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# Preliminary results from water-isotope characterization of groundwater, surface water, and precipitation in the Wilmot River watershed, Prince Edward Island

S.L. Liao, M.M. Savard, G.H. Somers, D. Paradis, and Y. Jiang

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**Abstract:** Agricultural activity, especially the application of fertilizers, is believed to be a major source of nitrates in groundwater and surface water in Prince Edward Island. Analyses of 107 groundwater and 17 surface-water samples from 4 seasonal field operations in the Wilmot River watershed, and 13 precipitation samples, indicate that average annual nitrate concentrations in groundwater are 6.5 mg/L N-$NO_3$, with 22% of domestic wells exceeding the health guideline of 10 mg/L N-$NO_3$. Concentrations in surface water average 6.2 mg/L N-$NO_3$, but all are below 8 mg/L N-$NO_3$. Stable isotopes of oxygen and hydrogen help delineate interactions between precipitation, groundwater and surface water. Groundwater values fall on or near the meteoric-water line for Charlottetown, indicating that groundwater may be derived entirely from modern local precipitation, although additional precipitation sampling is needed for confirmation. Surface waters have average isotope values similar to those for groundwater, implying that surface water is derived almost entirely from groundwater.

**Résumé :** L'activité agricole, en particulier l'épandage des engrais, est perçue comme étant une source majeure de nitrates dans les eaux souterraines et les eaux de surface de l'Île-du-Prince-Édouard. L'analyse de 107 échantillons d'eau souterraine et 17 échantillons d'eau de surface prélevés lors de quatre sessions de travaux saisonniers sur le terrain dans le bassin de la rivière Wilmot, et de 13 échantillons de précipitation indique que les concentrations annuelles moyennes de nitrates dans les eaux souterraines sont de 6,5 mg/L(N-$NO_3$), et que 22 % des puits à usage domestique ont des concentrations qui sont supérieures à la recommandation de 10 mg/L(N-$NO_3$) pour la qualité de l'eau. Les concentrations moyennes dans les eaux de surfaces sont de 6,2 mg/L(N-$NO_3$), toutes les valeurs étant inférieures à 8 mg/L(N-$NO_3$). Les isotopes stables de l'oxygène et de l'hydrogène aident à reconnaître les interactions entre les précipitations, les eaux souterraines et les eaux de surface. Les valeurs isotopiques des eaux souterraines se situent sur la droite des eaux météoriques de Charlottetown ou à proximité, et les eaux souterraines pourraient donc provenir entièrement de précipitations locales récentes. Toutefois, un échantillonnage plus poussée des eaux souterraines est nécessaire pour confirmer cette hypothèse. Les valeurs isotopiques des eaux de surface sont semblables à celles des eaux souterraines, ce qui suggère que les eaux de surfaces sont dérivées presque entièrement des eaux souterraines.

## INTRODUCTION

In many areas of Prince Edward Island (P.E.I.), nitrate concentrations in groundwater exceed background levels and, in some cases, the health threshold of 10 mg/L N-$NO_3$ (Somers, 1998; Somers et al., 1999). While there are many potential sources of nitrate (including atmospheric deposition, natural soil processes, manure and septic wastes, and the use of inorganic fertilizer), the prevalence of potato production has led investigators to postulate that the application of excess fertilizer to potato fields is a major source of nitrates (throughout this paper, the term 'nitrate' refers to the anions nitrate [$NO^{3-}$] and nitrite [$NO^{2-}$]). Groundwater is the sole source of potable water for the residents of P.E.I. and plays a dominant role in determining surface-water quality. In addition to being a concern for drinking-water quality, excessive nitrate levels contribute to eutrophication of surface water, especially in estuarine environments.

Over the past decade, several studies have documented the nitrate problem in P.E.I. groundwater (Somers, 1992; Somers, 1998; Somers et al., 1999; Young et al., 2003). These studies have shown that elevated nitrate levels are often associated with agricultural activities and result from the use of fertilizers for row-crop production. Some also suggest that groundwater nitrate levels in many areas of P.E.I. are increasing over time, a trend also seen in surface water.

### Objectives

The Prince Edward Island N-Cycle Project, a collaboration between the Geological Survey of Canada (GSC), the Prince Edward Island Department of Environment, Energy and Forestry (PEI-EEF), and Agriculture and Agri-Foods Canada (AAFC), was implemented in 2003 to study the dynamics of nitrogen transfer from soils to groundwater in the Wilmot watershed. The Wilmot watershed is an area of intense agriculture, including potato cropping, and the groundwater system is susceptible to contamination given the unconfined nature of the Wilmot aquifer. This paper examines the stable oxygen ($\delta^{18}O$) and hydrogen ($\delta^2H$) isotope characterization of groundwater, surface water, and precipitation in the watershed, in order to better understand the dynamics among these three reservoirs. Other aspects of this project will be published elsewhere (e.g. Savard et al., 2004).

## STUDY AREA

The Wilmot watershed is located in west-central P.E.I. (Fig. 1). The river drains an area of about 87 $km^2$ and flows southwesterly to the Northumberland Strait. The basin averages 17 km long and 5 km wide. Two-thirds of the river is tidally influenced. The elevation ranges from sea level in the tidal area to 90 m above sea level in the headwater area.

