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Groundwater nitrate concentration evolution under climate change and agricultural adaptation scenarios: Prince Edward Island, Canada

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16 Abstract

Nitrate (N-NO₃) concentration in groundwater, the sole source of potable water in Prince Edward 17 Island (PEI, Canada), currently exceeds the 10 mg/L (N-NO₃) health threshold for drinking water 18 19 in 6% of domestic wells. Increasing climatic and socio-economic pressures on PEI agriculture 20 may further deteriorate groundwater quality. This study assesses how groundwater nitrate 21 concentration could evolve due to the forecasted climate change and its related potential changes in agricultural practices. For this purpose, a tridimensional numerical groundwater flow and mass 22 transport model was developed for the aquifer system of the entire Island (5660 km²). A number 23 24 of different groundwater flow and mass transport simulations were made to evaluate the potential 25 impact of the projected climate change and agricultural adaptation. According to the simulations 26 for year 2050, N-NO₃ concentration would increase due to two main causes: 1) the progressive 27 attainment of steady-state conditions related to present-day nitrogen loadings, and 2) the increase 28 in nitrogen loadings due to changes in agricultural practices provoked by future climatic 29 conditions. The combined effects of equilibration with loadings, climate and agricultural 30 adaptation would lead to a 25 to 32% increase in N-NO₃ concentration over the Island aquifer 31 system. The change in groundwater recharge regime induced by climate change (with current 32 agricultural practices) would only contribute 0 to 6% of that increase for the various climate 33 scenarios. Moreover, simulated trends in groundwater N-NO₃ concentration suggest that an 34 increased number of domestic wells (more than doubling) would exceed the nitrate drinking water criteria. This study underlines the need to develop and apply better agricultural 35 36 management practices to ensure sustainability of long-term groundwater resources. The 37 simulations also show that observable benefits from positive changes in agricultural practices 38 would be delayed in time due to the slow dynamics of nitrate transport within the aquifer system.

39 1 Introduction

40 Significant increases in groundwater nitrate concentration ([NO₃]) are caused largely by sewage 41 leaks, wastewater treatment without denitrification, improper management of wastewater 42 effluents and overuse of fertilizers and/or animal waste. These nitrate sources are responsible for 43 the contamination of numerous aquifers, especially in those areas where groundwater is 44 replenished directly from the surface over large areas. Nitrate contamination is often associated with anthropogenic activities at ground surface, such as the fertilization of agricultural crops. 45 46 Once groundwater is contaminated, remediation is difficult, thus the prevention of contamination 47 is the primary strategy used for water quality management (Ghiglieri et al., 2009).

48 Groundwater is the sole source of potable water in the Province of Prince Edward Island (PEI) in 49 eastern Canada, and it plays a dominant role in surface water quality as well. Besides being a 50 concern for drinking water quality, excessive nitrate levels contribute to eutrophication of surface 51 waters, especially in estuarine environments (Somers and Mutch, 1999). Only one watershed 52 among the 50 watersheds delineated in PEI still has groundwater with a mean [NO₃] within 53 natural background levels (<1 mg/L N-NO₃). Furthermore 6% of supply wells exceed the 54 recommended maximum concentration limit of 10 mg/L (N-NO₃) for drinking water (Health 55 Canada, 2004; Somers, 1998; Somers et al., 1999). Over the past decade, several studies have 56 documented the nitrate problem in PEI groundwater (Somers, 1998; Somers et al., 1999; Young 57 et al., 2002; Savard et al., 2007) and suggested that elevated nitrate levels are often associated with agricultural activities, especially the use of fertilizers for row crop production. In addition, 58 59 water quality surveys have recorded important increases (more than doubling since 1980) of [NO₃] in groundwater and surface water in some areas of the province (Somers et al., 1999). 60

61 According to simulations made with the Global Circulation Model (GCM) for Canada, 62 temperature increases in the order of 2 to 4 °C by 2050 is expected at the country scale 63 (Hengeveld, 2000). Projected changes in annual precipitation over Canada remain within 10% of 64 present levels until 2050, with most of the increases occurring during winter months. Since global warming is expected to change the hydrologic cycle (Gleick, 1986) as well as the agricultural 65 66 practices (Olesen and Bindi, 2002; McGinn and Shepherd, 2003), it could, in turn, impact 67 groundwater [NO₃]. The overall impact on groundwater [NO₃] will likely depend on both the 68 magnitude of the change induced by climate change on the hydrologic cycle and how agriculture 69 will adapt to these changes. The combined pressures of climatic change on groundwater recharge

and agricultural practices, together with the need to preserve groundwater quality for the residents of PEI illustrate the importance of effective long-term strategies for water management. The aim of this study is then to assess the potential impact of both climate change and modified agricultural practices on future groundwater [NO₃] for the entire PEI (\sim 5 660 km²).

74 Nitrate concentration in groundwater depend on the mass loadings and the amount of water 75 infiltrating the soils down to the water table. In other words, future N-NO₃ concentration can be estimated as the mass of nitrate leached over the volume of recharge per unit area carrying out 76 77 this mass to the aquifer (groundwater recharge) under projected climatic conditions. Climate change impacts were simulated using different global circulation models (GCMs) and CO₂ 78 79 emission scenarios for the period of 2040-2069, to assess the sensitivity of the climatic variables. 80 The stochastic weather generator AAFC-WG (Hayhoe, 2000) was then used to adjust daily 81 temperature and precipitation of selected large-scale CGM scenarios to the scale of the Island and 82 allow simulations of groundwater recharge over the Island using the hydrologic infiltration model 83 HELP (Schroeder et al., 1994). The physical parameters used by this infiltration model allow an assessment of the impact of changing climatic parameters on the hydrological cycle, which 84 85 includes groundwater recharge. Moreover, the amount of nitrogen leaching to the aquifer was 86 estimated on the basis of the residual soil nitrogen (RSN) indicator (Yang et al., 2007) under 87 present-day conditions as well as considering agricultural adaptation scenarios in response to the 88 increase of crop heat units, effective growing degree-days and agro-economic trends (De Jong et 89 al., 2008).

90 Studying the impacts of climate change and agricultural management scenarios on groundwater 91 quality also necessitates understanding the aquifer system dynamics. Particularly, flow and 92 transport simulations are needed to assess the nitrate residence time and the aquifer response to 93 changes in practices or climatic conditions. While there have been many studies relating the 94 effect of climate changes on groundwater resources (e.g., Yussof et al., 2002; Allen et al., 2004; 95 Scibek and Allen, 2006; Green et al., 2007a, b; Hsu et al., 2007; Jyrkama and Sykes, 2007; Serrat-Capdevila et al., 2007; Woldeamlak et al., 2007; Holman et al., 2009; Allen et al., 2010; 96 97 Crosbie et al., 2010; McCallum et al., 2010; Okkonen et al., 2010; Rozell and Wong, 2010; Zhou 98 et al., 2010; Beigi and Tsai, 2015), there are few published studies which attempt to relate climate change to changes in groundwater [NO₃] (e.g., De Jong et al., 2008; Ducharne et al., 2007; 99 100 Holman et al., 2005a, b; Jackson et al., 2007). In their works, De Jong et al. (2008) and Jackson 101 et al. (2007) estimated mass of nitrogen (N) leaching through the unsaturated zone for different

102 scenarios to relate with [NO₃] measured in wells. That is, assuming a direct relationship between 103 nitrate leachate and groundwater [NO₃] regardless of the aquifer system dynamics. While the 104 semi-empirical hydrological model proposed by Holman et al. (2005a, b) to predict $[NO_3]$ in both 105 surface water and groundwater includes a groundwater store, such model does not simulate 106 spatial and temporal groundwater flow patterns that control nitrate transport in the aquifer 107 system. For instance, Ducharne et al. (2007) demonstrated that modeling of the aquifer system 108 using a physically based groundwater flow model allowed to simulate the inertia of the aquifer 109 system, which has a considerable impact on $[NO_3]$ measured in wells. In this study, the evolution 110 of groundwater [NO₃] under a changing climate was modeled using the physically-based 111 groundwater flow and solute transport numerical simulator FEFLOW (Finite Element subsurface 112 FLOW system; Diersch, 2010) considering the effect of the dual porosity of the fractured porous 113 medium (sandstone), identified by Jackson et al. (1990) as being responsible for the persistence 114 of pesticides in the aquifer system of PEI. In particular, the hydrogeological model developed for 115 the entire Province was based on knowledge gained from the Wilmot watershed (Jiang and 116 Somers, 2009; Paradis et al., 2006, 2007), which is representative of most other regions of PEI 117 regarding land use, soils, physiography, geology and hydrogeology. The hydrogeological model was calibrated with historical hydrogeological records of conditions specific to the Island: 118 119 hydraulic heads, groundwater discharge to river and [NO₃] measured in both wells and rivers.

