of CC impacts on GW resources have analyzed the effects of temperature and precipitation on stream flow and GW levels (Malcom *et al*., 2000; York *et al*., 2002; Yusoff *et al*., 2002; Allen *et al*., 2004; Sciebek *et al*., 2006), however the impacts on water quality have been studied to a much lesser extend.

In several agricultural regions of Canada, including PEI, the sustainability of aquifers is threatened by high nitrate concentrations. Groundwater is the sole source of potable water in PEI (Figure 1), and it plays a dominant role in determining surface water quality. Consequently, in addition to being a concern for drinking water quality, excessive nitrate levels contribute to eutrophication of surface waters, especially in estuarine environments (Somers *et al*., 1999). In most areas of the island, nitrate concentrations in GW exceed background levels and, in many cases, the recommended maximum concentration limit of 10 mg/L N-NO_3 for drinking water (Somers, 1998; Somers *et al*., 1999; Health Canada, 2004). Over the past decade, several studies have documented the nitrate problem in PEI, noting the association between elevated GW nitrate contents and the intensity of agricultural activities (Somers, 1998; Somers *et al*., 1999; Young *et al*., 2002). A trend of increasing GW and SW nitrate concentrations, in cases doubling, was also documented in some areas of the Province (Somers *et al*., 1999). In the past it has been assumed that application of inorganic fertilizers on row crops constitutes the dominant source of nitrate and that bacterial nitrification leading to labile nitrate is of only limited importance during winters and spring in Northern regions.

Considering the situation described above, we have designed a study which aims at: (1) evaluating the potential impacts of CC and APC on nitrate concentrations in GW over PEI; and (2) assessing the source and fate of nitrate on a seasonal basis in a watershed/aquifer system located in an intense potato-cropping region to more fully examine the potential impacts of climate change on nitrate production and transport to GW.

Methodology

Modelling of groundwater flow and nitrate transport at the island scale

Simulation of recharge

Groundwater recharge was simulated with the quasi-two-dimensional deterministic, hydrologic model HELP (Schroeder, 1994). This model simulates daily movement of water in the ground and accounts for the effects of surface storage, snowmelt, runoff, infiltration, evapotranspiration, vegetative growth, soil-moisture storage and lateral subsurface drainage. The distribution of GW recharge over PEI was obtained by subdividing the Island (5684 km^2) into 21,168 cells of 500m^2.

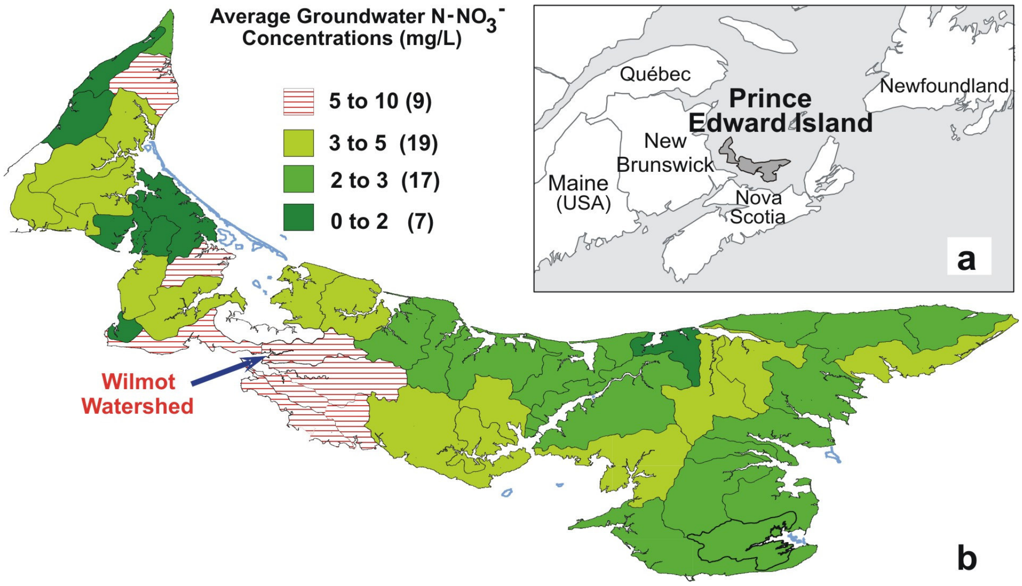

Figure 1. (a) Location of Prince Edward Island in eastern North America. (b) Distribution of watersheds in the Province with a shading code illustrating average nitrate-concentration class for domestic wells. The Wilmot watershed belongs to a class which is particularly at risk, as reflected by their high average GW nitrate concentrations (data from PEI-EEF).

The model was first run with historical records of temperature and precipitation (1960-2001), and calibrated with the average seasonal distribution of recharge and the runoff estimated from stream flow records. Calibration of the seasonal distribution of recharge was carried out using well hydrographs. Runoff was estimated using the filter analysis approach (Furey and Gupta, 2001), and calibration of the total annual runoff was carried out using data from hydrometric stations on three main rivers. Results of calibration show that seasonal recharge and runoff are respectively within 4-17% and 5-12% of the measured data. The average recharge over the entire province was estimated at 369 mm/yr between 1960 and 2001. The values based on HELP simulations vary locally from 0 mm/yr in wetland areas, to 704 mm/yr in areas of coarse sandy soils.