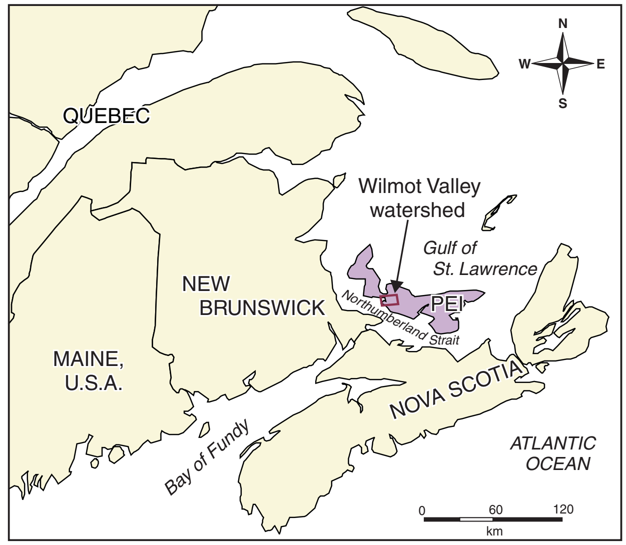


***Figure 1.*** *Location of the Wilmot watershed, west-central Prince Edward Island.*

### Land use

The Wilmot watershed is predominantly rural, consisting of 65% agricultural lands, 21% forests, and less than 10% residential use. The largest urban centre near the watershed is the City of Summerside, population 14 654 (Statistics Canada, 2002), located adjacent to the northwest corner of the watershed. Potato cultivation occupies more than 25% of the agricultural area under cultivation. Potatoes are part of a rotational system with grains and forage crops for hay in either two- or three-year sequences. Large-scale potato farming is concentrated in the southern half of the watershed.

### Climate and hydrology

The climate of P.E.I. is humid continental, with long, fairly cold winters and warm summers. Mean annual precipitation at Summerside Meteorological Station A is 1078 mm (1971–2000), most of which falls as rain (75%). The mean annual temperature is about 5.1°C, and mean monthly temperatures range from -8.6°C in January to 18.4°C in July. Streamflow data for the Wilmot River has been collected at a gauging station (Water Survey of Canada site #01CB004) located above the tidally influenced portion of the river. At the station, the mean annual discharge of the river is 0.92 $m^3/s$ (1972–1999), and the mean monthly discharge ranges from 0.45 $m^3/s$ in September to 1.88 $m^3/s$ in April during the spring freshet.

### Geology

Prince Edward Island is a crescent-shaped cuesta of continental red beds, Upper Pennsylvanian to Middle Permian in age, gently dipping to the northeast (van de Poll, 1983). The red beds have been mapped as a fining-upward series of cyclic deposits containing four 'megacycles' (van de Poll, 1983).

The Wilmot watershed is underlain by portions of Megacycles III and IVa of the Lower Permian Pictou Group (Fig. 2). These sequences are primarily composed of fine- to medium-grained fractured sandstone (80–85%), with lesser siltstone and claystone forming isolated lenses. The fractured sandstone also shows some matrix porosity in places, such that the bedrock is characterized as a dual-porosity medium. This sequence is almost entirely covered by a layer of permeable, unconsolidated glacial material, including sandy till, a few centimetres to several metres thick (Prest, 1973).

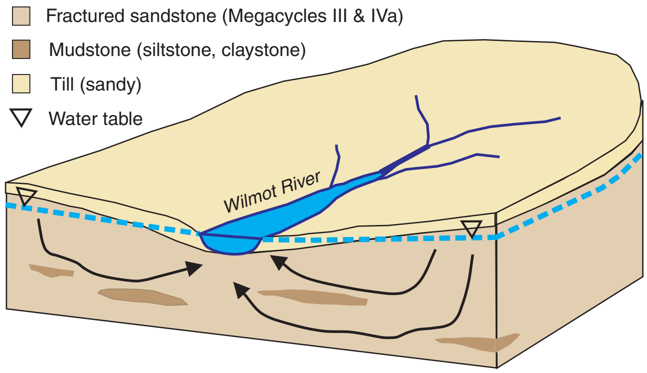


***Figure 2.*** *Hydrostratigraphy and conceptual model of groundwater flow, Wilmot watershed, west-central Prince Edward Island.*

## *Hydrogeology*

Hydraulic-conductivity estimates based on grain-size analyses and slug tests for the Winter River basin, located 50 km east of the Wilmot watershed, can be extended to the study area given the homogeneous geology of this sector of P.E.I. Hydraulicconductivity estimates for the till are $6.7 \times 10^{-8}$ to $1.3 \times 10^{-5}$ m/s for sand phases and $10^{-7}$ to $10^{-5}$ m/s for clay-sand phases (Francis, 1989). Hydraulic-conductivity estimates for the sandstone unit range from $10^{-7}$ to $10^{-3}$ m/s, determined from constant-head injection tests (Francis, 1989). Laboratorybased determinations of hydraulic conductivity range from $10^{-8}$ to $5 \times 10^{-7}$ m/s for sandstone and are less than $5 \times 10^{-10}$ m/s for mudstone (Francis, 1989). Hydraulic conductivities generally decrease with depth, a function of decreasing fracture aperture and frequency with depth, as seen during the multilevel hydraulic testing conducted by the authors during autumn 2004. Fractures represent the main groundwaterflow path, and matrix pores act as reservoirs.

Topography (Fig. 3) appears to be the major factor determining hydraulic-head distribution, with groundwater flowing from the highest to the lowest elevations, and surface-watershed boundaries generally coincide with the boundaries of groundwater-flow systems. The river functions as a groundwater-discharge zone. The aquifer is unconfined, except in small zones where less permeable mudstone beds alternate with sandstone to form semiconfined aquifers. There is a strong anisotropy within the bedrock, in which vertical flow is restricted and horizontal flow is favoured (Francis, 1989), causing the aquifer to behave like a semiconfined

