ESTIMATION OF GROUNDWATER RESIDENCE TIMES IN THE WILMOT RIVER WATERSHED ON PRINCE EDWARD ISLAND—IMPLICATIONS FOR NUTRIENT REDUCTION

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ABSTRACT
Groundwater residence times, and lag times between the reduction of sources of nitrate and the subsequent improvement in nitrate concentrations in surface water and groundwater in the Wilmot River watershed on PEI are examined through flow and mass transport modeling, and tritium age dating. A reduction in nitrate inputs could result in corresponding improvements of nitrate levels in shallow groundwater and associated base flow within 4-15 years. For groundwater at depths of 22-32 m and 52-70 m, similar reductions could take 11-40 and 33-50 years respectively.

1 INTRODUCTION

Groundwater and surface water in many agricultural watersheds on Prince Edward Island (PEI) exhibit nitrate (NO$_3$-N) concentrations elevated significantly above natural background levels, and in some groundwater cases, the human health threshold of 10 mg/l (Somers et al., 1998; Young et al., 2002). Groundwater is the sole source of potable water on PEI, and contributes a significant amount of water and nitrate to streams and their tributaries. Thus elevated nitrate levels are of concern with respect to both drinking water quality, and associated eutrophication in estuarine environments (Somers et al., 1998; Young et al., 2002). Evidence suggests that nitrate levels in both groundwater and surface waters are continuing to rise.

Reversing the trend of non-point source nitrate contamination is one of the top environmental priorities on Prince Edward Island. Isotope interpretation and modeling approaches are employed to investigate the nitrate contamination in the Wilmot River watershed. They provide the scientific basis for the development of an island-wide nutrient reduction strategy. Various evidences indicate that denitrification is not occurring in the aquifer and not significantly in riparian zones. Natural denitrification cannot be relied on for nitrate reduction in the watershed.

Elevated nitrate concentrations in groundwater are closely correlated with high intensity of farming and a large majority of the nitrate in the water bodies was identified as having originated from inorganic fertilizer residues (Savard, et al., 2004). Watersheds on PEI, like the Wilmot River watershed with as much as 60% of the land mass under potato production rotation, do not have much uncontaminated recharge to dilute the contaminated groundwater if potato acreage remains unchanged. To reduce the nitrate levels in groundwater and surface water, the loading from croplands must lessen through land-use changes. Two of the key questions that arise are 1) when the corresponding improvements will be observed in the receiving waters after reducing the source input and 2) how much reduction in loading to the groundwater is required to achieve water quality targets. The first question will be dealt with in this paper through modeling and tritium age dating and the second question will be discussed in a forthcoming paper. The timing of the response of groundwater/base-flow nitrate levels to land-use changes...
is translated into the estimation of the residence times of groundwater and nitrate mass in the aquifer.

Understanding the response time of groundwater and surface water nitrate levels to source changes is important. If the response time is quick, it is possible to demonstrate it through experiments in some sub-watersheds. If positive water quality changes can be detected within a short period of time, potato growers will be more receptive to land-use changes, which will make an island-wide nutrient reduction strategy widely accepted and workable. A water budget approach based on groundwater flow and tritium age dating approach is employed to estimate the residence times and ages of groundwater in the watershed. The estimates are compared against the simulated response of nitrate concentrations derived by mass transport modeling in this paper. The results will be helpful for the design of the demonstration experiments and provide input for the development of island-wide nutrient reduction strategy.

2 THE WILMOT RIVER WATERSHED

The Wilmot River watershed is located in the central west portion of Prince Edward Island (Fig. 1). The study areas include the Wilmot River watershed and two small adjacent watersheds (i.e. Barbara Weit River watershed and Rayners Creek watershed), which are collectively referred to as the Wilmot River watershed in this paper. The system is groundwater dominated, with groundwater derived base flow accounting for 66% of total stream flow (Jiang et al., in preparation).