Estimation of Residual Soil Nitrogen (RSN)

The RSN indicator is part of the CANB model (Yang *et al*., 2007), and it estimates the quantity of inorganic soil nitrogen immediately after harvest, for lands delineated by the Soil Landscape of Canada polygon (SLC). Prince Edward Island is divided into 23 of these polygons. RSN integrates inputs such as nitrogen fertilizers, manures and nitrogen fixation by plants, as well as outputs in the form of nitrogen in harvested crops.

The RSN values were estimated using the input values compiled from census years 1981, 1986, 1991, 1996 and 2001 (De Jong *et al*., 2007). These values in kilogram per hectare of cultivated land (kg/ha) were transformed to N-NO_3 concentration in GW for each SLC polygon by considering the farm land area and the quantity of water recharging the aquifer in this polygon. Using this approach, highest concentrations of nitrate in GW generally appear in the center of the province where agricultural activities are most intense.

Modelling of groundwater flow and nitrate transport

The aquifers of PEI consist of conglomerate, sandstone and siltstone red beds. These rock sequences are almost entirely covered by a layer of unconsolidated glacial material (till) from a few centimetres to several meters in thickness. These deposits are generally derived from local sedimentary rock and include both unsorted and water-worked glacio-fluvial and glacio-marine deposits. With few exceptions these surface deposits are not saturated, and do not represent significant aquifers. Upper portions of the aquifer are well fractured, and in most parts of the Island the rock aquifer is unconfined, responds rapidly to individual recharge events and is highly vulnerable to contamination. To represent the GW flow system and to simulate nitrate transport under various scenarios of CC and APC for the entire province, we have used the three-dimensional finite element numerical simulator FEFLOW (Diersch, 2004). The finite element grid design reproduces the conceptual model (Figure 2), for which we have used an effective diffusion of $1x10^{-9}$ m^2/s, and longitudinal and transverse dispersivities of 5 and 0.5m, respectively (see Table 1 for other properties).

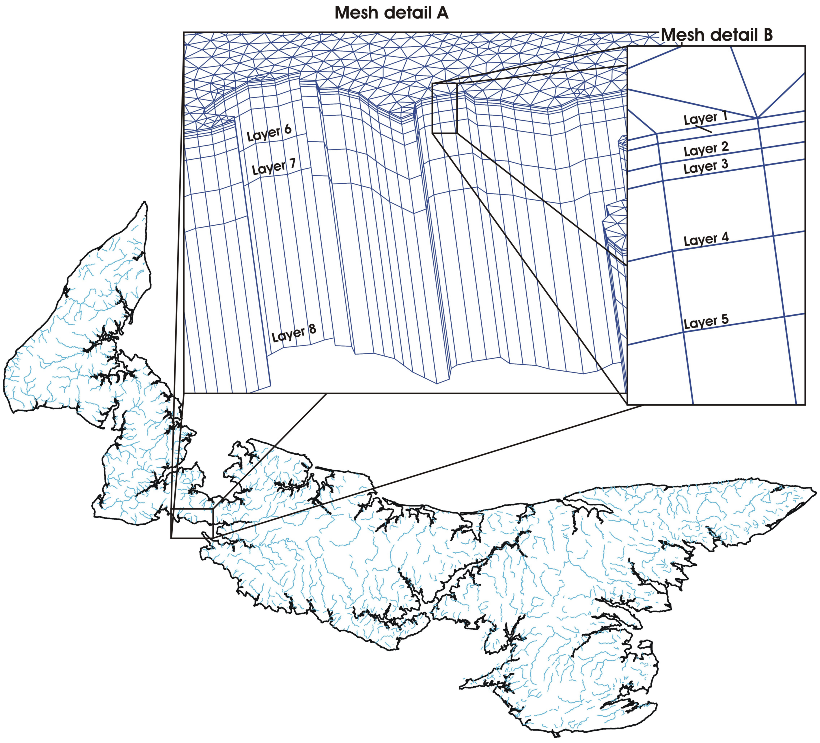

Figure 2. Conceptual model for numerical simulations of nitrate concentrations resulting from climate change and associated agricultural adaptation. Constant head boundary conditions are imposed to rivers and island-ocean limits (adapted from Vigneault *et al*., 2007).

The boundary conditions are constant heads around the Island in the first layer and no flow boundaries in the underlying layers to simulate flow along the saline front. Given that the rivers are hydraulically connected to the aquifers (Francis, 1989; Paradis *et al*., 2006), constant heads were applied on main rivers and streams. The FEFLOW model was calibrated using: (1) 17,000 GW head measurements in domestic wells between 2002 and 2005; (2) the mean base flow recession curve for three main rivers; and (3) records of GW nitrate concentrations in domestic wells compiled between 2000 and 2005.

The difference between measured and simulated nitrate concentrations per SLC polygon after calibration is 0.5 mg/L, meaning that the mass of nitrate on average is underestimated by modelling (Figure 3). However, we should note that nitrate concentrations are distributed randomly around the 1:1 line. This observation stresses the fact that the model reflects the average conditions existing on the Island but does not represent perfectly the concentrations within each watershed. Hence, model predictions will be used to discuss general trends, but not for assessing specific local conditions or absolute GW nitrate concentrations.

