A seasonal apportionment of nitrate sources has been conducted to investigate the dynamics of nitrogen (N) transfer from soils to groundwater. A mass balance model is used to link specific cropping practices to source contributions to GW. The model provides an independent source apportionment to be compared with a previous one based on nitrate isotope results. Both approaches demonstrate that chemical fertilizers dominate the growing-season load, whereas crop residues dominate the non-growing contribution, implying that simple changes to practices may help decrease N losses from agriculture.

1. INTRODUCTION

Elevated nitrate concentrations in groundwater (GW) can be a concern with respect to drinking water quality, and may also contribute to nutrient loading of surface waters with associated ecological concerns. Numerous investigations have linked nitrogen application rates on agricultural lands to GW quality. In contrast, the significance of bacterial nitrification during the colder, non-growing period has not been given much attention. Stable isotope methods using nitrogen isotope ratios ($\delta^{15}$N), and more recently $\delta^{15}$N and oxygen isotope ratios ($\delta^{18}$O) in GW nitrate have been used to investigate the relative source contributions of N in agricultural settings (Kendall and Aravena, 2000, Wassenaar 1995; Savard et al., in press).

In the current study area, Savard et al. (2007a, b) documented a distinct seasonal $\delta^{18}$O value in the nitrate ion present in GW and discriminated between the relative contributions of key nitrate sources during the growing and non-growing seasons. Using a geochemical mixing model with chemical fertilizers, manure and crop residues as end members the results confirm the importance of chemical fertilizers to N loading of GW during the warmer periods of the year, but also highlight the significance of bacterial nitrification of crop residues to the flux of N from soils during the colder non-growing season (Savard et al., 2007b).

These findings have important implications for the development of effective strategies for the reduction of N losses from agricultural lands, and it is therefore important to confirm these conclusions and link as closely as possible, specific N inputs, outputs and cropping practices with resulting N leaching losses to GW. Here, a mass balance model has been developed using data on the quantities, timing and cropping practices associated with various N sources for principle crops within an agricultural watershed throughout a typical yearly cycle. By this approach we attempt to evaluate the net contribution of different general types of N sources at different times of the year. We also aim at identifying, at least on a theoretical basis, the relative importance of specific crop inputs and crop practices responsible for the observed N fluxes from agricultural soils to GW. In addition to providing a theoretical framework for an investigation of the seasonal dynamics of N transport from agricultural soils to GW, we want to use this model for independent confirmation of the results derived from the parallel stable isotope source apportionment.
2. STUDY AREA

The subject area of this study is the Wilmot River watershed, situated in west central PEI. The watershed-aquifer system is ideally suited to the study of nitrate transfer from soils to aquifer due to the intensity of agricultural activity and to the availability of data from previous investigations in the watershed. The Wilmot River basin is approximately 5 km wide and 17 km long and drains an area of about 87 km². Elevations range from sea level in tidal portions of the river basin in the west to 90 m.a.s.l. in upland areas in the east. The climate of Prince Edward Island is humid-continental, with long, fairly cold winters and warm summers. Mean annual precipitation averages 1153 mm with 73% falling as rain and the remainder falling as snow. The mean annual temperature is 5.3°C with mean monthly temperatures ranging from −7.9°C in January to +18.5°C in July.

Groundwater resources are essentially limited to a sequence of “red bed” sediments of Upper Carboniferous to Lower Permian age, overlain by a thin veneer of glacial till. Rock lithology is dominated by sandstone with variable amounts of inter-bedded basal conglomerates, siltstone and claystone (van de Poll, 1983). These strata are essentially undisturbed and flat lying, with dips commonly to the northeast at about one to three degrees. The formation can be characterized as a fractured porous media, semi-confined aquifer, with fractures representing the main GW flow paths, and matrix porosity determining its storage characteristics. Increase in the spacing of horizontal bedding-plane fractures and decrease in the aperture of fracture sets significantly reduce permeability and flow below the aquifer depth of 30 m (Paradis et al., 2007). With near horizontal bedding plane fractures dominating the fracture network, GW flow is dominantly lateral, with the uppermost portions of the aquifer being the most active and responsive to seasonal recharge characteristics.