The novelty of this study is to provide a quantitative comparison of climate change effects and agricultural adaptation impacts on the future evolution of [NO₃], taking into account potential changes in groundwater recharge and nitrate leached. Also, the general framework developed for the integration of the knowledge related to the aquifer system, climatic parameters and agricultural practices into a comprehensive calibration approach with site-specific records to narrow uncertainty in model parameters, could be applied elsewhere to guide groundwater resource and quality management.

127 2 Prince Edward Island Study Area

PEI, located in eastern Canada, covers approximately 5 660 km² and is 225 km long by 3 to 65 km wide (Figure 1 and Table 1). Topographic elevation ranges from sea level to 140 m above sea level. PEI is predominantly rural, with 39% of its surface covered by agricultural lands and 45% by forests. Forests mostly cover the eastern and western portions of the Island, whereas 132 agricultural activities are mostly concentrated in the central part. Residential, urban and industrial

activities occupy less than 6% of the territory.

134 Figure 1

135 Table 1

136 2.1 Climate and Hydrology

137 The climate in the Island is humid continental, with long, fairly cold, winters and warm summers. 138 Data selected from four weather stations geographically distributed across the Island (Figure 1) show relatively similar conditions (Table 2). As an example of the climatic conditions found on 139 140 the Island, the mean annual precipitation at the Charlottetown weather station is 1173 mm, most 141 of which falls as rain (75%). The mean annual temperature is about 5.3 °C and means for 142 monthly temperature range from -8 °C in January to 18.5 °C in July. The Island can be divided 143 into fifty (50) watersheds comprising 241 sub-watersheds (Figure 1). River basins are typically 144 small, and the main rivers are estuarial over a significant portion of their length. Mean annual streamflow ranges from less than 0.66 to 2.88 m^3 /s (Table 3). 145

146 Table 2

147 Table 3

148 **2.2 Geology and Hydrogeological Framework**

PEI is a crescent-shaped cuesta of continental red beds, Upper Pennsylvanian to Middle Permian in age, dipping to the northeast at about one to three degrees that consist of conglomerate, sandstone and siltstone in which sandstones are dominant (Van de Poll, 1983). The rock sequence underlying the Island is almost entirely covered by a layer of unconsolidated glacial material from a few centimetres to several meters in thickness (Prest, 1973). These deposits are generally derived from local sedimentary rock and include both unsorted tills and water-worked glaciofluvial and glacio-marine deposits.

With few exceptions, the surficial sediments over PEI do not represent significant aquifers as they are not water saturated, so the sandstone constitutes the main aquifer. Because the geology of the Island is relatively homogeneous, the hydrogeological conceptual model for all PEI is assumed to be similar to the one defined for the Winter River and Wilmot River watersheds where Francis (1989) and Paradis et al. (2006, 2007) carried out extensive hydrogeological characterization. Based on these studies several observations relative to the hydrogeological framework of PEI can be made:

The sandstone aquifer comprises a shallow high-flow system overlying a deep low-flow system (Figure 2a). This is based on hydraulic conductivity profiles obtained from field multi-level packer tests in rock aquifer wells that show a rapid decrease of hydraulic conductivity with depth (Figure 2b). This decrease is significant under a depth of 18 to 36 m, according to location. The shallow interval with higher permeability is defined as the high-flow system. Most domestic wells tap potable water in this high-flow system (Mutch, 1998; Rivard et al., 2008).

- 170 The sandstone aquifer represents a double porosity system with fractures providing 171 groundwater flow paths and the porous matrix providing storage capacity, both for water and 172 solutes, including nitrate. The fractured sandstone is characterized by relatively high hydraulic conductivity, between 1×10^{-6} and 3×10^{-4} m/s (Figure 2b), but it has a low storage 173 174 capacity (1-3%), as obtained from modelling of baseflow recession curves (Paradis et al., 175 2006, 2007) and seasonal nitrate sources in groundwater from isotopes (Ballard et al., 2009). 176 In contrast, the matrix has a high porosity of about 17%, but a much lower hydraulic conductivity as measured from laboratory core permeameter tests: mostly between 1x10⁻⁸ 177 and 5×10^{-7} m/s but as low as 5×10^{-10} m/s for mudstone (Francis, 1989). 178
- 179 Comparison between field (Paradis et al., 2006, 2007; Francis, 1989) and laboratory (Francis, 180 1989) hydraulic conductivity measurements suggests that fractures play an important role in 181 the rock aquifer permeability, and the general decrease in hydraulic conductivity with depth 182 is the result of decreasing fracture aperture and frequency. Horizontal bedding of the 183 sandstone forms the main fracture network above 35 m depth (82% of all fractures; Francis, 184 1989). Over a large area, the relative homogeneity of the distribution and interconnection of 185 fractures provides a typical 'porous media' response to pumping, especially in the weathered 186 high-flow rock aquifer system (Francis, 1989).
- Tritium analyses on groundwater samples in the high-flow system indicate the presence of
 "modern groundwater" younger than 50 years. In the low-flow system, no tritium is observed
 but Carbon-14 analyses provide groundwater ages between 5 000 and 7 000 years at depths
 ranging between 50 and 85 m below the water table (Paradis et al., 2006, 2007).

Transient modelling of baseflow recession curves (the groundwater contribution to a river)
 for the Wilmot River watershed suggests that rivers gain water from the aquifer most of the
 year (Jiang and Somers, 2009) and there is a strong interaction between the high-flow system
 and the rivers (Paradis et al., 2007). This is also supported by seasonal sampling of nitrate
 carried out over a period of two years in domestic wells and in the Wilmot River that shows
 similar average [NO₃] as well as water and nitrate isotope properties (Savard et al., 2007;
 Savard et al., 2010).

198 In summary, it is inferred from the development of the conceptual hydrogeological model that 199 groundwater flow and nitrate transport predominantly occur in the high-flow system (Figure 2c). 200 The shallow high-flow system essentially follows the ground topography and is hydraulically 201 connected to rivers. Nitrate transported to the aquifer by infiltration of precipitation will first 202 reach the shallow high-flow system and then eventually reach rivers mainly through fractures in 203 weathered and fractured sandstone, which are fairly more permeable than the sandstone matrix 204 itself. Nitrate transport rate through the aquifer system could however be reduced as matrix 205 diffusion occurs due to the contrast in [NO₃] between fractures and matrices. The high porosity of 206 the sandstone matrix makes it an important repository for nitrate which could store or release 207 nitrate, depending on geochemical conditions in the adjacent fracture network. Finally, it is also 208 likely that a proportion of the nitrate transported in the high-flow system has also reached the 209 underlying low-flow system. Considering the reduced groundwater flow and the mostly old 210 groundwater ages encountered in the low-flow system, the nitrate that may be present in the low-211 flow system may not have reached rivers yet. Note that in the case of the entire PEI, oxidizing 212 aquifer conditions usually prevail in the sandstone aquifer and it was assumed that denitrification 213 processes are negligible within the aquifer. Moreover, no natural geological sources of nitrate are 214 expected to be present throughout the Island. The aquifer $[NO_3]$ would then be controlled by 215 water infiltration and nitrate leaching from the soil.

