

**APPLICATION OF A NITRATE FATE AND TRANSPORT MODEL TO THE  
ABBOTSFORD-SUMAS AQUIFER, WHATCOM COUNTY, WASHINGTON**

A Thesis  
Presented to the Faculty of  
Western Washington University

In Partial Fulfillment  
Of the Requirements for the Degree  
Master of Science

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February 2007

## ABSTRACT

The Abbotsford-Sumas aquifer is a shallow, unconfined aquifer located in an agriculturally intensive area in northwestern Washington and southwestern British Columbia. Due to aquifer characteristics and surface land use, the Abbotsford-Sumas aquifer has had a history of nitrate contamination from non-point sources. As such, nutrient managers are interested in predictive tools to evaluate management strategies. I assessed the effectiveness of a GIS based nitrate fate and transport model developed specifically for the Abbotsford-Sumas aquifer by Almasri and Kaluarachchi (2004) as a predictive tool for nutrient management. This model couples four sub-models that collectively estimate nutrient loading, predict soil-nitrogen dynamics (NLEAP), calculate groundwater velocity (MODFLOW), and nitrate fate and transport in groundwater (MT3D). The model was used to validate measured nitrate concentrations in the aquifer, and to assess the impact of land use changes and irrigation on nitrate concentrations.

Validating nitrate concentrations was difficult due to the model's design as a single layer aquifer. For those well sites with similar modeled and measured depths, the model was fairly effective at predicting nitrate concentration. Previous work has shown that nitrate is stratified in the Abbotsford-Sumas aquifer, but this fate and transport model estimates the same nitrate concentration for an entire water column. The model was sensitive to land use changes; however, the scale of the model is too coarse to capture local changes and seasonal variation. Changes in irrigation rate and concentration showed little change in resulting nitrate leaching. This lack of response is contrary to previous work, and indicates that the model underestimates irrigation's impact on groundwater nitrate concentrations.

## ACKNOWLEDGMENTS

I thank my advisor Bob Mitchell for his teaching, support, and encouragement during this entire process. Without his advisement much of this project would have never come together. He taught me how to both think and write critically as a scientist. I also thank my committee members Robin Matthews and Scott Babcock for being available to answer any questions and for very helpful editing critiques, and Chris Clark from Whatcom Conservation District for being generous with his time and helping me understand the impact of nitrate concentrations in the “real world”. I also acknowledge Stefan Freelan and Mike Hilles for their technical expertise and time in answering my questions, and Chris Sutton, and Vicki Critchlow from Western Washington University for their help during this process.

Getting to know the other graduate students in the geology program remain one of the highlights of this process. Their friendships brought me much joy during my time at Western.

Lastly I would like to thank my family for their support during this program, and for encouraging me in any endeavor I undertake.

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## 1.0 INTRODUCTION

Nitrogen can occur as many different species in the environment. The distribution of these species is shown in the nitrogen cycle (Figure 1). Nitrate comes from the fixation of nitrogen gas from the atmosphere to ammonia and then conversion to nitrate by nitrification, or from ammonification of organic nitrate and then nitrification. Nitrate is the most prevalent worldwide groundwater contaminant (Erwin and Tesoriero, 1997), and is often used as an indicator of groundwater quality (Gorres and Gold, 1996). Nitrate is very soluble and can be easily transported by groundwater. Cleaning up water contaminated with nitrate can be expensive and difficult, so there is great interest in understanding sources of nitrate (Nolan *et al.*, 1997) to prevent the occurrence of contamination. The presence of nitrate in drinking water can cause methemoglobinemia, particularly in infants, which affects the ability of blood to carry oxygen. Nitrate in drinking water is also linked with the occurrence of certain cancers in adults, such as non-Hodgkin's lymphoma (Nolan *et al.*, 1997). To mitigate the health effects, the U.S. E.P.A. and Health Canada set the maximum contaminant level (MCL) for nitrate at 10 mg-N/L.

Regions with a high percentage of urban or agricultural land-use and shallow coarse-grained aquifers are at a high risk to groundwater contamination by nitrate. One such aquifer, the Abbotsford-Sumas aquifer, located in rural western Whatcom County and southwestern British Columbia (Figure 2), is a major source of water for residents in this region (Erwin and Tesoriero, 1997). The source of nitrate in the aquifer is agricultural practices (Cox and Kahle, 1999; Mitchell *et al.*, 2005). Whatcom County is the highest exporter of raspberries in the country and is also Washington's second highest dairy producing county (Mitchell *et al.*, 2003). The Abbotsford area of southern British

Columbia (BC) is also a major raspberry producer, as well as home to numerous poultry farms (Hii *et al.*, 1999). Because groundwater in the Abbotsford-Sumas area flows south, land-use practices in BC can affect groundwater quality in Washington. Sources of nitrate in groundwater are from four general categories: natural sources, animal or human waste, agricultural loading, and irrigation. Typically, the greatest sources are animal waste from large-scale animal operations and over-application of fertilizers (Canter, 1997).

Previous work has documented elevated levels of nitrate in the Abbotsford-Sumas aquifer in British Columbia and Whatcom County (Garland and Erickson, 1994; Wassenaar, 1995; Erickson, 1998; Cox and Kahle, 1999; Hii *et al.*, 1999; Mitchell *et al.*, 2003; Mitchell *et al.*, 2005). Graduate students and professors (Gelinis, 2000; Nanus, 2000; Stasney, 2000; Mckee, 2004, Mitchell *et al.*, 2003; Mitchell *et al.*, 2005) from Western Washington University (WVU) undertook two water quality studies in a 2.5 mi<sup>2</sup> (6.4 km<sup>2</sup>) study area located north of Lynden and directly south of the Canadian border. The first study took place from April 1997 to February 1999, and the second from July 2002 to June 2004. Any later references to the study area will be referring to this WVU study area.

The nitrate in Whatcom County wells is believed to be a result of both local land-use and up gradient land-use in BC (Mitchell *et al.*, 2003). Because of the many possible sources of nitrate, it can be difficult to determine which land-use practices are responsible for the nitrate contamination in Whatcom County groundwater. Previous work measuring nitrogen isotopes on nitrate collected from wells in Whatcom County found that the majority of nitrogen was from organic and inorganic commercial fertilizers (Wassenaar, 1995; Mitchell *et al.*, 2003; Mitchell *et al.*, 2005), which indicates

contamination is likely from either up-gradient and local sources.

A nitrate fate and transport model was recently developed by Utah State University for the Abbotsford-Sumas aquifer (Almasri and Kaluarachchi, 2004). Almasri and Kaluarachchi integrated four different sub-models to develop a single model that estimates nitrogen loading on the land surface, models nitrogen-soil interactions and nitrate leaching to groundwater, determines groundwater velocity and head distributions throughout the aquifer, and simulates nitrate transport in groundwater. This model can be used to assess the impacts of surface activities on groundwater nitrate concentrations. Although the model was developed for the entire Abbotsford-Sumas aquifer, I have applied it to predict and validate nitrate concentrations in the WWU study area.

## 2.0 BACKGROUND

### 2.1 The Nitrogen Cycle

The nitrogen cycle describes the possible transformations of nitrogen in the atmosphere, geology, soil, animals, plants, and water (Figure 1). Nitrogen can form several different compounds depending on its oxidation state. Nitrogen will transform to different compounds through several mechanisms. These mechanisms include: fixation, ammonification, synthesis, nitrification, and denitrification. Canter (1997) provides an overview of these processes.

In fixation, nitrous gas undergoes a transformation to an organic nitrogen compound that can be more easily used by plants or animals. This transformation is predominately done by microorganisms and plants. Ammonification is the process in which organic nitrogen changes to the ammonium form of nitrogen. This is accomplished by microorganisms during the decomposition of animal or plant matter.

Through nitrification ammonium ions are oxidized to the nitrate form. This two-step process is accomplished by bacteria, which first convert the ammonium ions to nitrite and then to nitrate. The first step of oxidation of ammonium to nitrite is:

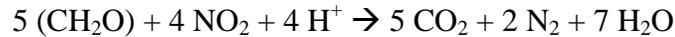


The transition to nitrate is fairly rapid, and there often is very little nitrite as a result of nitrification. Nitrite is then oxidized to form nitrate:

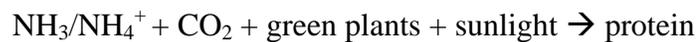


Nitrate is reduced to nitrogen gas through the biological process of denitrification.

Heterotrophic bacteria, anoxic conditions, and the presence of available carbon are necessary for this process to occur:



Synthesis/assimilation is a biochemical process that converts inorganic nitrate and ammonium into an organic nitrogen compound. Certain plants are able assimilate inorganic nitrates, making it possible for other plants and animals to obtain organic nitrate compounds:



These processes are all present in the study area. In particular, McKee (2004) documented the presence of denitrification along Pangborn Bog and Creek in the central part of the study area. Nitrogen transformations can be employed in the treatment of groundwater with excess nitrate (Cantor, 1997). The occurrence of denitrification in the study area helps to naturally lower nitrate levels to below EPA standards.