The watershed is underlain by terrestrial sandstone formations with unknown thickness. The formation consists of a sequence of Permo-Carboniferous sandstone red beds ranging in age from Carboniferous to Middle Early Permian (van de Poll, 1983). Regionally, the bedrock is generally either flat or dipping gently to the east, northeast or north. A thin veneer of glacial deposits (1-5 m) overlies the bedrock. The uppermost portion of the sandstone red bed formation forms a fractured-porous aquifer across the province. The aquifer is characterized by significant fracture permeability dominated by horizontal bedding plane fractures, in addition to intergranular porosity (Francis, 1989). These features are evidenced by the apparent “semi-confined” and delayed drainage effects observed in the pumping tests in the watershed. Multi-level slug tests in the watershed have shown that hydraulic conductivity (K) of the aquifer generally decreases with depth (Paradis et al., 2006), which agrees with previous findings by Francis (1989). Horizontal conductivities (K_h) decrease with depth at approximately one order of magnitude per 60 m (Francis, 1989). Vertical anisotropy in K is significant, with the ratio of K_v to vertical hydraulic conductivity (K_v) at a few orders of magnitude at a scale of tens of meters.

The watershed covers an area of 112 km². Topography is rolling with slopes generally ranging from 2 to 6%. Based on land-use data of 1995-2000, agricultural land accounts for ~80% of the land base, with the remainder either forested or under urban and residential development. The major crop is potato in rotation with barley, hay/grass for forage. About 60% of the land base (~75% of the farm land) is under potato rotation production in a given year.

A three-order stream network, which likely follows the bedrock fracture system, is present in the watershed. The width of the main stem of the Wilmot River varies from a half meter at the head waters to ~200 m at the tidal reach and the width of the tributaries varies from less than 0.5 m to a couple meters. The stream bed is covered with predominantly silty sand and sandstone fragments at a thickness of 0-1.5 m. Daily stream discharge data at the gauging station (1972-1992) indicate maximum, minimum and mean discharges are 19.1, 0.145 and 0.937 m³/s respectively with mean base flow of ~0.6 m³/s. Mean annual precipitation in the study area is ~1060 mm and annual recharge is estimated to be 400 mm (Jiang et al., in preparation; Jiang et al., 2004).

3 GROUNDWATER FLOW MODELING

A spatial three-dimensional groundwater flow model was developed using Visual MODFLOW to assess nitrate transport in the watershed. Details can be found in Jiang et al. (in preparation). The sandstone aquifer and the saturated portion of the till is conceptualized as a horizontally isotropic and vertically anisotropic (i.e. K_h=K_v>K_v), spatial three-dimensional laminar flow system. The model domain covers the whole Wilmot River watershed, as well as the Barbara Weit River and Rayners Creek watersheds. Groundwater divides along the external boundary of the model domain are assumed following surface water divides and considered impermeable. The groundwater divide between the Wilmot River watershed and adjacent Barbara Weit River and Rayners Creek watersheds may not be completely consistent with the surface water divides and as a result it is included into the model domain as an internal boundary. The coastlines are specified as constant head.
boundary with a head value of 0 m, which applies to the top layer only. The boundaries of Layers 2-15 along the coastlines are assumed impermeable, which simulates the effect of salt and fresh water interface. At the tidal estuary areas the rivers are defined as third type boundary, which is simulated using the River Package of Visual MODFLOW (McDonald and Harbaugh, 1988) and applies only to the top layer. The river stage is set as 0 m. The stream sediments are assumed to have a uniform thickness of 1 m and a vertical hydraulic conductivity of 2.8×10⁻⁵ m/s (Francis, 1989). Sources and sinks, consisting of precipitation infiltration, wells, stream/aquifer interaction and evapotranspiration, are included in the system. Vertically, the simulated formation starts from the ground surface to a depth of 213 m with 15 layers and uniform thickness varying from 6 to 26 m. Horizontal grid spacing is set at ~100 m.