216 Figure 2

217 **3** Study Methodology

Figure 3 presents the general workflow followed to model the evolution of [NO₃] in groundwater of the PEI aquifer system, which is briefly described below with further details provided in the following sections: Climate change can itself be predicted on the basis of meteorological models with a large degree of uncertainty. Therefore, different climate change scenarios have to be considered in order to represent the potential range of impacts related to predicted temperature and precipitation. In this study, four climate scenarios were selected to provide future daily weather conditions for the period 2040-2069. These scenarios are based on different global circulation models (GCMs) and CO₂ emission scenarios for the period 2040-2069.

- The daily temperatures and precipitations of the four selected large-scale CGMs were downscaled using historical meteorological records of existing weather stations using the stochastic weather generator AAFC-WG (Hayhoe, 2000) in order to provide more realistic climate conditions of the Island.
- Groundwater recharge was obtained from the HELP infiltration model (Schroeder, 1994),
 which uses daily climate conditions and soil properties as input. As done by Croteau et al.
 (2010), recharge obtained from HELP was calibrated on the basis of present-day climate
 conditions, so that future recharge could be estimated using the four climate scenarios.
- Nitrate leaching to the aquifer system was estimated under present-day conditions and agricultural adaptation scenarios. This mass of nitrate leachate is determined on the basis of the residual soil nitrogen (RSN) indicator (Yang et al., 2007).
- Using present-day nitrate mass and groundwater recharge, a three-dimensional numerical model of groundwater flow and nitrate transport was developed and calibrated to represent the specific hydrogeological conditions of PEI using FEFLOW (Diersch, 2004). This model was then used to simulate the future evolution of [NO₃] under different climate change and agricultural adaptation scenarios that implied potential changes in groundwater recharge and nitrate leachate.

244 Figure 3

245 **3.1** Climate Change Scenarios and Climate Data Downscaling

The Intergovernmental Panel on Climate Change Special Report on Emission Scenarios (Nakicenovic and Swart, 2000) provides 40 different scenarios, which are all deemed 'equally likely', but the A2 and B2 scenarios are widely adopted in climate change experiments and impact studies (IPCC, 2001). The A2 scenario envisions a population growth to 15 billion by year 2100 with rather slow economic growth and development. Consequently, the projected 251 equivalent CO₂ concentration rises from 476 ppm in 1990 to 1320 ppm in 2100. The B2 scenario 252 envisions slower population growth (10.4 billion by 2100) with a more rapidly evolving 253 economy, but with more emphasis on environmental protection. It therefore produces lower 254 emissions (CO₂ concentration of 915 ppm by 2100) and less warming than scenario A2. The A2 255 and B2 scenarios were simulated using two different GCMs, which are the CGCM2 (Flato and 256 Boer, 2001) developed at the Canadian Centre for Climate Modelling and Analysis, and HadCM3 257 (Gordon et al., 2000) developed at the Hadley Centre for Climate Prediction and Research of the 258 UK Meteorological Office. Daily outputs of maximum and minimum air temperature, and total 259 precipitation were obtained electronically from the Canadian Centre for Climate Modelling and 260 Analysis and the Hadley Centre through the Climate Impacts LINK project (Viner, 1996) for the 261 four climate change scenarios labelled hereafter: CGCM2-A2, CGCM2-B2, HadCM3-A2 and 262 HadCM3-B2.

263 The AAFC-WG (Hayhoe, 2000) was used to generate synthetic continuous daily weather records 264 for the historical period (1971-2000) and for two (2040-2069) climate scenarios using different 265 GCMs (Figure 3). The time period 2014-2069 is approximately corresponding to a doubling of 266 atmospheric CO₂ concentration (Qian et al., 2010). The AAFC-WG is a stochastic weather generator that was developed for and evaluated in diverse Canadian climates (Qian et al., 2004). 267 268 To obtain future climate data, daily outputs from the four climate change scenarios (CGCM2-A2, 269 CGCM2-B2, HadCM3-A2 and HadCM3-B2) were downscaled with observed historical climate 270 data from existing weather stations. A total of eleven weather stations were selected, covering 271 PEI fairly evenly and having the best available historical weather data for 1971-2000 (Figure 1). 272 Observed historical weather data, including daily maximum and minimum air temperatures and 273 daily precipitation, were provided by Environment Canada through their web site, and first used 274 to calibrate an AAFC-WG model for each weather station. The parameters for the various 275 statistical models used by the AAFC-WG were indeed estimated from historical observations 276 independently for each station. Note that historical climate from synthetic weather data generated 277 by AAFC-WG is generally not significantly different from observations (Qian and De Jong, 278 2007; Qian et al., 2011).

279 **3.2 Groundwater Recharge**

Groundwater recharge simulations serving as input for the FEFLOW model was carried out with the physically based hydrologic model HELP (Schroeder et al., 1994) (Figure 3). The model is quasi two-dimensional and the natural water balance components simulated include precipitation, interception of rainwater by leaves, evaporation by leaves, surface runoff, evaporation from soil, plant transpiration, snow accumulation and melting, and percolation of water through the soil profile. The advantage of using such a model is that temperature and precipitation resulting from climate scenarios may be directly used in the model to predict future groundwater recharge, once the model has been calibrated based on present-day data (e.g., Jyrkama et al., 2002; Allen et al., 2004; Croteau et al., 2010; Rivard et al., 2014).

The spatial estimation of groundwater recharge over PEI was obtained using 500x500 m cells (total of 21 168). For each cell, model parameters were retrieved and analyzed with geographical information software and a database management system. The HELP parameters used are summarized below.

293 Soil profile: The soil profile is the vertical combination of natural soil and geological • 294 materials that compose the vadose and saturated zones. The surface soil information was 295 assembled from various regional soil surveys conducted on the Island (Canadian Soil 296 Information System, 2000). There were a total of 953 unique soil types identified on PEI that 297 were regrouped into 6 distinct soil classes according to the dominant soil texture (A-Sand or 298 coarser; B-Loamy sand or gravelly; C-Sandy loam (<8% clay); D-Fine sandy loam or 299 very fine sandy loam; E-Loam or silt loam; and F-Sandy clay loam or clay loam). A typical 300 soil profile consisting of three layers was used to their representation. The top layer is 0.5 m 301 thick and consists of one of the 6-soil class; layer 2 is 1-17 m thick and consists of 302 unconsolidated glacial material; and bottom layer is 10 m thick and consists of weathered 303 sandstone (high-flow system).

Initial moisture content: The initial water content of each soil profile layers was computed by
 the model as steady state values. HELP indeed assigned values for the initial water moisture
 storage of layers and simulates a one-year period. These values were then used as initial
 values for the simulations. A sensitivity analysis of initial water content reveals that this
 parameter does not affect significantly groundwater recharge estimates as steady state
 conditions can be assumed over the long simulation period.

Surface runoff: Surface runoff (also known as overland flow) is the flow of water that occurs
 when excess rainfall or snowmelt flows over the soil surface. Surface runoff was estimated
 using modified Soil Conservation Service (SCS) curve-number method (USDA, 1986), as

proposed by Monfet (1979). The modified method allows a more reliable estimation of surface runoff in watersheds with short concentration time and for precipitation patterns found in eastern Canada. The modified SCS method allows estimation of surface runoff to a river following a rainfall or snowmelt event using soil characteristics, land use, type of vegetation, soil humidity, and surface slope. Digital land use and land cover data were obtained from Landsat-7 images (CanImage, 2001).

Solar radiation: The required daily values of precipitation, mean air temperature, and solar radiation were calculated. Precipitation and temperature were obtained from downscaled climate scenarios, while solar radiation data were generated using the weather generator provided by HELP. Solar radiation is computed according to precipitation (whether the day is wet or dry) and latitude.

Evapotranspiration: The multi-layer procedure for calculating evaporation values from snow,
 soil, and leaves, as well as transpiration based on type of vegetation used the evaporative
 zone depth, maximum leaf-area index, growing season start and end day, average wind
 speed, and relative humidity. These parameters were evaluated from existing land cover,
 agricultural and climatic data.