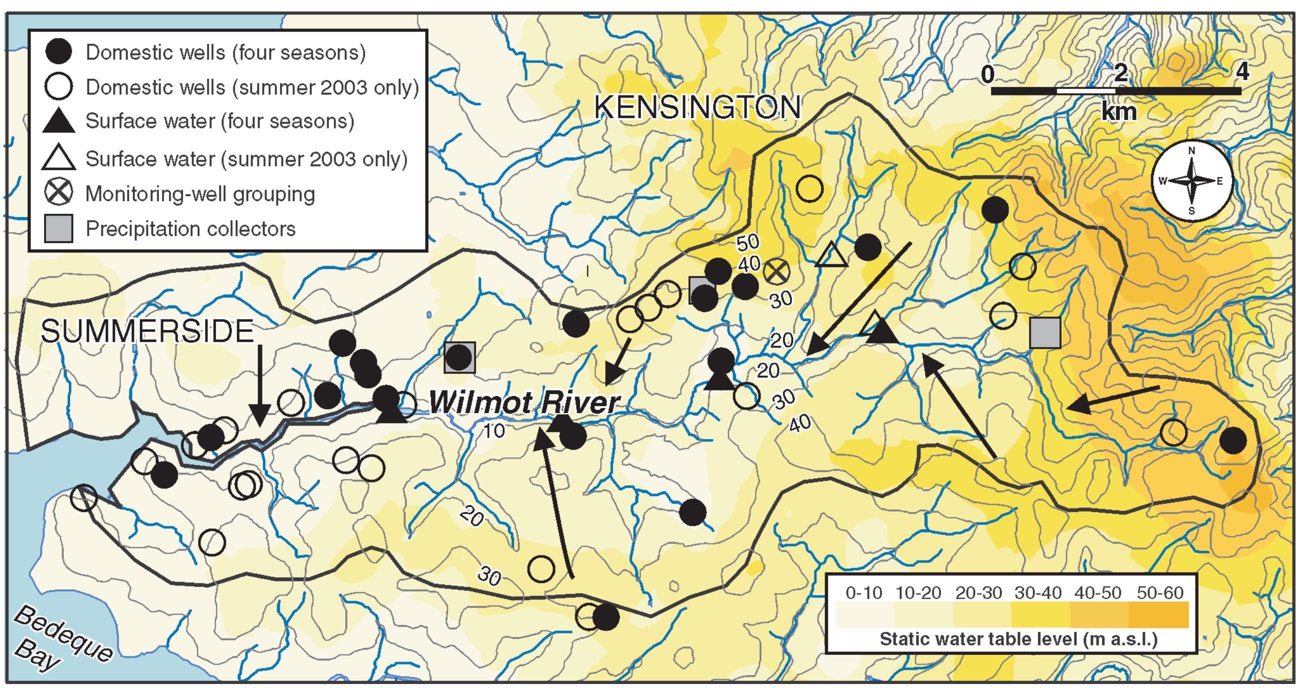


***Figure 3.*** *Wilmot watershed, west-central Prince Edward Island, showing water-table levels, topographic contours (10 m interval), and sampling sites. Solid black line defines the watershed boundaries. Arrows indicate the direction of groundwater flow. Topographic contour values in metres.*

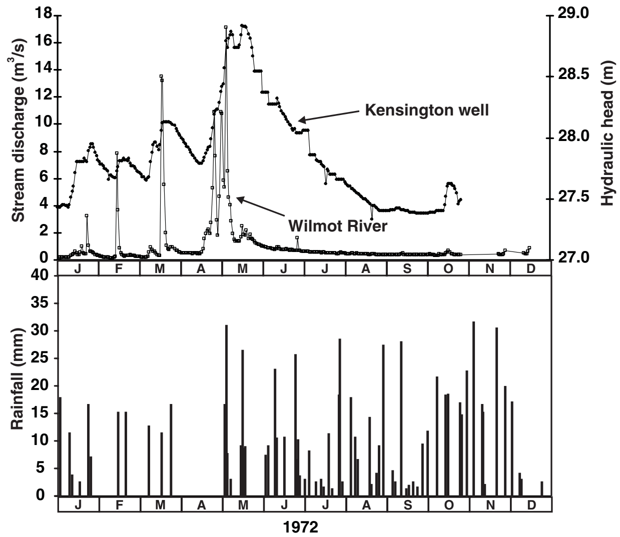


*Figure 4. Hydrographs of the Kensington well and Wilmot River for 1972, compared with 1972 precipitation amounts, west-central Prince Edward Island.*

aquifer. Preliminary modelling in the Wilmot watershed suggests an average Kxy:Kz ratio of 100:1. At the regional scale, the conceptual model of the aquifer can be represented by a permeable unit of sedimentary rock with mixed porosity (fractures and matrix pores), covered by permeable till of variable thickness (Fig. 2).

The fluctuations of the water level in a monitoring well in Kensington, just outside the study area, demonstrate the typical seasonal response to climate for the region (Fig. 4). This response includes a major spring recharge event followed by a summer water-table decline, a moderate autumn recharge event, and finally a decline in the water table through the winter, punctuated by significant winter recharge events.

The stream hydrograph for the Wilmot River indicates a short lag time (several days) between runoff events and the water-table response (Fig. 4). The presence of small seeps along the river and significant flow in the river and its tributaries even several weeks after precipitation events or snowmelt indicate the importance of groundwater discharge to streamflow. In the Winter River basin, runoff and baseflow account for 21% and 40% of precipitation, respectively (Francis, 1989). Baseflow may be the only source of water to the river during summer, however, when precipitation is intercepted by vegetation and subject to evapotranspiration. Given the similar topography, geology, and overall land usage in the Wilmot and Winter basins, runoff values for the Winter basin should apply to the Wilmot basin. Baseflow values could differ because Charlottetown's three well fields intercept and reduce baseflow in the Winter basin.

