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Land-use based modeling approach for determining freshwater nitrate loadings from small agricultural watersheds

Pierre Grizard, Kerry T. B. MacQuarrie and Yefang Jiang

ABSTRACT

Nitrate released from a variety of land-use activities is a major factor in the degrading conditions observed in many watersheds and estuaries. In this research a spatially lumped model is developed to estimate annual nitrate loads and concentrations from over 100 small watersheds in the Canadian province of Prince Edward Island (PEI). Nitrate source concentrations are associated with major land-use categories, and nitrate attenuation, based on the width of riparian zones, and transport delay due to groundwater residence time are simulated. To investigate the uncertainty of the results, model parameters were selected using a Latin hypercube sampling method. Nitrate concentrations from 12 watersheds were used for model calibration ($R^2 = 0.91$), while 118 other watersheds were used for verification purposes ($R^2 = 0.82$). Overall, the lumped parameter model is shown to be a useful tool for simulating annual nitrate loadings from agricultural watersheds when detailed spatiotemporal agricultural land-use data are available. For PEI the model results indicate that nitrate loadings to estuaries are strongly related to agricultural land, especially the land area in potato production.

Key words | land use, modeling, nitrate loading, watersheds

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HIGHLIGHTS

1. A new lumped parameter model was developed to estimate annual nitrate loadings
2. The model was calibrated and verified for the period 1996–2012
3. Better accuracy was achieved for watersheds larger than 6 km^2
4. For Prince Edward Island, 91% of the total nitrate load is simulated to come from agricultural areas

LIST OF SYMBOLS, NOMENCLATURE OR ABBREVIATIONS

BFI	baseflow index
C_i	initial nitrate concentration
C_L	annual average nitrate leaching concentration
C_o	average nitrate concentration of the water coming from the watershed
D	hydrodynamic dispersion coefficient
EW	excess water
EW_i	initial excess water
GIS	geographic information system
i	hydraulic gradient
K	hydraulic conductivity
L	average groundwater flow path length
M_D	delayed nitrate loading
M_O	total nitrate loading
N	nitrogen
n	porosity
NB	New Brunswick

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NorSt-EMP	Northumberland Strait – Environmental Monitoring Partnership
NS	Nova Scotia
pdf(s)	probability distribution function(s)
PEI	Prince Edward Island
r	ratio of water table elevation to ground surface elevation
RMSE	root mean squared error
S	slope
SSR	sum of squared residuals
t	time
TN	total nitrogen
V	flow velocity

INTRODUCTION

Maintaining an acceptable balance between agricultural land use and environmental quality especially in the case of nutrients in surface waters and groundwater can be difficult. This challenging task is not always fulfilled as evidenced by conditions in the Canadian province of Prince Edward Island (PEI), which is one of the most notable areas of the country with regard to the negative impacts of agricultural land use on water quality. In PEI, intensive potato production has contributed to elevated nitrate concentrations in both groundwater and surface water (Savard *et al.* 2007a; Zebarth *et al.* 2014), and more than a dozen anoxic events in estuaries have been recorded annually since 2002 by the PEI Department of Fisheries, Aquaculture and Environment. Danielescu & MacQuarrie (2011) have noted that although many factors may affect estuarine functioning (e.g. tidal flushing), the current poor conditions reported (e.g. anoxic events, proliferation of *Ulva* sp.) in two small estuaries in PEI are expected to be largely related to elevated nitrogen loadings from the adjacent watersheds.

Although nitrogen exists in several inorganic and organic chemical forms, nitrate has been shown to be the dominant species in waters in PEI, where it is estimated that more than 90% of the total nitrogen (TN) in fresh waters is nitrate (Danielescu & MacQuarrie 2011). The sources of nitrate in PEI groundwater and streams include chemical fertilizers, manure, sewage, soil organic matter, and atmospheric deposition (Savard *et al.* 2010). PEI has approximately 20% of its land area under potato production rotations (Jiang *et al.* 2011), and the large quantities of chemical fertilizer that are applied are not entirely taken up by the crops.

Calibrated models can be powerful tools for providing information regarding nitrogen loadings to water bodies over larger spatial areas and for various time frames. The simulation of nitrate transport and fate in watersheds may involve chemical, biological, and physical processes that can be modeled with widely varying levels of complexity. Spatially distributed groundwater flow models coupled with a solute transport simulator represent process-based models and, with sufficiently detailed parameter information, can accurately depict the dynamics of the processes involved. However, capturing this level of detail is made at the expense of two important criteria, the amount of input data required for model parameterization and calibration, and the computational time. To find a compromise, process complexity and spatial heterogeneity are often simplified to produce models that are more amenable for use by decision-makers at the spatiotemporal scales desired for management of watersheds.

The main goal of this study is to improve the ability to quantify nitrate loadings from small watersheds to coastal waters, in particular in the many estuaries surrounding PEI. The research objectives were to:

(a) improve upon existing watershed-based nitrate loading models for PEI,
(b) have the model run quickly and with readily available watershed information, so that it will be useful for decision-makers, and
(c) undertake a systematic parameter uncertainty analysis and determine the influence of uncertainty on key model outputs (e.g. flow, loadings, and concentrations).

DESCRIPTION OF THE STUDY AREA

PEI, located in the southern Gulf of Saint Lawrence, is the smallest Canadian province with a land area of 5,660 km^2. PEI agricultural land is mainly dedicated to the production

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of potatoes, which accounts for 20% of the total land area. Potato production increased from 11,982 ha in 1951 to 43,770 ha in 1996, and subsequently decreased to 35,030 ha in 2011. Potatoes are typically cultivated in the center and west of the island (Figure 1) in rotation with cereals for the second year and hay/grass for forage for the third year (Savard *et al.* 2010). A more detailed summary of the agricultural land uses and practices in PEI can be found in Jiang *et al.* (2015).

The land elevation in PEI reaches a maximum of 142 m, with an average of 30 m above sea level. The surficial geology consists of glacial till and glacio-fluvial deposits with an average thickness of 4 m (Rivard *et al.* 2008b). The bedrock of the island consists of 'red bed' fractured sandstone deposited from the late Carboniferous to early Permian. The upper most ~150 m of the bedrock forms an unconfined/semi confined fractured aquifer that provides 100% of the drinking water for the population. The aquifer yield potential is good with reported hydraulic conductivities ranging between 4.3×10^{-6} and 2.5×10^{-3} m/s, and total porosity averaging between 0.05 and 0.1 (Rivard *et al.* 2008a). Jiang & Somers (2009) also reported similar values for hydraulic conductivity, ranging between 1×10^{-7} and 7×10^{-4} m/s, and an effective porosity of 0.05–0.07 depending on depth.

The climate of PEI is characterized by long and cold winters and warm and dry summers. The mean annual temperature is 5.5 °C with a monthly average temperature varying between −7.7 °C in January and February and 18.5 °C in July based on historical data from 1960 to 2011 at the Charlottetown climate station. The annual precipitation is on average 1,165 mm with approximately 26% of the precipitation falling as snow from November to April. Infiltration of precipitation during the fall and early winter, when evapotranspiration is reduced, and snowmelt infiltration in the spring between March and May, are the primary periods of groundwater recharge (Lamb *et al.* 2019).

