Numerical modeling of the dynamics of multisource nitrate generation and transfer, PEI

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ABSTRACT
A numerical model of groundwater flow and nitrate transport was developed to quantify the seasonal contributions of nitrate sources leaching to the aquifer in the Wilmot River watershed, PEI. The transient model takes into account recharge and allows an estimation of seasonally-varying nitrate mass fluxes from chemical fertilizers, manure and soil organic matter, which are validated against isotopic analyses ($\delta^{15}N$ and $\delta^{18}O$). Differences in nitrate source proportions between the model and agronomic mass balance based on cropping practices suggest the nitrate types applied to the fields are modified prior to leaching.

RÉSUMÉ
Un modèle numérique d'écoulement et de transport de nitrate est développé afin de quantifier les contributions saisonnières des sources de nitrate atteignant la nappe dans le bassin versant de la rivière Wilmot. Ce modèle transitoire considère la recharge et permet d'estimer les variations saisonnières des flux de nitrate provenant des fertilisants chimiques, des fumiers et de la matière organique des sols – qui sont validées par des résultats isotopiques ($\delta^{15}N$ et $\delta^{18}O$). Les différentes proportions des sources de nitrate entre le modèle et un bilan de masse agronomique basé sur les pratiques agricoles suggèrent la modification des types de nitrate entre leur application et leur lessivage.

1 INTRODUCTION

Worldwide, groundwater pollution by nitrate is one of the most important environmental challenges of the coming decades, as groundwater in rural areas is often the sole source of potable water while the use of nitrogen-enriched fertilizers is required to meet increasing food production needs (WHO, 2007). Prince Edward Island (PEI), the most important potato producer in Canada, is typical of intensive agriculture that has led to widespread degradation of groundwater quality due to the presence of nitrate (Somers, 1998; Young et al., 2003; Savard and Somers, 2007; CNG, 2008). As a consequence, in many areas of PEI, the average nitrate concentration in groundwater now exceeds background levels (0-2 mg/L) with important increasing trends in the most intensive agricultural watershed (Vigneault et al., 2007).

From an agronomic perspective, the protection of groundwater consists in minimizing excess NO_3 in the root zone when the soil is vulnerable to leaching (Keeney and Follett, 1991). Estimations made for potato crops indicate that even at recommended fertilization rates, the leaching potential of NO_3 ranges between 25% and 50% of the total N input (Somers et al., 2007). A large part of NO_3 in groundwater is attributed to inorganic commercial fertilizers and manure spreading. However, there is transformation of the N-bearing components in the soil, especially the production of vegetal material that is later reintroduced in the N cycle through mobilization and nitrification of non harvested crops. These transformations delay NO_3 availability to leaching after the crop season.

In PEI, geological conditions mostly involve well drained soil and a highly fractured sandstone aquifer. Such conditions favour the rapid transit of excess nitrate to the shallow aquifer, in which most private wells are installed, and ultimately to rivers. NO_3 migration is on-going without attenuation due to well oxygenated waters that preclude denitrification (van Bochove et al., 2007). Groundwater flow, driven by recharge, thus plays a preponderant role on the fate of dissolved N-bearing components as it constitutes the main transport vector.

The study reported here consists of a follow up on previous work carried out in the Wilmot River watershed, which is typical of PEI hydrogeological conditions and has intense agricultural activities (Figure 1). A hydrogeological and geochemical characterization was carried out in that watershed. On this basis, Paradis et al. (2007) developed a numerical model of groundwater flow and nitrate transport. This model reproduced present-day hydraulic conditions, stream flow and nitrate concentrations in the underlying aquifer. Matching of the model with available NO_3 data allowed it to represent the historical evolution of nitrate loadings in the watershed from 1955 to 2000. Savard et al. (2007) seasonally characterized stable isotopes of N ($\delta^{15}N$) and O ($\delta^{18}O$) of nitrate ions in groundwater in the watershed. Their findings were that NO_3 originated from chemical fertilizers, manure and soil organic matter (crop residues), but that the proportions of NO_3 from these various sources changed seasonally.

The overall objective of our study is to better understand the dynamics of nitrate production and leaching to the aquifer. For this purpose, a numerical model was developed to represent transient conditions resulting from the combined effect of groundwater recharge and leachable NO_3 production originating from chemical fertilizers, manure and soil organic matter. Recharge is provided from the infiltration model HELP

(Schroder et al., 1994) using weather data and based on Vigneault et al. (2007) on PEI. Based on Paradis et al. (2007), the numerical model was developed using FEFLOW (Diersch, 2004), a finite element groundwater flow and mass transport simulator. NO_3 mass production in the model was iteratively changed and combined with recharge from HELP, which results in variable NO_3 concentrations and mass fluxes to the aquifer. This mass flux mixes with the groundwater already present in the saturated zone to yield a resulting variable NO_3 total concentration and proportions from the three sources. These values can be compared to the measured NO_3 concentrations and source proportions derived from isotopic analyses. Finally, the model-derived annual NO_3 mass from chemical fertilizers, manure and soil organic matter can be compared to the agronomic mass balance of applied NO_3 fertilizer derived by Somers et al. (2007) based on cropping practices. This comparison can reveal transformations that have occurred to the applied NO_3 sources prior to NO_3 leaching to the aquifer.