The model is calibrated to average conditions as represented by groundwater level measurements from private wells (some measurements are nonsynchronous with those of 2003) and multi-level piezometer measurements and average base flows for the period 1979-1999. Given 27 measurements, the calculated water levels agree with the measurements with a normalized RMS (Root Mean Squared) of 7% and a correlation coefficient of 0.97. The simulated heads compare with the measured heads from 9 multi-level piezometers with a normalized RMS of 14% and a correlation coefficient of 0.94. The model is further checked against the monthly stream base-flow series for 1995-2001 and the recharge used in the model is based on Jiang et al. (2004). The model reproduces the dry season flows with a good agreement. It is noted that the recharge used in July, August and September of the simulated hydrogeological windows usually are very small and therefore the simulated base flows basically represent the recession processes of aquifer discharge. Specific yields determined by simulating the recession processes of aquifer discharge include the simulated base flows basically represent the recession processes of aquifer discharge. Specific yields determined by simulating the recession processes of aquifer discharge include the simulated base flows basically represent the recession processes of aquifer discharge.
water particles. The water in Layer 1 may be older or younger than 4 years because of these effects. In addition, the residence times are averages for discretized layers with thicknesses varying from 6 to 26 m and in reality the flow is continuous. Thus, waters discharged from the vicinity of the stream may have residence times as short as only a few days, depending on the setback distance between the recharging point and the gaining stream. The implications are that water in Layer 1 may not be fully replaced within a 4-year framework due to dispersion (see next section) and nitrate entering the aquifer at the vicinity of the stream could be released in a few days.

Table 1 Model-layer water budget under steady state

<table>
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<th>Zone</th>
<th>CH</th>
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<th>R</th>
<th>ZT</th>
<th>ZB</th>
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</table>

Notes: CH = constant head (m³/d); RLP = river leakage + pumpage (m³/d); ET = evapotranspiration (m³/d); R = recharge (m³/d); ZT = zone top (m³/d); ZB = zone base (m³/d); S = sum (m³/d) and D = depth of layer base (m).

Discretized tritium samples were taken from the multi-level wells along Cross Section A-A’ to examine the appearance ages of groundwater at various depths. Tritium data (TU) are plotted against the sampled depth in Fig. 2. Tritium readings decrease with depth at Wil-1 and Wil-3 but not at Wil-2. The decreasing trend suggests increasing ages of groundwater with depth, which generally agrees with the above estimation of residence times. The odd reading in Wil-2 may be attributed to a mixture of cross-portion circulation in the aquifer driven by a strong local vertical hydraulic gradient.

At depths greater than 37.2 m in Wil-3, tritium approaches undetectable, suggesting groundwater below ~40 m in depth at this point was recharged before 1953 (Clark and Fritz, 1997) and was older than 52 years. The residence times at this depth as indicated above are 21-25 years. Conceptually, residence times do not equal ages here. It is possible the sampled waters for tritium analysis contained water recharged from a higher area and circulated upward from the deep portions of the aquifer, undergoing as twice much time as (forth and back) the estimated residence times.

Figure 2. Groundwater residence time vs. depth.

Figure 3. Groundwater tritium vs. depth.

Tritium readings from Layer 1 in Wil-1, Wil-2 and Wil-3 varied from 2.3 to 7.6 TU. The relatively wide range again suggests the presence of water with various ages (with the involvement of post 1953 waters). At depths below 32 m in Wil-1 and Wil-2, tritium readings were 5.5 and 4.1 TU respectively, indicating that water younger than 52 years, driven by large vertical downward hydraulic gradients, had possibly penetrated into the deep portions of the aquifer in the higher elevation areas. Nitrate concentrations at depths from 32 to 75 m at these two sites varied from 4 to 12 mg/l. As a tracer, the elevated nitrates confirm waters with modern agricultural chemicals (1960s) have reached the deep portions of the aquifer in the upland areas of the watershed. This means the nitrate concentrations at the depths where many domestic wells reach in upland areas of the watershed have climbed to levels of concern probably due to improper well construction in some cases. While it could take relatively short time to replenish the water in the shallow portion of the aquifer, at depths of 32-75 m it could take longer than two decades to replace the water based on the estimated residence times, not to mention the lag time dictated by dispersion and dual-porosity effects. The long lag time and deep extent of the plume represent some of the challenges for nitrate remediation.