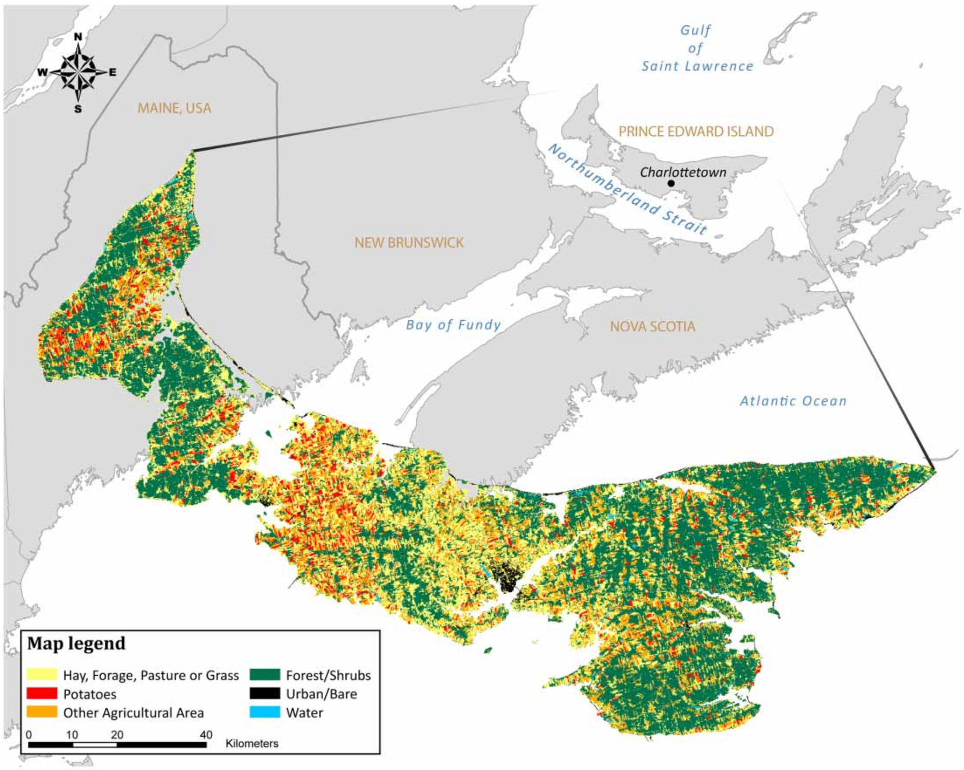

Figure 1 | Main land-use categories in PEI in 2009 adapted from Statistics Canada. The location of the province is indicated in the background map. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wqrj.2020.015.

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METHODS

Conceptual model

The model developed is designed to provide annual nitrate loadings and concentrations, which are particularly relevant to long-term watershed management. The model is spatially lumped, meaning that each watershed is considered as a single entity with no smaller subdivision, and no interaction occurs among adjacent watersheds. The conceptual model has some similarities with that presented by Jiang *et al.* (2015); however, the major advancements in the current model include the addition of a time (transient) formulation with an annual time step, nitrate attenuation based on riparian zone characteristics, and refinement of agricultural land-use categories.

The structure of the model is presented in Figure 2. The first component of the model involves estimating the average annual nitrate leaching concentration (C_L) for the selected watershed. This concentration is established by determining the contributing area of each land-use category within the watershed and assigning a corresponding nitrate leaching concentration for each of these categories. These latter concentrations are initially estimated from a literature review as summarized in Table 3, and subsequently adjusted during the model calibration process. Then, C_L is computed as an area-weighted average based on the land-use categories. Estimating the leaching concentration from the land uses, rather than applying a nitrogen mass balance, is a simplification that has been proposed in several previous studies (e.g. Volf *et al.* 2013). This approach has the benefits that (1) the various sources of nitrogen do not need to be individually estimated and (2) it is not necessary to explicitly simulate the complex transformations and interactions that the various nitrogen compounds undergo within the crop and root zone prior to leaching (e.g. mineralization and unsaturated flow).

The flow module (Figure 2) estimates the annual water discharge coming from the watershed and partitions this into rapid and future delayed flow. In the context of this study, rapid flow refers to the flow that will exit the watershed in less than one year, including surface runoff and shallow groundwater flow near the discharging zones, while delayed flow exits the watershed at some time in the future (i.e. beyond the current year). Delayed flow is mainly comprised of groundwater flow through bedrock aquifers. Such a division of the discharge agrees with the recent observations made on the Wilmot River watershed, which suggest a relatively rapid flow section in the upper part of the aquifer that quickly transports nitrate following seasonal recharge, and a deeper low flow section where nitrates slowly migrate (Paradis *et al.* 2018).

These two flows, once estimated, are multiplied with the area-weighted average nitrate concentration C_L for calculating nitrate loadings. This computation therefore leads to two loading components: rapid and future delayed loading. Delayed nitrate loadings are increased by adding the estimated contributions from home septic systems in the watershed following the approach of Jiang *et al.* (2015). The rapid loading, which is considered immediate because of the annual time step of the model, is reduced due to nitrate attenuation that is assumed to be correlated with the average width of the vegetated riparian zone (e.g. Vought *et al.* 1994; Kellogg *et al.* 2010). Finally, the rapid loading (M_R) and the delayed loading (M_D) for a particular year are added to obtain the total loading from the watershed (M_O). The annual average nitrate concentration (C_O) is obtained by dividing M_O by the total annual discharge from the watershed.

The model is developed for the time period from 1996 to 2012. Before 1996, no digital data are available for the distribution of land uses on PEI. The most recent data layer depicts land use in 2009, and because the land-use distribution tends to be more homogeneous with time (Crane C., 2013, personal communication), the study period was extended to 2012 by assuming the land-use distribution. Generally, the land-use data have not exhibited any major change since 1996 because the large increase in potato production happened progressively before 1996 according to Statistics Canada. This intensification is partially captured by the model when assigning the initial nitrate concentration (C_i) that affects the delayed flow concentration.

The model was developed using Matlab® software (The MathWorks) and all the spatial data were manipulated through Arcgis® software (ESRI).