2 STUDY AREA

2.1 Land Use, Climate and Recharge

Figure 1 shows the Wilmot River watershed and Table 1 summarizes its main characteristics. The Wilmot River watershed is located in the west central part of Prince Edward Island (PEI) and covers 84 km^2. Farming activities occupy 78% of the watershed area, potato being the main crop generally in rotation on a two to three year basis with cereals, hay or leguminous plants. A minor part of the agricultural land is also used as pasture for cattle. About 11% of land surface remains forested. The basin landscape is dominated by the presence of the Wilmot River that flows westward into Bedeque Bay. The last downstream third of the River is influenced by average tides of 2 m. The physiography is relatively smooth with elevations ranging from sea level to 90 m above mean sea level (AMSL).

The climate of PEI is humid-continental with warm dry summers and cold winters, with common warmer rainy periods during which recharge can occur. Daily recharge was computed using weather data with the quasi-2D deterministic vertical infiltration model HELP (Schroeder et al., 1994). HELP simulates daily movement of water in the ground and accounts for surface storage, snowmelt, runoff, infiltration, evapotranspiration, vegetative growth, soil-moisture and lateral subsurface drainage. Mean recharge over the last 46 years was estimated to be 380 mm/y (Vigneault et al., 2007). For this study, recharge was estimated for the period from June 1, 2003, through May 31, 2005, which was the groundwater sampling period. For these two years, annual recharge was respectively 316 mm/y and 237 mm/y. Figure 2 shows the distribution of daily recharge over these two years, compared to the mean daily recharge. Normally, over a year, the main recharge period is the spring, but there is also with a significant recharge period at the end of fall. It is worth noting that for the simulation period, total annual recharge was respectively 17 and 38% lower than the last 46 years mean value of 380 mm/yr.

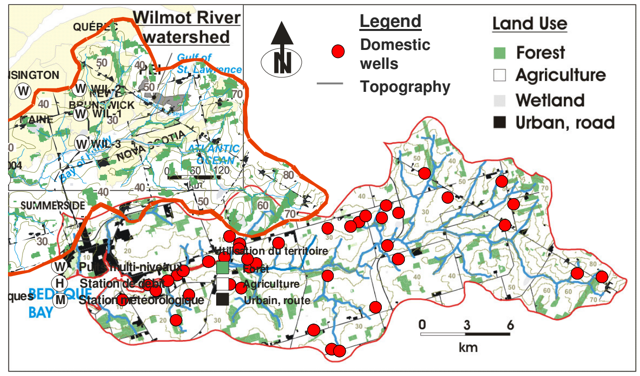

Figure 1. Wilmot River watershed location, physiography and land use. Sampled domestic wells (22) in 2003-2005 are also shown.

Table 1. Characteristics of the Wilmot River watershed

Physiography	
Area	84 km^2
Average Length	17 km
Average width	5 km
Elevation above sea level	0-90 m
Land Use	
Agriculture	76 %
Forest	11 %
Urban	9 %
Wetlands	4 %
Weather (1959-2004)	
Mean precipitation as rain	1140 mm/yr
Mean precipitation as snow	269 mm/yr
Mean annual temperature	5.1 °C
Maximum mean monthly temperature	18.4 °C
Minimum mean monthly temperature	-5.6 °C
Water Balance	
Mean annual evapo-transpiration	438 mm/yr
Mean annual runoff	230 mm/yr
Mean recharge (HELP 1959-2004)	380 mm/yr
Mean recharge (HELP 2003-2004)	316 mm/yr
Mean recharge (HELP 2004-2005)	237 mm/yr
Groundwater Quality (22 Wells)	
Mean nitrate concentration 2003-04	6.40 mg/L
Mean nitrate concentration 2004-05	7.38 mg/L
Standard dev. nitrate conc. 2003-05	4.6 mg/L

2.2 Hydrogeological Conditions

The entire PEI population relies on groundwater for potable water. Most of that groundwater is tapped in a productive sedimentary roc aquifer made up of Permian to Carboniferous cyclic sequences of fine to medium sandstone interbeded with siltstone and claystone. The high storage capacity of the roc matrix coupled with the important recharge provide sufficient water to meet domestic, industrial and agricultural needs. In the Wilmot watershed, most domestic wells are installed in the high yield zone of the top 20 m of the saturated zone in the sandstone aquifer (Mutch, 1998; Rivard et al., 2008).