Table 1. Field-based and calibrated hydraulic properties for the aquifer-system model over PEI. Kh and Kv are the horizontal and vertical hydraulic conductivities, respectively, and 'n', total porosity.

Layer # Depth (m)	Field K (m/s)	Numerical model		
		K (m/s)	K_h/K_v	n (%)
1 (0-5)	$4.5x10^{-4}$ to $8.1x10^{-5}$	$3x10^{-4}$	10	17
2 (5-10)		$1x10^{-4}$	10	17
3 (10-15))		$5x10^{-5}$	10	17
4 (15-30)		$1x10^{-5}$	100	17
(30-80)	$1.7x10^{-4}$ to $8.4x10^{-7}$	$1x10^{-5}$	1000	17
6 (80-180)	n.d.	$1x10^{-6}$	100	17
7 (180-380)	n.d.	$1x10^{-7}$	10	17
8 (380-880)	n.d.	$1x10^{-8}$	1	17

Climate change scenario

Climatic scenario CGCM2 A2 was selected to run predictive modelling. This scenario is based on the two times carbon dioxide (2xCO2) assumption which is expected to be reached in 2050. This scenario is provided by the Canadian Climate Center General Circulation Model (1959-2001; Table 2). The scenario characteristics were used as inputs to estimate GW recharge using the HELP infiltration model. To obtain a better spatial resolution for weather conditions, the Island was subdivided into four zones covering the area around the Environment Canada weather stations of O'Leary, Summerside, Charlottetown and Monticello.

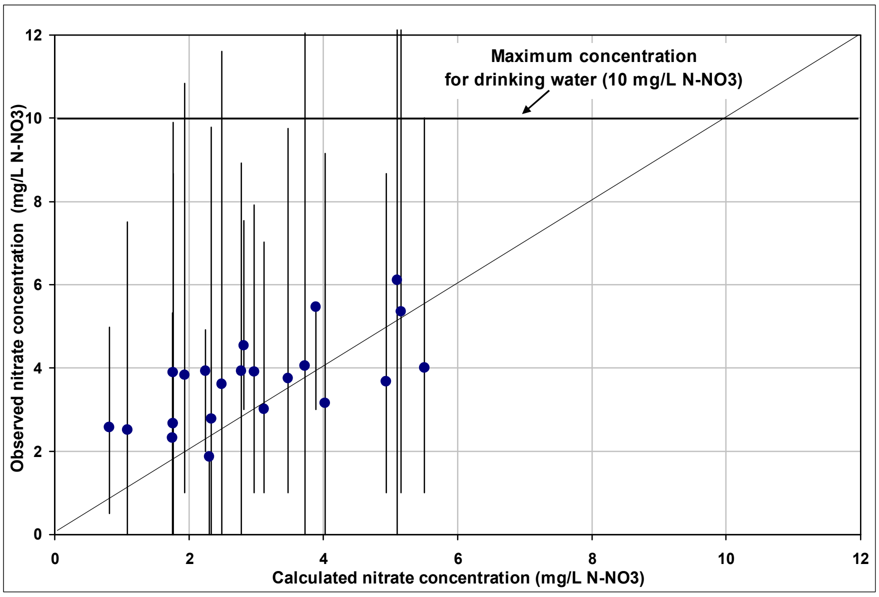

Figure 3. Comparison per SLC polygons (dots) of the average nitrate concentrations measured in groundwater of domestic wells, as a function of the modelled concentrations after calibration. Bars indicate the concentration interval from the 25 to the 75 percentiles. The line is the 45° perfect-fit illustrated for reference (modified from Vigneault *et al*., 2007).

The climatic scenario was used to estimate GW recharge for the 2040-2069 period (Table 2). On average, the CGCM2 A2 scenario predicts drier and warmer conditions than observed in historical data, implying that evapo-transpiration will increase, and runoff will decrease. The resulting APC for the period of 2040-2069 shows that the average RSN value will increase by 15% (5% to 30% depending on the SLC polygon), as based on estimates made by a group of Canadian experts in agriculture (Bootsma *et al*., 2001).

Groundwater flow and mass transport simulations were performed to estimate the potential impact of CC coupled with APC. The simulations with the CGCM2 A2 scenario uses the RSN values, including APC modelled for the 2040-2069 period, along with the GW recharge based on the values obtained from this CC scenario.

Table 2. Changes in climatic conditions for the period 2040-2069 relative to historical conditions (1959-2001) for Prince Edward Island. Values in brackets are % of change.

Scenario	Precipitation (mm)	T (°C)	Evapo-transpiration (mm)	Runoff (mm)	Recharge (mm)
Historical	1173	5.3	583	197	369
CGCM2 A2	1109 (-5)	8 (+51)	618 (+6)	131 (-33)	336 (-9)

Source apportionment of nitrate using dual isotope characterization of seasonal samples

To shed more light on how climate change may affect GW nitrate values, it is pertinent to examine the specific sources and processes involved in the transfer of N from agricultural soils to the aquifer. To better understand these factors we have analyzed nitrate $\delta^{15}N$ and $\delta^{18}O$ values and water $\delta^{2}H$ and $\delta^{18}O$ values in GW, SW and key N sources in the intensively cultivated Wilmot watershed. The Wilmot aquifer has been characterized as a fractured porous media, with fractures representing the main GW flow paths. Samples were collected on a seasonal basis over 8 seasons between July 2003 and May 2005 (Figure 4).