329 Groundwater recharge values simulated from HELP were calibrated against baseflow values 330 estimated using the method of hydrograph separation with streamflow records (Furey and Gupta; 331 2001) to narrow uncertainty in the input parameters of HELP (e.g., Croteau et al., 2010). 332 Baseflow is the groundwater contribution to river discharge (streamflow) and it is often used as 333 an approximation of groundwater recharge when underflow (groundwater flow beneath and by-334 passing a river), evapotranspiration from riparian vegetation, and other losses of groundwater from the watershed are minimal (Risser et al., 2005). Hydrograph separation methods estimate 335 336 the part of the streamflow hydrograph attributed to baseflow using semi-empirical filter 337 techniques. The calibration was done with the historical records of temperature and precipitation 338 (1971-2000) for three gauged streamflow stations with the most comprehensive time series 339 (Morell, Wilmot and Winter, Figure 1 for location). For each watershed, groundwater recharge 340 with HELP was estimated by summing all individual 1D soil profiles included in the watershed 341 assuming that water reaching the aquifer for each soil profile contributes to the streamflow within 342 the year. The most relevant parameters to calibrate were the evaporative zone depth and the heat 343 insulation of the snow cover. The trend in groundwater recharge simulated with HELP is 344 comparable to baseflow estimated with the Furey and Gupta (2001) method (Table 4), with a 345 correlation coefficient of 0.64 and no significant bias (relative error close to 0) in the annual
346 values. The error in the simulated values is 19% as expressed by the RMS error.

347 Table 4

348 **3.3** Mass of Nitrogen Available for Leaching and Agricultural Adaptation Scenario

349 The mass of nitrate available for transfer to groundwater was estimated with the residual soil 350 nitrogen (RSN) indicator (Drury et al., 2007; Figure 3). The RSN indicator estimates the quantity 351 of inorganic soil N at the time of harvest, at the Soil Landscape of Canada (SLC) polygon level 352 (Soil Landscapes of Canada Working Group, 2006). The RSN indicator is the difference between 353 N inputs from chemical fertilizer N, manure, biological N fixation by leguminous crops, and 354 atmospheric deposition and outputs in the form of N in the harvested portion of the crops and 355 pasture, and gaseous (N₂ and N₂O) losses to the atmosphere via denitrification. The total 356 chemical fertilizer N is based on fertilizer recommendation applied to crops adjusted to the total 357 manure N available for crops and improved pasture. The amount of available inorganic N from 358 manure applied to crops and pasture take into consideration losses from storage and handling. It 359 is estimated that 15% of manure N is lost during storage and handling (Burton and Beauchamp, 360 1986), 35% is added to the soil as organic N (Ontario Ministry of Agriculture and Food, 2003), 361 and consequently 50% of N originally present in manure is inorganic N which would be available 362 to crops during the year of application. Of this available N, 1.25% is lost as N₂O emissions, and 363 an equal portion is assumed to be lost through N₂ production. Although soil mineralization and 364 immobilization also occur on a seasonal basis, it is assumed that soils are in a steady-state 365 situation, with no net change in soil organic N from one year to the next.

366 The main inputs of the RSN model consist of acreages for all major agricultural crops and their 367 associated crop yields, as well as the type and number of livestock. These data are collected every 368 five years through the census made by Agriculture and Agri-Food Canada and are allocated to 369 SLC polygons based on the methodology described by Huffman et al. (2006). The RSN model 370 was run for all five-census years (1981, 1986, 1991, 1996 and 2001) and the output was averaged 371 to obtain a 'historical' RSN value for each of the 23 SLC polygons covering PEI (De Jong et al., 372 2008). The RSN values at the SLC polygon level could not be validated because independent 373 data sets are not available at that scale. However, Yang et al. (2007) compared the total adjusted 374 chemical fertilizer N recommendation (fertilizer recommendation minus available manure) with 375 the total amount of N fertilizer sold in PEI. For the five census, the average ratio between the 376 adjusted fertilizer recommended rates and the amount of N fertilizer sales is 1.0 (between 1.35 to

0.82) indicating that fertilizer recommendations are generally well followed in the province.

Many different agricultural adaptation scenarios can be devised, either with increased or decreased production intensity as compared to the present level. For the purpose of our study, a «worst case» scenario was selected because none of the adaptation scenarios is verifiable. Based on consensus expert opinion of Agriculture and Agri-Food Canada at the Research and Policy Branch, it was assumed that agricultural production in PEI would intensify over the next 50 years. Hence, relative to the 2001 census provincial totals, the following sequential agricultural land use scenario was developed for the 2040-2069 period (De Jong et al., 2008):

The area of alfalfa, improved pasture, tame hay and other grain cereals reduces by 40, 30, 30
and 15%, respectively (total 'freed-up' area: 29 794 ha);

• The berries and vegetable area increases by 100% (remaining 'freed-up' area: 25 179 ha);

• Of the remaining 'freed-up' area, 20, 40 and 40% is allocated to potatoes, grain corn and soybeans, respectively;

Buffer strips, a legislative requirement, reduce the increased total area of potatoes by 5%,
with this area going into the 'other land' category;

- For SLCs 538001, 537002 and 537003, the total area of potatoes decreases by 6%, because
 these SLCs contain fields with steep slopes, and the 'freed-up' area is allocated equally to
 tame hay and spring wheat;
- As a consequence of the decrease in perennial forages, the number of cattle decreases by
 10%; and
- The number of poultry and pigs increases by 30%.

398 To calculate RSN for this agricultural adaptation scenario, the 1996 crop yields and N 399 fertilization recommendations of Ontario were used because crop heat units and effective 400 growing degree-days for this year were reported to be similar than those reported for the 2040-401 2069 period in PEI (Bootsma et al., 2001). Thus, the agricultural adaptation scenario depends on 402 land use, crop yield and N fertilization recommendation changes induced by climate change. As 403 done by De Jong et al. (2008), the RSN model was then run with this scenario to obtain 23 404 projected RSN values one for each polygon. The N mass was applied on the SLC polygons 405 because RSN values are estimated over these entire polygons. RSN units are provided in kg of N 406 per hectare of farmland area but farmlands are not defined within the SLC polygon. To provides 407 conservative scenarios, it was assumed that the total RSN was nitrified and leached to the aquifer 408 within the year. Moreover, to be compatible with the FEFLOW model, the transformed mass of 409 N applied at the surface of the model was estimated by multiplying the RSN values by the ratio 410 of farmland area over SLC polygon area. This operation maintains the total mass of nitrate over 411 the SLC polygon but reduces the applied rate.

412 **3.4** Numerical Groundwater Flow and Nitrate Transport Model

413 The physically based FEFLOW model used to simulate groundwater flow and nitrate transport 414 was divided into eight layers (4 layers for each of the two flow systems). The base of the model is 415 deep at 800 m below water table to include the different flow patterns that can develop within the 416 PEI aquifer system (e.g., Tóth, 1963). The flow in the vadose zone was neglected due to the short 417 lag-time response (few days) between precipitations and water table fluctuations. Boundary 418 conditions include constant heads around the Island in the first layer, and no flow boundaries in 419 the underlying layers to simulate the flow along the saline front around the Island. Constant heads 420 were also applied to rivers on the first layer to represent the hydraulic connection between rivers 421 and the high-flow system. Note that non-pumping conditions were considered for the calibration 422 and future scenarios, as most of the Island is supplied by individual domestic wells sparsely spread over the Island (approximately 145 000 inhabitants in 2014, over 5 660 km²). The impact 423 424 of pumping wells on the water table is thus expected to be low (<2 mm/y based on a daily 425 individual consumption of 200 L), except in few localized areas where potable water is supplied 426 by production wells (e.g., Charlottetown). Irrigation water for agriculture and associated return 427 flow were not considered either because rainfall generally supplies the needed water demand for 428 crops irrigation. The resulting three-dimensional grid contains 4 896 246 6-node prismatic triangular elements with an average element area of 0.0925 km² (with triangle edges of 429 430 approximately 430 m).

The calibration of the FEFLOW model, which is an important step to narrow uncertainty in historical and future groundwater [NO₃], was carried out sequentially with three independent data sets: (1) hydraulic heads measured in domestic wells; (2) baseflow-recession curves for the main rivers and; (3) groundwater [NO₃] recorded in domestic wells.