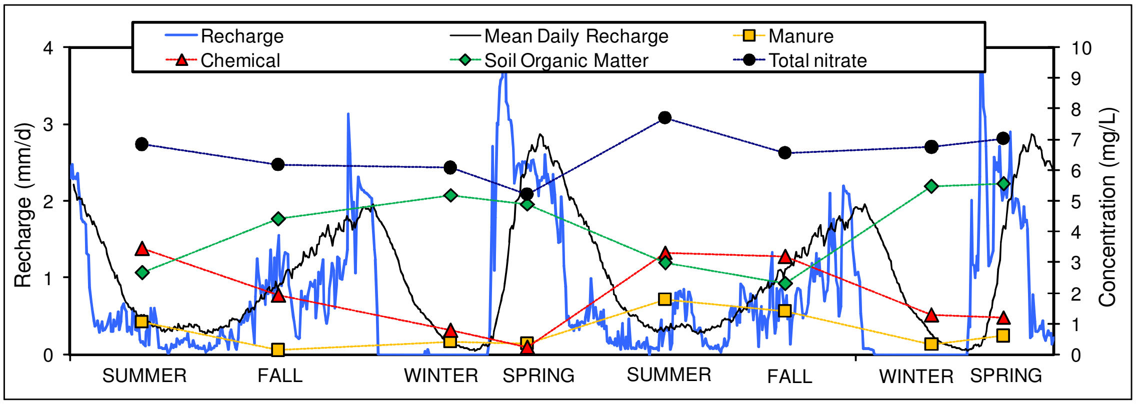

Figure 2. Recharge and nitrate in groundwater during the study period: 1) daily recharge obtained from the HELP infiltration model is compared to the mean recharge over the last 46 years; 2) mean seasonal total nitrate concentration for all sampled wells in the watershed and proportions of this concentration for each NO_3 source (chemical fertilizers, manure and soil organic matter) derived from isotopic analyses (Savard et al., 2007).

The sandstone aquifer represents a double porosity system with fractures providing groundwater flow paths and the porous matrix providing storage capacity. Horizontal bedding of the sandstone forms the main fracture network above 35 m depth (82% of all fractures) (Francis, 1989). These sandstones are characterized by relatively high hydraulic conductivity, between 10^{-6} and 10^{-4} m/s, but with a low storage capacity (1 to 3% under unconfined conditions). Over a large area, the relative homogeneity of the distribution and interconnection of fractures provides a typical 'porous media' response to pumping, especially where the upper fractured bedrock is saturated (Francis, 1989). In contrast, the matrix has a high porosity of about 17%, but a much lower hydraulic conductivity as measured from core permeameter: mostly between 10^{-8} to $5x10^{-7}$ m/s but as low as $5x10^{-10}$ m/s for siltstone (Francis, 1989).

There is a rapid decrease of the aquifer hydraulic conductivity with depth based on profiles measured with packers in open wells (Paradis et al., 2007). This decrease is more important under 20 m depth. The rock aquifer is covered by a permeable unconsolidated sandy till, which averages 4.6 m in thickness but can vary locally (Prest, 1973). Over most of the watershed, this till is unsaturated. The permeable surface soil and fractured rock aquifer represent a relatively vulnerable system to surface contamination.

2.3 Agricultural Nitrate Sources

Most of the Wilmot River watershed (6500 ha, Table 1) is used for farming, 80% of which being dedicated to potato crop, which is made in a two to three year rotation with cereals and hay. Therefore, each year, about 2200 ha are planted for potato, 2200 ha for cereals and 880 ha for hay (Atlantic Agritec Inc., 2006). From these data, an agronomic mass balance was made by Somers et al. (2007) to estimate the total annual N requirements for the watershed. The calculation uses the quantities, timing and cropping practices associated with various N sources for the main crops throughout the entire watershed.

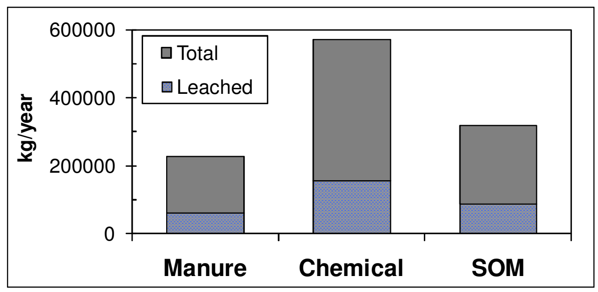

Figure 3. Mass balance of applied fertilizer nitrate sources (manure, chemical and soil organic matter, SOM), as total and leaching to groundwater (Somers et al., 2007).

The mass balance takes into account three major N sources: chemical fertilizers, manure and vegetal crop residues (including N fixed by legume plants and direct atmospheric deposition). The agronomic model also provides an estimate of the N available for leaching based on the portion of nitrate input that is harvested. Figure 3 illustrates results of Somers et al. (2007) for total applied nitrate and the proportion available to leaching, which represents about 27.5% of the total input. Overall, for the entire watershed, the total inorganic and organic nitrate input from entropic and natural sources represents more than 1 million kg/yr, or a nitrate mass flux of 133 kg/ha·yr. Chemical fertilizers represent more than 50% of the input, vegetal crop residues (soil organic matter) about 30% and manure the remaining 20%.

2.4 Nitrate Sources in Groundwater from Isotopes

Total nitrate and nitrate ion isotopes ($\delta^{15}N$ and $\delta^{18}O$) in groundwater were obtained over the entire watershed from 22 domestic wells sampled between June 2003 and May 2005 for 8 consecutive seasons (Figure 1). Total nitrate concentrations ranged from undetected to 14.6 mg/L, with an average of 6.9 mg/L (Table 1) (Savard et al., 2007). The high variability of concentrations between wells, without spatial trend, results from variations in land use, field conditions and well installation. However, seasonal average concentration shows a narrow range of variation between 5.5 mg/L, in the spring time of the 1st year, to 8.1 mg/L, in the summer of the 2nd year. The mean concentration for the 1st year is slightly lower (6.40 mg/L) than for the 2nd year (7.38 mg/L), presumably due to the lower recharge in the 2nd year (237 mm from June 1, 2004, to May 31, 2005), compared to the 1st year (316 mm from June 1, 2003, to May 31, 2004). The dilution effect of recharge on nitrate concentration is further discussed in the next section on model results.