## FIELD METHODS

### *Location of sampling sites*

To date, 101 groundwater samples from domestic wells (41 summer, 20 autumn, 20 winter, 20 spring), 6 groundwater samples from 3 monitoring wells (3 winter, 3 spring), 17 samples from the Wilmot River (6 summer, 4 autumn, 3 winter, 4 spring), and 13 precipitation samples (7 rain, 6 snow) have been collected and analyzed for $\delta^2$H and $\delta^{18}$O in $H_2O$. Three monitoring wells were installed at one site in January 2004, each dedicated to a discrete level of sampling (Fig. 3).

During the initial field-sampling trip to P.E.I. (summer 2003), precipitation collectors were installed at three locations in the watershed (Fig. 3). Precipitation samples were obtained from all three collectors for the first few months, and then only at a single location after it had been established that the results were similar to those of the other two. Snow samples were obtained on March 31 and April 6, 2004 from an area near the three precipitation sites.

## SAMPLING METHODS

Prior to sampling domestic wells, water-table measurements were obtained where possible. Groundwater was generally sampled from an outdoor tap. Prior to sampling, water-treatment systems were disabled and the wells purged of two to three well volumes until temperature, pH, and specific conductivity values were stabilized. Sampling and purging the monitoring wells was accomplished with a Wattera inertial pump. Groundwater samples were collected in high-density polyethylene (HDPE) 60 mL narrow-mouth bottles for water-isotope analysis. A duplicate sample was obtained for every water-isotope sample. Samples for nitrate-ion analysis were collected in 60 mL polypropylene bottles, frozen, and analyzed within 28 days. A blank was collected at each site by filling a sample bottle with deionized water. A duplicate was collected at the start of each sampling day to determine laboratory precision.

Surface-water samples were collected from the stream's edge at least 10 cm below the water surface and in portions of the stream where flow was swift. None of the sampling trips coincided with any major precipitation events; hence, during sampling, the Wilmot River was under baseflow conditions.

Precipitation samples were obtained for water-isotope analysis only and were sampled from plastic collectors that were 30.5 cm in diameter and 45 cm in height. Buckets were fitted with a funnel, 30.5 cm in diameter at the top, narrowing to 3 cm in diameter at the lower end, to reduce exposure to air. To further minimize evaporation, a layer of Canola oil at least 2.5 cm thick was added to the bottom of the collector. The bucket was fastened to a steel post. Each collector was left for a one-month period (or longer), during which time a composite precipitation sample, representing all precipitation that fell during the month, was collected. A 60 mL plastic syringe was used to obtain water samples from below the layer of oil.

For water-isotope analyses, snow samples were obtained by inserting a plastic cylinder, 1 m long with a 3.8 cm inner diameter, vertically into the snow pack, transferring the snow to a plastic bag and repeating until sufficient snow had been collected for a sample representative of the snow pack plus a duplicate. The samples were allowed to melt at room temperature, then homogenized and transferred into 60 mL HDPE bottles.

## ANALYTICAL METHODS

All samples were analyzed for stable isotopes at the Delta-Lab of GSC Quebec. Isotope results are reported using standard delta (δ) notation in parts per thousand (per mil or ‰) relative to Vienna Standard Mean Ocean Water (VSMOW; Coplen, 1994). Oxygen-isotope analyses were performed by $CO_2$-$H_2O$ equilibration and hydrogen-isotope analyses were performed by $H_2$-$H_2O$ equilibration with a platinum catalyst (Horita and Kendall, 2004). An online isotope-ratio mass spectrometry (IRMS) water-equilibration system (Gas Bench-Delta PlusXL) was used to analyze $\delta^2H$ and $\delta^{18}O$ ratios. Precisions on $\delta^{18}O$ and $\delta^2H$ ratios were 0.07 and 0.8‰, respectively.

Analysis of nitrogen-species concentrations was conducted at the AAFC-Québec laboratory. Nitrate concentrations were determined by the flow-injection analysis (FIA) colorimetric method (LACHAT), for which the detection limit was 0.04 mg/L N-$NO_3$ (1.53 mg/L $NO_3$) and the precision was 0.09 mg/L N-$NO_3$ (0.4 mg/L $NO_3$).

## RESULTS AND INTERPRETATION

### *Concentration of nitrates in groundwater and surface water*

The sampled groundwater exhibits a broad range of nitrate concentrations, from below the detection limit to 14.6 mg/L N-$NO_3$. Maximum concentrations are 14.6, 12.7, 13.4, and 12.2 mg/L N-$NO_3$ for summer, autumn, winter, and spring groundwater samples, respectively. Annual nitrate concentrations in groundwater average 6.5 mg/L N-$NO_3$, with seasonal averages of 7.2, 6.5, 6.3, and 5.5 mg/L N-$NO_3$ for summer, autumn, winter, and spring, respectively. Overall, 22% of the summer groundwater samples have N-$NO_3$ concentrations above the threshold of 10 mg/L established for human health (Health Canada, 2004), whereas 7% of summer groundwater samples have concentrations within the natural range (<1 mg/L). Average nitrate concentrations in the monitoring wells are 6.7 and 6.0 mg/L N-$NO_3$ for winter and spring, respectively.

Surface waters exhibit a much narrower range of values (5.1–7.7 mg/L N-$NO_3$) than that of groundwater, likely because they represent an integration of the wider range of groundwater nitrate concentrations. All values are below the 10 mg/L threshold, yet well above natural levels. Seasonal maximum values are 7.4, 7.7, 6.5, and 5.6 mg/L N-$NO_3$ for summer, autumn, winter, and spring, respectively. On average, nitrate concentrations in surface water are very similar to those for groundwater, with an average annual value of 6.2 mg/L N-$NO_3$, and seasonal averages of 6.6, 6.5, 6.2, and 5.4 mg/L N-$NO_3$ for summer, autumn, winter, and spring, respectively.