Nitrogen was found as nitrate, nitrite and ammonia in the Abbotsford-Sumas aquifer. Previous work (Mitchell *et al.*, 2003 and Mitchell *et al.*, 2005) found that the majority of nitrogen in the WWU study area is present as nitrate. Ammonia and nitrite are present in low amounts.

## **2.2 Geologic Setting**

The Abbotsford-Sumas aquifer is glacial sediments from the Fraser glaciation (Cox and Kahle, 1999). These Pleistocene-age glacial deposits form the current land surface of the study area. The unconsolidated glacial deposits of the area are estimated to

be 1000 to 2000 ft (300 to 600 m) thick over sandstone bedrock of the Tertiary Huntington Formation in the study area (Cox and Kahle, 1999). The Fraser Glaciation is divided into four units: the Evans Creek Stade, the Vashon Stade, the Everson Interstade, and the Sumas Stade (Easterbrook, 1969). Sumas Stade deposits comprise the Abbotsford-Sumas aquifer (Mitchell *et al.*, 2005).

The Sumas Stade lasted from 11,600 to 10,000 years B.P., and began with the retreat of marine waters and emergence of the lowlands. Kovanen and Easterbrook (2002) documented four phases of the Sumas Stade, two of which contributed to the formation of the Abbotsford-Sumas aquifer. Phase III (10,980-10,250 years B.P.) began with retreat of the ice margin to the north, and the subsequent deposition of the Sumas Outwash. The Sumas Outwash consists of glaciofluvial and glaciolacustrine deposits that are dominated by coarse-grained sands and gravels (Kovanen, 2002). Phase IV of the Sumas Stade (10,250-10,000 years B.P.) began with readvancement of the ice margin and continued sand and gravel deposition. Melting blocks of ice formed kettles in the outwash plain. Some of these kettles are believed to be the site of peat formation. Localized peat bogs present in the glacial outwash unit are significant to note because of their importance in contributing to natural denitrification in the aquifer (McKee, 2004).

All units of the Sumas Outwash represent the unconfined Sumas aquifer (Cox and Kahle, 1999). The Sumas aquifer varies in thickness from 15 to over 200 ft (5 to 60 m) thick, but is typically about 40 to 80 ft (12 to 24 m) thick (Cox and Kahle, 1999).

### **2.3 Hydrostratigraphy**

The hydrostratigraphy of an area controls the direction and rate of groundwater transport.

An accurate picture of the hydrostratigraphy of the Abbotsford-Sumas aquifer is necessary in order for a meaningful prediction of the transport of nitrate by groundwater.

Four major hydrostratigraphic units are found in the region: the Sumas aquifer, the Everson-Vashon unit, the Vashon unit and Tertiary bedrock, represented by the Huntington Formation (Figure 3). The Everson-Vashon unit, Vashon unit and the Huntington Formation typically act as confining units, but can yield water in localized areas (Cox and Kahle, 1999).

The unconfined Sumas aquifer is the most productive aquifer in the study area. Cox and Kahle (1999) completed a study that defined the hydraulic characteristics of the units in the study area. Data from 170 wells completed in the Sumas aquifer were used to calculate a range of horizontal hydraulic conductivity values. Hydraulic conductivity, given in units of length per time, represents the rate at which a volume of water will pass through a cross-sectional area. Since glacial deposits can be highly variable, the calculated hydraulic conductivities cover a wide range. Values range from 6.8 to 7800 ft/day (2 to 2377 m/day) with a median of 270 ft/day (82 m/day) (Cox and Kahle, 1999). Using techniques from Cox and Kahle (1999), Mitchell *et al.* (2005) estimated the horizontal hydraulic conductivity of the study area by using specific capacity data from 8 wells. The geometric-mean of their results was 532 fet/day (162 m/day). The median values for hydraulic conductivity of the Everson-Vashon, Vashon and Chuckanut units are 81, 52 and 0.55 ft/day (25, 16, and 0.17 ms/day) respectively, indicating a much lower ability to transfer water (Cox and Kahle, 1999). Researchers at Simon Fraser University developed a MODFLOW model of the Abbotsford-Sumas aquifer by using data from 2500 borehole lithology logs (Scibek and Allen, 2006). They divided all

glacial sediments deposited on top of the Tertiary bedrock into seven different hydraulic zones based on their lithology, and assigned each zone a unique hydraulic conductivity and specific storage. Sumas Drift, which represents the material of the Abbotsford-Sumas aquifer, was separated into four hydraulic zones with mean hydraulic conductivities from 62 to 344 ft/day (19 to 105 m/day) (Scibek and Allen, 2005).

Velocity of the Sumas aquifer in the WWU study area is calculated from the values of hydraulic conductivity, hydraulic gradient and the literature values for effective porosity (Mitchell *et al.*, 2005). Using a hydraulic conductivity of 532 ft/day (162 m/day), a porosity of 0.30, and a hydraulic gradient of 0.0056, Mitchell *et al.* (2005) estimated the average horizontal pore-water velocity for the WWU study area at 10 ft/day (3 m/day).

## **2.4 Climate, Soils, and Recharge**

The climate, soils, and recharge of an area affect the rates of precipitation, irrigation, infiltration, and temperature. These factors impact nitrogen loading, soil-nitrogen processes, and the movement of nitrogen species through the unsaturated zone, all of which affects nitrate transport.

### **2.4.1 Climate**

The WWU study area has a temperate, maritime climate that is strongly influenced by moist winds coming off the Pacific Ocean. The majority of yearly precipitation falls between November and April, with the growing and harvest season typically drier.

Precipitation will typically fall as rainfall that has light to moderate intensity (Cox and Kahle, 1999).

Summers are typically warm and dry, and irrigation is necessary for many crops. Depending on the season and the crop, annual irrigation needs are usually between 6 to 17 inches of water (Cox and Kahle, 1999). Raspberries in the area may require 18 inches of irrigated water during the growing season (Ellers, 2005).

#### **2.4.2 Soils**

The development of soils in an area is influenced by climate and the underlying geologic formations in an area. The WWU study area is underlain by glacial and alluvial deposits. Several different soil types have developed in the area because of the variability in underlying geology, surface relief and drainage; however, these soils are similar in thickness and permeability. The permeability rate of these soils is usually 0.6-2.0 inches/hour (1.5-5 cm/hour), with upward rates of 20 inches/hour (50 cm/hour) and down to 0.06 inches/hour (0.15 cm/hour). Generally, the permeability rate of these soils is greater than the rate of precipitation (Cox and Kahle, 1999). Generally soils above the aquifer are well-drained. If clay is present, it typically decreases with depth allowing increasing infiltration. Peat deposits exist locally within the study area. They are characterized by high organic content and high moisture content (Cox and Kahle, 1999).

#### **2.4.3 Recharge**

Recharge to the Abbotsford-Sumas aquifer is primarily from precipitation. Cox and Kahle (1999) determined that 60% of yearly precipitation acts to recharge the aquifer.

Crop irrigation, losing stream reaches, and leachate from manure lagoons and septic systems also help to contribute to aquifer recharge, but by a much lesser degree (Cox and Kahle, 1999).

## **2.5 Land Use and Nutrient Loading**

Land-use activities and the physical properties of the unconfined Sumas aquifer increase its susceptibility to nitrate contamination. Characterizing the surface activities in the study area and in British Columbia is required to accurately define sources and amounts of nutrient loading. Areas most at risk for nitrate contamination have coarse, well-drained soils, a high population density, a high cropland to woodland ratio, and high nitrogen input from land-use activities (Nolan *et al.*, 1997). Since the Nolan *et al.* (1997) study was on a national scale, they were not able to include all factors that could impact nitrate concentrations in groundwater. Other regional factors considered to have a possible impact are “local land use, aquifer type, rainfall and irrigation amounts, and the timing of rainfall in relation to fertilizer and manure applications” (Nolan *et al.*, 1997).

Tesoriero and Voss (1997) predicted the vulnerability of aquifers in the Puget Sound basin to nitrate contamination by determining both the susceptibility of the aquifer and availability of nitrate in the area. After quantifying these values using available data for land use, surficial geology, and well depth, they developed a logistic regression equation that determined the probability that a well would have a nitrate concentration at or above 3 mg/L. Concentrations above 3 mg/L suggest that nitrate sources are possibly anthropogenic in nature. Tesoriero and Voss (1997) found that the shallow wells located in areas with coarse-grained glacial deposits at the surface and with a high percentage of

the land surface in either residential, commercial, industrial or agricultural use were the most vulnerable to nitrate contamination. Agricultural areas in the Lower Nooksack River Valley in Whatcom County were found to be highly vulnerable using these criteria.

