



Evaluation of Nitrate Impacts at a Municipal Well in an Agricultural Setting using Mass Balance Modeling Techniques

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ABSTRACT

Current and future nitrate concentrations at a production well were evaluated using a mass balance model which linked nitrogen loading to groundwater concentrations at the production well. The nitrate loading function was developed using detailed agricultural information from within the capture zone. The nitrate loading function captured historical changes to agricultural practices suggesting it can be an effective tool for qualifying the implementation of Beneficial Management Practices. Combining the nitrate loading function with the mass balance model it was possible to quantitatively predict nitrate concentrations at the production well. The following details the nitrate loading function and introduces the preliminary mass balance modeling results.

RÉSUMÉ

Une évaluation des concentrations présentes et futures en nitrate a été réalisée pour un puits de production d'eau potable au moyen d'une modélisation du bilan massique qui établit un lien entre les charges d'azote et les concentrations dans l'eau souterraine au niveau du puits. Le modèle d'évaluation des charges de nitrate a été développé à l'aide d'informations détaillées sur les pratiques agricoles employées dans la zone de captage du puits. Le modèle d'évaluation des charges de nitrate incorpore les changements historiques des pratiques agricoles, ce qui suggère que ce modèle pourrait s'avérer un outil efficace pour qualifier l'implémentation des pratiques de gestion bénéfiques. En combinant le modèle d'évaluation des charges de nitrate avec le modèle du bilan massique, il a été possible de faire une prédiction quantitative des concentrations de nitrate au niveau du puits. Ce qui suit détaille le modèle d'évaluation des charges de nitrate et introduit les résultats préliminaires du modèle du bilan massique.

1 INTRODUCTION

The Regional Municipality of Waterloo (RMOW), alerted by elevated nitrate concentrations at some of their well fields, recognized that work was required to better evaluate the potential impacts of historic and/or current agricultural practices on groundwater supplies. To optimize the implementation of Beneficial Management Practices (BMPs) a method to evaluate future nitrate trends and the impacts of potential nitrate reduction measures was required.

Three-dimensional (3-D) unsaturated-saturated solute transport modeling represents the most sophisticated method for simulating the migration of solutes in the subsurface. However, development of regional scale 3-D solute transport models can be very difficult both computationally, and from a data quality perspective. In addition, where multiple wells require evaluation, the evaluations can be very costly to complete.

As an alternative, we have developed a mass balance modeling approach that integrates previously developed time related capture zones with a database program in an easy to use model interface. The mass balance model results will be compared with results from a detailed solute transport model that is being completed

for one of the well field areas as part of a validation process of the mass balance model.

Once the model has been calibrated and validated, future work will include the evaluation of various BMP scenarios to determine a cost effective method of managing nitrate concentrations at the production well.

2 NITRATE LOADING FUNCTION

The ability to predict the nitrate concentration in groundwater beneath agricultural areas is dependent on the understanding of fertilization practices and the amount of nitrogen that leaches beneath the root zone. The mass of leachable nitrogen can be estimated by a nitrogen budget:

$$N_{pl} = N_{inputs} - N_{outputs} - \Delta N_{storage} \quad [1]$$

where the potentially leachable nitrogen (N_{pl}) is the sum of the sources of nitrogen (N_{inputs}) minus the sum of the sinks of nitrogen ($N_{outputs}$) minus the change in long term storage of nitrogen in the soil ($\Delta N_{storage}$).

Sources of nitrogen (N_{inputs}) considered in the nitrogen budgets included commercial fertilizer and manure

application; crop residue, and cover crops; nitrogen from seed; symbiotic and non-symbiotic N_2 fixation; and atmospheric deposition of nitrogen.

Sinks of nitrogen (N_{output}) considered included nitrogen removed during crop harvest; volatilization of fertilizer and manure nitrogen; immobilization of nitrogen in manure, crop residue and cover crops; gaseous losses during plant senescence; loss by erosion and runoff; and denitrification.

2.1 Data Collection

Producers who managed fields within the 10-year surface to well advective travel time (SWAT) capture zone of the production well were surveyed to determine agricultural and fertilization practices. Data received generally included crop rotation and yield; fertilizer application rates; manure application rates and types; method of fertilizer and/or manure applications; timing of fertilizer and/or manure applications; and/or tillage practices.