There is no apparent spatial trend of nitrate concentrations in the watershed (Fig. 5). There is no apparent correlation between well depth and groundwater nitrate concentrations. It is suggested that the apparent lack of systematic distribution of nitrate concentrations in space can be at least partly interpreted as an expression of a diffuse source of nitrates at surface, unevenly distributed over soils.

### *Water isotopes in precipitation, groundwater, and surface water*

#### Precipitation

Precipitation is the ultimate source of water in all catchment basins, and long-term sampling of precipitation allows for delineation of a local meteoric-water line (LMWL) on a $\delta^2H$ versus $\delta^{18}O$ graph, which is a critical baseline against which the stable-isotope ratios can be compared and the processes affecting them deduced. Precipitation waters plotting at the more positive end (enriched in heavy isotopes of O and H) of a LMWL are derived from summer precipitation, whereas those plotting at the more negative end (depleted in heavy isotopes of O and H) are derived from winter precipitation, a function of the temperature effect (Dansgaard, 1964). The meteoric-water line for Truro, Nova Scotia, the closest long-term site (MWLT: $\delta^2H = 7.30\ \delta^{18}O + 3.59$; Fritz et al., 1987) is derived from 7 years of precipitation data (1975–1982). It represents the average composition of modern local meteoric water. Precipitation at Charlottetown has been examined on a shorter time scale (40 months), yielding a meteoric-water line for Charlottetown (MWLC: $\delta^2H = 6.86\ \delta^{18}O + 6.23$; Francis, 1989).

Only a few months of precipitation and snow data have been analyzed in the present study, not enough to make a full assessment of whether the MWLT or MWLC can be suitably applied to the Wilmot watershed. The existing rain data points for the Wilmot watershed plot near the MWLT and the MWLC, although there is some scatter and the data points are clustered at the enriched (in heavy isotopes) end of each line (Fig. 6). The clustering results from the rain samples being collected only during a time when precipitation is enriched in the heavy isotopes (June to September). The MWLC is a better fit with the data than the MWLT, as the groundwater data sit in approximately equal portions above and below the MWLC, and roughly equal numbers of rain data points lie above and below the MWLC.

The snow samples cannot be considered in the same way as the rain samples because, during the several months it takes the snow to accumulate, the isotopic signature of the precipitation that originally fell is often altered. Snow originates with depleted isotope values because of the temperature effect (Dansgaard, 1964). As the snow begins to melt, sublimation on the surface of the snow occurs, causing kinetic

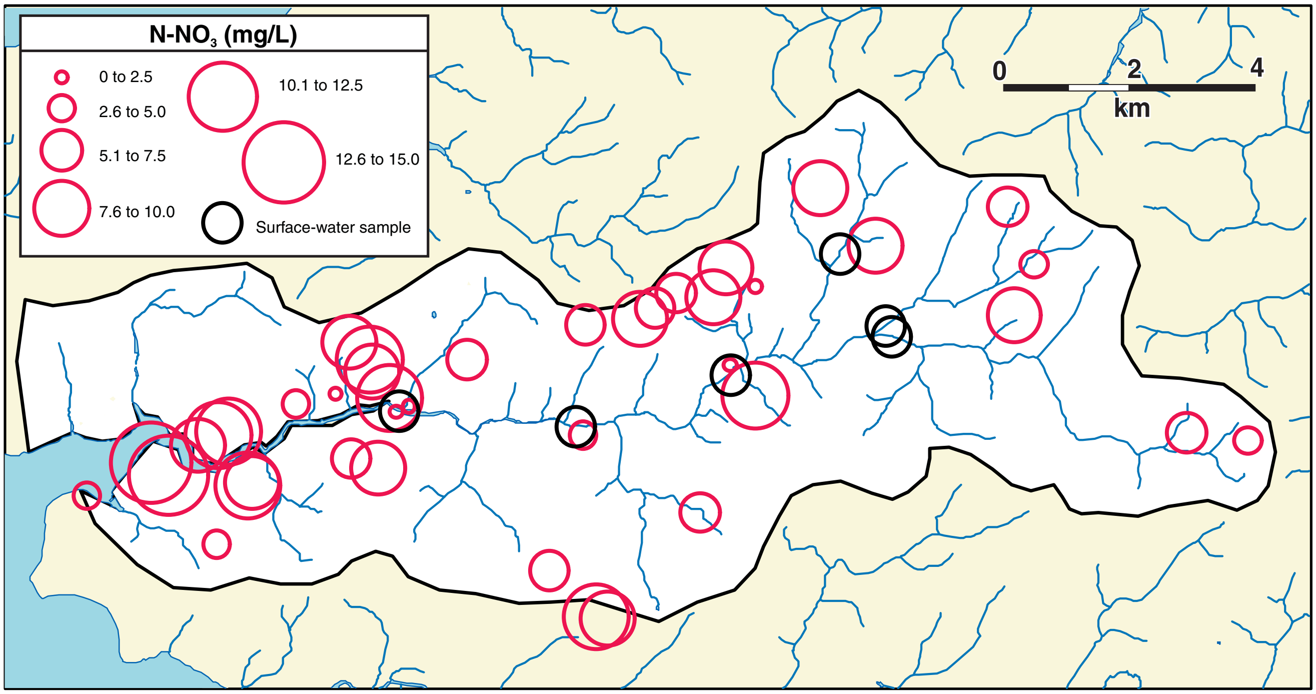


***Figure 5.*** *Spatial distribution of nitrate concentrations in summer 2003 samples, Wilmot watershed, west-central Prince Edward Island.*