## **2.6 Previous Work**

### **2.6.1 Nitrate Fate Models**

Modeling can be a useful tool for predicting land use influences on water quality. Attempts have been made to model the nitrogen cycle on the surface and subsurface, and subsequent groundwater nitrate concentrations (Geng *et al.*, 1996; Ling and El-Kadi, 1998; Puckett *et al.*, 1999; Shamrukh *et al.*, 2001). Many of these models are based on a mass-balance equation to estimate nitrogen loading, soil-nitrogen interactions, and subsequent nitrate leaching to groundwater. These models differ in their application, detail to input data and soil-nitrogen processes, and form of output data. Since agriculture is the major source of nitrate in groundwater, these models were all based in agricultural areas where a nitrate fate model could be utilized for prediction and the assessment of groundwater management scenarios.

Geng *et al.* (1996) developed a coupled model, called MORELN, to calculate nitrate leaching magnitudes into groundwater and linked it to a third model, NEWSAM, to simulate the movement of nitrate in an aquifer system. MORELN treated the aquifer as one layer. Aquifer parameters were differentiated horizontally but not vertically. There was also no modeled vertical movement of groundwater, only horizontal movement. These models were tested on three different scales in agricultural areas in

France. The first test was done on a soil plot of 21.5 ft<sup>2</sup> (2 m<sup>2</sup>), then in a 2.2 mi<sup>2</sup> (5.8 km<sup>2</sup>) basin, and then in a more heterogeneous basin of 290 mi<sup>2</sup> (750 km<sup>2</sup>). The authors found that the model was fairly accurate in predicting water drainage and nitrate leaching in the smaller test areas. In the larger test area, the model did succeed in reproducing the overall spatial trend of nitrate distribution; it did not exactly reproduce observed local nitrate concentrations. Geng *et al.* (1996) determined that this was because the nitrogen loading information was averaged over each “nitrogen zone”. Point observations are also difficult because of the nature of the model being a single layer. The measured nitrate concentration often represents a different depth in the aquifer than is being modeled. However, the authors believe that this model is effective as tool to use for identifying critical zones of nitrate contamination.

Shamrukh *et al.* (2001) developed a three-dimensional groundwater modeling system that incorporated MODFLOW and MT3D to simulate present groundwater flow and contaminant concentrations, and also to predict future concentrations based on current land use in the Nile Valley aquifer in Egypt. The contaminants of interest were chloride and nitrate. The only nitrate loading considered in the model was fertilizers. After calibration, the authors found that the model was able to accurately predict nitrate concentrations in the aquifer. The authors also used their model to predict future nitrate concentrations based on current land use.

Puckett *et al.* (1999) used mass-balance equations to predict nitrate concentrations in an agricultural aquifer in Minnesota. The authors measured water quality at 29 wells in their 82 mi<sup>2</sup> (212 km<sup>2</sup>) study area, and used the results to refine their predicted nitrate concentrations. Their mass-balance model was designed as a set of equations in a

spreadsheet and was modeled to be five layers with different hydraulic attributes. The degree of denitrification in the study area was estimated by adjusting its value until the measured nitrate concentrations and predicted nitrate concentrations matched. According to their results, denitrification was responsible for removing almost half of the excess nitrate from the soil. Puckett *et al.* (1999) were able to accurately determine nitrate concentrations, and also predict nitrate concentrations for different scenarios.

The nitrate leaching model developed by Ling and El-Kadi (1998) uses less detailed inputs than more sophisticated models (e.g. Geng *et al.*, 1996), but their lumped parameter model (LPM) provides a user-friendly way of predicting nitrate leaching. The authors tested their LPM against two other leaching models and measured field data on five different crop fields. They found that although the other predictive models often fell within the range of field data, the LPM was the best fit to the median of the field data. However, the simplistic nature of this model limits its applicability. The model estimates the mean concentration of nitrate throughout the unsaturated zone and does not consider any vertical distribution of nitrate concentration or spatial variability of soil or hydraulic properties.

### **2.6.2 Nitrates in the WWU Study Area**

The first water quality study by WWU in the Abbotsford-Sumas aquifer served to answer questions about the hydrogeology of the area and the temporal and spatial variation of nitrate concentrations. The field work from this study was performed from 1997-1999. The water quality was monitored at 26 wells and several surface water sites for 15 months.

Stasney (2000) identified three hydrostratigraphic units within the study area. He found the Sumas aquifer to be composed of Sumas outwash gravel and sand, Sumas outwash sand, and peat deposits. Using grain size analysis and empirical equations, he determined the average hydraulic conductivity of the unit. Stasney used measured water levels to determine water table contours and hydraulic gradients. This hydrogeologic information was used to calculate and model groundwater velocities, and model nitrate transport simulations. Stasney's results from the nitrate transport model suggested that contamination from Canadian sources was likely to be in the northeast and northwest portions of the study area.

Nanus (2000) used nitrogen isotope analysis to demonstrate that the main sources of nitrate in the study area were from animal waste and inorganic fertilizers. Nanus also found that a majority of the wells with high nitrate concentration (average of 10 mg/L or higher) had dairy farms or berry fields as the up-gradient land use. The nitrogen isotope ratios measured at surface water sites also indicated both animal waste and inorganic fertilizers as nitrate sources. Nitrate concentration peaks in surface water were shown to be directly related to irrigation events in the study area. Generally, nitrate concentrations were lower in the summer with less infiltration, and higher in the winter when infiltration was greater.

Gelinas (2000) found through statistical analysis that wells tended to fall into three groups: shallow wells with high nitrate, deep wells with high nitrate, and shallow and deep wells with low nitrate. Gelinas concluded that shallow wells with high nitrate were affected by local nutrient loading, deep wells with high nitrate were affected by nutrient loading in BC, and denitrification was possible at the wells with low nitrate

concentrations.

All researchers in the WWU 1997-1999 study concluded that denitrification was likely occurring in the study area, but further work needed to be done to confirm this occurrence. Another water quality study undertaken by WWU from 2002-2004, revealed that denitrification was occurring in peat deposits along Pangborn Creek (McKee, 2004). Higher concentrations of nitrate were measured north of the creek, and several water quality parameters indicate that denitrification is taking place in the peat deposits.

Mitchell *et al.* (2005) compiled a comprehensive report on the WWU water quality study from July 2002 to June 2004. The objectives of the report were to compare water quality parameters to local agronomic information, estimate the nitrate concentration in groundwater from Canada, and assess the effectiveness of Dairy Nutrient Management Plans (DNMP) that were to be implemented in the study area by December 2003. Twenty-one of the 26 wells sampled had median nitrate concentrations above 3 mg N/L, and both streams sampled had median nitrate concentrations above 5 mg N/L indicating anthropogenic sources. Wells in the northern half of the study area generally had higher nitrate concentrations than the southern half due to denitrification in bogs along Pangborn Creek. Other wells throughout the study area are likely experiencing denitrification as indicated by water quality parameters. Nitrate concentrations in the northern half of the study area are higher due to a combination of groundwater transport from British Columbia and leaching from local sources. Nitrogen isotopes measured at wells in the study area suggest organic manure, or a mix of organic and inorganic nitrogen as the source of nitrate. The effectiveness of DNMPs was assessed by comparing groundwater nitrate concentrations measured between 1997-1999 to those

measured in 2002-2004. Seven of the 14 wells sampled had increased median nitrate concentrations after implementation. Comparison of groundwater concentrations measured November 2002-April 2003 to November 2003-April 2004 found that 15 of the 24 wells had nitrate concentration increase after DNMPs were implemented. The authors estimate that nitrate concentrations of 10 mg-N/L or more are transported across the border into Whatcom County. In order to accurately assess the impact land use practices have on groundwater nitrate concentrations, the authors recommend analyses of soil and soil pore-water data, monitoring of shallow groundwater, and numerical modeling of nitrogen in the surface and subsurface.

Previous work documents that agricultural practices in Canada have contributed to the elevated nitrate concentrations in groundwater in the WWU study area (Gelinias, 2000; Mitchell *et al.*, 2005). A relationship has also been found to exist between nitrate concentrations and up-gradient land use. Surface processes such as degree of irrigation and fertilizer application have an impact on down-gradient groundwater nitrate concentrations.

Previous work by WWU students and faculty has done much to characterize nitrate concentrations temporally and spatially in the WWU study area, and to determine the extent denitrification affects water quality. The relationship between surface activities and nitrate concentrations has been explored, but not extensively. With nitrate being a non-point source pollutant and part of a complex natural system, it is difficult to directly correlate groundwater nitrate concentrations with surface activities. Modeling makes it possible to represent nitrate loading, soil transformations, and groundwater nitrate transport within the Abbotsford-Sumas aquifer, and explore the relationship

between groundwater nitrate concentrations and surface activities.

Through a nitrate fate and transport model developed specifically for the Abbotsford-Sumas aquifer (Almasri and Kaluarachchi, 2004), I tested the influence agricultural activities in the U.S. and Canada have on the resulting groundwater nitrate concentrations, and estimated the extent and degree to which Canadian agriculture affected groundwater nitrate concentrations in Whatcom County. Groundwater and surface water measurements from the July 2002 to June 2004 Western Washington groundwater quality monitoring of the Abbotsford-Sumas aquifer were used in this thesis.