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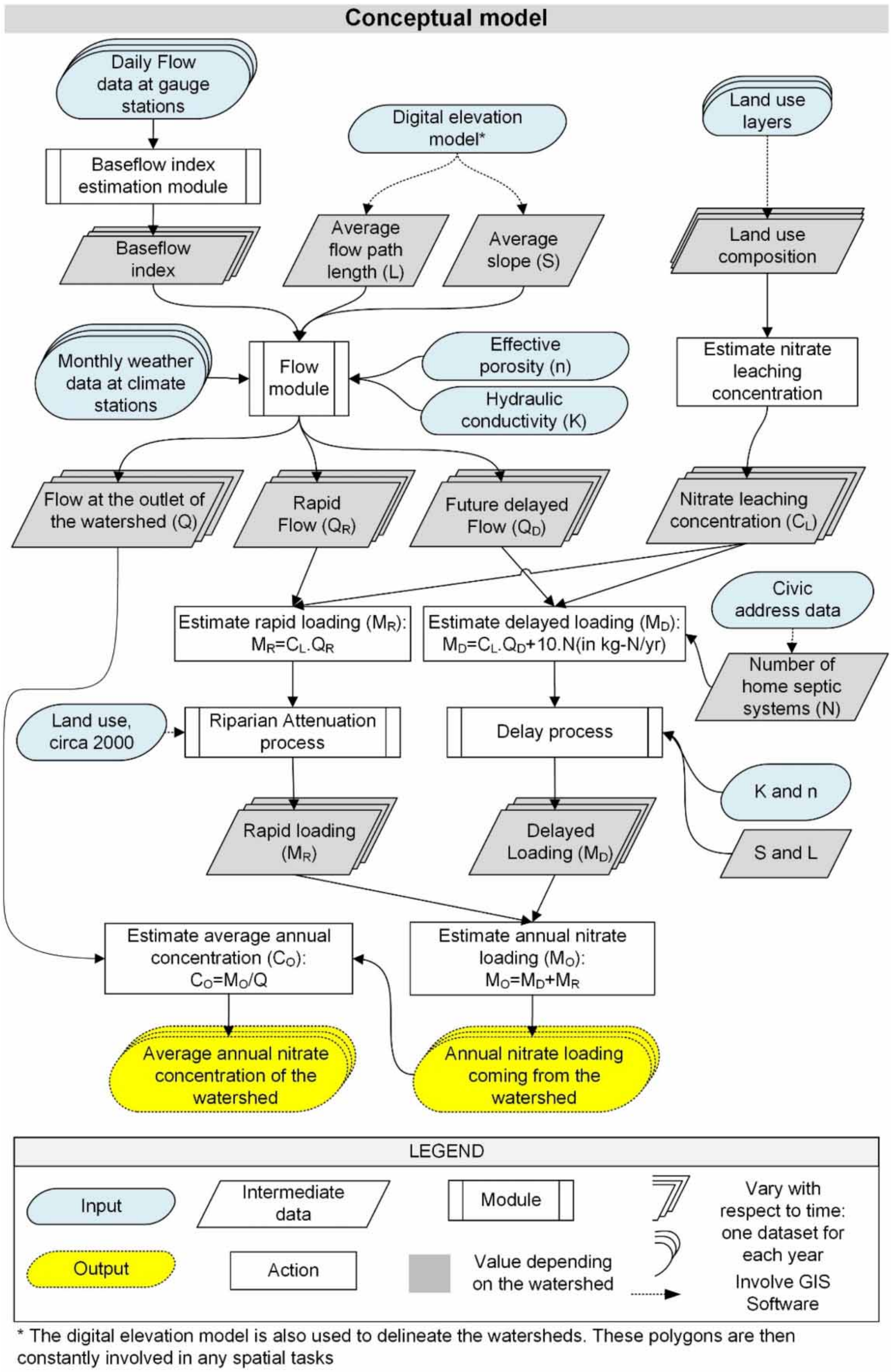

Figure 2 | Flowchart depicting the components of the conceptual model.

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Land use

Jiang *et al.* (2015) considered four different land-use layers that emphasize the land area under potato crop rotation, which covers 20% of PEI (Jiang *et al.* 2011). However, this is not the only commercial crop, and the types of crops being cultivated are changing.

Creating a particular land-use layer and assigning a nitrate leaching concentration for each possible crop rotation that occurs in PEI would be too cumbersome and data intensive. Firstly, the layers would be constantly evolving and, secondly, the number of different crop rotations would be too numerous to document and capture in a model. An alternative approach is to consider each crop grown in a particular year and to assign a nitrate leaching concentration to each crop type. One of the main problems with this approach is that the nitrate leaching concentration also depends on the cropping history. A compromise for estimating the nitrate leaching concentrations is to group the land uses into complementary categories that reflect the current and previously cultivated crop(s) in the selected area. Table 1 shows the different categories that have been chosen. Category RC and RCp include row crops other than potatoes, including soybeans and corn which are the only other row crops identified in the land-use layers obtained from Statistics Canada. The land area of each watershed is subdivided into these nine land-use categories and assigned a corresponding nitrate leaching concentration as discussed in the model calibration results. If significant land-use changes occur in the future, additonal categories could easily be added to the model.

Table 1 | Land-use categories chosen for the current model

Category	Description
P	Land in potato production this year
RC	Land in row crop production (other than potato) this year, which was *not* in potato production the previous year
RCp	Land in row crop production (other than potato) this year, which was in potato production the previous year
G	Land in grain production this year, which was *not* in potato production the previous year
Gp	Land in grain production this year, which was in potato production the previous year
HPG	Land in pasture, forage, hay, or grass this year, which was *not* in potato production the previous year
HPGp	Land in pasture, forage, hay, or grass this year, which was in potato production the previous year
OA	Other agricultural area
BG	Other area (non-agricultural)

Flow module

The flow calculation process consists of, first, evaluating the excess water, which is computed as the total precipitation minus evapotranspiration, the latter being estimated using the monthly method presented by Thornthwaite & Mather (1955). This excess water represents the water that will contribute to stream flow and groundwater recharge. The baseflow index (BFI), which is the percentage of groundwater that contributes to annual stream discharge, is then used to provide an estimation of how much water goes into the delayed and rapid flow paths. This method may overestimate the quantity of delayed flow because it is expected that part of the actual baseflow is composed of shallow subsurface flow having a residence time less than one year. However, more detailed models for estimating the delayed flow would require significantly more hydrogeological data (e.g. Jiang & Somers 2009) for each watershed, and such information is only available for relatively few watersheds in PEI.

A recursive digital filter with a filter parameter of 0.925, as discussed by Nathan & McMahon (1990), was used to compute the BFI for hydrometric stations located in PEI. The computations were based on climate records from 20 climate stations across the island, and discharge data from six hydrometric stations in PEI monitored from 1990 to 2010 obtained from the database of Water Survey of Canada. An inverse squared-distance weighted interpolation was used to spatially extend the results from the locations of these stations to the rest of the island.

Nitrate transport delay process

When nitrate enters groundwater it may take many years before this mass reaches a stream or estuary (e.g. Howden *et al.* 2011). This lag time can be approximated by the

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groundwater residence time, that is, the time required for water to move through the aquifer and arrive at a discharge location. This approximation implies that there is no significant nitrate storage in the matrix of the sandstone bedrock aquifer and that nitrate in groundwater is not attenuated during transport. These assumptions have been made in the development of previous models applied to PEI aquifers (Jiang & Somers 2009).