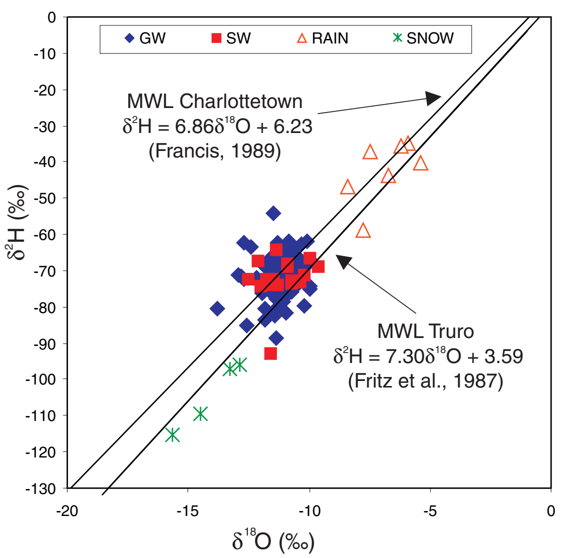


***Figure 6.*** *Oxygen- and hydrogen-isotope values of groundwater, surface water, rain, and snow in the Wilmot watershed (annual), west-central Prince Edward Island. Abbreviations: GW, groundwater; SW, surface water.*

isotope enrichment in the remaining snow (Árnason, 1981). As the snow within the snowpack melts, it mixes with the more enriched surface snow to produce snowmelt with progressively higher δ values. The first meltwaters plot above the LMWL, whereas subsequent waters plot below this line. Depending on when in the melt cycle sampling occurred, snow samples from the Wilmot watershed could fall above or below the meteoric-water line for the watershed. Wilmot watershed snow data plot just below the MWLT and well below the MWLC. This could indicate that the sampled snow had already experienced several phases of melting and was contaminated with late-season meltwater, a reasonable explanation given that sampling was carried out late in the winter.

## Groundwater

Oxygen-isotope ratios of the Wilmot groundwater range from -13.8 to -10.0‰, with an annual average of -11.1‰ and seasonal averages of -11.1, -11.2, -11.0, and -11.2‰ for summer, autumn, winter, and spring, respectively (Fig. 6, 7). Hydrogen-isotope ratios of groundwater range from -89 to -54‰, with an annual average of -72‰ and seasonal averages of -70, -72, -73, and -75‰ for summer, autumn, winter, and spring, respectively (Fig. 6, 7). Average oxygen-isotope values in the monitoring wells are within 0.1‰ of averages observed in domestic wells. Similarly, average $\delta^2$H values in the monitoring wells are within 1‰ of averages observed in domestic wells.

The oxygen- and hydrogen-isotope ratios of the majority of the groundwater fall on or above the MWLT, implying that the MWLT may not be applicable to the Wilmot watershed because there are only a few processes in nature that can cause waters to plot above the LMWL. In the Wilmot watershed, the stable-isotope ratios of groundwater fall within the range (-6 to -14 ‰ for $\delta^{18}$O) expected for groundwater derived from modern precipitation in the Maritimes (International Atomic Energy Agency, 2001). The fact that approximately equal numbers of groundwater data points lie above and

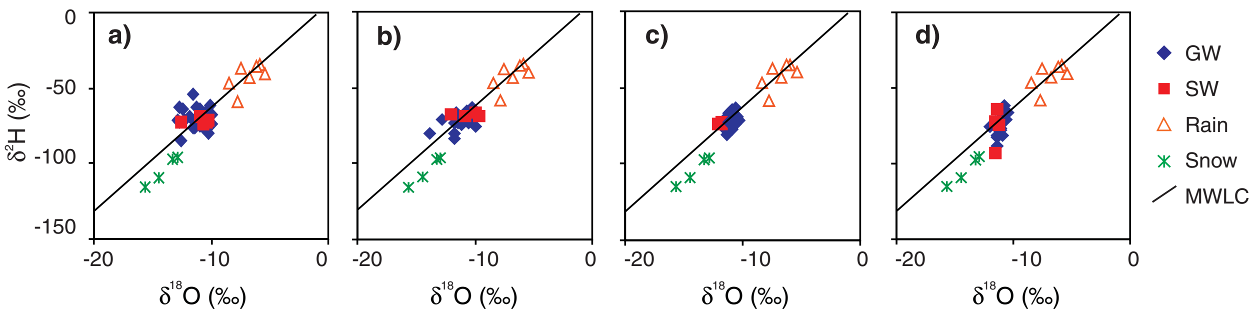


*Figure 7. Oxygen- and hydrogen-isotope values of groundwater, surface water, rain, and snow in the Wilmot watershed for a) summer, b) autumn, c) winter, and d) spring samples. Abbreviations: GW, groundwater; MWLC, meteoric-water line for Charlottetown; SW, surface water.*

below the MWLC implies that groundwater in the watershed may be derived entirely from modern local precipitation. Once there are sufficient data to construct a LMWL for the Wilmot watershed, it will be possible to confirm this. There is no evidence that the isotopic signature of the groundwater was altered by evaporation from a shallow water table, mineral exchange, or mixing with isotopically distinct waters.

The cluster of all groundwater data is positioned halfway between the precipitation that fell during June to September and the winter snow precipitation, implying that the groundwater system may be affected approximately equally by precipitation events and spring snowmelt (Fig. 6). Although climatic data show that a larger proportion of precipitation at Summerside falls as rain (75%), there is likely very little infiltration of summer precipitation, as evapotranspiration is high during the summer. During the cooler months, when evapotranspiration is negligible, a larger proportion of precipitation is likely to infiltrate. A well hydrograph at Kensington (several years of data) indicates that almost 50% of recharge is from autumn precipitation and the other 50% is from the spring melt. In order to confirm the relative proportions of groundwater recharge, stable-isotope analysis of at least a full year of precipitation data is needed.