My research objectives for this work were to:

- become familiar with the model elements and functions;
- validate modeled concentrations with measured nitrate concentrations;
- assess model sensitivity to nitrate loading and irrigation changes;
- predict nitrate contributions from Canadian and U.S. sources; and
- evaluate the model's effectiveness as a management tool for the Whatcom Conservation District.

### **3.0 METHODS**

#### **3.1 Field Sampling and Laboratory Analysis**

The 2002-2004 WWU water quality study monitored groundwater and surface water in the Abbotsford-Sumas aquifer (Figure 5). Field sampling and laboratory analyses followed an approved Quality Assurance Project Plan (Mitchell *et al.*, 2002). The wells used in this study as groundwater collection sites were chosen based on their location, finished depth below the water table, presence of nitrate noted from previous studies, existence of a well log, and physical access (Mitchell *et al.*, 2005). The well names were based on the road names nearest to the wells' locations: Halverstick Road (H), Pangborn Road (P), Van Buren Road (V), Trap Line Road (T), and Kraght Road (K). Wells were classified as shallow (<25 ft) or deep (>25 ft) based on median depth of the finished below the water table. The shallow wells include: H1, H2, H5, H6, H8, P3, T1, V1, V4, V5, V6, V9, and V10. Deep wells include: H3, H4, H7, K1, P1, P2, T2, V2, V3, V7, V8, V11, and V12. Data indicate that well H7 is breached or has a leaky seal so it could be considered a shallow well. In November 2003, deep well V12 was added to the sampling. Well H6 was sampled inconsistently due to problems with the on-site pump.

Groundwater samples were taken from a standpipe at 25 wells every other month from July 2002 to June 2004. Thirteen wells were monitored monthly because of their high nitrate values (H1, H2, H3, H4, H5, H7, T1, T2, K1, V5, V6, V8, and V9). Overall, 466 groundwater samples from 26 wells were processed during the study.

During field collection, the standpipe closet to the well was purged until the dissolved oxygen, specific conductance, and temperature values were stable. Dissolved

oxygen, specific conductance, and temperature were measured in the field using a YSI model 85 analyzer. Dissolved oxygen was calibrated at each site. At the beginning of each sampling day, conductivity was checked with a known standard and temperature was checked with a mercury thermometer. Three bottles were collected at each site for laboratory analysis. These samples were analyzed for nitrate+nitrite, ammonium, total phosphorus, total nitrogen, chloride, iron, and manganese in the IWS laboratory at WWU. The amount of nitrite measured in samples was negligible, therefore for the sake of brevity the samples were referred to as nitrate only. The depth that each well was completed came from the well logs for each well (Mitchell *et al.*, 2005).

Water quality data from four piezometers in southern BC directly above the study area was available from Environment Canada. These piezometers (BC3, BC4, BC5, and BC6) were sampled on a monthly basis during the same time period as the WWU water quality study.

### **3.1.1 Land Use Data**

Land use in the WWU study area is predominately agricultural. Raspberry fields comprise approximate 40% of the study area. Grass fields used as dairy pastures are almost 25% of the study area. The rest of the land is used for blueberries, corn, nuts, pasture and residential homes. Across the border in BC, the land use is a mix of raspberry fields, pasture, poultry farms, and gravel pits (Figure 6). Land use maps from Mitchell *et al.* (2005) were used to replicate land use from 2002-2004 in the WWU study area. The fertilizer and manure application rates used in the model were confirmed by the Whatcom Conservation District to be realistic for the area (Clark, 2006).

### **3.2 Fate and Transport of Nitrate Model**

The fate and transport of nitrate model (Almasri and Kaluarachchi, 2004) couples four sub-models (Figure 7). This paper will refer to Almasri and Kaluarachchi's fate and transport of nitrate model as the A&K model. The first sub-model quantifies the spatial and temporal on-ground nitrogen loadings, the second sub-model simulates the physical and chemical changes to this nitrogen mass as it travels through the soil, the third sub-model is used to determine the variations in groundwater velocity due to changing parameters in the aquifer, and the fourth sub-model determines the fate and transport of nitrogen in the groundwater. The visual display of the A&K model was developed in ArcView GIS 3.2, and the fate and transport model is run through this program. The GIS environment for the A&K model facilitates the calculations and display of model parameters. Almasri and Kaluarachchi at Utah State University were commissioned by Whatcom County to develop the A&K model as part of a group of models to serve as a Decision Support System for managing water resources in WRIA 1. Water Resource Inventory Area 1 consists of the Nooksack River drainage basin, and the DSS will help in management of water quality, water quantity, instream flow, and fish habitat with the drainage (WRIA 1 website). The model domain is larger than the Abbotsford-Sumas aquifer and extends into parts of British Columbia (Figure 8). The model domain is divided into 39 drainages (Figure 9).

Each sub-model provides different output results. The nitrogen loading sub-model provides the monthly and annual on-ground nitrogen loading for each land use class within each drainage. The soil-nitrogen dynamics sub-model provides the monthly and annual distribution of nitrate leaching. The groundwater flow sub-model provides

the head distribution, flow velocity field and cell fluxes, and the nitrate fate and transport sub-model provides the distribution of nitrate concentration in the groundwater.

### **3.2.1 Nitrogen Loading**

Nitrogen loading is one of the four sub-models in the A&K model that considers sources of nitrogen to on-ground loading in the model domain to be dairy manure, fertilizer, septic systems, dairy farm lagoons, wet and dry deposition, lawns, irrigation recharge and legumes (Almasri and Kaluarachchi, 2004). The model is divided into 100 meter cells. Nitrogen loading values are calculated for each cell.

The steps taken to determine the amount of on-ground nitrogen loading are as follows:

1. The distribution of land-use classes was established within the study area (Figure 10). The authors used the USGS National Land Cover Data (NLCD) grid in this study. This grid consists of 21 land-use classes that are applied throughout the United States. Since there is not a dairy farm land-use class, the authors obtained the spatial distribution of dairy farms within the study area from the Whatcom County Conservation District.
2. The contribution of on-ground nitrogen sources was determined for each land class present in the study area. This was done on a monthly time-scale with the distribution of land-use classes within a single drainage.
3. The amount of nitrogen deposited by each nitrogen source was calculated for every land-class within each drainage by month.

Calculations are done on a monthly basis because of the temporal variations from some on-ground nitrogen sources. See Appendix A, Section 1.0 for further explanation

of equations used.

Each on-ground nitrogen loading source will consist of different fractions of the nitrogen constituents: nitrate, ammonia, and organic nitrogen. It is necessary to determine the composition of each source so that volatilization losses of ammonia and organic nitrogen and the soil-nitrogen dynamics of each nitrogen species can be correctly modeled. The nitrogen-species compositions of each source were values gathered from literature sources.

There are some on-ground nitrogen losses to consider before nitrogen travels to the unsaturated zone. These losses are due to runoff and volatilization. Runoff losses are applied to all nitrogen species. Percentage of nitrogen lost to runoff depends on soil conditions at application, amount of precipitation after application, and source of nitrogen. The authors decided to use a 10% loss value from literature (Meisinger and Randall, 1991). Runoff losses do not apply to dairy farm lagoons and septic tank systems that deposit directly into the unsaturated zone.

Volatilization occurs when nitrogen is lost as gaseous ammonia from manure or fertilizers. Estimating volatilization rates can be complex because of the variety of factors involved. Ammonia loss can be affected by the N source, method of N application, soil pH, soil cation exchange capacity, and weather conditions (Meisinger and Randall, 1991). Generally, the higher the air temperature, the greater amount of nitrogen that will be lost to volatilization. The value for percentage volatilized was estimated from the range of losses published by Meisinger and Randall (1991). The values used in the model are 10% loss for fertilizers and 23% loss for manure.

### **3.2.2 Soil-Nitrogen Dynamics**

Another sub-model in the A&K model simulates soil-nitrogen dynamics. After surface application and losses, nitrogen travels down to groundwater through the unsaturated zone. The nitrogen that leaches to the groundwater is the result of the many chemical, physical and biological interactions with the soil. In order to correctly model the amount of nitrogen in the groundwater, it is important to understand and quantify soil-nitrogen dynamics. Kaluarachchi and Almasri (2004) based their model off the already existing Nitrate Leaching and Economic Analysis Package (NLEAP), which was developed in the Midwest to estimate nitrate leaching to groundwater. The authors developed their model using many of the same NLEAP calculations, but reformatted them for better integration into their GIS platform. The processes accounted for in the A&K model are fixation, mineralization, immobilization, nitrification, denitrification, plant uptake and water available for leaching. For further explanation of the calculation of these variables, please see Appendix A, Section 2.0.

McKee (2004) found the process of denitrification to be significant in reducing nitrate concentrations in parts of the Abbotsford-Sumas aquifer with peat bogs. The nitrogen loss due to denitrification in the soil was calculated using an equation from Shaffer *et al.* (1991).

### **3.2.3 Groundwater Flow**

The development of a groundwater flow sub-model within the integrated A&K model was necessary to calculate groundwater velocity within the aquifer. These values of groundwater velocity would then be used within the fate and transport model.