Howden et al. (2011) have proposed a simple approach, and one that is consistent with the concept of a lumped parameter approach, for the Thames River watershed. Howden et al. (2011) used a 1D model based on the Ogata & Banks (1961) analytical solution:

$$A(t) = \frac{1}{2}\left\{ erfc\left[\frac{L - Vt}{\sqrt{4Dt}}\right] + e^{LV/D} \cdot erfc\left[\frac{L + Vt}{\sqrt{4Dt}}\right]\right\} \tag{1}$$

where V is the average groundwater flow velocity (L/T), D is the hydrodynamic dispersion coefficient (L^2/T), L is the average groundwater flow path length (L), and t is the time (T). $A(t)$ is the mathematical solution of the 1D advection–dispersion equation for the injection of a solution with a constant concentration at the time $t = 0$. As C_L changes annually, the principle of superposition is applied and the delayed loading at year t, $M_D(t)$, is a linear composition of functions $A(t)$ as shown in Equation (2):

$$\begin{aligned} M_D(t) &= M_i \quad \text{if } t = 1 \\ M_D(t) &= M_i + \sum_{k=1}^{t-1} (M_{k+1} - M_k) \cdot A(t-k) \quad \text{if } t \geq 2 \end{aligned} \tag{2}$$

Equation (2) is presented for the nitrate loading; however, it can also be applied to determine future delayed flow. One important characteristic of Equation (2) is that the input of the current year will be considered only from next year onwards. The initial delayed loading (M_i) is obtained by multiplying the initial concentration (C_i) by the initial delayed flow (Q_i). The estimation of C_i was computed to reflect the land use in PEI in 1991. Potato area was 28% less in 1991 than 1996, so the proportions of categories P, RCp, Gp, and HPGp were all reduced by this percentage (Table 1). The aforementioned factor of 28% was determined by comparing total agricultural land in potato in 1991 and 1996, data from Statistics Canada. The initial delayed flow, Q_i, was assumed equal to the average delayed flow over the study period.

Equation (1) contains three parameters that need to be estimated for each watershed: L, V, and D. Darcy's law is used to estimate the average linear groundwater velocity (Schilling & Wolter 2007; Basu et al. 2012):

$$V = \frac{K \cdot i}{n} \tag{3}$$

where K is the hydraulic conductivity (L/T), i is the hydraulic gradient (Ø), and n is the effective porosity (Ø).

K and n are assumed to be constant values for the entire province, and their values have been determined during the flow module calibration. The hydraulic gradient (i) is computed using the average slope (S) for each watershed (Schilling & Wolter 2007; Basu et al. 2012) multiplied by a coefficient of $r = 0.65$. This factor, r, represents the ratio of the groundwater table elevation to ground surface elevation and experience has indicated that the water table in PEI is at an elevation that is usually between 60 and 70% of the ground surface elevation (Somers G., 2013, personal communication). Under the assumption that the groundwater table mimics the topography, L can be estimated by the actual surface flow path length using a digital elevation model. For the same reason that the computed i is adjusted, the average value over the watershed L is multiplied by the factor $r = 0.65$.

The mechanical dispersion is, for assumed 1D transport, equal to the product of the longitudinal dispersivity α and the average linear velocity V. Longitudinal dispersivity is known to be dependent on the scale of the problem (Neuman 1990), which can be estimated by L, the average flow path length. The empirical equations presented by Neuman (1990) are then used to estimate α:

$$\alpha = 0.32 \cdot L^{0.83} \quad \text{if } L > 100 \text{ m} \tag{4}$$

The condition $L > 100$ m is always satisfied for PEI watersheds.

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Nitrate attenuation

Nitrate attenuation can occur in reservoirs, lakes, streams, groundwater, wetlands, and riparian zones (Kellogg *et al.* 2010). This research focuses only on riparian zone attenuation that may occur within the permanently vegetated land along a river or stream that marks the interface between terrestrial and aquatic ecosystems. Runoff and shallow subsurface flow have to cross this region before discharging into a river or other water body. In doing so, nutrients such as nitrate may be partially removed by denitrification and plant uptake.

The nitrate removal rate in riparian zones depends on several parameters including the degree of anoxia, the amount of available organic carbon, the width of the riparian zone, the type and density of vegetation, the topography, and the root zone depth (Fennessy & Cronk 1997). Considering all these parameters would overly complicate the model and not fulfill one of the study objectives, which is to use readily available data. Thus, only the width of the riparian zone, which can be obtained from a land-use data base, is considered as shown in Equation (5). This equation is based on the findings of Kellogg *et al.* (2010) and Vought *et al.* (1994). Kellogg *et al.* (2010) developed a simple riparian attenuation model that assigns nitrate attenuation with respect to the width of vegetated riparian area with hydric soil. Hydric soil maps do not exist for PEI, and so this parameter was not included in the current model. In Equation (5), the attenuation rate is directly proportional to the riparian zone width as suggest by Vought *et al.* (1994).

$$\%\text{Reduction} = 80 \cdot \frac{\text{Min (Average riparian zone width, 30 m)}}{30\text{ m}} \tag{5}$$

A study conducted in PEI (Dunn *et al.* 2011) determined that a 10 m wide grassed area removed approximately 38% of nitrate in runoff after rainfall events. For a 10 m wide riparian zone, Equation (5) predicts a 27% reduction in the nitrate load, which is considered to be sufficiently close to the findings of Dunn *et al.* (2011) for the present modeling purposes.

Model calibration

First, the flow module was calibrated independently using the annual discharge data from six hydrometric stations. Subsequently, the model was calibrated with respect to the nitrate concentrations in surface water at 12 long-term monitoring sites.

Flow module calibration

The flow module was calibrated by varying K, n, and r and using the total annual discharge at six hydrometric stations in PEI over a period of 21 years, except for the Bear River which only had a 16-year record. This information resulted in 121 calibration data points. The sum of the squared residuals (SSR) has been used for assessing the results of the calibration.

The hydraulic conductivity, K, and the effective porosity, n, have a significant impact on the lag time. During the flow module calibration, K was varied from 10^{-7} to 10^{-3} m/s with an increment of 1×10^{-7} m/s, and the effective porosity was varied between 0.01 and 0.2 with an increment value of 0.01. These values capture the ranges reported in the previous studies discussed above. Moreover, the extreme values of 0 and 0.2 were also tested for effective porosity as these were reported by Jiang & Somers (2009). The parameter r, the ratio of groundwater table elevation to ground surface elevation, was varied between 0.6 and 0.7 with a 0.01 increment.

Nitrate concentration calibration

In this component of the calibration, the nine different nitrate leaching concentration values were first estimated with the software PEST (Doherty 2005) and then adjusted manually to honor the parameter ranges reported in the literature while maintaining a low objective function. All other nitrate module parameters were held constant. The objective function was taken as the sum of the squared residuals (SSR).

Annual nitrate loadings to streams or estuaries are rarely measured directly in PEI, and this limitation is the reason the calibration was carried out with respect to surface water nitrate concentrations. Concentration data were

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obtained from Environment Canada and the PEI Department of Environment, Labour, and Justice for the 12 long-term surface water quality monitoring sites displayed in Figure 3. This resulted in having 204 data points available for model calibration. These 12 sites were chosen because they have been more routinely monitored compared to other sites in PEI.

Model verification

The purpose of the verification was to evaluate how well the calibrated model was able to predict the average annual nitrate concentrations for other watersheds in PEI. The verification was performed in two steps. The first step was to assess whether the fit between measured and simulated concentrations was influenced by the area of the watersheds. To answer this question, the root mean squared error (RMSE) was computed for groups of watersheds having approximately the same surface area. A minimum of five watersheds per group was used to compute this indicator. This analysis was conducted on the watersheds presented in Figure 3, which vary in area between 1 and 152 km^2. This includes data from the calibration and 196 other watersheds having recorded nitrate concentration data for any years between 1996 and 2012. The data for these 196 sites were obtained from the water quality database of the PEI Department of Environment, Labour, and Justice and were usually scattered in time and not as complete as the data sets used for calibration.

The second step of the verification process was to test if the model was accurately representing the system by analyzing the residuals. The number of watersheds used for this phase was restricted according to their drainage area.