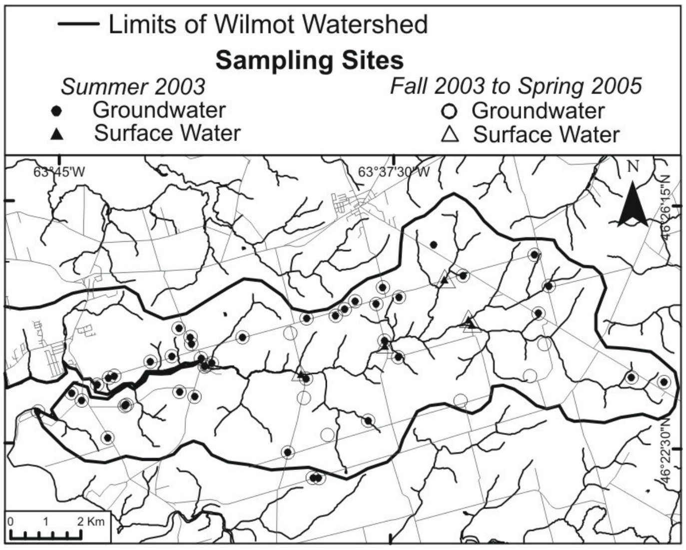

Figure 4. Distribution of samples used for seasonal analyses of nitrate and water isotopes in surface water and groundwater (modified from Savard *et al*., 2007a).

All isotope analyses were performed at the Delta-Lab of the Geological Survey of Canada (Quebec Division; Table 3). An isotopic equilibration peripheral on-line with an isotope ratio mass spectrometer (IRMS) was used to analyze water $\delta^{2}H$ and $\delta^{18}O$ ratios; the precisions obtained on each of these analyses were generally better than 1‰ and 0.2‰, respectively.

Nitrate was concentrated and extracted using the ion-exchange resin and silver nitrate protocols; analyses of the $\delta^{15}N$ and $\delta^{18}O$ values were performed with combustion and pyrolysis peripherals on-line with IRMS, respectively. The average precisions obtained on sample duplicates were 0.2‰ or better (for details see Savard *et al*., 2007a, b).

The sources of nitrate in the Wilmot watershed are atmospheric N chemical species, inorganic fertilizers, manures (including a minor component of sewage) and soil organic matter which includes plant residues, microbial organic matter, etc. Crop residues most likely constitute the main component of soil organic matter because other sources of N immobilized in soil biota are continuously mineralized but in relatively small amounts (Cortez and Schnitzer, 1979; Smith *et al*., 1989). Nitrate isotope data can be used to estimate the relative proportions of nitrate derived from the three main sources in the Wilmot watershed, i.e. inorganic fertilizers, manures and soil organic matter, assuming that the amount of nitrate deposited from the atmosphere is constant during the year. Prince Edward Island receives around 6 Kg/ha/year of atmospheric $N\text{-}NO_3^-$+NH_4 (Environment Canada, public data). Consequently we can assume that the wet and dry atmospheric N input represents approximately 5% of the total annual load in the Wilmot watershed (estimated at approximately 120 Kg-N-NO_3^-/ha/year on the basis of data presented in Atlantic and Agritech, 2006).

Table 3. Summary of sample types used in this study (modified from Savard *et al*., 2007b).

	Tracer	n
Precipitation		
H_2O	δ^2H, $\delta^{18}O$	18
Surface water		
H_2O	δ^2H, $\delta^{18}O$	27
NO_3	$\delta^{15}N$	35
	$\delta^{18}O$	37
Groundwater		
H_2O	δ^2H, $\delta^{18}O$	240
NO_3	$\delta^{15}N$	272
	$\delta^{18}O$	274

n: number of samples.

We can assume that the GW pool of nitrate was not affected by denitrification because the average concentration of dissolved oxygen is 8.8 mg/L, and individual measurements are never below the upper limit for denitrifying conditions of 0.5 mg/L. To obtain the relative proportions of nitrate from the principle sources present in the Wilmot watershed we solve a problem of three equations and three unknown fractions:

$$\delta^{15}N_{measured} = 0.95 \text{ x } (F_s \text{ x } \delta^{15}N_s + F_m \text{ x } \delta^{15}N_m + F_{if} \text{ x } \delta^{15}N_{if}) + 0.05 \text{ x } \delta^{15}N_{atm} \quad \text{(eq. 1),}$$
$$\delta^{18}O_{measured} = 0.95 \text{ x } (F_s \text{ x } \delta^{18}O_s + Fm \text{ x } \delta^{18}O_m + F_{if} \text{ x } \delta^{18}O_{if}) + 0.05 \text{ x } \delta^{18}O_{atm} \quad \text{(eq. 2), and}$$
$$1 = F_s + F_m + F_{if} + 0.05 \quad \text{(eq. 3),}$$

where F stands for fraction, and s, m and if indicate soil organic matter, manures and inorganic fertilizers, respectively. The conditions we have stipulated in making these calculations include (Table 4): (1) the three main sources of N account for 95% of the N loading, assuming an atmospheric contribution of 5%; (2) seasonal $\delta^{15}N$ and $\delta^{18}O$ averages obtained for GW samples from domestic wells reflect the nitrate export from soils to GW at the top of the Wilmot aquifer; (3) the $\delta^{15}N$ average for soil organic matter is assumed to be