For years where estimates of fertilizer application rates were not obtained a linear interpolation between estimates was made. Crop yields are dependent on weather and farming practices and therefore a linear interpolation of crop yield estimates was not applicable. Estimates of crop yield by year and region is available from the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) (2009a). The current and historic yields that producers provided were compared with estimates (OMAFRA, 2009a) to aid in the interpolation of crop yields for years in which there was no data. For example, Producer C typically produced 25% greater yields than the OMAFRA reported yields. In years which estimates were not provided by Producer C the OMAFRA reported crop yield including a 25% increase was applied.

The information was compiled and a nitrogen budget was calculated on a field by field basis for which data was available. Producers have been assigned an alphabetical identifier with the fields the producer managed identified numerically.

2.2 Sources of Nitrogen

2.2.1 Fertilizer

Fertilizer application rates are dependent on crop type with corn having the greatest nitrogen requirement, followed by wheat. Legumes crops such as soybeans and alfalfa fix nitrate from the atmosphere and therefore do not require nitrogen fertilizer.

Producers provided current and historic nitrogen fertilizer application rates for each crop and each decade. Where data was not available for a particular decade the application rate was interpolated based on a linear extrapolation.

2.2.2 Manure

Manure application rates were estimated by the producers and based on livestock operations that the producers managed. The availability of nitrogen from manure is dependent on the proportion of ammonium and organic nitrogen in the manure. Nitrogen in the form of

ammonium is immediately available to the crop in the year applied. The remaining nitrogen in the manure is in the organic form which becomes available to crops over time as the nitrogen mineralizes (OMAFRA, 2009b).

To calculate the amount of nitrogen applied based on the amount of manure spread, OMAFRA (2006) standard estimates of nitrogen content of various types of manure were used. Poultry manure has the highest nitrogen content, with beef, dairy and swine having about a third of the nitrogen content of poultry. Solid manure has greater nitrogen content than liquid.

Only a portion of the total nitrogen is available to the crop in the year it is applied, the remaining nitrogen is immobilized. OMAFRA (2009b) presents estimates of available nitrogen from late summer and fall applied manure. For the purpose of the nitrogen budget it was assumed that all manure was spread in the late summer or early fall and incorporated with the soil within 3 days. It was assumed the nitrogen available in the year applied was primarily ammonium nitrogen (minus any volatilization losses as discussed in Section 2.3.2) with a minor amount of organic nitrogen.

2.2.3 Mineralization of Manure

The ammonium nitrogen in manure is generally consumed within the year the manure is applied through either crop uptake and/or volatilization. The remaining organic nitrogen within the manure becomes available in succeeding years as the organic material is mineralized. The amount of nitrogen available from the organic form is dependent on the type of manure, and the microbial activity which is dependent on temperatures and adequate moisture content (OMAFRA, 2009b).

The organic nitrogen available from previously applied manure is estimated as 10% of the organic nitrogen applied one year previous, 5% of the organic nitrogen applied two years previous, and 2% of the organic nitrogen applied three years previous (OMAFRA 2009b; NMAN, 2008).

2.2.4 Seed

The nitrogen content of seed was calculated using estimates of nitrogen removal in the grain for a given crop in combination with the typical seeding rate and the seed weight OMAFRA (2006). It was assumed that only the grain or seed is harvested and therefore the nitrogen removal at harvest would represent the nitrogen content of the seed. This assumption combined with the typical seeding rate and seed weights were used to calculate the nitrogen content of seed. Nitrogen loading from seed is low, especially for crops such as corn and wheat (<2.1 Kg-N/Ha).

2.2.5 Symbiotic N_2 Fixation

Symbiotic N_2 fixation is the process of fixing atmospheric nitrogen (N_2) to nitrogen compounds by symbiotic bacteria living in the root nodules of certain plants, primarily legumes such as soybeans, red clover and alfalfa. Although legumes have the ability to fix nitrogen from the atmosphere they will preferentially utilize

available nitrogen in the soil as it requires less energy. Therefore it was assumed that any nitrogen taken up by the legume less any other nitrogen inputs (e.g. manure mineralization, atmospheric deposition, fertilizer application, manure application, etc) would represent symbiotically fixed nitrogen by the legume (OMAFRA, 2006).

2.2.6 Non-Symbiotic N₂ Fixation

Non-symbiotic N₂ fixation is estimated to represent a small component of nitrogen loading. Estimates provided by Barry et al. (1993) indicate that non-symbiotic nitrogen fixing microorganisms contribute no more than 7 Kg-N/Ha to soils. This is likely to occur under optimal conditions with high soil moisture content, residue cover and low soil nitrogen content. Havlin (1993) estimates under normal conditions, periodic dry soil, non-symbiotic N₂ fixation is likely less than 5 Kg-N/Ha per a year. The study area generally consists of well drained sandy soils and as a result a value of 5 Kg-N/Ha/Yr was assumed.