A groundwater flow model (MODFLOW) developed by the USGS was used within this model. MODFLOW is a three-dimensional model that can be modified for various applications. It is necessary to note that the A&K model assumes a single layer model, and only horizontal flow throughout the aquifer. However, transmissivity differed spatially throughout the aquifer and ranged from less than 3200 ft<sup>2</sup>/day to over 29,000 ft<sup>2</sup>/day (300 m<sup>2</sup>/day to over 2700 m<sup>2</sup>/day) (Figure 11). In the model, the area of flow is divided into “blocks” in which the hydraulic properties are uniform. At each time step in the model, mass balances are calculated as well as a cumulative volume from each source or discharge. The fate and transport model (MT3D) is interfaced with MODFLOW so that output values calculated by MODFLOW can be used directly in MT3D. See Appendix A, Section 3.0 for the equation used to calculate groundwater velocity.

### **3.2.4 Fate and Transport of Nitrate in Groundwater**

The fourth sub-model uses the model MT3D to simulate the fate and transport of nitrate in the groundwater. MT3D was developed by Zheng (1990) and is used to model the dispersion, diffusion, advection, decay and sorption of contaminants in a three-dimensional system. Since the authors developed this model as a single layer, transport of nitrate was simulated in two dimensions. See Appendix A, Section 4.0 for the equation used to calculate nitrate transport. Boundaries of specific head or flux conditions can be simulated that supply water into the model (Figure 12).

Denitrification is also modeled as occurring in groundwater in the aquifer. Average denitrification rates came from previous work in the aquifer (Tesoriero *et al.*, 2000), and ranged between 1.3 to 2.7 mM of nitrate per year in part of the aquifer, and

0.1 mM per year in deeper parts of the aquifer. In calibration of the model, the rate of denitrification in groundwater was one of the parameters that was altered for greater agreement between measured and modeled groundwater nitrate concentrations.

### **3.2.5 Model Assumptions and Limitations**

There are many factors that can affect a nitrate concentration measured at a particular well. These factors include: timing and degree of precipitation, irrigation, and nutrient loading events, thickness of vadose zone, residence time in soil, depth of well below water table, denitrification and other soil-nitrogen dynamics, amount of nitrate present in south-flowing groundwater, and vertical and horizontal mixing of nitrate plumes within the aquifer. Due to the size and scope of the study area, the A&K model cannot capture all these details. As such, simplifying assumptions had to be made.

The following assumptions and limitations were made due to lack of data on certain aspects of the nitrogen cycle, or because the scope of the model limited the amount of detail possible.

- The model assumes a uniform distribution of nitrogen across each land cover class. In reality application will not be uniform, and this method will underestimate in high intensity agricultural areas, and overestimate in low intensity areas.
- Some model parameters are estimated from literature: percentage of nitrogen species in manure and inorganic fertilizers, lagoon seepage rate, percentage of nitrogen species in atmospheric deposition, loading from septic systems, nitrogen fixation rate by legumes, and inorganic fertilizer application rate. To gain the

most accurate results, it would be best to measure these values in the study area, since these literature values could either over- or underestimate these values.

- Values for soil-nitrogen dynamics are estimated using literature values. Rates of mineralization, nitrification, denitrification, manure volatilization, and fertilizer volatilization either cannot be measured directly in the field or the cost of obtaining accurate values for the entire study area is prohibitive. Values for these parameters were calculated from equations from Shaffer *et al.* (1991).
- A travel time of three months for nitrate through the unsaturated zone. It is set at a three-month lag time that was estimated by the response time of groundwater levels to precipitation (Hii *et al.*, 1999). While this would likely not affect the magnitude of nitrate leaching for each month, it would affect the timing of nitrate concentration peaks in the groundwater. Travel time would be a function of the amount of water, the porosity, and permeability of the unsaturated zone.
- The Abbotsford-Sumas aquifer is modeled as a single layer. Aquifer characteristics are modeled as varying horizontally, but they cannot be modeled as varying vertically. Due to the glacial genesis of the aquifer, this assumption is a major simplifying aquifer characteristic and will lead to a less accurate estimation of groundwater flow. Scibek and Allen (2006) modeled the Abbotsford portion of the aquifer into four distinct hydraulic zones that vary horizontally and vertically through the aquifer. Based on their work, modeling the Abbotsford-Sumas aquifer as a single layer is oversimplifying aquifer characteristics.
- Nitrate concentrations are calculated as uniform within groundwater throughout the depth of the aquifer because of the single layer aquifer assumption. Previous

work has shown that there is stratification of nitrate values within the aquifer, but the model gives volume averaged values for the entire column of groundwater within the aquifer. Since the source of nitrate in groundwater is from surface activities, nitrate concentrations would be greater at shallower depths and decrease further down. They would not be completely mixed throughout a water column.

- Nitrogen loading in Canada is distributed evenly across all land classes. When the model was developed, the authors did not have detailed information on land use in the Canadian portion of the study area (Almasri and Kaluarachchi, 2004). The pasture/hay land class in the Canadian portion does not receive the same nitrogen loading as in the U.S. portion, but is a combination of what the authors refer to as “large farm and small farm agricultural land area” (Almasri and Kaluarachchi, 2004). The application rates of fertilizer and manure are calculated for each of the four drainages in the Canadian portion, and then applied equally throughout each drainage. While this estimation of Canadian loading would not have a great impact over the majority of the model’s U.S. area, it does have an impact on the WWU study area. If the calculated applied amount was higher than what actually occurs, it would overestimate the impact of Canadian land use, and if it is lower, than the impact of Canadian land use would be underestimated.

### **3.2.6 Scenario Descriptions**

Different scenarios can be created in the A&K model by altering the land use and nitrogen inputs. Several scenarios were created to test the impacts Canadian and U.S.

land use had on groundwater nitrate concentrations

#### *No Land Use*

To determine the modeled background concentration for the WWU study area, all land in the study area and a portion of land north of the study area in Canada was converted to the Mixed Forest land class. This land class would result in minimum nitrogen loading in the study area.

#### *Basic Land Use*

The Basic Land Use scenario was set up to validate measured groundwater values. In this scenario, land uses were changed to represent the study area during the time of the study (Whatcom Conservation District). Dairy loading values (Tables 1 & 2) and fertilizer applications (Table 3) were set to generalized default parameters defined by the authors as representative of the Sumas aquifer. Basic Land Use scenarios were also run with the default inputs for wet and dry deposition, septic systems, dairy lagoons, lawns and gardens, irrigation, and legumes.

#### *No Canadian Land Use*

The No Canadian Land Use scenario was designed to test what groundwater concentrations would be if there was only agriculture in the WWU study area. All Canadian land directly above the WWU study area was changed to the Mixed Forest land class. All land use in the U.S. is the same as in the Basic Land Use scenario.

#### *No U.S. Land Use*

The No U.S. Land Use scenario was intended to show the effects that Canadian land use has on groundwater in the U.S. Canadian land use was left the same as in the Basic Land Use scenario, but all land use in the WWU study area was converted to the

Mixed Forest land class.

### *Irrigation Influence*

Five scenarios were set up to study the influence irrigation of crops has on groundwater nitrate concentrations. To determine the impact that irrigation has on nitrate concentrations in groundwater, scenarios were set up in which nitrate, ammonia, and organic nitrogen concentrations in irrigation water were doubled, halved, and set to 0 mg/L; and scenarios in which the irrigation rate was doubled and halved.

Almasri and Kaluarachchi recommend running the model until it reaches a “steady-state” in which values remain fairly constant, since land use practices have been occurring in the study area for many years, the build-up of nitrogen in the soil and groundwater is expected to be in a quasi-steady state (Kaluarachchi and Almasri, 2004). Running the model for shorter periods of time would introduce less nitrate into the system. Each of the land use scenarios were run for a simulation time of 30 years. The irrigation scenarios were run for a simulation time of 20 years. A time-series of values from the Basic Land Use at well site H1 shows the increasing nitrate concentration through time (Figure 13).

## **4.0 RESULTS & DISCUSSION**

After each scenario was successfully run in the A&K model, shapefiles of well sampling sites within the study area were overlain over the output maps within the model. Nitrate time series data were calculated at each well site within each scenario. The median value of the final 36 months of each scenario was taken to represent the groundwater nitrate concentration at each site. The following is a summary of the scenarios' results.

### **4.1 No Land Use**

Nitrate can enter groundwater from environmental sources such as precipitation, atmosphere, nitrogen fixation by plants, etc. To estimate the amount that these sources contribute to nitrate in groundwater, and to determine what the background concentration of nitrate in the study area would be, the entire U.S. study area and BC section above were converted to a no-agricultural land use. With the entire U.S. portion of the study area and the BC section above the study area converted to "Mixed Forest", the groundwater nitrate concentration would be the result of environmental factors (Table 4). These modeled nitrate concentrations could be considered the background concentration of nitrate in the aquifer. The average modeled concentration of nitrate in groundwater was 1.5 mg/L. Cox and Kahle (1999) predicted the background concentration to be less than 1.0 mg/L.