Savard et al. (2007) derived the proportions of nitrate sources from nitrate ions isotopes ($\delta^{15}N$ and $\delta^{18}O$) in groundwater based on a geochemical mixing model and the average seasonal values, and assuming atmospheric contribution was constant. Figure 2 shows these proportions as equivalent nitrate concentrations from chemical fertilizers, manure and vegetal crop residues compared to total nitrate concentration. The three nitrate sources represent 95% of the total concentration; the remaining 5% coming from assumed constant direct atmospheric deposition. Although seasonal total nitrate concentrations remain steady, there is seasonal variability in the proportions of the three nitrate sources making up this concentration: chemical fertilizers and manure have higher proportions during summer (respectively about 50% and 20%), whereas soil organic matter is the main source of nitrate in winter and spring.

From an agronomic standpoint, high proportions of chemical fertilizers in summer and fall agree with a unique late spring to mid-summer application at the start of growing seasons. For manure, this single high proportion season is in contradiction with the two known periods of application, one in late spring or early summer and one in the fall. The proportion from soil organic matter is above 30% all year. This is a strong evidence of bacterial nitrification leading to nitrate leaching, even in winter.

3 NUMERICAL MODELING

3.1 Numerical Model Description

The overall objective of the model is to better understand the dynamics of nitrate production and leaching to the aquifer. Specifically, the model was used to obtain plausible nitrate mass production rates from the three sources (chemical fertilizers, manure and soil organic matter). Combined with recharge independently derived from HELP, these sources of nitrate had to match the total nitrate concentration and the proportions of each source found in groundwater in the Wilmot watershed.

The model was based on the one developed by Paradis et al. (2007) to represent historical nitrate accumulation in the entire aquifer and its potential evolution in the future under climate changes and agriculture adaptation scenarios. That first model represented groundwater flow under steady state with an equivalent porous media having a porosity of 17% taking into account fractures and the porous matrix. This was adequate to show long-term nitrate transport and accumulation in the entire aquifer.

Modifications had to be made to that original model since the focus of the study is the upper part of the aquifer, where domestic wells are installed, and the model has to represent short-term transient changes in nitrate concentration and proportions from three nitrate sources over the two-year period for which geochemical data are available. Besides changing the simulation mode to represent both flow and transport under transient conditions, the two main conceptual changes made to the model were 1) the representation of only the upper part of the fractured aquifer and 2) the use of only fracture porosity, rather than total porosity. The rationale for these changes is further explained.

First, only the upper part of the aquifer was represented in the model. This part is the most fractured and permeable and it is the main groundwater flow path (Paradis et al., 2007). Also, the model has to predict changes in nitrate concentrations in domestic wells, most of which are installed within the first 20 m of the saturated aquifer. Finally, this part of the aquifer is the one that will respond to short-term transient changes in nitrate fluxes.

Second, in preliminary simulations, it was found that only fracture porosity had to be considered in the equivalent porous media to reproduce the magnitude of seasonal changes in nitrate source proportions. Although total porosity controls long-term nitrate accumulation and migration at the scale of the entire watershed, short-term changes in nitrate geochemistry observed in domestic wells seem to be controlled by the storage volume represented only by fracture porosity. Using analytical models, Paradis et al. (2007) found that concentrations in matrix porosity could take about 2 years to equilibrate with fracture porosity concentrations. Since the time scale of seasonal changes in nitrate geochemistry is on the order of weeks or months, exchanges between matrix and fracture porosity thus seem too slow to significantly modify the groundwater isotopic signature. Furthermore, fracture porosity in the upper 20 m of the aquifer was estimated to have a total pore volume representing about 50% of the annual recharge volume. This fracture pore volume is thus flushed twice each year with new recharge. New recharge with distinct nitrate source proportions can impart a new isotopic signature to the groundwater in domestic wells.

The model was developed with the finite element numerical simulator FEFLOW (Diersch, 2004). The 3D numerical grid reproduces the physiography and geology of the watershed (Figure 4). The grid contains 45055 six-node triangular elements and 28506 nodes with an average element area of around 11 250 m^2 (≈150 m x 150 m). The outer limit of the model is the hydrologic water divide on topographic highs, which is presumed apply to groundwater as well and is thus a no flow boundary. The Wilmot River is where groundwater outflow occurs and it was represented by imposed hydraulic heads at the elevation of the river. The outlet of the Wilmot River corresponding to Bedeque Bay was imposed an elevation of 0 m AMSL. Relatively homogenous distribution of surface conditions throughout the watershed (Figure 1; land use, vegetation, slope, soil type, precipitations) allowed the application of uniform recharge and nitrate loads over the model.