The recharge rate of the aquifer is high; in the range of 30% of annual precipitation or on average 410 mm/y, and GW discharge (base-flow) constitutes a high portion of total stream flow. Hydrogen (δ²H) and oxygen isotope results for GW samples fall on or near the meteoric water line (MWL) for the region, indicating that GW is likely to be derived entirely from modern local precipitation. Surface waters (SW) have average isotope values similar to those for GW, implying that SW is derived almost entirely from GW (Liao et al., 2005), confirming the importance of base-flow processes to total stream flow.

Approximately 21% of the watershed is covered by forest, and another 4% is accounted for by residential development, with the population distributed throughout the watershed, although concentrated somewhat in the vicinity of several rural communities. The remaining 75% of the watershed is occupied by agricultural land, with potatoes being the principle cash crop, produced as part of a rotational system with cereals and forage crops. Lands in potato rotations account for approximately 80% of agricultural land use in the watershed (Atlantic AgriTech 2006, Jacques Whitford and Associates 2001).

At any one time approximately 50% of the crop land in the Wilmot watershed will be in a two-year crop rotation and 50% of the land will be in a 3 year crop rotation. Typical agricultural practices are characterized by seeding and fertilization of crops during late spring and crop harvest in the fall, with plant residues left in the field after harvesting. Other agricultural land uses include a few livestock operations.

Nitrate concentrations in GW and SW of the watershed have been subject to considerable study, with average values from domestic wells sampled during this study ranging from below detection to 14.6 mg/L and averaging 7.09 mg/L. In spite of the wide range of nitrate concentrations, seasonal values derived from individual wells through this study remain relatively stable throughout the year (Savard et al., 2007b). There is evidence for progressively increasing nitrate concentrations in the watershed over longer time periods (Somers et al., 1999) and continuation of this trend is suggested by the results of numerical GW flow and transport modelling (Jiang and Somers, 2007, Paradis et al., 2007). Surface water nitrate results were similar to GW results, but with a narrower range of values. The mean SW nitrate concentration from samples collected from the Wilmot River was 5.57 mg/L with values ranging from 2.72 mg/L to 7.68 mg/L. Surface water samples were collected at times when the water should represent primarily GW base-flow. Historical samples from the same river and representing base-flow conditions reflect the same historical trend toward increasing nitrate levels noted for GW (Somers et al., 1999).

3. METHODS

For the development of a nitrogen mass balance model, data were collected for the proportions of the watershed occupied by specific land uses within the watershed, representative input and outputs rates for key N sources and sinks and the timing and prevalence of the main agronomic practices. The nitrogen inputs considered in the model can be considered to fall into four categories: chemical fertilizers, organic sources (manure + domestic sewage) crop residues and direct atmospheric deposition (Savard et al., 2007a). Data specifically applicable for the Wilmot watershed were assembled under contract by Atlantic AgriTech (2006), and supplemented by information from Jacques Whitford Environment Ltd. (2001).

3.1 Annual Mass Balance

Annual contributions from major N sources were initially tabulated for major N sources based on information on the spatial proportions of specific land uses and cropping practices within the watershed. Principle N sources considered included chemical fertilizers, manures, domestic sewage, mineralization and nitrification of residual plant (crop) material, and atmospheric deposition. Land use proportions form GIS resources (Atlantic AgriTech, 2006) were used to estimate the proportions of land occupied by specific crops. Land used
for potato production was divided evenly into two-year (potato – hay) and three-year (potato – cereal – hay) rotations. In addition the proportion of crop lands planted with cover crops, and the frequency of use of straw mulch were included in the model.

Nitrogen inputs from chemical fertilizers were derived by weighting N application rates for individual crops by the proportion of the watershed occupied by that crop. The crop rotations considered were split evenly between a three-year rotation including potato, cereal and forage crops and a two-year rotation consisting of just potato and cereal crops. The N contribution from the mineralization and subsequent nitrification of crop residues was estimated using the N content of the un-harvested portion of the crop, weighted again by the proportion of the relevant fraction of the watershed for that crop.

Table 1. Annual nitrate mass balance for the Wilmot watershed.