Parameter uncertainty analysis

Nitrate leaching under each specific land use is not constant in time and space and depends on many parameters that have not been explicitly accounted for in the preceding model (e.g. the agricultural practices of individual farmers, soil property variations within watersheds, etc.). This is reflected in the literature (Table 3), which shows that many of the land-use categories can have a large variation in nitrate leaching concentration. Also the hydrogeological parameters (i.e. K, n, and r) are assumed spatially constant for the province, but the reality shows a range in values

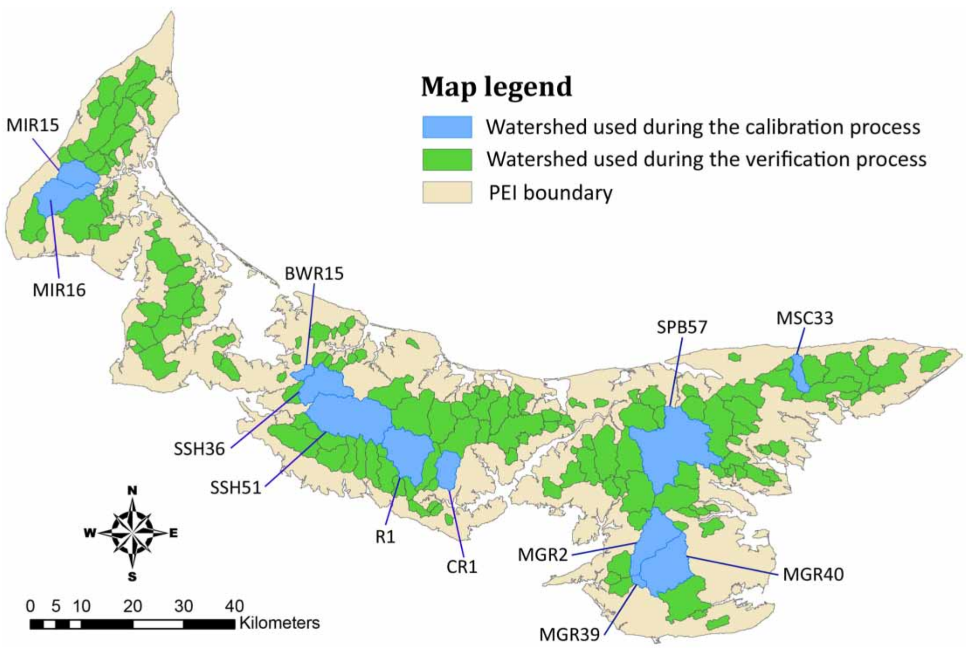

Figure 3 | Watersheds used for the model calibration and validation with respect to nitrate concentration. The 12 sites indicated with the alphanumeric codes are the locations where long-term surface water nitrate concentration data were available.

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depending on the location (Rivard *et al.* 2008a; Jiang & Somers 2009).

The above arguments support the need for considering parameter uncertainty in the modeling process. The method used in this study consists of ascribing each parameter a probability distribution function (pdf) and then running the model many times (~1,000) with a set of parameters drawn from the pdf by a LHS method. The flow, the loading, and so, the nitrate concentration results are bounded by two intervals determined from quartiles and percentiles of the set of results obtained from such an approach. The 50% interval is defined as the difference between the lower and upper quartiles, while the 90% interval represents the difference between the 5th and 95th percentiles.

Table 2 summarizes the pdfs used, and each of them has been defined so that the central value of the distribution matches the value obtained during the model calibration; however, the final pdfs may be slightly changed if the distribution encompasses nonphysical negative values. The pdfs generally represented the variation observed in the literature (e.g. Table 3 for the different nitrate leaching concentration) but if no data were found, then the interval of variation was set to what was judged to be a reasonable value. The choice between normal or uniform distributions was typically equivocal, and it should be noted that these pdfs can easily be changed in the future when more data become available.

RESULTS AND DISCUSSION

Model calibration

Flow module calibration

The parameter r was found to have a very small influence on the objective function and was therefore set to a fixed value of 0.65. The minimum of the objective function is obtained for a surface where K and n varied proportionally. To find a unique solution, n was fixed to 0.07 and K was then found to be 2×10^{-5} m/s.

Table 2 | Pdfs selected for the different input parameters

	pdf	Parameter *a*	Parameter *b*
K – hydraulic conductivity (m/s)	Log-normal	$\mu = \log(2 \times 10^{-5})$	$\sigma = 1.25$
n – effective porosity	Beta	$\alpha = 7$	$\beta = 80$
S – slope	Normal	$\mu = S$	$\sigma = 0.2S$
L – average flow path length (m)	Normal	$\mu = L$	$\sigma = 0.2L$
r – ratio surface elevation to water table elevation	Uniform	Min = 0.6	Max = 0.7
Category P – (mg-N/L)	Normal	$\mu = 18$	$\sigma = 3$
Category RC – (mg-N/L)	Uniform	Min = 2	Max = 6
Category RCp – (mg-N/L)	Uniform	Min = 7	Max = 15
Category G – (mg-N/L)	Normal	$\mu = 1$	$\sigma = 2$
Category Gp – (mg-N/L)	Normal	$\mu = 7$	$\sigma = 2$
Category HPG – (mg-N/L)	Normal	$\mu = 1$	$\sigma = 1$
Category HPGp – (mg-N/L)	Normal	$\mu = 4$	$\sigma = 2$
Category OA – (mg-N/L)	Normal	$\mu = 1$	$\sigma = 3$
Category BG – (mg-N/L)	Normal	$\mu = 0.1$	$\sigma = 0.1$
Home septic system load (kg-N)	Normal	$\mu = 10$	$\sigma = 1$
C_i – (mg-N/L)	Normal	$\mu = C_i$	$\sigma = 0.2C_i$
EW_i	Normal	$\mu = \hat{\mu}$ (EW)	$\sigma = \hat{\sigma}$ (EW)

μ is the 'mean' and σ is the 'standard deviation'.

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Table 3 | Nitrate leaching concentration results and composite parameter sensitivity obtained from the nitrate module calibration – bold values have been obtained by manual adjustment

		Potential nitrate leaching concentration (in mg-N/L)	
Land-use category	**Composite parameter sensitivity**	**Range from literature**	**From calibration**
P	6.98×10^{-3}	7–45[a,b,c,d,e]	18
RC	5.26×10^{-4}	0.6–6[f,j]	**4**
RCp	2.16×10^{-4}	–	**11**
G	5.33×10^{-3}	0.6–4.1[j]	1
Gp	5.63×10^{-3}	2.9–28[a,b,c,d,e]	7
HPG	1.35×10^{-2}	0.75–3[a,f,g,j]	1
HPGp	1.24×10^{-3}	–	4
OA	4.75×10^{-3}	0.6–4.1[j]	1
BG	2.76×10^{-2}	0.06–1.6[e,h,i]	0.1

Sources: [a]Milburn *et al.* (1990); [b]Milburn *et al.* (1997); [c]Jiang & Somers (2009); [d]Jiang *et al.* (2011); [e]Savard *et al.* (2007b); [f]Milburn & Richards (1994); [g]Eastern Canada Soil & Water Conservation Centre (1998); [h]Jiang *et al.* (2015); [i]Haith & Shoemaker (1987); [j]Volf *et al.* (2013).