There are no obvious seasonal trends in the water-isotope results obtained for groundwater, although the summer data, particularly the $\delta^2$H results, show the greatest amount of scatter (Fig. 7). The lack of seasonal trends and the relative constancy of the results imply that the groundwater system represents a well mixed aggregate of waters from different seasons. The scatter is likely a function of the greater sample set and variation in well depths for the summer sampling period, although no correlation has yet been observed between well depth and groundwater d$^{18}$O or d$^2$H values. The relative constancy of $\delta^{18}$O and $\delta^2$H values for all seasons implies that the groundwater system is well enough mixed that seasonal signals are muted out. There are no $\delta^{18}$O or $\delta^2$H spatial trends in the watershed (Fig. 8 and 9, respectively) and no correlation between groundwater nitrate concentrations and groundwater $\delta^{18}$O or $\delta^2$H values.

### Surface water

The $\delta^{18}$O values of Wilmot surface water range from -12.5 to -9.6‰, with an annual average of -11.1‰ and seasonal averages of -10.9, -10.7, -11.8, and -11.4‰ for summer, autumn, winter, and spring, respectively (Fig. 6, 7). The $\delta^2$H values of surface water sampled throughout the year range from -74 to -64‰, with an annual average of -71‰ and seasonal averages of -72, -68, -74, and -76‰ for summer, autumn, winter, and spring, respectively (Fig. 6, 7).

All surface-water bodies undergo evaporation from their surfaces at humidities of less than 100% (Gat, 1970). Evaporation is a nonequilibrium fractionating process that causes the heavy isotopes of oxygen and hydrogen to be concentrated in the more dense phase (residual liquid phase). Such waters typically plot along an evaporation line that diverges from the LMWL (Craig and Gordon, 1965), making them distinguishable from precipitation and groundwater. In moderate climates, evaporation of river water is not significant. Therefore, stable-isotope values of river water often reflect the source waters. In environments where surface runoff is the dominant source of water to a river, the isotopic values of river water will resemble those of precipitation, displaying seasonal extremes. In environments where groundwater baseflow into rivers is significant, the values of river water will have a less seasonably variable signature.

The fact that the stable-isotope values obtained for the Wilmot River do not exhibit strong seasonal variations implies that the river water is not derived directly from precipitation, at least not during the four sampling trips (Fig. 7). Surface-water values plot in the middle of the groundwater values, implying that the surface water is likely derived entirely from local groundwater. This idea is supported by the fact that the average annual value of $\delta^{18}$O in groundwater is identical to that of surface water (-11.1‰). The average annual $\delta^2$H values for groundwater and surface water are also nearly identical. The absence of surface-water excursions from the MWL (no local evaporation line) indicates that the river is not undergoing evaporation during the time of year when evaporation is expected to be highest. Surface runoff (during heavy precipitation) could, however, provide an additional source of water to the Wilmot River. Surface water was sampled immediately following a major precipitation event in spring 2005, and will be assessed.

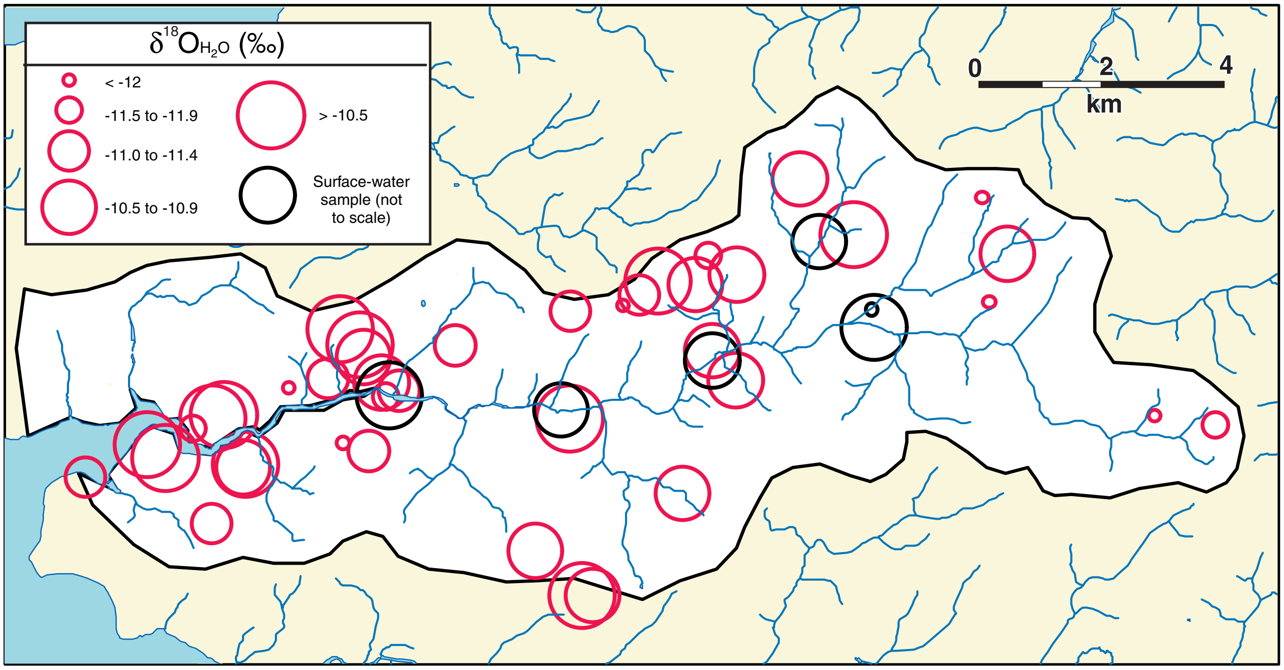


*Figure 8.* Spatial distribution of $\delta^{18}O$ values obtained for summer 2003 samples.