5 DISPERSION AND LAG TIME OF NITRATE RELEASE FROM THE AQUIFER

A spatially three-dimensional transient nitrate transport model was developed using MT3DMS to estimate the current distribution of nitrate throughout the aquifer and to predict groundwater nitrate conditions in the future, both under existing nitrogen input rates and under several scenarios of differing N inputs. The results of the simulations shed light on the long-term implications of
current land use practices and on the degree of adjustment to these practices that may be required to effect positive water quality changes in the watershed. Details can be found in Jiang et al. (in preparation). The model is also utilized to estimate the lag time between lowering N input and improvement in water quality in the watershed.

Groundwater receives nitrate leaching from residual fertilizer, mineralization-nitrification of soil organic nitrogen, manure, sewage, and atmospheric deposition. Land uses are grouped into two categories, i.e. under potato production rotation and not under potato production, based on GIS data from 1995 to 2000. To simplify the model, the spatial change of land use practices is assumed fixed for the period of 1965 and 2005. Low potato acreage before the 1980s is offset by practices is assumed fixed for the period of 1965 and 2005. Low potato acreage before the 1980s is offset by

It is assumed that advection-dispersion processes control nitrate transport in the groundwater. Dispersivity is scale-dependent (Gelhar et al., 1992; Schulze-Makuch, 2005) and in the Wilmot case, longitudinal dispersivity ($\alpha_L$) is set at 10 m and the ratios of horizontal/longitudinal and vertical/longitudinal dispersivities are set at 0.1 and 0.01 respectively. The effective porosity used was 0.05-0.07. Based on evidence from N, H and O isotope and hydrogeochemical analyses (Savard et al., 2004), nitrate is further assumed to be non-reactive, with retardation and absorption being negligible. The initial nitrate concentration in groundwater is set at 1 mg/l, representing background levels derived from groundwater base flow concentrations at that time. The model was calibrated against the measured nitrate levels in the Wilmot River from 1985 to 1998.

Aquifer-scale groundwater residence times dominated by advection processes were discussed in the previous section. Lag time dictated by the effect of dispersion is examined through simulations with nitrate leaching concentration decreased to natural level 1 mg/l from croplands are compared in Fig. 4. Results were extracted from depths of a point (Wil-1) mid-way between the watershed boundary and the discharge point of the flow system at the river at depths of 14 m, 27 m and 60 m.

The results indicate, as expected, a larger $\alpha_L$ leads to a longer tailing off of the nitrate concentrations when source reduction is modelled. The lag time of predicted groundwater nitrate concentrations in response to source reduction, especially the deep groundwater concentration at Wil-1, is sensitive to variations of dispersivity. If nitrate source input to groundwater is reduced to the pre 1965 level from 2005, the model predicts 7-15, 30-40 and 40-50 years are needed for the base-flow/shallow, intermediate and deep groundwaters to recover to pre 1965 nitrate levels respectively. The lag time is defined as the time required for base flow and groundwater concentrations to recover to pre contamination levels after the reduction of loads to pre contamination levels. Note that the lag time and residence times of Layers 2-15 are not comparable because loading reduction in Layer 1 will not lead to immediate input reduction in Layers 2-15.

When $\alpha_L=0$ m, both the Upstream Finite Different Method (UFDM) and Modified Method of Characteristics (MMOC, numerical dispersion free) (Zheng et al., 1998) solvers are used to deal with the advection term and they produce nearly identical base-flow/groundwater concentrations. This suggests that numerical dispersion imposes minimal impacts on the estimation of the lag time in the Wilmot case. The potential impact of a dual-porosity effect on the response of groundwater nitrate concentration to source reduction is not conceptualized in the model and needs further study.