Figure 4 presents the simulated annual total flow versus the observed annual total flow with the calibrated parameters. The coefficient of determination for the linear regression is 0.93. The model residuals (not shown) were found to be approximately normally distributed and centered on zero. The calibrated annual flows are considered to be quite acceptable given the limited amount of data used. The flow module has not been separately verified as no other independent flow data were available. The variables K, n, and r were held constant for the nitrate model calibration and verification.

Nitrate concentration calibration

The final results of the nitrate concentration calibration obtained using the combination of PEST and manual parameter assignment are presented in Table 3 and Figure 5. The coefficient of determination is equal to 0.91, and the RMSE is equal to 0.51 mg N/L. These two statistics indicate an acceptable quality model calibration.

The nitrate leaching concentration for land-use categories RC and RCp could not be adequately defined using PEST relative to the seven other categories as indicated by their relatively low composite parameter sensitivity (Table 3); thus, they were assigned manually. These two categories represent a small percentage of the total area (less

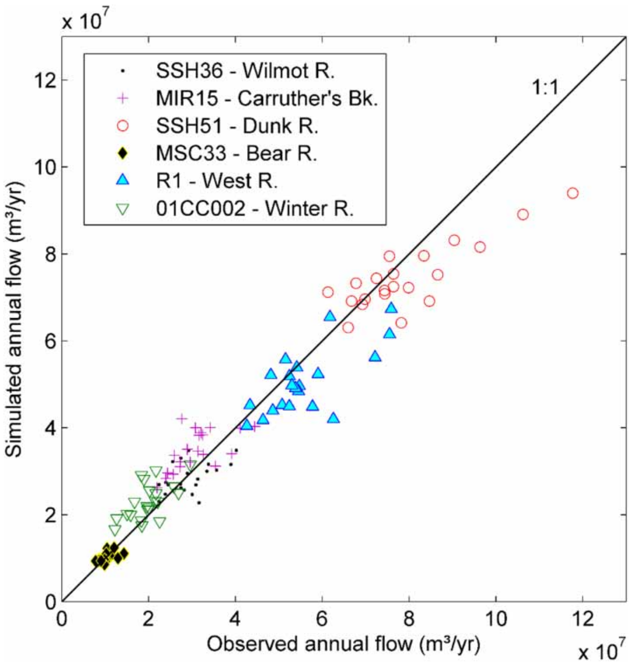

Figure 4 | Flow module calibration results: simulated versus observed annual total flows for the six calibration watersheds ($R^2 = 0.93$; RMSE $= 6.5 \times 10^6$ m^3/yr; SSR $= 5.1 \times 10^{15}$ m^6/yr^2).

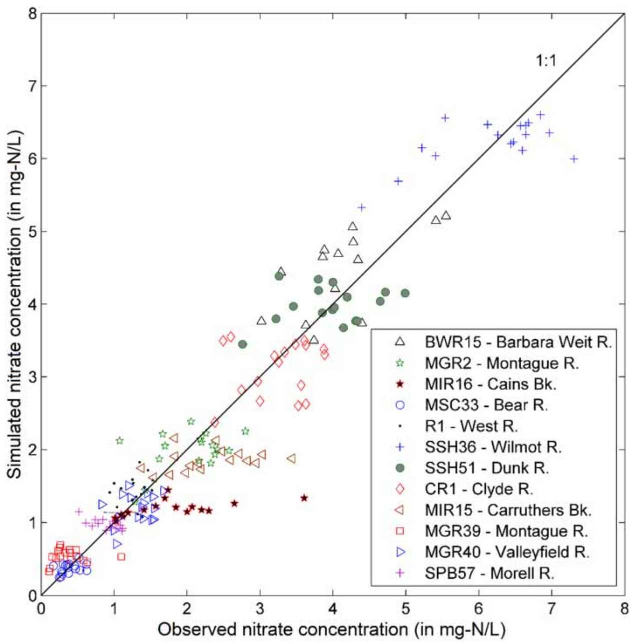

Figure 5 | Nitrate module calibration results: simulated versus observed annual nitrate concentrations for the 12 calibration watersheds ($R^2 = 0.91$, RMSE $= 0.51$ mg-N/L, SSR $= 50.54$ (mg-N/L)^2).

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than 1% of the island), explaining why the sensitivity is low compared to the other categories. Generally, the composite sensitivity of a category is explained by its relative surface area with a quasi-proportional relationship ($R^2 = 0.99$). Hence, category BG (other area) is the most sensitive because it accounts for an average of 47% of the area of the watersheds used for the model calibration.

As category RC (row crops *not* following potatoes) only includes corn and soybeans, and because the latter was only present in significant proportions after 2006, a concentration of 4 mg N/L has been used. This concentration represents the average annual nitrate leaching concentration measured beneath land in corn production (Milburn & Richards 1994). As no previous value has been found in the literature for category RCp (row crops following a year of potato production), a concentration of 11 mg N/L has been assumed. There is no strong justification for this value and the impact of this assumption is explored during the parameter uncertainty analysis.

Some particular sites are not well simulated, especially MIR15 (Cains Brook) and MIR16 (Carruther's Brook) in the west of the province (Figure 3). The simulated concentrations were essentially constant at these locations because the watersheds had a fairly stable land use from 1996 to 2012, while the observed concentrations varied over a range of 2 mg N/L. There are two possible explanations for this misfit. First, it may indicate that something other than land use and home septic tanks has an impact on the nitrate concentration of these streams (e.g. different land-use practices or unidentified point-source pollution). The second explanation involves the residence time of these watersheds, which was computed to be higher than the PEI average of 3.2 years (using the calibrated values of K and n); 9 years for MIR15 and 6 years for MIR16. The residence time for these two watersheds may not be long enough to completely explain the misfit, but if K was lower than the calibrated value in these watersheds, then the measured concentrations may reflect land-use activities prior to 1996.

Model verification

The RMSE, computed on groups of watersheds having approximately the same size, indicated that the nitrate concentrations for small watersheds are poorly represented compared to larger watersheds. This finding may arise for several different reasons. For example, the spatial land use obtained from geographic information system (GIS) data may not provide a representative picture of small watersheds because of the resolution of the land-use layer. Another cause could be local unresolved heterogeneities in land-use and agricultural management activity. A relatively small area of unresolved land use in a large watershed would not have a large impact on the computed nitrate concentrations; however, in a smaller watershed the same absolute area could have a large influence on the simulated loading or concentration. There is no obvious delimitation between the 'small' and 'large' watershed categories, and a threshold of 6 km^2 has been chosen.

The final verification was conducted using the data from 118 watersheds. Figure 6 shows that the model tends to slightly over predict the nitrate concentration when the concentration is less than approximately 1 mg N/L, and under predicts when the concentration is above 4–5 mg N/L. On average, the sum of the residuals was close to zero (4.0×10^{-2} mg-N/L), and the distribution is visually similar to a normal distribution (histogram not shown).