Kaluarachchi and Almasri (2004) found that wet and dry atmospheric deposition contributed only 6% of the total nitrogen loading in the study area. However, atmospheric deposition is significant because it occurs over the entire study area, and atmospheric deposition deposits more nitrate than both manure and fertilizer applications.

Wet deposition refers to nitrate and ammonium in precipitation, and dry deposition refers to particulate fallout and the sorption of nitrogen gas. Dry deposition would be greater in an area with dairy farms because volatilization of nitrogen gas from the manure would be redeposited in the area at the rate of 15 lbs-NO<sub>3</sub>/acre-year. The dry deposition rate for non-agricultural areas is 1lb-NO<sub>3</sub>/acre-year (Kaluarachchi and Almasri, 2004). Thus, nitrate is still present in the groundwater.

#### **4.2 Basic Land Use**

To test the validity of the Basic land use scenario, the modeled values calculated at each well site were compared to the measured values. For each well site, the median of the measured values was compared to the final three years of the modeled data (Table 5).

The time series of modeled nitrate concentrations at a selection of the well sites reach steady-state conditions between 60-260 months (Figure 14). The time to reach steady-state conditions varied for each well, and was likely a combination of the amount of up-gradient nitrogen loading, transmissivity of the aquifer, and depth at each well site. There was very little seasonal change in modeled concentrations, which is dramatically different than most measured nitrate concentrations at the same well sites which can show significant change throughout the sampling period (Figure 15). The lack of seasonality in modeled concentrations documents the insensitivity of the model to short-term changes. Well site K1 is also affected by denitrification. The modeled nitrate concentrations for that well site are consistently high because the model simulates no denitrification in the study area.

Difficulties in comparing modeled values to measured values was due to the

differences in depth that each modeled value represents, and the presence of denitrification in the study area. For the difference in well depths, the measured values represented the nitrate concentration at the depth of the completed well below the water table and the modeled values represented the nitrate concentration of the entire water column. The authors set the layer thickness of each cell in the model to the depth at which the nitrogen was less than the baseline concentration of 1 mg/L (Figure 16). The depths that the modeled values and the measured values represent were often different, making comparisons of values at specific well sites difficult. Wells H4, P1, P2, BC4, and BC5 had measured depths and modeled depths within a difference of 10 ft (3 m) (Table 5). Well H4 had a measured median value of 12.0 mg/L and a modeled median value of 11.6 mg/L. Wells P1 and P2 had measured median values of 7.0 and 3.9 mg/L and modeled median values of 6.1 and 5.1 mg/L, respectively. British Columbia piezometers BC4 and BC5 had measured median values of 8.15 and 13.5 mg/L and modeled median values of 10.8 and 5.7 mg/L. The average difference between the medians of the measured and modeled values at these wells is 2.6 mg/L, and the average difference for the rest of the wells with a greater difference between depths is 6.9 mg/L.

Denitrification is known to occur in the WWU study area (McKee, 2004), and is thought to cause lower nitrate concentrations at wells P1, P2, P3, K1, V1, V2, V3, V4, V7, V11, and V12 (Mitchell *et al.*, 2005; Table 5). Denitrification was simulated in the model, but the spatial distribution of denitrification rates was applied through the process of “trial and error” by the authors. The same denitrification rate was applied over the entire model domain and during the calibration process; this rate was then altered in different areas of the model domain until the modeled nitrate concentrations more

accurately predicted the measured nitrate concentrations. Figure 17 shows the final spatial distribution of denitrification rates, which shows the denitrification rate in the WWU study area to be 0. The A&K model is not able to predict denitrification on a small-scale, which is another limitation. This lack of accurate prediction also makes comparisons difficult between measured and modeled values.

These results are comparable to other models used to predict nitrate groundwater concentrations. However, those models that have three-dimensional groundwater flow and transport and were able to predict nitrate concentrations at depth (Shamrukh *et al.*, 2001; Puckett *et al.*, 1999) were more successful than the models that were single layer (Geng *et al.*, 1996; Ling and El-Kadi, 1998). Being able to model nitrate concentrations at varying depths through a multi-layered aquifer would greatly improve this model as a water management tool.

The original fertilizer and manure loading amounts were both doubled and then halved to test the loading sensitivity of the model. The change in median modeled nitrate concentrations is shown in Figure 18. When the manure and fertilizer loading was doubled, the median groundwater nitrate concentrations at the majority of the wells doubled as well (Table 6). Those wells that did not show as great an increase or decrease in nitrate concentration were H8, V7, V8, V9, V10, BC3, BC4, BC5, and BC6. The modeled nitrate concentration at these wells increased between 3-6 mg/L. These wells are either located in BC or are the closest to the Canadian border. In the model, the authors used a different method to apply loading to Canadian lands, so the loading in Canada was averaged over the entire drainage, unlike in the U.S. where it was specific to a certain land use. Changes in manure and fertilizer loading in the Canadian portion of

the model are not as great as in the U.S., but were still significant.

Well sites H1, H2, H3, T1, and T2 showed significant increases in median nitrate concentration when nitrogen loading was doubled. All of these well sites were modeled to have depths between 20-40 ft (6-12 m), and are also located in the area of lowest transmissivity (Figure 11). Lower transmissivity values would translate to lower groundwater velocities, which mean that over time nitrate leaching to the groundwater at that site would not travel and mix with other groundwater, but would affect concentrations at that well site. This is a possible explanation for the large increases in nitrate concentrations seen at the above-mentioned well sites.

The depth of each well site has an impact on the degree to which well sites will show changes in nitrate concentrations. Those well sites that were located at greater depths might not show as great a change in nitrate concentration because the increased nitrate would be averaged over a greater water column. Differences between Basic Doubled and Basic Land Use at each well site were plotted by well site depth (Figure 19). Although the data are scattered, there is a negative regression indicating that the well sites with greater depths show less of a change in median nitrate concentration.

In the scenario for halved loading, the median groundwater nitrate concentrations of a majority of the wells were approximately half of the original values (Table 5). Again, the wells that did not show as great a change were V8, V9, V10, BC3, BC4, BC5, and BC6 because these wells were more affected by the Canadian nitrate loading.

In their model validation, Kaluarachchi and Almasri (2004) found that manure contributed 69% of total nitrogen loading to the model domain, and fertilizer application was 19% of total nitrogen loading. Although the exact percentage contribution for

manure and fertilizer in the Basic Land Use scenario was probably different, the application of manure and fertilizer represents the greatest contribution of nitrogen in the WWU study area. According to the A&K model, doubling and halving these contributions would effectively double and halve the resulting groundwater concentrations.

#### **4.3 No Canadian Land Use Loading**

To estimate the impact that U.S. land use has on groundwater in the study area, agricultural land use in BC north of the study area was converted to the Mixed Forest land class. With the Mixed Forest land class, groundwater nitrate concentrations in the study area would be a result of environmental deposition in Canada and U.S. land use. Wells in the U.S. portion of the study showed an average decrease of 1.0 mg/L from Basic Land Use (Table 4). This decrease in nitrate concentration affected some well sites more than others (Figure 20). Wells V7-V10 showed the greatest change in the U.S. study area with an average decrease of 4.7 mg/L from Basic Land Use. Since well sites V7-V10 were located the closest to the Canadian border, they were impacted the most by land use in BC. This range of influence predicted in the model is not as extensive as previously observed (Mitchell *et al.*, 2005). This decreased influence could be due to the fact that transport is modeled as occurring through the entire aquifer as a single layer.

The BC piezometers had the greatest average decrease from Basic Land Use, with an average background concentration in the BC section of 1.2 mg/L. While the model shows that BC agriculture directly impacts BC well sites, the range of influence of BC agriculture appears to be underestimated.

#### **4.4 No U.S. Land Use Loading**

To estimate the impact Canadian land use has on groundwater nitrate concentrations, the entire U.S. study area was converted to a Mixed Forest land class. With the entire U.S. portion of the study area converted to the Mixed Forest land class, the groundwater nitrate concentration would be a result of environmental deposition and Canadian land use influence. As stated earlier, since nitrogen loading from Canadian land use was calculated differently from U.S. loading, these estimations of the Canadian influence on groundwater are less reliable.

Wells in the U.S. portion of the study area had lower nitrate concentrations when compared to the Basic Land Use concentration (Table 4). Well sites showed variable changes in median modeled concentrations (Figure 20). Wells that did not show a significant change from the Basic Land Use were V8, V9, V10, BC3, BC4, BC5, and BC6. The median concentrations at V8 and V10 slightly decreased, but the concentration at V9 remained the same. Since these wells are located about 0.1 miles (0.16 km) away from the Canadian border, it is obvious that these wells are strongly influenced by Canadian sources.

The modeled nitrate concentrations given for each well site represent the average nitrate concentration for the entire water column. In reality, nitrate is not present at the same concentration throughout the entire water column. Previous work (Mitchell *et al.*, 2005) has shown that nitrate concentrations are generally higher in shallower wells, and decrease with depth.