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Application rate (kg/ha)</th>
<th>% area of watershed</th>
<th>Nitrate contribution (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical fertilizers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potatoes</td>
<td>200</td>
<td>26</td>
<td>52</td>
</tr>
<tr>
<td>Cereals</td>
<td>42</td>
<td>26</td>
<td>16.1</td>
</tr>
<tr>
<td>Forages</td>
<td>0</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Organic sources</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manure</td>
<td>-</td>
<td>-</td>
<td>24.7</td>
</tr>
<tr>
<td>Domestic sewage</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
</tr>
<tr>
<td>Atmosphere</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct deposition</td>
<td>7</td>
<td>100</td>
<td>7</td>
</tr>
<tr>
<td>Fixation by legumes</td>
<td>-</td>
<td>5</td>
<td>31</td>
</tr>
<tr>
<td>Total N inputs</td>
<td></td>
<td></td>
<td>133.1</td>
</tr>
<tr>
<td>N removed with crops</td>
<td></td>
<td></td>
<td>96.6</td>
</tr>
<tr>
<td>N available for leaching</td>
<td></td>
<td></td>
<td>36.5</td>
</tr>
</tbody>
</table>

Manure inputs for the watershed were taken directly from Jacques Whitford Environment Ltd. (2001), and were estimated on the basis of livestock numbers, annual manure production and average N content of respective manure types. An estimation of the N contribution from residential sewage discharges was made based on residential population and average nitrate concentrations in typical domestic wastewater streams. Direct atmospheric deposition of nitrate over the entire watershed was provided by Bob Vet (pers. comm. 2004, Environment Canada). Nitrogen fixed from the atmosphere by legumes was accounted for in the model indirectly by assuming that the entire N content of leguminous crops is derived from atmospheric N.

N outputs from the system included N removed with the harvested portion of the crop, and N leached from the soil to GW. The former were estimated from typical crop yields in the watershed and literature values for the N content of the harvested portion of the specific crop. The quantity of N available for leaching to GW was taken simply as the difference between total N inputs and N removed from the system by the crops. Table 1 summarizes the annual N inputs and outputs considered in the model. Based on this information an annual nitrogen balance for the watershed was developed using equation 1:

$$N_{\text{leached}} = N_{\text{cf}} + N_{\text{man}} + N_{\text{cr}} + N_{\text{atm}} + N_{\text{leg}} - N_{\text{hc}}$$

Where N sources or sinks are identified as:

- $N_{\text{cf}}$ = chemical fertilizers
- $N_{\text{man}}$ = manure + domestic sewage
- $N_{\text{cr}}$ = nitrification of crop residues
- $N_{\text{atm}}$ = direct atmospheric deposition
- $N_{\text{leg}}$ = fixation by legumes
- $N_{\text{hc}}$ = N removed with harvested crop
- $N_{\text{leached}}$ = N available for leaching

The results of the annual balance were subsequently verified by comparison with independent estimations of N leaching from the Wilmot agricultural soils (van Bochove et al., 2007, Jiang et al., 2007).

3.2 Seasonal Mass Balance

After an annual N balance was developed, specific N inputs and outputs from the system associated with main agronomic practices were assigned either to the growing season or non-growing season. To capture both the key elements of major agronomic processes, and the natural hydrologic and biological processes affecting nitrogen behaviour and transport, a number of simplifying assumptions were necessary. The growing season is defined here as the period following the main spring recharge event, commencing with planting and fertilization of crops and extending through crop harvest, terminating after the fall recharge event. Thus the growing season as defined here includes the main period of crop growth as well as a period of time during which crop growth is essentially negligible. The non-growing season as defined in the model extends from the period after the fall recharge period, where the only significant plant growth is limited to that associated with cover crops, through the winter and spring until the end of the spring recharge event.