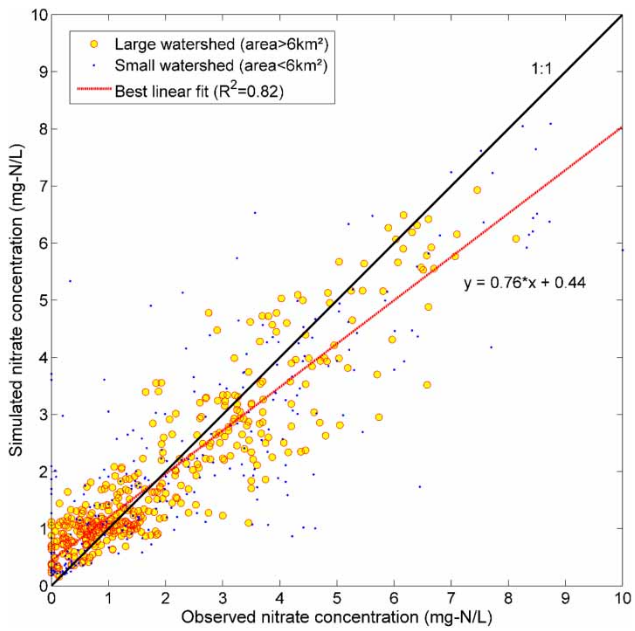

Figure 6 | Concentration module verification, observed vs. simulated (for the regression performed with only the large watersheds: $R^2 = 0.82$; RMSE = 0.74 mg-N/L).

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Model results comparison

In Table 4, the model results are compared to other studies that estimated nitrate loadings in PEI. The results of these studies are usually similar or included within the 90% confidence interval computed by the model.

Application of the calibrated model to the entire province

The computed annual flows vary significantly temporally and spatially as shown by comparing Figures 7(A) and 7(D). Precipitation is one of the main factors explaining these variations.

The simulated annual nitrate loadings in PEI watersheds range from 1.2 to 45 kg-N/ha watershed/yr, with an average of 12 kg-N/ha watershed/yr (or 6.7×10^6 kg-N/yr) for the period 1996–2012. Figures 7(B) and 7(E) show the spatial distribution of the loading for 1996 and 2009, respectively. The average annual nitrate loading has an increasing trend and varies between 8.7 kg-N/ha watershed/yr in 1996 to 13.8 kg-N/ha watershed/yr in 2011. The regions having the highest watershed-based nitrate loadings are mainly in the center and west of the island as already noted in the general overview.

Figures 7(C) and 7(F) show the simulated nitrate concentrations in different watersheds of the island in 1996 and 2009. The computed concentrations in 1996 were usually lower than in 2009. High concentrations are found in watersheds where potatoes are grown in relatively large quantities and these regions were mainly in the center and west of the island.

Annual flow and annual nitrate loading are well correlated ($R^2 = 0.6$). The model assumes that nitrates are transport limited, rather than supply limited, on an annual time scale. This assumption was made in the conceptual model by considering the leaching concentrations rather than nitrogen budgets for different land uses. This assumption is considered most appropriate for the delayed flow, where the reservoir of nitrates in the aquifer is large and capable of buffering the variations of concentration (Basu et al. 2010; Paradis et al. 2018). In PEI, groundwater nitrate concentrations remain quite constant with respect to time (i.e. Savard et al. 2007b; Bartlett 2011). This observation partially supports the aforementioned assumption that irrespective of the discharge, the nitrate concentration of the delayed flow will remain relatively constant. However, this may not be as valid for small watersheds. In Figure 7, the smallest watersheds have been aggregated with adjacent ones in order to avoid having watersheds smaller than 6 km^2. For the rapid flow, the nitrate concentration may vary significantly with time, and the current model may overestimate the rapid loading component for years with very high precipitation. Potential ways of improving future versions of the model could include simulating the rapid flow loading component as source limited, rather than transport limited. This would require the collection of more detailed spatial and temporal data sets, including land use, flows, and nitrate concentrations, for a few selected watersheds.

Table 4 | Comparison of current model results with other studies and data from PEI

Location	Period	Means	Estimated from source Nitrate loading (kg-N/ha/yr)	Estimated from model Nitrate loading (kg-N/ha/yr)	Source
Trout River watershed	2005–2007	Flow and nitrate concentration measurements	9.0 ± 0.7	8.9	Danielescu & MacQuarrie (2011)
Part of Trout River watershed	2009–2011		12.1	10 (9.4–12.3 for the 50% interval)	Bartlett (2011)
27 watershed in PEI island	2006–2009	Modelling	12	12	Jiang et al. (2015)
Wilmot River watershed	2004		25	23.3 (20.7–26.6 for the 50% interval)	Jiang & Somers (2009)
Tracadie Bay watershed	2002–2003	Nitrogen budget	6–8.5 (TN not nitrate)	8.4 (6.9–18.9 for the 90% interval)	Cranford et al. (2007)

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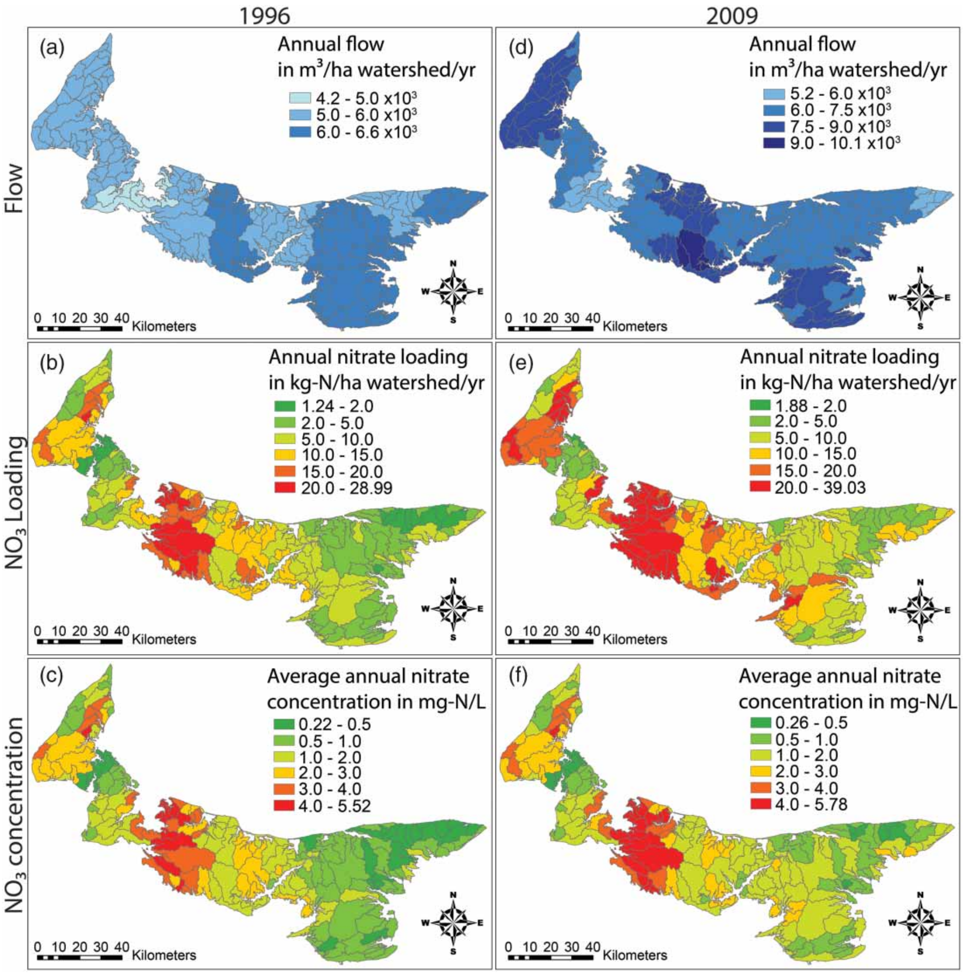

Figure 7 | Simulated results for 1996 (a, b, and c) and 2009 (d, e, and f). (a) and (d) represent the annual water flow, (b) and (e) represent the annual nitrate loading, and (c) and (f) represent the average annual nitrate concentration. PEI was divided in 172 watersheds larger than 6 km^2.