+4.7‰, based on isotopic values from PEI watersheds where soil material can be the only source of nitrate; (4) the proportions of nitrate-based and ammonium-based chemical fertilizers used in the Wilmot area are assumed to be 24 and 76%, respectively, i.e., the average proportions of fertilizers sold annually in PEI; (5) aside from nitrate from inorganic fertilizers, seasonal $\delta^{18}O$ values for nitrate derived from soil organic matter, manures and ammonium-based fertilizers must be calculated according to the fact that they are the product of bacterial nitrification, during which two oxygen atoms are taken from soil water and one from free O_2 from the atmosphere (Savard *et al*., 2007a); (6) soil-water $\delta^{18}O$ values involved in the calculation of the $\delta^{18}O$ ratios for the products of bacterial nitrification are assumed to be equal to the $\delta^{18}O$ average for local precipitation measured for each season; (7) the recharge during fall 2003 and summer and fall of 2004 (47, 19, 20mm) was significantly lower than during the other seasons (average of 85mm), so that dilution of the current season water by the former season GW needs to be accounted for to estimate the $\delta^{15}N$and $\delta^{18}O$ ratios of soil water for these periods; and (8) it is assumed that ammonium-based chemical fertilizers present in fall, winter and spring loads were nitrified during the previous summer, and that there is a small portion of the summer load, associated with the period immediately after fertilizer application, that is nitrified during the preceding spring.

Table 4. Model conditions (‰) for the source apportionment based on results obtained for groundwater and potential source samples.

season	**1** Sum 03	**2** Fall 03	**3** W 03-04	**4** Spr 04	**5** Sum 04	**6** Fall 04	**7** W 04-05	**8** Spr 05
GW $\delta^{15}N$	**3.7**	***3.1***	**4.5**	**4.9**	***4.9***	***4.4***	**4.0**	**4.5**
$\delta^{15}N_s$	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
$\delta^{15}N_m$	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2
$\delta^{15}N_{if}$	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6
GW $\delta^{18}O$	**10.9**	***5.9***	**-1.1**	**0.3**	***11.3***	***9.8***	**-0.2**	**2.5**
$\delta^{18}O_s$	3.1	-0.2	-7.4	-4.0	3.1	-0.2	-7.4	-4.0
$\delta^{18}O_m$	17.1	11.0	10.0	12.0	17.1	11.0	10.0	12.0
$\delta^{18}O_{if}$	11.6	12.7	12.7	12.7	11.6	12.7	12.7	12.7

Sum, summer; W, winter; Spr, spring; s, soil organic matter; m, manures and sewages; if, inorganic fertilizers.

Results & Interpretations

Impacts of CC and APC on nitrate concentrations in the watersheds of PEI

The numerical modelling produced average nitrate concentrations per watershed (Figure 5), for the first four layers of the conceptual schema (Figure 2; Table 1), representing the aquifer depths normally exploited by domestic wells. Watersheds are grouped into four classes according to these average-nitrate concentrations. Simulated averages of current concentrations (Figure 5a) are lower than observed concentrations during the 2001-2005 period (Figure 1). This implies that predictions from the numerical simulations for the impact of CC and APC will be somewhat conservative.

The simulated class distribution of watersheds as based on average nitrate concentrations associated with both CC and APC reveals an important increase in contamination levels (Figure 5b), with the number of watersheds at background levels predicted to be 0. The numbers of watersheds belonging to the medium and high classes would become 21 and 11, respectively, representing increases of over 120 and 275% when compared to the simulation for current conditions.