While the depth of the aquifer within the model cannot be changed, the nitrate concentrations given by the modeled can be recalculated to estimate what the nitrate

concentrations would be at a different depth. For example, the well sites V8, V9, and V10, which are located closest to the Canadian border, have fairly deep modeled depths of 65, 65, and 95 ft (20, 20, and 20 m), respectively. In reality, these wells have measured median depths of 37.7, 18.3, and 17 ft (11.5, 5.6, and 5.2 m). To recalculate nitrate concentrations, I estimated the total volume of water in a model cell, assuming a porosity of 0.30, to the modeled depth. Each cell in the model is 328 ft (100 m) on each side. The volume was first calculated in m<sup>3</sup> and then multiplied by 1000 to convert to liters.

$$Water\ Volume(L) = \left[ \text{site depth}(m) \times \text{cell area}(m^2) \right] \times \text{porosity} \times 1000$$

I then calculated the amount of nitrate applied to this area by multiplying the water volume by the modeled nitrate concentration.

$$Total\ amount\ of\ nitrate(mg) = Water\ Volume(L) \times Modeled\ Concentration\ (mg - N/L)$$

I then divided this amount of total nitrate by a new water volume. This new water volume was calculated using the above method, but by using a new well site depth.

$$New\ Concentration\ (mg - N/L) = \frac{Total\ Amount\ of\ Nitrate(mg)}{New\ Water\ Volume(L)}$$

In the No U.S. Land Use scenario the modeled nitrate concentrations at sites V8, V9, and V10 are 7.0, 7.2, and 7.5 mg/L. I decided to recalculate these concentrations at 25 ft (7.6 m) depth to estimate what the nitrate concentrations might be like closer to the actual median well depths. The recalculated nitrate concentrations produced values closer to what was measured and show the impact on the modeled nitrate concentrations (Table 7).

The No U.S. Land Use Scenario was designed to estimate the impact that

Canadian surface activities has on groundwater in the WWU study area. These recalculated concentrations show a larger impact by Canadian land use on those well sites closest to the border. In the model, these well sites were greatly influenced by Canadian land use. In the No Canadian Land Use scenario, the median nitrate concentrations at these well sites had the greatest decrease (Table 4). If it can be assumed that they were mostly influenced by Canadian land use, then these recalculated concentrations show groundwater flowing south from B.C. with a nitrate concentration of close to 20 mg/L. This is higher than the estimate of Mitchell *et al.* (2005) of a nitrate concentration of 10 mg/L in groundwater flowing south from BC based on measured nitrate concentrations in piezometers directly north of the WWU study area.

While the influence of Canadian land use might not be accurately modeled due to model limitations, this model was somewhat helpful in showing what sections of the WWU study area and northern Whatcom County are most influenced by Canadian sources.

#### **4.5 Irrigation Influences**

Irrigation waters are believed to have an impact on groundwater nitrate concentrations by either Mechanism A) serving as a means to leach nitrates out of the unsaturated zone into the groundwater, or Mechanism B) adding more nitrate into the soil by recirculating groundwater having a significant nitrate concentration.

Previous work has found that irrigation can lead to greater groundwater concentrations by increased percolation and solute leaching through the unsaturated zone (Close, M.E., 1987; Spalding *et al.*, 2001; Rodvang *et al.*, 2004). Stites and Kraft (2000)

found that nitrate concentrations average 21 mg/L under irrigated vegetable fields, and 1 mg/L up-gradient of the same fields. Chang and Entz (1996) compared irrigated and non-irrigated fields that were receiving manure applications at differing rates. Non-irrigated fields had a significant accumulation of nitrate in the root zone, while irrigated fields had less total nitrate in the root zone and had greater leaching rates of nitrate. For agricultural fields where fertilizers or manure are being applied, irrigation can have a significant impact as a means for increased transfer of nitrate to the groundwater.

Irrigation water can also be a source for nitrate. Water used to irrigate fields is often pumped from groundwater below that same field. A significant nitrate concentration in the groundwater can build up as that same water is used for irrigation. The recirculation of groundwater as irrigation water has been found to cause increased nitrate concentrations in the groundwater below the irrigated fields. Through work on irrigated corn fields in Nebraska, Spalding *et al.* (2001) found that when irrigation water with a nitrate concentration of 30 mg/L was applied to the field, the crops would partially utilize the nitrate already in the water. The irrigation water unused by the crops would travel down the unsaturated zone to the groundwater, leaching more nitrate along the way. The leached nitrate, as well as the nitrate already in the groundwater, delivered nitrate spikes to the shallow groundwater after irrigation.

Guimerà (1998) found that recirculating groundwater in a coastal aquifer in Spain with restricted outflows led to an average nitrate concentration of 44 mg/L throughout the aquifer. Crop fields in the recharge area of the aquifer were over-fertilized, and the excess nutrients traveled to the groundwater. When water for irrigation was extracted from the aquifer, the natural hydrodynamics of the aquifer changed. Water that would

naturally outflow to the ocean was being intercepted for irrigation, and nutrient buildup in the aquifer was not able to discharge. This recirculating of groundwater led to nitrate concentrations as high as 160 mg/L within the aquifer.

Almasri and Kaluarachchi (2004) determined a standard nitrate concentration in irrigation water by assuming a default mean concentration of groundwater in each drainage. This mean nitrate concentration came from their earlier work in the aquifer (Kaluarachchi and Almasri, 2004). The study area is located over the boundary of two drainages: Fishtrap (northern section) and Johnson (southern section). Nitrate concentrations in irrigation water are 7.93 mg-N/L in Fishtrap and 7.30 mg-N/L in Johnson. Approximately 60% of the study area received irrigation: Transitional, Orchards/Vineyards/Other, Grassland/Herbaceous, Pasture/Hay, Row Crops, Small Grains, and Fallow. Each drainage has a standard irrigation rate for each month that was applied to every irrigated land class within that drainage.

To test mechanism A, I set up two scenarios: one that doubled the irrigation rate, and another that halved the irrigation rate. There was no significant difference between each wells' median modeled concentrations when comparing these two scenarios to the Basic Land Use scenario (Table 8) (Figure 21). From these results it appears that the amount of water used in irrigation was not a factor in increasing leaching to the groundwater.

To test mechanism B, I set up three scenarios: one in which irrigation water has a concentration of 0 mg/L of nitrate, ammonia, and organic N; one that has double the standard concentration given in the model, and one that has half the standard concentration. There was no significant difference between each wells' median modeled

concentrations between these three scenarios and the Basic Land Use scenario (Table 8) (Figure 22). From this model it appears that the presence of nitrate in the irrigation water has little effect on the groundwater concentrations. Perhaps the concentration in the irrigation water was not significantly greater than the nitrate concentration already in the groundwater, therefore recirculation of the irrigation water would not have added more nitrate to the groundwater.

Kaluarachchi and Almasri (2004) state that in their model, deposits from irrigation contribute 1% of total nitrogen loading. Limitations within the model may make it so that the impact of irrigation water is misrepresented. The use of the same monthly irrigation rate for every irrigated land class within each drainage may not be detailed enough to reflect actual irrigation practices. Leaching due to irrigation water could be overestimated in some parts and underestimated in others.

Using the same nitrate, ammonia, and organic nitrogen concentration within each drainage also does not accurately represent what is happening. Irrigation water can be a meaningful source of nitrate for some fields, and using a general nitrate concentration rather than one that is scaled by the modeled nitrate groundwater concentration can significantly overestimate or underestimate the nitrate concentration. In some parts of the study area, the modeled nitrate concentrations were significantly greater than the nitrate concentrations in irrigation water, which leads to an underestimation of the impact of irrigation. The irrigation concentration constants could also lead to an overestimation of nitrate concentration if significantly greater than groundwater concentrations in the area.

Based on these results, it seems that the equations to estimate nitrate loading and leaching due to irrigation are not accurate enough within this model.

## 5.0 CONCLUSIONS

Due to its aquifer characteristics and land use, the Abbotsford-Sumas aquifer has high vulnerability to nitrate contamination. Nitrate is a non-point source pollutant from the intensive agriculture present in the area. The use of a predictive tool with a GIS interface would be of great interest to nutrient managers to develop nutrient management strategies. The A&K model predicts the complex path of nitrate from land surface to groundwater through the combination of four sub-models that estimate nutrient loading, soil-nitrogen dynamics (NLEAP), groundwater velocity (MODFLOW), and nitrate fate and transport in groundwater (MT3D). I assessed the capabilities of the A&K model to accurately predict measured nitrate concentrations, as well as range of sensitivity to changes in nutrient loading.

Overall, the effectiveness of the A&K model as a predictive tool is compromised mainly due to its development as a single-layer model. Previous work in the WWU study area has shown nitrate to be stratified within the aquifer. However, the A&K model simulates groundwater flow within a single layer aquifer, which means that a nitrate concentration is averaged over the entire water column at a well site. This limitation makes it difficult to predict nitrate concentrations at depth, which restricts the use of the model as a predictive tool.

The A&K model was sensitive to changes in fertilizer and manure loading, but the scale of the model made it impossible to see seasonal variations. Land use changes predicted that only those wells closest to the border were influenced by Canadian land use. This range of influence is not as great as previously thought, and perhaps reflects on

the design of the model as a single-layer aquifer system.