435 3.4.1 Hydraulic Heads Calibration

436 The calibration of the FEFLOW model was first carried out under steady-state conditions with 437 hydraulic head values measured at the time of drilling in more than 700 wells. These wells are 438 domestic water wells, of varying depth, which generally end in the shallow high-flow system. 439 Hydraulic heads were used to adjust the horizontal and vertical hydraulic conductivities within 440 the reported range of values (Table 5) while keeping calibrated groundwater recharge values from 441 the HELP model unaltered. The mean annual groundwater recharge for the 1971-2001 period was 442 used. Using a time-averaged recharge value per model cell to represent present-day groundwater 443 recharge conditions is justified by the facts that: (1) no significant changing trend is observed in 444 water table elevation at available long-term monitoring well hydrographs over the Island (Rivard 445 et al., 2009); and (2) measured head data were collected over a considerable period of time (>40 446 years). A comparison of the observed and predicted hydraulic heads indicates a similar trend with 447 a relatively high correlation coefficient of 88%, but show a fair amount of scatter and simulated 448 heads slightly underestimated (Table 4). This is consistent with the fact that the observed head 449 data were measured over several decades and likely reflect transient intra and inter-annual head 450 variations, which results in large uncertainty in mean head values, which is what the numerical 451 groundwater flow model represents.

452 Table 5

453 3.4.2 Baseflow-Recession Calibration

454 Once an acceptable match was obtained under steady-state conditions, the resulting model was 455 used to simulate transient baseflow under recession conditions for the main rivers (Morell, 456 Wilmot, Winter) to estimate specific yield (Table 5). With this procedure, groundwater recharge 457 for the model is set to zero and daily discharge through the river nodes are compared to specific 458 baseflow-recession events extracted from streamflow records. Baseflow-recession events for PEI 459 occur generally at the end of summer during long periods of time without rainfall, when rivers are 460 solely sustained by groundwater. The rate of decline of baseflow-recession curves is sensitive to a specific yield value, which controls the amount of water that can drain from the aquifer to the 461 462 connected rivers (Mendoza et al. 2003; Sánchez-Murillo et al., 2015). A lower specific yield 463 value is thus associated to a faster drainage of the aquifer. This dynamic is linked with 464 groundwater and nitrate residence time that have a direct impact on the capabilities of the 465 numerical model to predict meaningful groundwater [NO₃]. The modelling of baseflow-recession 466 events shows the best adjustment for a specific yield value of 1% (Table 4), which is attributed to 467 the fractures in the sandstone aquifer. Note that recession curves are mostly sensitive to the high-468 flow layers, and specific yield values for underlying layers were progressively lowered to 469 represent the decreasing number of fractures with depth (Table 5).

470 3.4.3 Nitrate Concentrations Calibration

471 After calibration of the groundwater recharge with HELP and the aquifer system dynamics with 472 FEFLOW through head and baseflow-recession data, the historical mass of N leaching to the 473 aquifer was adjusted to match present-day (2000-2005) [NO₃] measured in more than 17,000 474 domestic wells. In PEI, intensive agriculture began around 1965 with the introduction of 475 chemical fertilizers and steadily increased since that time. The model of Paradis et al. (2006, 476 2007) for the Wilmot River watershed has illustrated the considerable time lag between increased 477 leaching of nitrate and the build up of groundwater [NO₃] corresponding to this increased input. This lag time is due to both the large capability of the PEI aquifer system to accumulate nitrate 478 479 because of the large porosity of the sandstone, and the typically long residence time of 480 groundwater from its recharge to its outflow in rivers. The maximum residence time of the high-481 flow and the shallow low-flow systems before discharge to the Wilmot River watershed was up 482 to 20 and 10 000 years, respectively. It can be assumed that a similar situation exists over the 483 entire PEI aguifer system and that groundwater $[NO_3]$ is presently not in steady state equilibrium 484 with the nitrate leachate that have historically prevailed in watersheds throughout PEI. 485 Consequently, the numerical model needs to be run under transient conditions with the historical 486 record of the mass of nitrate reaching the aquifer to ensure realistic predictions of groundwater 487 [NO₃]. Because RSN values were only estimated based on the 5 census years (1981, 1986, 1991, 488 1996, 2001), no RSN estimate is available prior to 1981. Thus, for the onset of intensive 489 agriculture in PEI from 1965 to 1981, an average mass of nitrate representative for this period 490 was adjusted to match observed present-day $[NO_3]$. The estimates of mass of nitrate leaching to 491 the aguifer based on the last 5 census years were not modified during the calibration process and 492 it was assumed that all available RSN is transferred to the aquifer within the year of application.

493 As previously demonstrated by Savard et al. (2007), no significant denitrification occurs in the 494 PEI aquifer system, and then only advective-dispersive transport was considered. Groundwater 495 flow and nitrate transport were then run under steady-state and transient conditions, respectively, 496 using hydraulic parameters summarized in Table 5. Total porosity needed for the transport 497 simulations were based on average laboratory values (Francis, 1989), whereas the effective 498 diffusion coefficient, and longitudinal and transverse dispersivities were 1×10^{-9} m²/s, 5 m and 0.5 499 m, respectively, considering typical groundwater flow path lengths (Gelhar et al., 1992).

As reported in Table 4, the average [NO₃] measured in wells generally agrees with the simulated concentration for the SLC polygons for which RSN values are available. Simulated concentration is the average [NO₃] for the first four layers representing the high-flow system within which most domestic wells are installed. However, the simulated concentration slightly underestimates measurements (approximately 0.5 mg/L lower), as expected from the procedure of nitrate mass application at the surface of the model previously discussed. Based on the RMS value, the error in groundwater [NO₃] predicted by the FEFLOW model is 30%.

507 4 Results of Modelling

508 On the basis of the previous calibration results, it is assumed that the FEFLOW model provides a 509 good representation of groundwater flow conditions and nitrate transport in the PEI aquifer 510 system as well as of present-day [NO₃] in drinking water. For the purposes of this study, and 511 knowing the uncertainty about groundwater recharge, hydraulic conductivity, specific yield, 512 porosity and nitrate mass, consideration will thus be given to the relative changes of future 513 scenarios with respect to the calibrated FEFLOW model.

514 4.1 Future Climate Scenarios

515 The generated future climate scenarios show considerable warming from both GCMs (Table 6), 516 although CGCM2 projected much greater warming than HadCM3 for the Charlottetown weather 517 station (Figure 1). Also, minimum temperature increases more markedly than maximum 518 temperature, and warming under scenario A2 is more noticeable than under B2, as expected from 519 higher CO₂ emissions. While warming is expected throughout the entire year (July and January) 520 for all scenarios, changes in precipitation appear uncertain, with total monthly precipitation and number of days with precipitation increasing or decreasing according to a specific scenario or 521 522 season. Indeed, CGCM2 projects a slight decrease in precipitation for January with the opposite 523 for HadCM3, even though the number of days with precipitation decreases in January for all 524 scenarios. However, the projected July precipitation for 2040-2069 shows an increase or no 525 change relative to the 1971-2000 averages for all four scenarios.

Scenario CGCM2-A2 shows a decrease in precipitation intensity during July (summer), as the number of days with precipitation increases and total precipitation remains unchanged. This can thus have an impact on surface runoff because a decrease in precipitation intensity results in less excess water to runoff during rainfall events. The scenario HadCM3-A2 shows on the contrary an increase in precipitation intensity for July. For January (winter), the surface runoff dynamics is more complex as snowpack thawing and form of precipitation (snow vs rain) should be taken into account as previously done with the HELP model.

533 Table 6

534 4.2 Hydrologic Cycle Components and Groundwater Recharge

Simulation results for the historic period (1970-2001) show that almost 50% (583 mm) of the annual precipitation is returned to the atmosphere by evapotranspiration (Table 7). Another 19% (221 mm) is flowing to the rivers by surface runoff, and 31% (369 mm) infiltrates the soil down to the sandstone aquifer as groundwater recharge. Moreover, groundwater recharge over the Island varies from 0 mm/yr in wetland areas, to 704 mm/yr over coarse sand soil (Figure 4). The standard-deviation for groundwater recharge values is 50 mm/yr, in accordance with the homogeneity observed at the Island scale for climate as well as for the soil and geology.