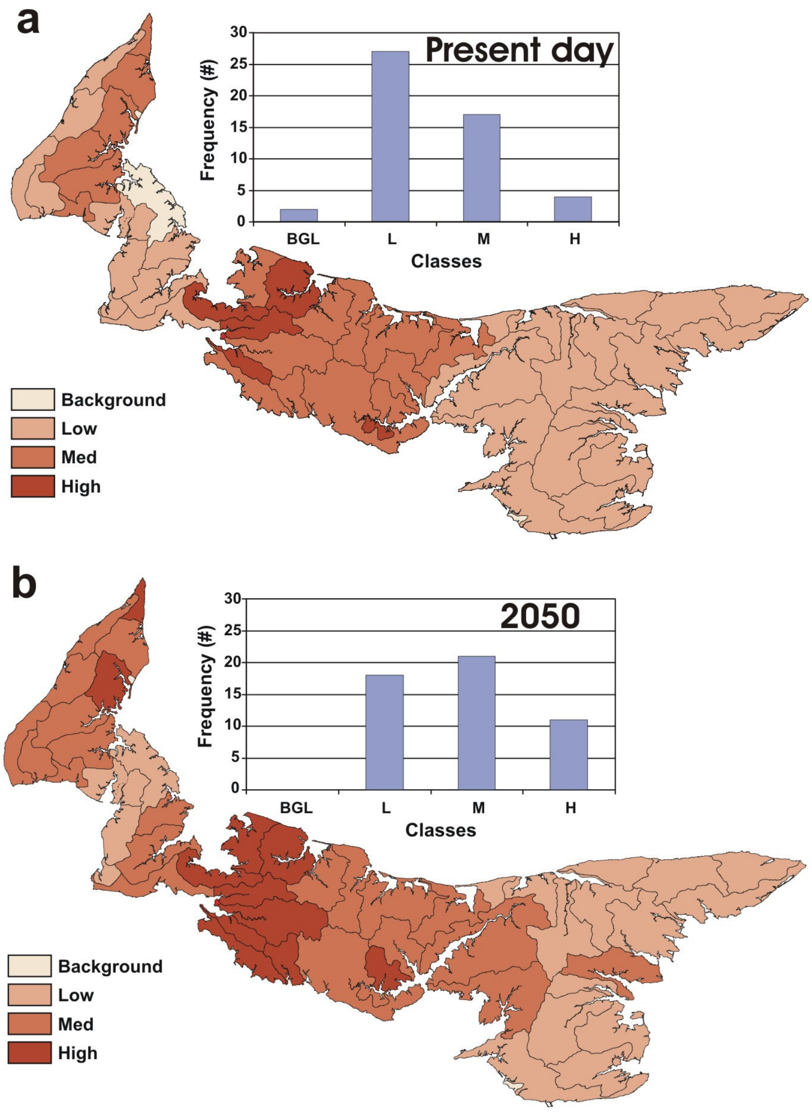

Figure 5. Simulated class distribution of mean nitrate concentrations per watershed, and histogram of the number of watersheds in each class: (a) for present day (2001); (b) for year 2050 with a 20% increase in nitrate loading relative to today, reflecting impact of climate change and the predicted adaptation of the agricultural sector. The background class represents averages lower than 1 mg/L, low, between 1 and 3, med, between 3 and 5, and high, greater than 5 mg/L.

Source apportionment of nitrate in the agricultural Wilmot watershed

Hydrogen and oxygen isotope values for precipitation form the local meteoric water line (Figure 6a). GW and SW isotopic ratios are all appearing on or near the meteoric line, clustering around average δ^2H and δ^{18}O values of -72.5 and -11.1‰, and 73.0 and -11.5‰, respectively (Figure 6b). This data set indicates that GW is derived from local meteoric water and, in turn SW is derived from GW base flow. Such straightforward dynamics from atmospheric precipitation to GW can also be understood as freshwater representing a transport vector dissolving nitrate in air and soil horizons and transporting this load to the top of the aquifer and, by groundwater discharge (base flow), to the river. Combined water and nitrate isotope results also suggest that most nitrate in the Wilmot River are derived from GW as nitrate isotopes of river water and GW also define a common field (Savard *et al*., 2007a, b).

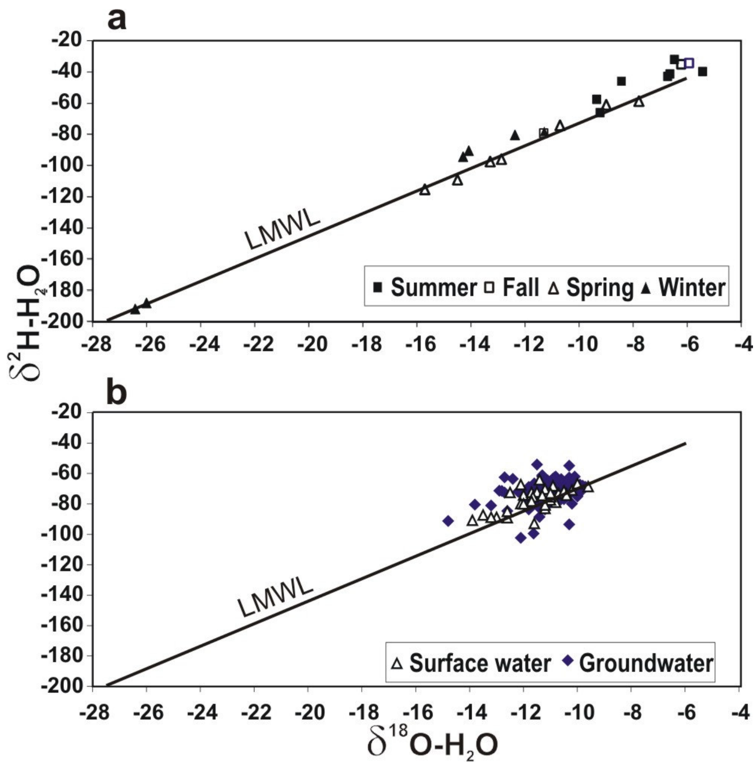

Figure 6. Dual isotope graph for freshwater in the Wilmot river area. (a) Precipitation data form the local meteoric water line (LMWL). (b) Groundwater and surface water data define a common field centered on the LMWL.

Nitrate isotope results plotted in δ^{18}O-δ^{15}N space can help identify the main sources of nitrate, and determine if denitrification or seasonal nitrification have affected the nitrate load to the aquifer (Figure 7). We previously established that nitrification produced by biological mediation is occurring year round in the Wilmot watershed (Savard *et al*., 2007a). Here, we compare the nitrate isotope averages with the domains of potential N sources as determined during this study (Figure 8). It is clear that the δ^{18}O averages for summer and fall are higher than winter and spring values for year 2003-2004 (Figure 8a), indicating that nitrification using winter and spring precipitation with light oxygen isotopes (relative to summer and fall precipitation, Figure 6a) is imprinting the nitrate characteristics of nitrate present at the top of the aquifer during these seasons. The winter average is also lower than the ones for the 2004-2005three other seasons, suggesting again seasonal effects.