Numerical modeling conditions are transient both for groundwater flow, driven by variable recharge, and for nitrate mass transport. The model was run fully saturated with the adaptive mesh option for the first 2 top layers whose thickness varies according to water table elevation changes. The minimum total thickness of the model was 18 m, corresponding to the average depth of domestic wells. To minimize the total number of cells and ease the computing process, the aquifer was vertically divided into 5 layers. The interpolated water table elevation was used as initial hydraulic head for steady state calibration, whose results were used as initial values for transient simulations. To extract representative model results, 22 observation points were placed in the model at the same locations as the domestic wells sampled in 2003-2005. Since there is no information on exact depths of observation wells, observation points were placed in all 5 model layers and concentrations for each layer were weighted based on layer transmissivities.

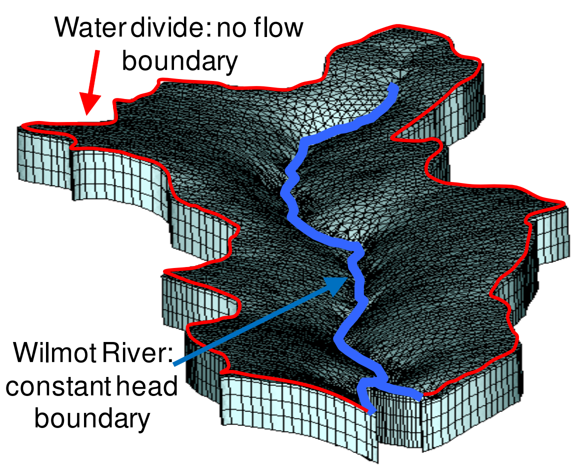

Figure 4. Numerical model grid (vertical x 50).

3.2 Flow Calibration

Water input to the model only occurs as uniform recharge applied on surface nodes. Recharge values estimated from HELP on the basis of weather data were directly used without changes. As done by Paradis et al. (2007), calibration of the hydraulic parameters controlling flow was carried out in two steps. Under steady state, the first step involved the adjustment of hydraulic conductivity (*K*) of each layer to obtain an acceptable fit between simulated and measured hydraulic heads obtained from PEI's Drillers Database. Calibrated parameters presented in Table 2 led to a R^2 of 0.87, no systematic bias and an error generally below 5 m over a range of 50 m. Under transient conditions, the second calibration step consisted in fine tuning *K* and obtaining a representative specific yield (S_y) by comparing model outflow to the river with master baseflow recession curves (MBR) of the Wilmot River. A S_y of about 2% is required to reproduce the MBR, which is in agreement with Paradis et al. (2007).

Table 2. Model parameters for all layers: thickness *b*, horizontal K_h and vertical K_z hydraulic conductivity, specific yield S_y and porosity *n*.

Layer	*b* (m)	K_h (10^{-4} m/s)	K_z (10^{-4} m/s)	S_y (%)	*n* (%)
1	>1*	6	6	1.5	1-3
2	>1*	5	0.5	1.5	1-3
3	5	3	0.3	1.5	1-3
4	5	1	0.01	1.5	1-3
5	5	0.5	0.05	1.5	1-3

* Adaptative mesh option. The same dispersivity was applied to all layers (5 m longitudinal, 0.5 m transverse) and the diffusion coefficient was set at $1x10^{-9}$ m^2/s.

3.3 Nitrate Sources Based on Isotopes

Transient transport simulations were carried out for each individual nitrate source to reproduce its measured equivalent seasonal concentration (Figure 2). Daily nitrate fluxes were defined to match the time step of daily recharge provided by HELP. In FEFLOW, nitrate mass was applied as a second kind (Neumann) condition (mass flux in $g/m^2 \cdot d$) at surface nodes, independent of recharge, which allow the evaluation of the potential dilution effect of recharge on nitrate concentrations. To simplify the calibration process, nitrate inputs were defined as simply as possible using square (on/off) functions, although gradual changes in nitrate production are expected in the natural system.

The initial nitrate mass flux functions were based on isotopic results of Savard et al. (2007) following a three-step process. First, the proportion of each nitrate source was used to apportion their respective seasonal nitrate concentrations based on total concentration, thus providing an equivalent concentration (Figure 2). Second, an estimate of the seasonal mass production for each source was obtained from the product of concentration by the seasonal recharge volume. Third, the nitrate mass flux ($g/m^2 \cdot d$) was obtained from the ratio of total mass production by the number of days of source application and recharge considered.

Porosity controls the volume of groundwater in the aquifer available for the mixing of leached nitrate concentrations. To reproduce the observed magnitude of changes in equivalent concentrations of the three nitrate sources, parametric simulations were carried out with values of porosity initially ranging from 0.1% to 10%. Simulations then focussed on the more probable range of 1% and 3%. Figure 5 shows simulated concentrations for each nitrate compared to observations. Simulated values are average for of the 5 layers of the model weighted by layer transmissivities at the 22 observation points where sampled domestic wells are located. These calibrated results were obtained by iteratively adjusting nitrate mass fluxes and their timing for three porosity values (1, 2 and 3%), with the best fit obtained for 2% porosity. Individual source and total nitrate concentrations (6.51 mg/L for the model and 6.89 mg/L for field measurements) for the same period are well represented by the model.