Distribution of nitrate sources for the entire province

Figure 8 presents the annual contribution computed for each nitrate source category for the entire island. Domestic septic systems contribute around 4% of the total provincial nitrate loadings. Even if the contribution of septic systems seems insignificant, it can locally be an important component, especially in residential watersheds not connected to any municipal sewage treatment system. For example, the sample location TRB 44 in the Winter River, located at Hardy Mill Pond inlet, has an average nitrate loading of 16 kg-N/ha watershed/yr and 42% of this is calculated to be derived from domestic septic systems. Regarding the entire island, most of the nitrate loading comes from potato fields represented by land-use category P, but also partially from category RCp, Gp, and HPGp (row crop; grain; hay, pasture, forage, and grass; all following a year of potato production respectively, Table 1). According to the model results, 57% of the loadings are due to potato production and 91% from agricultural land in general. Category OA exhibits a large variation over the simulation period, which is directly linked to the interpolation method used to fill the missing land-use information (Grizard 2013). The delayed and rapid flow carry annually, on average, 70% (min = 55%, max = 80%) and 30% (min = 20%, max = 45%) of the nitrate loadings, respectively. Riparian attenuation is simulated to remove 37% of the nitrate loadings coming from the rapid flow.

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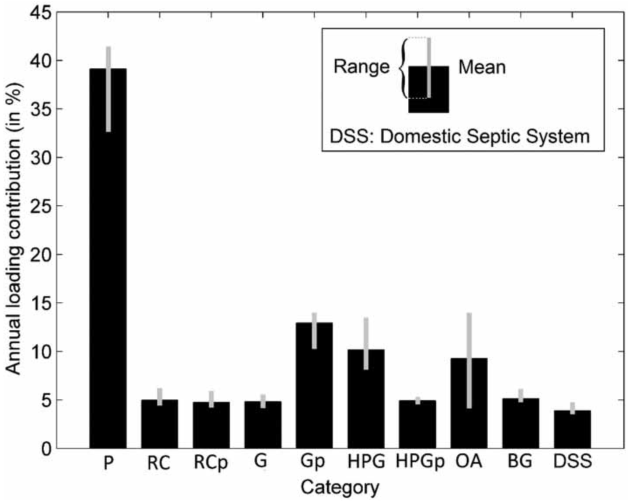

Figure 8 | Annual contribution of each land-use category (Table 1) to the total annual nitrate loadings coming from PEI for the period 1996–2012.

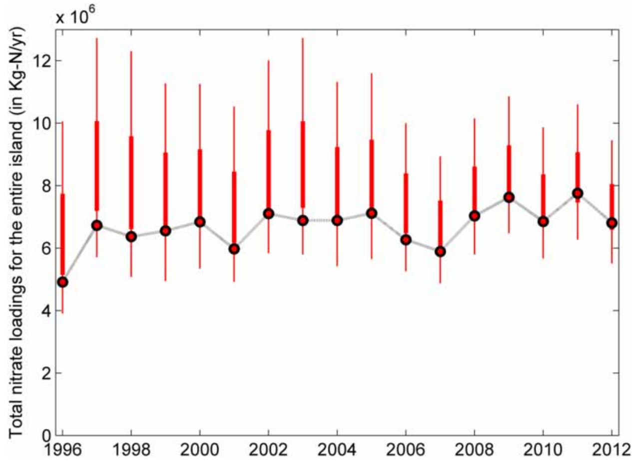

Figure 9 | Sensitivity analysis on the annual nitrate loadings coming from the entire island. Dots represent the annual simulated loading obtained with the calibrated parameters and bars represent 5th, 25th, 75th, and 95th percentiles.

Application of the parameter uncertainty analysis for the entire province

The annual flow obtained with the parameter uncertainty analysis is equal to $3.6 \times 10^9\,m^3$ on average over the study period. This is identical to the value found with the calibrated model. The 5th and 95th percentiles are only ±8% away from this value, respectively 3.3 and $3.9 \times 10^9\,m^3$, indicating a small uncertainty for this result.

The average of the total annual nitrate loadings from the parameter uncertainty analysis over the study period is equal to 7.9×10^6 kg-N/yr (Figure 9), which is higher than the 6.7×10^6 kg-N/yr found with the set of calibrated parameters. The calibrated model results tend to be lower than the mean of the parameter uncertainty analysis because the average of a pdf for a particular parameter is not always equal to its calibrated value. This is the case for categories where the pdf could not be adjusted with the range of values observed in the literature by keeping the central value of the pdf equal to the calibrated value.

CONCLUSIONS

The goal of this research was to improve upon existing land-use based nitrate loading models, while at the same time enabling simulations to be conducted with readily available data sets for the watersheds in PEI. A lumped GIS-model developed by Jiang et al. (2015) was used as the conceptual basis for model development and further improved by adding significant new components, including: a time component including groundwater delay that defers the arrival of nitrates in the receiving waters, a flow module accounting for rapid flow which is affected by riparian zone attenuation depending on the average width of the riparian zone, land-use categories that consider the current year's crop as well as the influence of the previously cultivated crops, and a parameter uncertainty analysis that quantifies the uncertainty of the results by assigning each parameter an appropriate pdf and by using a LHS method.

The model was implemented to simulate conditions in PEI for the period 1996–2012. The simulated results show good agreement with the observed concentrations, especially for agricultural watersheds larger than $6\,km^2$. On average, 70% of the nitrate loadings come from delayed flow, taking longer than one year to be transported through the watershed, while the remainder comes from rapid flow. More confidence is attached to simulated delayed loadings compared to rapid loadings. Indeed, few studies have investigated nitrate loadings from runoff, rapid subsurface flow, and riparian attenuation in PEI. Also, the one-year time step of the model makes it difficult to accurately capture the rapid loading processes. Nitrogen attenuation in riparian

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zones also requires further investigation to increase the confidence in the estimates of rapid N loadings.

It is concluded that lumped parameter models can be accurate and useful tools for simulating annual nitrate loadings from agricultural watersheds such as those found in PEI. However, such models require accurate temporal and spatial agricultural land-use data and cannot be expected to perform well when such data are missing.

Because the simplified structure of lumped parameter models allow them to run quickly, a thorough parameter uncertainty analysis can be performed to account for the variability and uncertainty associated with key parameters. Such methods increase the credibility of the results by quantifying the limitation and reliability of the available data.

For PEI, it is concluded that nitrate loadings to estuaries are strongly related to agricultural land, especially the land in potato production, and reductions in loading will have to address nitrate leaching from such areas.

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