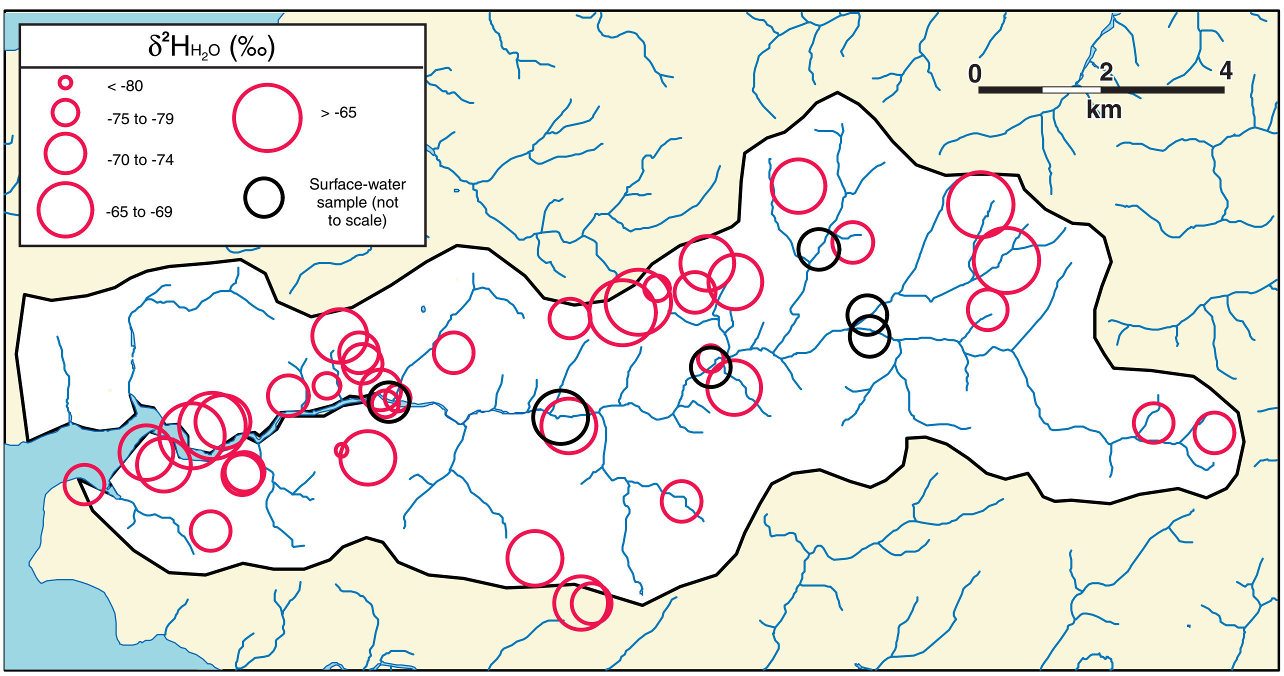


*Figure 9.* Spatial distribution of $\delta^{2}H$ values obtained for summer 2003 samples.

There are some differences between the average seasonal values of $\delta^{18}O$ in groundwater (-11.1, -11.2, -11.0, and -11.2‰ for summer, autumn, winter, and spring, respectively) and those of surface water (-10.9, -10.7, -11.8, and -11.4‰ for summer, autumn, winter, and spring, respectively; Fig. 7). There is only a 0.2‰ difference between summer values and spring values; however, there is a 0.5‰ difference between autumn values and a 0.8‰ difference between winter values, with groundwater being more negative than surface water in autumn and less negative than surface water in winter. Surface water shows a greater range of values than groundwater, with the seasonal averages for surface water being farther from the annual average of -11.1‰ than the seasonal averages for groundwater. For surface water, autumn values tend to be more positive than summer values. This further supports the idea that evaporation is not the primary control on the surface-water values, or summer values would be more positive.

## FUTURE INVESTIGATIONS

Five additional seasonal sampling trips from summer 2004 to summer 2005 will be used to confirm and constrain these preliminary interpretations. This includes sampling of six additional monitoring wells and six domestic wells, drive-point sampling (a type of shallow groundwater sampling in which a narrow steel tube, with internal plastic tubing for sampling, is driven a few metres into unconsolidated sediment to sample groundwater in locations where the water table is shallow) of shallow groundwater near river discharge points, and sampling of stream water immediately following precipitation events. Samples from all nine monitoring wells will be sent for tritium analysis to establish groundwater age and to assess groundwater recharge. Precipitation sampling will continue until autumn 2005, and additional snow sampling occurred in winter 2005.

## CONCLUSIONS

The Charlottetown meteoric-water line (MWLC), although based on less data than the Truro meteoric-water line (MWLT), is a more suitable match to Wilmot precipitation and for comparison with Wilmot groundwater and surface water.

Stable-isotope ratios of groundwater fall within the range predicted for P.E.I. groundwater (International Atomic Energy Agency, 2001). The position of the groundwater data relative to the MWLC implies that groundwater in the Wilmot River basin is derived entirely from modern local precipitation, although additional precipitation sampling will confirm this. Once there are sufficient data to construct a LMWL for the Wilmot watershed, it will be possible to determine proportions of groundwater derived from rain versus snowmelt. Two-dimensional modelling and recharge analysis will assist in this determination. The lack of seasonal trends in groundwater-isotope results and their relative constancy imply that the groundwater system represents a well mixed aggregate of waters from different seasons.

The stable-isotope ratios of water in the Wilmot River do not exhibit strong seasonal variations, implying that it is not derived directly from precipitation, at least not during the four sampling trips discussed here. The average annual $\delta^{18}O$ and $\delta^{2}H$ values of groundwater are nearly identical to those of surface water, and the overlap of groundwater and surface-water clusters in $\delta^{2}H$-$\delta^{18}O$ space suggests that most nitrates present in the Wilmot River during baseflow are derived from groundwater. Future sampling will enable an assessment of whether surface runoff during heavy precipitation events is also a source of water and nitrates to the Wilmot River.

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