The lag time of predicted groundwater nitrate concentrations in response to source reduction should be expressed in range formats due to the uncertainty of dispersivity and unknown effect of dual porosity. Ignoring the effect of dual porosity, the estimated lag time from mass transport modeling can be considered as the upper bounds of time required for nitrate release from the aquifer. The above estimations are summarized in Table 2 for comparison purposes.
6 CONCLUSIONS

Spatially three-dimensional groundwater flow modeling suggests laterally-dominated flows are present in the aquifer in the Wilmot River watershed mainly due to the large contrast in the hydraulic conductivity ($K_h >> K_v$), the partially-penetrated streams and topography. The model layers are approximately orientated parallel to the flow directions and water budget is performed for individual model layers. Residence times in each layer are calculated as water storage divided by the in-layer flow rate. Results from this exercise show groundwater between water table and 22 m below the land surface, which is the most contaminated and contributes >80% of base flow (53% of total stream flow), has a residence time <4 years. Groundwater at depths tapped by typical domestic wells (22-32 m) has a residence time of 11 years. At depths of 52-70 m, the residence times range from 33 to 90 years. Below 70 m, the residence times increase to >90 years. The estimates represent watershed-scale discretized-layer averages based on pure advection assumptions.

Discretized tritium measurements suggest the ages of groundwater generally decrease with depth and sampled groundwater demonstrates a mixture of water with various ages. Both tritium and nitrate measurements indicate water contaminated by modern agricultural nitrate have reached as deep as 30-75 m in the aquifer in the upland areas probably due to deep well construction (> 75 m). However, domestic wells in the Wilmot River watershed generally do not reach that depth. Nevertheless, this result suggests that caution is needed in the well construction to limit cross-contamination between shallow and deep aquifer. The long lag time, wide and deep spreading extent of the plume and the high intensity of farming represent the large challenges to deal with the nitrate contamination issues in the watershed. Tritium age dating generally agrees with the estimations of residence time adding weight to the gravity of the conclusion.

To understand the impacts of dispersion on the lag time of mass release from the aquifer, the estimations of residence time are compared against spatial three-dimensional advection-dispersion mass transport simulations. A range of $\alpha_L$ is examined and the lag time of groundwater/base-flow nitrate level responses to source changes were found to be sensitive to variations of $\alpha_L$. Larger $\alpha_L$ leads to a longer tailing off effect on concentrations after N input reduction. If pure advection is considered, seven years are needed on average to see a
quasi steady-state mass transport in the base flow and shallow groundwater (Layer 1), which agrees fairly well with the estimation (4 years) of the model layer average. Neglecting dual-porosity effect and considering the uncertainty with dispersion, if nitrate source input is reduced to pre-1985 level from 2005, one would see pre-1965 nitrate concentrations in base flow/groundwaters at depths from water table to 22 m, 22-32 m and 52-70 m in about 7-15, 30-40 and 40-50 years respectively. These estimations basically represent the quasi steady-state concentrations and could be considered as the upper bounds of lag time between adoption of land-use changes and improvement in water quality. In Fig. 4, the scenario with complete elimination of N applications shows that an 80-percent reduction in shallow groundwater and base-flow concentrations could occur in about 5 years. The aquifer is porous-fractured and studying the effect of dual-porosity on mass transport should provide further refinement of time-lag estimations.

The implication for nutrient reduction is that a reduction in N inputs through changes in farming practices could likely result in corresponding improvements in nitrate levels in shallow groundwater and associated base flow within 4-15 years with 80% of the total improvement occurring in about 5 years, and gradually reverse the trend of increasing levels in the aquifer in the Wilmot River watershed. For groundwater at depths of 22-32 m and 52-70 m, similar reductions could take 11-40 and 33-50 years respectively. However, in a small sub watershed, monitoring should detect positive water quality changes in shallow groundwater and associated tributaries upon a reduction in N inputs through land-use changes within less than 5 years due to the relatively short groundwater flow path. The relatively short period of lag time is promising for validating the findings through sub watershed experiments. How much changes should be made on land uses to reach water quality objectives will be discussed in a forthcoming paper.

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REFERENCES