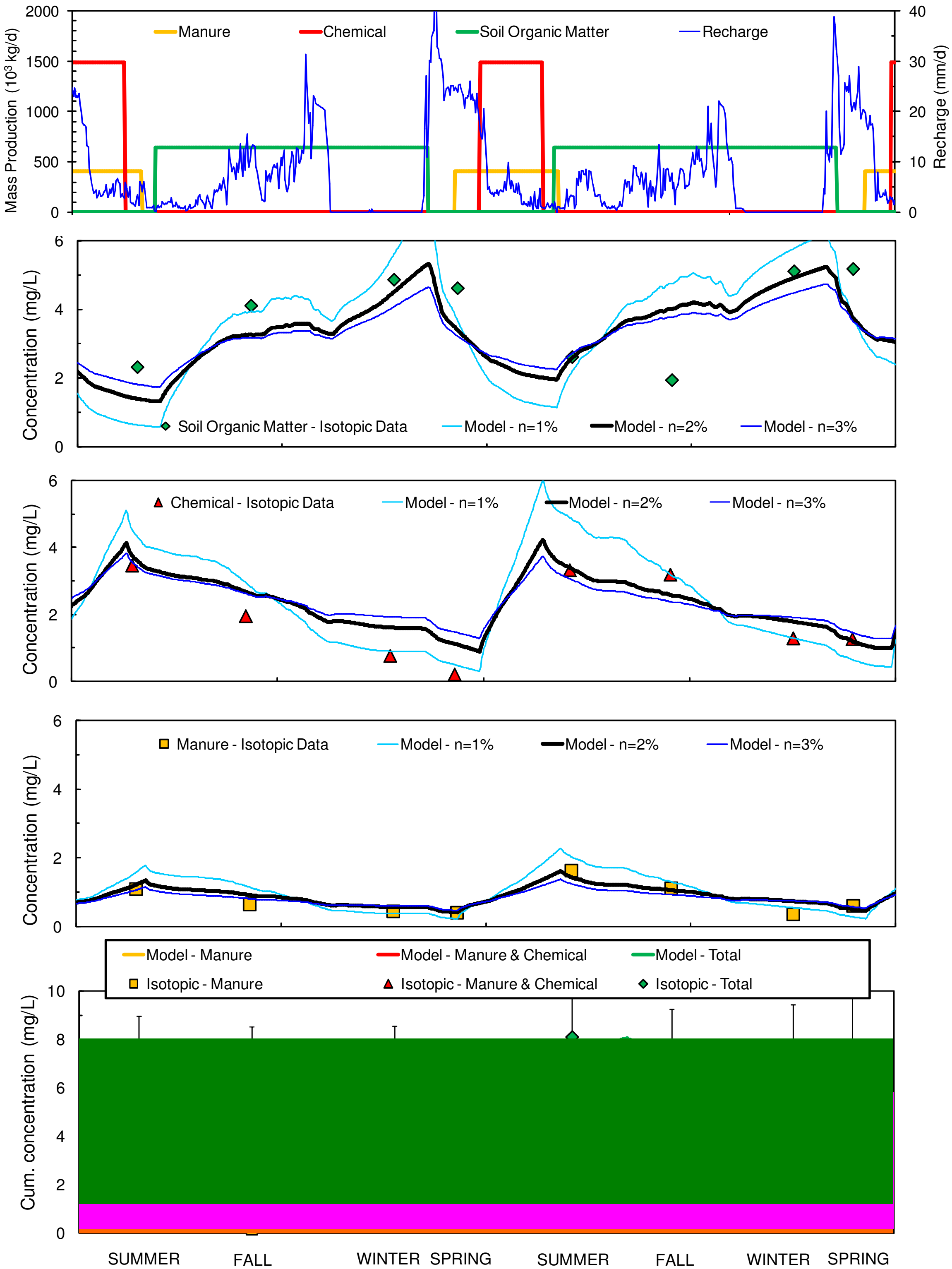

Figure 5. Calibrated nitrate mass productions and concentrations for the three nitrate sources. The top figure shows the input functions for recharge obtained from HELP and the nitrate mass productions for each source represented by square functions. For three porosity values (*n*=1, 2 and 3%), the central three graphs compare simulated concentrations to values derived from isotopes for each source. The lower graph compares simulated (*n*=2%) and observed total nitrate concentration and the proportions of the total concentration made up of each nitrate source. The bars associated with total concentrations for the lower graph represent the standard deviation of measurements in the 22 wells.