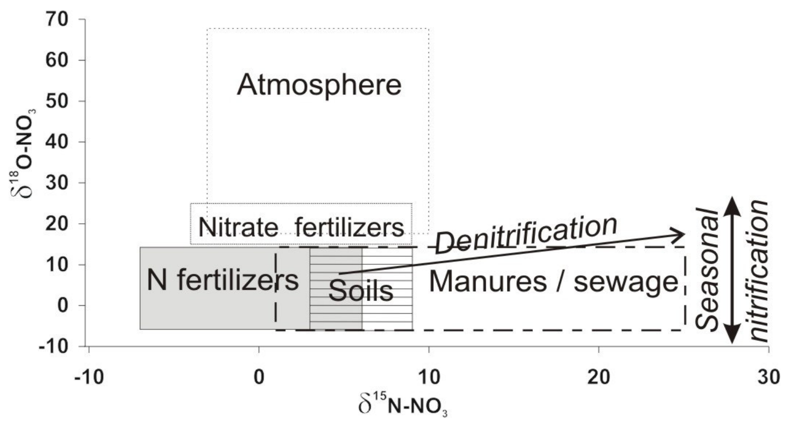

Figure 7. Potential sources of nitrate in agricultural settings and processes modifying nitrate loads in GW (modified from Savard *et al*., 2007a).

The nitrate isotope averages appear in the left half of the soil organic matter domain, between the domains of inorganic fertilizers and manures (Figure 8). Using the averages for each of the eight seasons, we have solved the three equations problem and found important seasonal changes in terms of sources (Table 5).

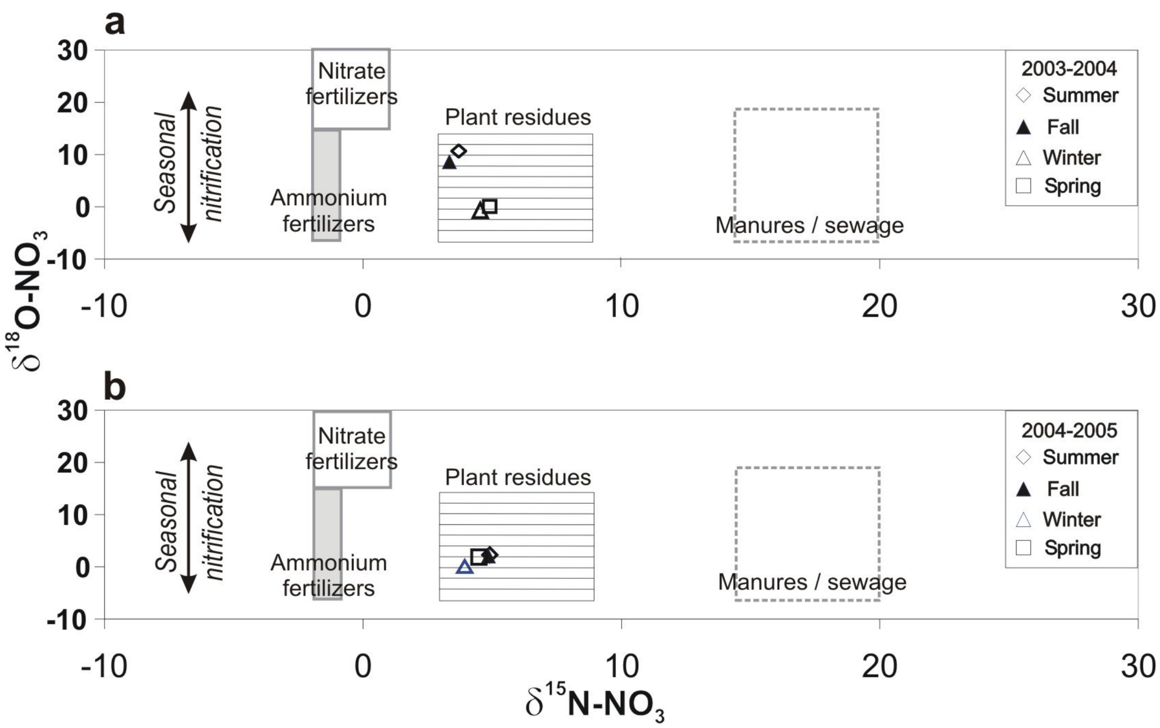

Figure 8. Nitrate isotope results obtained for groundwater of the Wilmot watershed for the eight sessions of seasonal sampling (modified from Savard *et al*., 2007b).

Over the two years of investigation, between 30 and 48% of summer and fall nitrate loads present at the top of the aquifer derive from inorganic fertilizers, and between 28 and 63%, from soil organic matter. Manures and sewage contribute a charge varying between 2 and 20% during these seasons (Table 5). Between 70 and 84% of nitrate originate from transformation of soil organic material during winter and spring, whereas 4 to 18%, and 5 to 8% derive from inorganic fertilizers and manures, respectively. Overall, the nitrate load in GW during the warm period (summer, fall) derives from a mixture of inorganic fertilizers (average of 41%), soil organic matter (39%) and manures (15%), whereas the loads during the cold period (winter, spring) are largely dominated by nitrate from soil organic matter (76%).