The approach adopts a rigid assignment of specific processes or inputs to either the growing or non-growing seasons even though under real world conditions these may occur dominantly in one season, but still have some influence on nitrate availability at other times of the year. By way of example, it is generally considered that a certain amount of nitrate remains in the soil into the winter period (MacLeod et al., 2002), although it has not generally been possible to identify the specific source of this N. Without detailed information on the relative degree of this carry-over, it is not possible to correctly assign the proportions of this N source between these adjacent seasons. In the model, all chemical fertilizer inputs are assigned to the growing season and are assumed to be taken up by the crop, or leached to GW by the end of the growing season, after the end of the fall recharge period.
Similarly, it is logical to assume that the mineralization of crop residues takes place to some extent year round, and that the rate of mineralization will vary from crop to crop and with prevailing weather conditions. Nonetheless, in the model, the timing of mineralization and nitrification is tied to major agronomic practices such as the ploughing down of forage crops or the presence of “un-harvested” portions of crops left behind as residual plant material after harvest. Furthermore the model does not attempt to mimic the rate of mineralization and subsequent nitrification and assumes all N contained in the crop residual is made available within the same season. It should be noted however that it is the timing of significant recharge events that will determine when this nitrate is exported to the aquifer. Thus as the growing and non-growing seasons are defined here, the rigid assignment of these factors in time should not overly affect the main conclusions regarding relative source influences drawn from the model.

Another assumption is that manure spreading occurs in equal proportions in the fall and the spring periods. While manure spreading practices are likely to vary from farm to farm, in the absence of definitive information on the timing of manure application it is assumed here that 50% of the manure generated during the year is applied post-harvest, in part to free up manure storage capacity over the winter when manure application is prohibited, and the manure generated and stored over the winter is applied the following spring.

As a consequence of these factors the model can produce only a generalized picture of the influence of particular agronomic practices on a seasonal basis and direct comparison with real world results for a specific year is difficult. Thus the model is not intended to mimic actual field conditions precisely, but at least at a first order, identify the key practices and processes that dominate the growing and non-growing seasons as a whole. Table 2 shows the assignment of specific N inputs and outputs to one of four seasons, subsequently aggregated into the two principle periods of interest, namely the growing and non-growing seasons.

### 4. RESULTS AND DISCUSSION

#### 4.1 Results of Mass Balance Models

The mass balance model suggests that on an annual basis, N inputs from various sources to the system, including chemical fertilizers, manures and sewage, and residual crop material (including N fixed by legumes) sum up to the equivalent of approximately 133 kg/ha. Of this amount a little over 70% (95.1 kg/ha) is from anthropogenic sources, a value in the same range for anthropogenic inputs (97.9 kg/ha) estimated by Jacques Whitford Environment Ltd. (2001) for the watershed. On an annual basis, chemical fertilizers account for nearly 70% of these anthropogenic sources. N sinks considered include N removal with the harvested portion of crops and N leached to GW. Based on average crop yields, the portion of the crops removed from the system at harvest, and the N content of these harvested crop fractions, we estimate N removal by crops amounts to approximately 97 kg/ha when prorated over the watershed. Subtracting N removed with the crop fraction from N inputs to the system, it is suggested that approximately 36 kg/ha N is available for leaching to GW, a figure in reasonable agreement with the average value of 30.1 kg/ha over a three year period calculated by van Bochove et al. (2007), and a 5 year mean of 34.6 kg/ha calculated by Jiang et al., 2007).

When N sources and processes are assigned to the growing season and non-growing season the overall significance of chemical fertilizers is preserved, however the important influence of mineralization and nitrification of crop residual material during the non-growing season becomes apparent. It is important to note that whereas the magnitude of N sources during the growing season is

<table>
<thead>
<tr>
<th>N sources (kg/ha)</th>
<th>Growing season</th>
<th>Non-growing season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Summer</td>
<td>Fall</td>
</tr>
<tr>
<td>Inorganic inputs:</td>
<td>Chemical fertilizer application</td>
<td>68.12</td>
</tr>
<tr>
<td>Organic inputs:</td>
<td>Manure application</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Sewage inputs</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Total organic sources</td>
<td>0.57</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>Direct deposition - wet and dry</td>
<td>1.75</td>
</tr>
<tr>
<td>N from residual plant material</td>
<td>N in residual crop material</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Plow down of forage crops**</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Plow down of cover crops</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Total residual plant material</td>
<td>0.00</td>
</tr>
<tr>
<td>Sum of inputs by period</td>
<td>103.40</td>
<td>46.32</td>
</tr>
</tbody>
</table>

---

Table 2. Assignment of principle nitrate sources and processes to growing and non-growing seasons (values are prorated over the entire watershed).
more than double that of the non-growing season, there is little plant uptake of N during this latter period, and as a consequence actual quantity of nitrate leached to the water table during the non-growing season is comparable to that of the growing season (Savard et al., 2007a).