542 For the 2040-2069 period, evapotranspiration values increase for all climate scenarios, as 543 expected from the increase in temperature for the same period (Table 7). However, the variation 544 in evapotranspiration is less marked than the variation in temperature. For surface runoff, values 545 are predicted to be unchanged or decreased, with large variations ranging from 0 to 66 mm (Table 7). Those variations between scenarios are mainly related to the total precipitation available. 546 547 evapotranspiration, decrease in precipitation intensity and snowpack dynamics as previously 548 discussed. Total precipitation and groundwater recharge variations between scenarios follow 549 similar patterns with increased values for the A2 scenarios (CGCM2 and HadCM3) and 550 decreased values for the B2 scenarios with respect to the historic period (Table 7). In general, a 551 decrease in groundwater recharge is expected for the 2040-2069 period (between 2.1 to 12.4%); 552 only the CGCM2-B2 scenario leads to an increase in recharge of 6.7%.

553 Table 7

554 Figure 4

555 4.3 Residual Soil Nitrogen

The components of the N balance were averaged over the 23 SLC polygons in PEI (Table 8). The total amount of N input from fertilizer, manure, leguminous crops and atmospheric deposition is 102.3 kg N/ha/yr. The outputs consist in N removed by cropping and gaseous losses, which total 71.5 kg N/ha/yr. The province-wide average RSN is therefore 30.8 kg N/ha/yr. The spatial variability of historical RSN values ranges from less than 25 kg N/ha/yr to approximately 40 kg N/ha/yr according to the local agricultural management practices (Figure 5a).

562 With the agricultural adaptation scenario, N inputs from fertilizer were predicted to increase by 563 8.4 kg N/ha/yr relative to historical inputs (Table 8). The other inputs from manure, fixation and 564 deposition remained relatively constant. N removal by crop uptake increases by 3.1 kg N/ha/yr, 565 and consequently residual soil N at the end of the growing season increases significantly from 566 30.8 kg N/ha/yr under historical management, to 35.7 kg N/ha/yr with the simulated adaptation 567 scenario (16% increase). The spatial variability of RSN under the adaptation scenario ranges 568 from 28.3 kg N/ha/yr to 46.1 kg N/ha/yr (Figure 5b). The increase in RSN relative to historical 569 data ranges from 10 to 23%.

- 570 Table 8
- 571 Figure 5

572 4.4 Nitrate Concentration Evolution Simulations

573 To assess the potential impact of climate change and agriculture adaptation in the future, nine 574 groundwater flow and mass transport simulation scenarios were defined:

Scenario 1 (Figure 6b): This is the baseline scenario, which uses the mean historical groundwater recharge (steady-state flow) and the present-day agricultural practices (steady-state transport with RSN values from the 2001 census) from 2001 until 2069. This scenario is used to assess when aquifer concentrations are reaching steady-state conditions using present-day nitrate mass (equilibrium between nitrate inputs and outputs from the aquifer system).

• Scenarios 2 to 5 (Figures 7a-d): These scenarios use the present-day agricultural practices (steady-state transport) in the SLC polygons but their groundwater recharge is based on the

values obtained from the four climate scenarios (transient flow). The mass of nitrate applied
over the watershed is kept constant for the 23 SLC polygons from 2001 until 2069. This
mass represents the mean RSN value from the 5 past censuses (1981, 1986, 1991, 1996 and
2001). These scenarios combine the impact of aquifer system equilibrium and groundwater
recharge change related climate changes on [NO₃].

Scenarios 6 to 9 (Figures 8a-d): These simulations use the RSN values modelled for the 2040-2069 period (transient transport) with the four climate scenarios along with the groundwater recharge based on the values obtained from these climate scenarios (transient flow). These scenarios combine the impact of [NO₃] equilibrium, groundwater recharge change and agricultural adaptation (land use and climate changes).

593 For the modelling purposes of this study, the gap between the last year of the calibration period 594 (2001) and the beginning of the scenarios (2040) was then filled with gradual changes in 595 groundwater recharge and RSN values to provide meaningful [NO₃] in the future. A linear 596 interpolation between values established for 2001 and 2040 was thus applied.

597 Figure 6a presents map of the average [NO₃] per watershed for the present-day (2001) conditions 598 obtained from the calibrated FEFLOW model. For comparison purposes, modelled groundwater 599 [NO₃] were divided into four classes: background (<1 mg/L), low (1-3 mg/L), medium (3-5 600 mg/L) and high (>5 mg/L). These classes are used to emphasize that the model is more indicative 601 of relative spatio-temporal changes in groundwater [NO₃] rather than absolute concentration 602 values. This map shows that the most impacted watersheds are in the center of the Island where 603 most agricultural activities are taking place. Histograms of the number of watersheds in each 604 class reveal that 42% of the watersheds are in the medium (17) or high (4) $[NO_3]$ classes (Figure 605 6a; Table S1). This observation reflects the critical situation PEI is in regarding groundwater 606 quality related to nitrate contamination.

Note that for simplicity results are presented for 2050 (middle of the period 2014-2069). Compared to the present-day situation (Figure 6a), the average increases in [NO₃] for the 2050 baseline scenario (scenario 1; Figure 6b) is 11% for the Island (Table S1). This increase reflects steady-state in groundwater concentration due to gradual loading of nitrate using present-day concentration. Under the 2050 baseline scenario, the average nitrate content of several watersheds moves in a higher concentration class, 50% to the medium (17) and high (8) classes. The 2050 results show no more watershed at the background level (Figure 6b; Table S1). 614 Moreover, in the Western part of the Island, several watersheds are predicted to reach the higher 615 class, likely due to the longer residence times, i.e., a longer period before reaching equilibrium.

616 The average increase in groundwater $[NO_3]$ over the Island for the four climate scenarios (2-5; 617 Figures 7a-d) range between 11 and 17% (Table S1) with respect to the present-day scenario 618 (Figure 6a). The departures from the baseline scenario suggest that the impact of groundwater 619 recharge change alone (without the equilibrium effect) on [NO₃] is 6% for CGCM2-A2 and 620 HadCM3-A2, 4% for HadCM3-B2, and zero for CGCM2-B2. There is thus also no significant 621 change in [NO₃] classes and only two watersheds moving from the low to the medium class for 622 all climate scenarios (Figure 7a-d; Table S1). These simulations indicate that modification of the 623 groundwater recharge regime caused by climate change (scenarios 2-5) has less impact on future 624 water quality than reaching equilibrium with current nitrate mass (scenario 1).

625 The Island average concentration for each climate scenario integrating the agricultural adaptation 626 scenario (6 to 9; Figures 8a-d) indicates a nitrate increase between 25 and 32 % (Table S1) 627 relative to the present-day simulation (Figure 6a). The scenarios with CGCM2-A2 (scenario 6, 628 Figure 8a) and HadCM3-A2 (scenario 8, Figure 8c) predict the highest impacts with 64% of the watersheds in the medium (17) or the high (8) class, while the scenario with CGCM2-B2 629 630 (scenario 7, Figure 8b) has the lowest impact (58% in medium or high class). The center of the 631 Island is more strongly affected by high [NO₃], as expected from the intensification of 632 agricultural activities for the 2049-2069 period (Figure 5b). Moreover, the comparison of 633 scenarios 6 to 9 with the baseline scenario indicates that changes in agricultural practices (land 634 use and fertilization) and crop yields induced by climate change would have an impact on the 635 increase of average [NO₃] between 14 and 21% (Table S1). Thus agricultural adaptation will 636 potentially have a greater effect on future groundwater [NO₃] in PEI than groundwater recharge 637 change induced by climate change (0-6%) or the reach of $[NO_3]$ equilibrium in the aquifer system 638 (11%).