Table 5. Solution (in %) to the posed problem of 3 equations for the 8 seasons of sampling during the 2003-2005 period.

Season	1	2	3	4	5	6	7	8
Potential source								
Soil organic matter	32	63	76	84	32	28	72	70
Inorganic fertilizers	48	30	12	04	41	46	18	17
Manures and sewages	15	2	7	7	22	20	5	8

Percentages add to 95% as a yearly atmospheric input of 5% is assumed. 1=summer 2003; 2= fall 2003; 3= winter 2003-2004; 4= spring 2004; 5= summer 2004; 6=fall 2004; 7= winter 2004-2005; 8= spring 2005.

Discussion and Conclusion

The results of large scale modeling for CC and APC impacts will exacerbate the nitrate problem in PEI. On top of increases in average nitrate concentrations simply resulting from current land-use practices (11%), CC is expected to generate an increase of 6%. The largest effect is expected from APC which would raise the total increase on the island to 32%. Based on the current statistical distribution of nitrate concentrations in individual wells, this increase in average nitrate levels could translate into a 66% increase in the number of wells exceeding the health threshold in the Province by the year 2050. These figures give an indication of the overall CC impacts in PEI and clearly, the magnitude of these changes is likely to be most severe in the intensively cultivated watersheds such as the Wilmot watershed.

On a watershed scale, using seasonal variations in oxygen isotope ratios in nitrate, we have inferred that nitrification due to microbial activities is effective all year long, and that nitrate export from soils to GW takes place whenever recharge is occurring, even during winter. The amount of nitrate transferred seasonally can be estimated using seasonal recharge, the source proportions calculated with the isotopic method (Table 5), and the measured concentrations of GW in the aquifer (Savard *et al*., 2007b). It is particularly interesting to quantify the amounts of nitrate transferred seasonally (Figure 9). On average, over 184 Tonnes of $N\text{-}NO_3^-$ were transferred to the aquifer yearly. Soil organic matter, inorganic fertilizers, manures and the atmosphere contributed an average total of 101, 51, 23 and 9 Tonnes $N\text{-}NO_3^-$, respectively. On a seasonal basis 94 Tonnes (11.27Kg/ha) were transferred during the warm period, and 90 Tonnes (10.75Kg/ha) during the cold period, underlining the importance of the winter transfer in the N cycle of agricultural settings in temperate regions. Knowing that global warming will raise temperatures, it is reasonable to expect the contribution from winter nitrification to increase, and more frequent winter thaws would result in a greater export of N from soils to aquifers during winter.

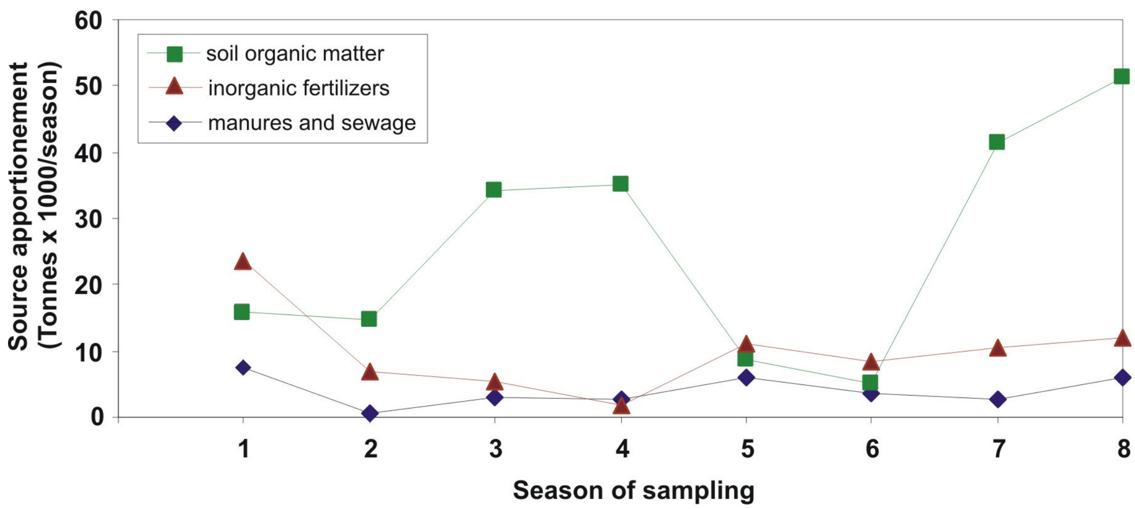

Figure 9. Estimated load of nitrate transferred seasonally from the three main sources to the Wilmot aquifer. This source apportionment is seen as conservative as it is based on nitrate contents of groundwater which are likely lower than in soil water recharging the aquifer.

Collectively, these findings have important implications for strategies to prevent further degradation of water quality in PEI. It is clear that timely and significant changes in agricultural practices are required in order to see improvements in water quality in the future. Even if we ignore the potential impact of CC and if current practices are maintained throughout the next 50 years in PEI, a significant increase of 11 % is predicted to occur. Truly effective strategies aimed at a reduction of N leaching will need to focus not solely on reducing the application rates of inorganic fertilizers, but also on carefully considering the management of the main source of nitrate during winter, namely residual crop material. This is likely to pose special challenges as it will be necessary to utilize organic matter in soils more effectively to reduce its contribution to winter N-leaching to aquifers.

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