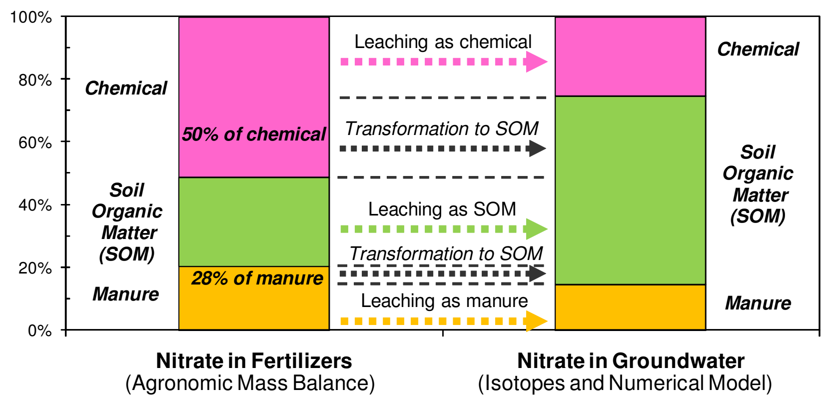

Figure 6. Proportions of the sources of leached nitrate applied as fertilizers (Somers et al., 2007) compared to the proportions of nitrate sources found in groundwater according to numerical modeling and isotopic analyses (Savard et al., 2007). Comparison allows the inference of the transformation of fertilizers into soil organic matter prior to leaching.

4 NITRATE TRANSFORMATION

Figure 6 compares the agronomic nitrogen mass balance for the Wilmot River watershed estimated by Somers et al. (2007) to the proportions of nitrates sources in groundwater estimated by modeling. Results from the mass balance represent the proportion of the three sources of nitrate applied as fertilizers that could have leached to the aquifer. Numerical modeling results represent the proportions of the nitrate mass originating from these three sources that have actually reached the aquifer. Comparison of these proportions thus allows the inference of the proportions of chemical and manure fertilizers that were integrated into vegetal and organic matter prior to their nitrification and leaching to the aquifer. Although total nitrate mass input to the aquifer estimated from the numerical model, 257 000 kg, is 26% lower than the total agronomic estimates of 307 000 kg, these results are considered equivalent due to the large uncertainty related to the agronomic mass balance. Since numerical modeling results are constrained by hydraulic heads, MBR recessions and isotopic data, they are considered more representative.

Figure 6 indicates that more than 50% of nitrates originate from chemical fertilizers, which only represent about 25% of nitrates present in groundwater, thus implying a 50% transformation into vegetal and soil organic matter prior to leaching to groundwater. A similar process is inferred to occur for manure. The year-long transformation of soil organic matter (including crop residues) into leachable nitrate, even during winter months, and the large proportion of nitrate originating from this source make removal of crop residues an important practical means of reducing nitrate leaching.

5 CONCLUSION

In order to better understand the dynamics of nitrate production and leaching to the Wilmot River watershed aquifer, a numerical model was developed to represent conditions resulting from the combined effect of groundwater recharge and leachable NO_3 production originating from chemical fertilizers, manure and soil organic matter. NO_3 mass production is combined with recharge to obtain variable NO_3 concentrations and mass fluxes to the aquifer. Total NO_3 concentration and source proportions were compared, respectively, to the available NO_3 concentrations in private supply wells and the source proportions derived from isotopes ($\delta^{15}N$ and $\delta^{18}O$). Model-derived annual NO_3 mass from chemical fertilizers, manure and soil organic matter were compared to the agronomic mass balance of applied NO_3 fertilizer derived by Somers et al. (2007) based on cropping practices.

Results provide insights on hydraulic properties of the aquifer and on nitrate production and transformation. The model used recharge estimated by the HELP infiltration model using weather data. Model calibration relied on measured hydraulic heads to determine hydraulic conductivity and transient modelling of river flow rates to specify a representative specific yield (1.5%).

Nitrate concentration and isotopes were used for the calibration of porosity (2%). These values correspond mostly to fracture porosity as the total porosity of the aquifer is estimated at about 17% (Paradis et al., 2007). The relatively large annual recharge corresponds to about twice the pore volume of fractures in the more permeable upper part of the aquifer. This condition leads to a rapid exchange of the groundwater present in the upper part of the aquifer by recharge, which induces rapid seasonal changes in groundwater NO_3 concentration and source proportions according to the variations in nitrate fluxes from chemical fertilizers, manure and soil organic matter.

Domestic wells are installed in the shallow part of the aquifer (first 20 m of the saturated zone). Hydrogeological conditions are such that it is the aquifer's most vulnerable part in which groundwater can easily be contaminated by surface agricultural activities. On the other hand, the rapid renewal of shallow groundwater in the fracture network of the top part of the aquifer implies that rapid groundwater quality changes could occur in fractures if nitrate influx were reduced. Counter-diffusion in fractures of nitrate accumulated in the porous matrix could partly offset or delay groundwater quality recovery, but this process was not represented by the numerical model used in this study. This quality recovery is not expected to be as fast for deeper parts of the aquifer and surface water due to the large accumulation of nitrate in the porous matrix of the entire aquifer system (Paradis et al., 2007).

Nitrate source proportions reaching the aquifer, based on the model, are different from nitrate mass proportions applied to fields as fertilizers based on cropping practices (Somers et al., 2007). This comparison indicates that 50% of chemical and 28% of manure fertilizers are first transformed to vegetal and soil organic matter, which is later nitrified and leached to the aquifer. NO_3 from soil organic matter is the dominant nitrate source to groundwater in fall and winter. This finding implies that efforts in minimizing NO_3 leaching to the aquifer should focus on better managing plant residues in order to reduce nitrate availability to leaching during non-growing periods when there is no plant uptake.