Figure 1. Results of mass balance calculation of relative proportions of key N sources for a) the growing and b) the non-growing season.

4.2 Comparison with Source Apportionment Based on Nitrate Isotope Results

The dual isotope δ^{15}N and δ^{18}O approach combined with a program of seasonal sampling was used to quantify the relative contribution of the same key N sources considered above during the four seasons (Savard et al., 2007a, b).

Figure 2 depicts the average end members and seasonal GW samples in the δ^{15}N and δ^{18}O space showing the typical isotopic fields of N sources and points derived from measurements of Wilmot sources. The model is described in Savard et al. (2007a) and will be discussed in detail in Savard et al. (in prep.). Only pertinent details are reproduced here. Main sources of nitrate were characterized with isotopic analyses. Using classical mixing models and the average nitrate isotopic values obtained for the various seasons, the relative contributions of chemical fertilizers, manure + sewage and the mineralization and nitrification of crop residues were estimated and expressed for the growing and non-growing seasons. The relative apportionment of individual N sources assumes that the atmospheric load is constant over the year and that the total of N sources can be attributed to a mixture of the three main sources cited above. Relative source proportions were determined using the approach of solving 3 equations for 3 unknowns. Solution of the equations for the summer of 2003 suggests that chemical fertilizers dominate the nitrate load at 62%, followed by organic sources (manure and sewage) at 21%, and crop residues at 12%. In contrast, the same calculations for the winter of 2004 attribute only 22% to chemical fertilizers, 14% to organic sources and, perhaps most significantly, 59% to crop residues.

As with the mass balance model, this source apportionment based on nitrate isotope results does not aim to provide precise values for the contribution of various sources, but rather at assessing which source contributes most significantly to the seasonal loads during the period of investigation. Both approaches demonstrate the importance of understanding not just net annual results of the processes involved in the transfer of N from agricultural soils to GW but also the complex seasonal behaviour of the soil N system.

The figures drawn from the isotopic mixing model are in general agreement with the mass balance model, but perhaps the isotopic data more accurately reflect real-world conditions. Even if watershed-wide seasonal average values were used for calculations, the isotopic model benefits from the fact that it is based on actual field values, providing a more representative assessment of relative N source proportions in GW. As noted before the mass balance model assumes that the influence of manure can be distributed over two discrete periods.
In addition, the mass balance model assumes that all chemical fertilizers are either taken up by plants, or flushed from the soil by the fall recharge event whereas the isotopic model reflects the carry over of some portion of the inorganic and organic N into the growing and non-growing seasons.

From another angle, the mass balance model represents an idealized picture of soil N processes under generalized weather and cropping conditions which allows for the identification of key agricultural practices associated with seasonal N loads. In contrast, the isotopic model lacks the ability to identify the role of specific agronomic practices in relation to the N contributions of various sources. Results using the stable isotope approach are also dependant on the weather and cropping conditions for the sampling period, and while results for a subsequent yearly sampling cycle (not reported here, see Savard et al., 2007a) demonstrate the same general apportionment of seasonal N sources presented here, the temporal trends vary somewhat between yearly cycles. Briefly, the two models complement each other, and taken together, they provide independent confirmation of results and allow greater insight into the links between specific agronomic practices and resulting nitrogen losses to GW than would be possible independently.

5. CONCLUSIONS

Mass balance calculations were made, based on land-use distribution of various crops, timing of principle agronomic practices and N content of harvested and residual crop materials. Results in terms of contributing sources to the GW load during the growing and non-growing seasons compare well with results previously obtained using a 3 equations-3 unknowns solution model based on average GW nitrate isotopic results. The two models highlight the importance of considering the complex seasonal behaviour of the soil N system in developing strategies for the reduction of nitrogen losses from agricultural lands. The models complement each other by collectively providing information that could not be derived from either model independently. They also demonstrate the significant differences in N sources between growing and non-growing periods of the year, and the importance of nitrification of crop residual material to the availability of N for leaching to GW during winter.

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