2.2.7 Mineralization of Crop Residues and Cover Crops

Crop residues or cover crops help protect the soil surface of a field from wind and water erosion. Legume cover crops can supply an appreciable amount of nitrogen due to their nitrogen fixing abilities. Cover crops and crop residues on the fields immobilize a portion of the nitrogen applied in the year the crop was grown. Over time as the plant residue breaks down nitrogen is slowly released. OMAFRA (2009b) estimates of nitrogen credits for cover crops and residue from the previous crop were used in the nitrogen budgets.

2.2.8 Atmospheric Deposition

Barry et al. (1993) summarized estimates of nitrogen loading from atmospheric deposition for nine studies conducted in southern Ontario. Estimated nitrogen loading ranged from 10.8 Kg-N/Ha to 33.0 Kg-N/Ha. The higher estimates of atmospheric deposition were associated with nitrogen that had been emitted from nearby sources such as manure piles, livestock housing, or manure spreading.

For the purpose of the nitrogen budget a total atmospheric deposition of 18.4 Kg-N/Ha was considered representative and treated as a constant for the nitrogen budget calculations.

2.3 Sinks of Nitrogen

2.3.1 Harvested Nitrogen

The amount of nitrogen removed during harvest for a given year was calculated based on crop yield and OMAFRA estimates of nitrogen content of various crops (OMAFRA, 2006).

2.3.2 Volatilization of Manure Nitrogen

The volatility of ammonium nitrogen in manure can result in a significant loss during collection, storage, and

spreading of manure. The amount of ammonium lost through volatilization is dependent on soil moisture and weather conditions. OMAFRA (2006) presents a summary of ammonium nitrogen loss from manure under different weather and soil conditions. It was assumed that manure would be spread in either the spring or fall, with average temperatures likely between 10 to 20 °C and producers would incorporate the manure within 2 days of spreading. The average ammonium loss due to volatilization was therefore assumed to be 22% (OMAFRA, 2006).

2.3.3 Volatilization of Fertilizer Nitrogen

Nitrogen loss from fertilizer is associated with the volatilization of ammonia and influenced by the type of fertilizer, method of fertilizer application, and weather conditions. The majority of producers interviewed applied nitrogen fertilizer to the crops in the form of urea ammonia nitrate (UAN) by broadcast or dribble. It was assumed that soil in the study area had a pH of approximately 7 and the climate was considered sub humid. With these assumptions it was estimated that 5% of the nitrogen applied from fertilizer was lost through volatilization based data from Meisinger & Randall (1991).

2.3.4 Denitrification

Denitrification is the microbial facilitated process of reducing nitrate to its elemental form (N₂). Literature values of nitrogen loss due to denitrification vary from 15 to 30 % of nitrogen input (Barrey et al, 1993; Meisinger & Randall, 1991). Meisinger & Randall (1991) provide estimates of percent of inorganic nitrogen that is denitrified for various soil drainage types and soil organic matter content. The study area is characterized by well-drained sandy loam soils. The soil organic matter content is unknown but assumed to be low to moderate. Therefore, an estimate of 6% inorganic nitrogen lost as a result of denitrification was assumed in the nitrogen budgets, with 12% of manure nitrogen also lost as a result of denitrification.

2.3.5 Gaseous Losses During Plant Senescence

Gaseous losses of nitrogen as ammonia and volatile amines occur as a plant ages. Nitrogen loss by this process has not been studied extensively. Meisinger & Randall (1991) reviewed available literature which indicated losses in the range of 4 to 18 Kg-N/Ha annually. The higher end is representative of a high producing region, where temperatures are generally higher and the growing season is extended relative to the study area. For the purpose of the nitrogen budgets a value of 9 Kg-N/Ha was assumed.

2.3.6 Erosion and Runoff

Nitrogen lost by soil erosion is dependent on the nitrogen content of the soil and the amount of soil leaving the site. The extent of soil erosion at a farm will depend on the ground surface topography, soil type, vegetative cover, tillage practices and climate. Producers interviewed as

part of this study indicate they use no-till practices and/or leave a cover crop or crop residue on the fields over the non-growing season. Both practices limit the extent of erosion that may occur. Soil nitrate concentrations near ground surface are less than 10 µg/g. Assuming less than 10,000 Kg/Ha of soil is lost annually at a soil concentration of 10 µg/g the nitrogen lost through soil erosion would be <1 Kg-N/Ha.