ACKNOWLEDGEMENTS

The authors would like thanks Yves Michaud for the critical review of the manuscript. This study was supported by the Geological Survey of Canada under the Groundwater Resources Inventory program (GSC contribution 11739), by the Climate Change Action Fund and by a NSERC Discovery Grant held by R.L.

REFERENCES

Atlantic Agritec Inc., 2006. Agricultural land use practices in the Wilmot River watershed area of PEI. Report to the Department of Environment, Energy and Forestry, February 2006.

Commission on Nitrate in Groundwater (CNG), 2008. *Report of the Commission on Nitrate in Groundwater*. Document Publishing Centre, Prince Edward Island, June 2008, 56 p. www.gov.pe.ca

Diersch, H.J.G. 2004. FEFLOW: Finite Element Subsurface Flow and Transport Simulation System – Reference Manual. WASY Institute. 277 pp.

Keeney, D.R., Follett, R.F., 1991. Managing nitrogen for ground water quality and farm profitability: Overview and introduction. In: R.F. Follet et al. (eds) *Managing nitrogen for ground water quality and farm profitability*, 1–7. Soil Science Society of America, Madison, WI.

Francis, R M. 1989. Hydrogeology of the Winter River Basin Prince Edward Island. Report, Dep. of the Environment, Water Resources Branch, Prince Edward Island, 117 pp.

Mutch, J., 1998. The hydrologic cycle and water movement. Nitrate – agricultural sources and fate in the environment – perspectives and direction. *Proceedings of the workshop,* Eastern Canada Soil and Water Conservation Centre (1998), 3–7.

Paradis, D., Ballard, J.-M., Lefebvre, R. 2007. Watershed-scale numerical modelling of nitrate transport using spatially uniform averaged N inputs. *In* Savard. & Somers, ed., *Consequences of climatic changes on contamination of drinking water by nitrates on Prince-Edward-Island*. Climate Change Action Fund, A881/A843, 52-65.

Prest, V.K., 1973. Surficial deposits of Prince Edward Island. Geological Survey of Canada, Map "A", 1366A.

Rivard, C., Paradis, D., Paradis, S.J. , Bolduc, A., Morin, R.H., Liao, S.L, Pullan, S., Gauthier, M.J., Trépanier, S., Blackmore, A., Spooner, I., Deblonde, C., Fernandes, R., Castonguay, S., Michaud, Y., Drage, J., Paniconi, C. 2008. Canadian groundwater inventory: Regional hydrogeological characterization of the Annapolis-Cornwallis Valley aquifers. GSC Bulletin 589, 86 p. & Appendix.

Savard, M.M., Paradis, D., Somers, G., Liao, S., van Bochove, E. 2007. Winter nitrification contributes to excess NO_3^- in groundwater of an agricultural region: A dual-isotope study. *Water Resources Research* 43, W06422, doi:10.1029/2006WR005469.

Savard, M.M. Somers, G., ed., 2007. *Consequences of climatic changes on contamination of drinking water by nitrates on Prince-Edward-Island.* Climate Change Action Fund, A881/A843.

Schroeder, P.R., Aziz, N.M., Lloyd, C.M., Zappi, P.A., 1994. The Hydrologic Evaluation of Landfill Performance (HELP) Model: User's Guide for Version 3. EPA/600/R-94/168a, U.S. EPA, 116 pp.

Somers, G.H., 1998. Distribution and trends for the occurrence of nitrate in Prince Edward Island groundwater. Proceedings, *From nitrate-agricultural sources and fate in the environment - Perspectives and Direction*, Eastern Canada Soil and Water Conservation Center, Grand Falls, N.B., 19-26.

Somers, G., Savard, M.M., Paradis, D., 2007. Mass balance calculations to estimate nitrate proportions from various sources in the agricultural Wilmot watershed on Prince Edward Island. GeoEdmonton '08, *61th Canadian Geotechnical Conference and 9th Joint CGS/IAH Conference*, Edmonton, Canada, Sept. 21-24, 2008, 212-218.

van Bochove, E., Thériault, G., Chérif, R., Ziadi, N. MacLeod, J., 2007. Nitrogen Leaching from Agricultural Soils at the Watershed Scale. *In* Savard. & Somers, ed., *Consequences of climatic changes on contamination of drinking water by nitrates on Prince-Edward-Island*. Climate Change Action Fund, A881/A843, 21-28.

Vigneault, H., Paradis, D., Ballard, J.-M., Lefebvre, R., 2007. Numerical modelling of the evolution of groundwater nitrate concentrations under various Climate Change scenarios and agricultural practices for Prince Edward Island. *In* Savard. & Somers, ed., *Consequences of climatic changes on contamination of drinking water by nitrates on Prince-Edward-Island*. Climate Change Action Fund, A881/A843, 93-109.

World Health Organization (WHO), 2007. *Nitrate and nitrite in drinking-water: Background document for development of Guidelines for Drinking-water Quality*. WHO/SDE/WSH/07.01/16.

Young, J., Somers, G.H., Raymond, B., 2003. Distribution and trends for nitrate in Prince Edward Island groundwater and surface waters. Proceedings, *2002 National Conference on Agricultural Nutrients and their Impact on Rural Water Quality*, 313-319.