- 639 Figure 6
- 640 Figure 7
- 641 Figure 8

642 **5 Discussion**

643 5.1 Comparison with Previous Studies

644 De Jong et al. (2008) document the only other study on the assessment of the impact of climate 645 and agricultural practice changes on groundwater quality for PEI. Similar to our study, they 646 showed that the impact of the projected climate change on N leaching is small compared to the 647 effect of agricultural intensification that could increase soil N leaching well above historical 648 levels. While they showed that there was a reasonable qualitative agreement between simulated N 649 leaching and groundwater [NO₃] in domestic wells, the sole simulation of N movement through 650 the unsaturated zone does not allow a quantitative assessment of the effect of the aquifer system 651 dynamics on [NO₃] in groundwater. Nevertheless, their simulations of N movement on a daily 652 basis during the non-growing season indicated that a few percentages of the RSN was not 653 reaching groundwater each year. On average, for all SLC polygons, 91% of the RSN was indeed 654 lost via soil leaching, with a range from 87 to 96% over the Island. In comparison, we assumed 655 that 100% of the RSN was reaching the aquifer system each year. On the other hand, De Jong et 656 al. (2008) neglected N leaching during the growing season, which is contradicted by the findings 657 of Savard et al. (2010) and Ballard et al. (2009), which showed important input of nitrate in 658 groundwater throughout the year, including during the growing season.

659 The results obtained for PEI can also be compared to those reported by Ducharne et al. (2007) for 660 the Seine basin (France). The main findings of this study are indeed similar to those obtained for 661 PEI. First, the dynamics of the aquifer system of the Seine basin leads to an important increase in 662 future $[NO_3]$. This increase is however at least twice the percentage obtained for PEI by 2050, 663 which suggests that the residence time of nitrate in the PEI aquifer system is shorter and it could 664 equilibrate faster to a change in nitrate mass. This could be explained by the different geology 665 between the two aquifer systems. For the Seine basin, the influence of climate on groundwater 666 recharge also has a minor impact on the increases of future [NO₃], as indicated by small to 667 moderated decreases in river low flows (baseflow), so the reason why climate change leads to 668 higher [NO₃] in groundwater is the increased nitrate leaching from the soils. This increased 669 leaching is mainly related to enhanced crop biomass and yield as well as soil N mineralization 670 (this process was not considered in our study). In our study, the increased nitrate leaching results 671 from larger agricultural land, increased fertilizer use and higher crop yield. Thus, future studies in 672 PEI should include a comprehensive simulation of nitrate movement through the unsaturated cone with a consideration of soil N mineralization to be more representative of actual and futureagricultural conditions.

675 5.2 Assessing Model Uncertainty through Calibration

676 In this study, the proposed workflow includes numerous modelling steps, which involve many 677 hypotheses and conceptual choices. While a sensitivity analysis could be made on each of the 678 many model parameters to quantify and propagate the uncertainty on groundwater [NO₃] 679 predictions, the strength of our approach is rather to capitalize on known conditions that are used 680 in a comprehensive calibration approach that constrains the possible range of model parameters. 681 As reminded in Figure 9, [NO₃] in groundwater depends on the mass of nitrate combined with the 682 amount of water reaching the water table and the mixing of that infiltration with the flowing 683 groundwater. Obviously, different combinations of nitrate mass, recharge and water flux could 684 lead to the same [NO₃], and at least two of the three parameters need to be independently 685 calibrated to obtain meaningful predictions of [NO₃] in groundwater. For this study, the flux of 686 water coming from the surface (groundwater recharge) and flowing within the aquifer system 687 were carefully calibrated with river baseflow and groundwater hydraulic head data. However, the 688 mass of nitrate applied at the soil surface through RSN estimates was more uncertain at the scale 689 investigated, and measurements in wells were instead used to calibrate [NO₃] in groundwater. 690 Thus, the estimated mass of nitrate and flux of water (recharge and within the aquifer system) are 691 likely representative of the actual conditions in PEI, and the performance of the FEFLOW model 692 to predict $[NO_3]$ in groundwater could be used to quantify the uncertainty propagated during the 693 modelling process.

694 Figure 9.

695 **5.3** Assessing Uncertainty in Future Predictions

696 Uncertainties in the projections related to climate models and forcing scenarios could be large, 697 although the objectives of this study were to develop methodologies for assessing climate change 698 impacts on groundwater [NO₃] and demonstrate their application in PEI. Projected climate 699 changes by the two state-of-the-art GCMs, CanESM2 (Arora et al., 2011) and HadGEM2 (Johns 699 et al., 2006; Martin et al., 2006), from the same climate modelling centres of CGCM2 and 691 HadCM3, are presented in Table S2 under the Representative Concentration Pathways (RCP) 4.5 and 8.5. The projected temperature changes are larger in these new simulations. It is also noticed
that an increase in July precipitation by over 20% was projected with little change or a decrease
in the number of rainy days. Such changes could indicate increased precipitation intensity.

705 As reported by De Jong et al. (2008), N leaching in PEI is however considerably less sensitive to 706 increases in daily precipitation than to decreases. For instance, a 15% increase in annual 707 precipitation resulted in a 2.5% increase in N leaching, which is likely due to the high level of 708 soil water saturation throughout much of the year in this temperate-humid climate. Thus, 709 increased precipitation intensity could not result in a significant increase in N leaching to the 710 aquifer system because much of the excess water will drain as surface runoff. Nevertheless, the 711 projected groundwater [NO₃] under these new climate scenarios might differ from those based on 712 CGCM2 and HadCM3 and uncertainties in the projections should be taken into account when 713 results are used to develop adaptation strategies and policies.

Finally, while we considered only a single "worst case" agricultural adaptation scenario, it should be understood that this scenario was designed to explore the upper limits of potential future conditions. Thus, any adaptation strategy (e.g., better agricultural practices) will have to make sure that such an upper limit it not actually reached. This study thus serves as an indicator of the magnitude of the reduction needed on N leaching by agricultural adaptation strategies to counteract the projected increase in [NO₃] in groundwater.

720 6 Summary

To assess the potential impact of climate change and the foreseen agricultural adaptation on [NO₃] in groundwater over the PEI, nine different groundwater flow and mass transport scenarios were considered. Simulations of these scenarios and their results expected for 2050 show that:

- The progressive change of groundwater [NO₃] simply due to reaching steady-state conditions
 related to present-day loading would generate an 11% increase of concentrations.
- Groundwater recharge change related to climate change would only account for an increase
 of 0 to 6%, whereas agricultural adaptation that include land use, fertilization and crop yield
 changes induced by climate change would generate an increase of 14 to 21%.
- The combined effect of equilibration with loadings, groundwater recharge change and agricultural adaptation would create an increase in [NO₃] between 25 and 32% over the PEI aquifer system.

As a consequence, the predicted general trend from 2001 to 2050 is that a significant number of watersheds would belong to the highly impacted group of watersheds having a mean $[NO_3]$ exceeding 5 mg/L (N-NO₃) with a recommended maximum concentration limit of 10 mg/L (N-NO₃) for drinking water. In 2001, 4 watersheds over a total of 50 were in this group compared to greater for 2050 after reaching steady-state conditions and having undergone some of the climate change, or 9 to 11 after agricultural adaptation is also considered.

738 Finally, predicting the impact of climate change on groundwater quality in agricultural contexts 739 represents a complex challenge that we have attempted to address using the case study of PEI. In 740 that particular example, the main finding in support to decision making for sustainable 741 development is that predicted climatic conditions combined with agricultural practices adapted to 742 these conditions may be expected to generate significant degradation of water quality that would 743 require modifying water servicing infrastructures, and develop better agricultural management practices to reduce nitrate leaching to the aquifer system (e.g., Zebarth et al., 2015; Somers and 744 745 Savard, 2015). At a broader scale, we also have made progress in pinpointing key steps to be 746 considered in predictive modelling, particularly in highlighting the need to produce sound and 747 realistic scenarios of region-specific agricultural adaptation to climate change while considering 748 the specificity of the hydrogeological processes taking place, and applying a comprehensive 749 calibration process to narrow the uncertainty in model parameters and results.

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Table 1. Main physiographic and land use characteristics of Prince Edward Island (land use based on a LANDSAT image for 2000).