Similarly, Meisinger & Randall (1991) estimate nitrogen lost by surface runoff to be small, approximately 3 Kg-N/Ha a year or less. For the purpose of the nitrogen budgets it was assumed there was 3 Kg-N/Ha lost by erosion and/or surface runoff.

2.3.7 Immobilization of Nitrogen by Crop Residue

Cover crops and crop residue on the fields are considered to immobilize a portion of the nitrogen applied in the year the crop was grown. The credits that are applied for a previous year crop residue or crop cover are therefore subtracted from the total nitrogen applied in the year it was grown. The amount of nitrogen that is removed for the crop residue or cover crop for a given year is stated in Section 2.2.7.

2.4 Change in Storage

The change in stored nitrogen ($\Delta N_{\text{storage}}$) is represented by the nitrogen immobilized over the long term in organic material (e.g., manure, cover crops). Meisinger & Randall (1991) estimate that a typical hectare of soil may contain 3,400 Kg of organic nitrogen in the top 15 cm of soil with only 2 to 5% of this actively decomposing annually. The change in stored organic nitrogen from manure sources was calculated as the total nitrogen applied minus the nitrogen available to the crop, and the nitrogen lost through volatilization, denitrification, and mineralization.

Therefore in years that manure was applied to the fields a substantial amount of nitrogen enters storage. In subsequent years, a small portion of nitrogen is removed from storage through mineralization of organic nitrogen. Cover crops were not grown in the study area until recently (2007, 2008) and therefore were not included in the change in storage term.

2.5 Results

Detailed agricultural data was obtained for greater than 90 percent of the land within the 3, 5, 10, and 15 year SWAT capture zones of the production well. Greater than 40% of lands within all SWATs were accounted for except for the 30 year SWAT where only 33% of the land had detailed data. Overall, detailed nitrogen balances were completed for 53% of the land within the steady state capture zone of the production well.

Prior to 2000, estimates of N_{pl} ranged from 0 Kg-N/Ha to 92 Kg-N/Ha. Since 2000, Producers A and C have altered their farming practices which reduced N_{pl} to a maximum of 40 Kg-N/Ha. Producer A removed manure as a form of fertilizer yet maintains a similar crop yield due to the organic nitrogen available from long term storage in the soil. Producer C began applying fertilizer

during several stages of crop growth allowing the crop to utilize more of the nitrogen which resulted in higher crop yields. Producer C applies the greatest amount of fertilizer of all the producers interviewed but also receives the greatest crop yields due to the timing of fertilizer application which resulted in a low N_{pl} .

Producer B has a cattle operation that results in the use of manure as a fertilizer source. The manure is commonly applied in addition to commercial fertilizer resulting in high values of N_{pl} . The combined input of manure and commercial fertilizer is similar to Producer C; however, Producer B does not receive similar crop yields. The high input of nitrogen from fertilizer and manure combined with the low output of nitrogen due to crop yield, results in significantly higher estimates of N_{pl} .

The nitrogen budgets highlight fields within the capture zone of the production well which may benefit from the implementation of BMPs and illustrate the effect of BMPs on the N_{pl} . The calculated N_{pl} for each field was subsequently used with a mass balance model to predict nitrate concentrations at the production well.

3 MASS BALANCE MODELING

3.1 Model Conceptualization

To better understand the impacts of agricultural practices on groundwater, and the benefits of potential reduction measures being considered, a mass balance model was developed for the production well. The mass balance model integrates a database program and a GIS program through an easy to use model interface. The model utilized particle tracking data from existing groundwater flow models to provide travel time estimates from ground surface. This data was combined with the individual nitrogen budgets for farm fields within the capture zone of the production well. Using the mass balance model, nitrate within the well field capture zone was allowed to travel to the well, providing an estimate of nitrate concentrations over time.

The predicted nitrate concentrations at the production well are determined by the integration of the nitrate mass from each SWAT capture zone over time. The predicted nitrate concentrations at each well field are dependent on the following model parameters: SWATs, recharge; nitrate loading function; and denitrification.

The SWATs represent the particle travel time from the ground surface to the well and include both saturated and unsaturated travel times. The SWATs were delineated using an existing groundwater flow model prepared as part of a watershed planning study (CH2M Hill and S.S. Papadopoulos & Associates Inc., 2003).