Physiography					
Area	$5 660 \text{ km}^2$				
Width	3-65 km				
Length	225 km				
Elevation (above sea level)	0-140 m				
Land Use (%)					
Forest	45				
Agriculture	39				
Wetland	7				
Residential, urban, industrial	5.9				
Recreational	0.3				
Miscellaneous	2.8				

Table 2. Weather for Prince Edward Island (meteorological data for the 1971-2000 period). See
 Figure 1 for locations of the weather stations.

Weather Characteristic	Station					
weather Characteristic	O'Leary	Summerside	Charlottetown	Monticello		
Mean annual total precipitation (mm)	1141	1078	1173	1164		
Mean annual rain (mm)	860	806	880	903		
Mean annual snow (mm)	281	282	311	261		
Mean annual temperature (°C)	5.2	5.6	5.3	5.5		
Minimum mean monthly temperature (°C) (January)	-8.6	-7.9	-8.0	-7.4		
Maximum mean monthly temperature (°C) (July)	18.5	19.1	18.5	18.4		

Table 3. Streamflow characteristics of selected rivers in Prince Edward Island (records are for
1972 to 2005, 1961 to 1995 and 1965 to 1991 for Wilmot, Morell, and Winter rivers,
respectively). See Figure 1 for locations of the rivers.

Streamflow Characteristics	Watershed (drainage area in km ²)				
(m^3/s)	Morell	Wilmot	Winter		
(11/5)	(133)	(45)	(38)		
Mean annual	2.88	0.92	0.66		
Minimum monthly mean (Sept.)	1.10	0.44	0.24		
Maximum monthly mean (April)	6.77	1.89	1.61		

1004Table 4. Statistical analysis of model performance on calibration of different independent data1005sets for the simulation of groundwater flow and nitrate transport in the Prince Edward Island1006aquifer system.

		Model Error			
Model	Model Calibration Target		Relative Error (Bias in %)	Root Mean Square Error (RMS in %)	
HELP	Groundwater recharge from baseflow	<mark>0.64</mark>	0.8	19	
FEFLOW	Hydraulic head in open wells	<mark>0.88</mark>	-66.8	46	
FEFLOW	Baseflow recession in rivers	<mark>0.96</mark>	0.3	3	
FEFLOW	Nitrate concentration in wells	<mark>0.64</mark>	-0.3	30	

1009	Table 5. Field-based and calibrated hydraulic properties of the FEFLOW numerical model for the
1010	Prince Edward Island aquifer system.

Model Layer (depth in m)	Field K _h	Numerical Model				
	(m/s)	K_h	K_{v}/K_{h}	S_y	n (%)	
1 (0-5)		$\frac{(11/3)}{3 \times 10^{-4}}$	0.1	1	17	
2 (5-10)	4.5×10^{-4} to 8.1×10^{-5}	1×10^{-4}	0.1	1	17	
3 (10-15)		5×10^{-5}	0.1	1	17	
4 (15-30)	1.7×10^{-4} to 9.4×10^{-7}	1×10^{-5}	0.01	1	17	
5 (30-80)	1./X10 10 8.4X10	1×10^{-5}	0.001	0.1	17	
6 (80-180)	n.d.	1×10^{-6}	0.01	0.1	17	
7 (180-380)	n.d.	1×10^{-7}	0.1	0.1	17	
8 (380-880)	n.d.	1×10^{-8}	1	0.01	17	

 K_h and K_v : are horizontal and vertical hydraulic conductivity, respectively; S_y : specific yield; n: total porosity

1012 Table 6. Temperature and precipitation changes for the future period (2040-2069) relative to the

1013 historical period (1971-2000) for each selected climate change scenarios at the Charlottetown

1014

weather station, Prince Edward Island (Qian and De Jong, 2007).

	Т	emperati	ure chan	ge	Precipitation change			
Scenario	Monthly Mean Maximum (°C)		Monthly Mean Minimum (°C)		Monthly Total (%)		Days with Precipitation (%)	
	Jan.	July	Jan.	July	Jan.	July	Jan.	July
CGCM2-A2	1.7	2.5	4.6	3.1	-5.3	0.0	-2.1	5.0
CGCM2-B2	1.1	1.8	4.0	2.2	-8.1	5.0	-3.8	1.8
HadCM3-A2	1.4	1.8	1.7	2.0	4.1	7.7	-5.0	-4.6
HadCM3-B2	1.2	1.4	1.5	1.5	5.1	1.4	-3.0	-1.9

1017Table 7. Summary of mean annual temperature and hydrologic cycle components (precipitation,1018evapotranspiration, surface runoff and groundwater recharge) simulated with the HELP model for1019the historical period (1970-2001) and the four climate scenarios (2040-2069) in Prince Edward1020Island. Values provided in brackets are the change in mm or °C for the 2040-2069 period1021compared to historical conditions (1970-2001).

Scenario	Temperature (°C)	Precipitation (mm) (mm) Evapo- transpiration (mm)		Runoff (mm)	Recharge (mm)
Historic	5.3	1173	583	221	369
CGCM2-A2	8.0 (+3.31)	1109 (-64)	618 (+35)	155 (-66)	336 (-33)
CGCM2-B2	7.0 (+2.3)	1223 (+50)	620 (+37)	209 (-12)	394 (+25)
HadCM3-A2	6.7 (+1.4)	1141 (-32)	616 (+33)	202 (-19)	323 (-46)
HadCM3-B2	7.1 (+1.8)	1197 (+24)	615 (+32)	221 (0)	361 (-8)

1024	Table 8. Average components of the nitrogen balance as simulated with historical crop and
1025	animal husbandry practices and with an adapted agricultural management scenario (De Jong et
1026	al., 2008).

Period	Nitrogen Inputs (kg N/ha/yr)						RSN (kg N/bg/yr)	
	Fertilizer	Manure	Fixation	Deposition	Crop	Gas	(kg 1\/11a/yr)	
Historical	52.8	17.4	29.6	2.5	70.3	1.2	30.8	
Adapted	61.2	16.8	30.1	2.5	73.2	1.6	35.7	

RSN: residual soil nitrogen.

1029 Figure Captions

Figure 1. (a) Location of Prince Edward Island (PEI) in eastern Canada. (b) Limits of the watersheds (numbered area delineated with brown lines, see names Table S1), with identification of the major rivers (names in blue), along with land use (see legend) and location of the weather stations (names in black).

Figure 2. (a) Schematic conceptual model of the groundwater flow system along with (b) a typical profile of hydraulic conductivity showing distinct shallow high-flow (red) and deeper low-flow (blue) systems; and (c) a conceptualization of nitrate transport in the double-porosity sandstone aquifer with advective fracture flow and matrix diffusion.

Figure 3. Workflow for the study of the potential impact of climate and agricultural practicechanges on future groundwater nitrate concentration in the Prince Edward Island aquifer system.

Figure 4. Spatial distribution of groundwater recharge from simulations with the calibrated HELP infiltration model for the historical period (1970-2001). Cell values are averages for the 1970-2001 period. Groundwater recharge is not shown for the 2040-2069 period as no significant changes were obtained from HELP based on climate change scenarios.

Figure 5. Simulated residual soil nitrogen (RSN) using (a) historical management practices and
(b) the adaptation scenario presented in Table 8 (De Jong et al., 2008). RSN values are for each
Soil Landscape of Canada (SLC) polygon.

Figure 6. Class distribution of simulated mean nitrate concentration per watershed and histogram of the number of watersheds in each class for: (a) present-day (2001); (b) 2050 baseline scenario with present-day (2001) nitrate loading and groundwater recharge.

Figure 7. Class distribution of simulated mean nitrate concentration per watershed and histogramof the number of watersheds in each class for the four climate change (CC) scenarios (a, b, c andd).

Figure 8. Class distribution of simulated mean nitrate concentration per watershed and histogram of the number of watersheds in each class for the four climate change (CC) scenarios with ensuing agricultural practice adaptation (APC) (a, b, c and d). Figure 9. Schematic of the constraints exerted by conditions considered (in blue) in the calibration of model parameters for the simulation of processes controlling groundwater nitrate concentration (NO₃ mass leached and water fluxes, including recharge and groundwater flow).

