The recharge estimates were provided from previous modeling studies which were based on the GAWSER continuous simulation surface water model. The GAWSER modeling utilized 14 soil-type/land cover combinations, commonly referred to as hydrologic response units (RUs).

The nitrate loading function, defined as the amount of nitrate applied at surface and available to leach to the groundwater was mainly dependent on agricultural practices, as described in Section 2.0. Using aerial

photography three land use categories were identified; agricultural fields, forest/pasture, other and quarries. A GIS program was used to calculate the area of land for each category that was within each SWAT of the production well. A nitrogen loading function was then assigned to the land. Agricultural fields for which detailed agricultural information was obtained have a nitrogen loading function calculated on a per year basis. For fields in which agricultural information was not available an average of the nitrate loading function for the detailed fields for that year was used. Future loading was determined for each field with detailed data based on the average nitrate loading over the past 10 years. For fields with no detailed agricultural data, the average nitrate loading from all fields for the past 10 years was used for future loading. Land that was classified as forest/pasture were assigned a nitrate loading value of 6 Kg/Ha and land that was considered gravel pits or roads/subdivision were assigned a nitrate loading function of 0 Kg/Ha.

Denitrification within the aquifer was calculated as the estimated rate of denitrification (mg/L) multiplied by the recharge volume within the SWAT and the time of travel for the SWAT zone. The mass is then subtracted from the total mass that migrates to the well. For the purpose of the model simulation a denitrification value of 0.01 mg/L was applied.

3.2 Preliminary Modeling Results

Preliminary model estimates are presented in Figure 1. Predicted nitrate concentrations are presented for 1980 to 2050 with observed nitrate concentrations extending back to the 1980's. Nitrate concentrations at the production well ranged from 6.0 to 7.6 mg/L from 1985 to 1999. Predicted concentrations for this time period correlate well, ranging from 6.4 mg/L to 8.0 mg/L. Since 2000, nitrate concentrations have reached a maximum of 8.5 mg/L in 2004, with predicted concentrations reaching a maximum of 8.5 mg/L in 2008. Model results of future nitrate trends at the production well, assuming agricultural practices remain the same, indicate that concentrations at the well will likely decrease with concentrations consistently below 8.0 mg/L from 2020 onwards.

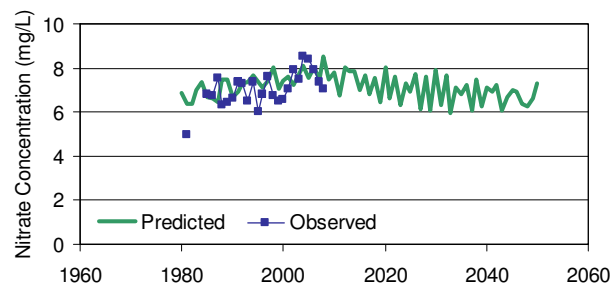


Figure 2. Preliminary results of mass balance modeling of nitrate concentrations at the Production Well.

3.3 Next Steps

The next steps with the mass balance model is to refine the early time data (pre-1960's) in which no specific agricultural information is available and which there is no nitrate concentration data available for the production well. We expect the nitrate input function will weight the loading data based on historical fertilizer sales and recommended application rate data for the time period.

Soil cores being collected to measure shallow nitrate concentrations beneath the agricultural fields as well as a bromide tracer to quantify recharge will be used to aid in calibration of the mass balance model.

Following calibration to observed nitrate concentrations, the model will be used to evaluate future nitrate concentrations under a variety of BMPs. The result of the mass balance modeling will be compared with detailed 3-D numerical solute transport modeling completed using the University of Waterloo flow model WATFLOW and transport model WTC.

4 CONCLUSIONS

This study describes the development of the nitrate loading function for use in a mass balance model to predict nitrate concentrations at a municipal production well. The nitrate loading function was calculated for select fields within the capture zone. The nitrate loading function was able to capture historic changes to agricultural practices suggesting it can be an effective tool for qualifying the implementation of BMPs. When combined with the mass balance model, preliminary results suggest a good correlation of predicted and observed nitrate concentrations at the Production Well. Following calibration, the model will be used to evaluate various BMPs with the objective of reducing nitrate concentrations at the production well. The mass balance model has shown the potential to be an effective tool to quantitatively evaluate nitrate concentrations at a production well in an agricultural setting.

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