Modeled changes in irrigation application rate and the concentration of nitrate in irrigation water resulted in little changes in modeled nitrate leaching to the aquifer. This lack of response to irrigation changes is inconsistent with previous research (Close, 1987; Spalding *et al.*, 2001; Rodvang *et al.*, 2004), which found that increases in irrigation rate and nitrate concentration resulted in more nitrate leaching to the aquifer. Based on the response of the model to irrigation changes, it seems that assumptions the authors made proved to be limiting when assessing the sensitivity of irrigation.

While the sub-models that might effectively estimate nitrate loading and leaching, the resulting modeled nitrate groundwater nitrate concentrations do not accurately reflect the observed conditions of nitrate in the aquifer. Overall, the A&K model is inadequate as an assessment tool.

## **6.0 FUTURE WORK**

This model would benefit greatly from being transformed into a multi-layer three-dimensional groundwater flow and transport model. Previous work in the Abbotsford-Sumas aquifer (Gelinias, 2000) has found that a stratification of nitrate concentrations exists within the aquifer. Gelinias (2000) attributed this to land use further up-gradient affecting deeper groundwater. Currently the model is not able to make any stratification of nitrate concentrations, making it difficult to compare to actual measured values.

Making this a three-dimensional model would also give the opportunity to add in aquifer heterogeneity by layers throughout the model. Scibek and Allen (2005) have developed a three-dimensional model of the Abbotsford-Sumas aquifer, and its combination with the nitrogen loading and leaching component of the A&K model would create a powerful tool for modeling nitrate concentrations in the aquifer.

I would recommend the creation of a “berry” land class to the model. Since the NLCD does not have a dairy farm land cover class, the model authors created one by merging a shapefile of dairy farms in Whatcom County with the NLCD for the area (Kalulachchi & Almasri, 2004). Berry farms represent a major agriculture land use in Whatcom County. Currently in the model, nitrogen loading from berry fields is distributed between Orchards/Vineyards and Row Crops land use classes. I think it would improve the loading accuracy of the model if there were a berry field specific land class. Canadian land use should also be updated to more accurately reflect current land use. Nitrogen loading in Canadian portion should also be changed to be specific to each land class, rather than averaged over several different land classes.

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Drainage ID	<i># of milking cows</i>	<i># of dry cows</i>	<i># of heifers</i>	<i># of calves</i>
Deer	152	19	108	30
Fourmile	1199	193	588	352
Ten Mile	3305	483	1322	550
Nooksack Channel	0	0	0	0
Blaine	0	0	0	0
California	1980	295	1004	330
Haynie	0	0	0	0
Lower Dakota	0	0	0	0
North Fork Dakota	225	28	110	60
South Fork Dakota	4554	472	1192	343
Schneider	461	76	205	167
Scott	2934	368	542	389
Wiser Lake/Cougar Creek	1150	173	312	217
Lummi Peninsula West	280	30	40	40
Schell	151	14	62	0
Bertrand	8160	1078	1364	770
Fishtrap	5695	868	1860	1057
Kamm	3442	567	900	704
Nooksack River Delta	0	0	0	0
Silver	100	20	75	25
Breckenridge	7565	1030	1606	1050
Dale	2234	349	185	405
Johnson	4326	688	659	591
Saar	2055	231	544	256
Swift	260	40	0	18
Lower Anderson	223	29	22	69
Nooksack Deming to Everson	1190	200	20	30
North Fork Anderson	0	0	0	0
Smith	172	25	0	60
South Fork Anderson	0	0	0	0
Fazon	55	27	40	14
Fingalson	70	20	45	45
Jordan	1200	250	0	0
Lake Terrell	40	2	1	7
Lummi Peninsula East	0	0	0	0
Lummi River Delta	0	0	0	0
Sandy Point	0	0	0	0
Semiahmoo	0	0	0	0
Cherry Point	0	0	0	0

Table 1. This input table for the A&K model shows the default number of cows per drainage (Kaluarachchi and Almasri, 2004). Each cow type has a different nitrogen production rate.

	Pounds of nitrogen produced each year
milking	266
dry	159
heifer	51
calf	85

Table 2. This input table for the A&K model shows the default values for pounds of nitrogen produced per year for each cow type (Kaluarachchi and Almasri, 2004).

	hay	berries	corn	seed potatoes	nursery	vegetables	fruits/nuts	pasture	grains
January	0	0	0	0	0	0	0	0	0
February	0	0	0	0	0	0	33	0	0
March	0	71	0	0	0	0	0	0	0
April	0	71	87	75	49	0	0	109	134
May	159	71	87	75	49	120	0	0	0
June	0	0	0	0	0	0	0	0	0
July	0	0	0	0	0	0	0	0	0
August	0	0	0	0	0	0	0	0	0
September	0	0	0	0	0	0	0	0	0
October	0	0	0	0	0	0	0	0	0
November	0	0	0	0	0	0	0	0	0
December	0	0	0	0	0	0	0	0	0

Table 3. An A&K input table for the default nitrogen application rates (lb/acre) within the model by crop type (Kaluarachchi and Almasri, 2004).

Well Site	Basic Land Use (mg/L)	No Land Use (mg/L)	No Canada Land Use (mg/L)	No US Land Use (mg/L)
H1	6.1	2.0	5.6	2.6
H2	7.5	2.1	6.9	2.4
H3	7.0	2.0	6.5	2.4
H4	11.6	1.9	11.1	2.3
H5	13.4	1.7	13.0	2.1
H6	12.6	1.4	9.8	2.0
H7	5.0	0.5	4.6	0.9
H8	4.2	0.4	3.2	1.4
V1	6.3	1.7	6.2	1.7
V2	7.9	1.5	7.3	1.6
V3	3.3	0.5	3.3	0.6
V4	7.7	1.0	7.5	1.3
V5	10.2	1.7	10.2	1.8
V6	6.5	0.6	6.1	1.1
V7	7.7	0.8	4.5	4.1
V8	8.4	1.2	2.5	7.0
V9	7.2	4.0	4.0	7.2
V10	7.6	1.1	1.2	7.5
V11	7.8	1.6	7.3	1.6
V12	8.9	1.8	8.8	1.9
K1	17.9	1.7	17.9	1.7
T1	6.3	1.8	6.2	1.8
T2	5.9	1.8	6.4	1.8
P1	6.1	1.8	6.0	1.9
P2	5.1	1.7	4.6	1.9
P3	4.6	1.7	4.4	1.9
BC3	12.6	1.4	1.4	12.6
BC4	10.8	1.3	1.3	10.8
BC5	5.7	1.0	1.0	5.7
BC6	6.1	1.2	1.2	5.8

Table 4. Median modeled groundwater nitrate values for Basic Land Use, No Land Use, No Canada Land Use Loading, and No U.S. Land Use Loading scenarios.

Well site	Median of measured values (mg/L)	Median of modeled values (mg/L)	Median depth below water table (ft)	Modeled thickness of aquifer (ft)
H1	14.2	6.1	10.0	35
H2	13.1	7.5	13.6	25
H3	11.3	7.0	55.5	25
H4	12.0	11.6	35.0	25
H5	12.1	13.4	6.3	25
H6	16.3	12.6	5.4	65
H7	11.2	5.0	38.0	65
H8	15.1	4.2	17.0	65
K1*	7.1	17.9	29.0	35
P1*	7.0	6.1	26.6	35
P2*	3.9	5.1	38.0	35
P3*	10.8	4.6	6.7	35
T1	18.8	6.3	15.0	35
T2	8.6	5.9	53.1	35
V1*	2.4	6.3	17.7	85
V2*	0.0	7.9	105.0	85
V3*	2.2	3.3	58.0	85
V4*	7.3	7.7	7.8	85
V5	27.1	10.2	1.4	35
V6	18.7	6.5	7.5	85
V7*	4.0	7.7	33.8	65
V8	16.3	8.4	37.7	65
V9	19.2	7.2	18.3	65
V10*	8.2	7.6	17.0	95
V11*	2.2	7.8	30.5	85
V12*	0.4	8.9	48.1	35
BC3	17.0	12.6		35
BC4	8.2	10.8	25.0	25
BC5	13.5	5.7	55.8	55
BC6	22.4	6.1	95.1	95

Table 5. Comparison of measured and modeled well depths and median nitrate concentrations. Shaded values indicate well sites where modeled and measured depths are within 10 feet. Wells that are believed to be influenced by denitrification are marked with an asterix.

Well Site	Basic Land Use (mg/L)	Basic Doubled (mg/L)	Basic Halved (mg/L)	median of measured values (mg/L)
H1	6.1	16.4	2.7	14.2
H2	7.5	18.8	3.1	13.1
H3	7.0	19.1	2.9	11.3
H4	11.6	22.5	5.2	12.0
H5	13.4	23.4	5.6	12.1
H6	12.6	20.0	6.0	16.3
H7	5.0	7.3	2.5	11.2
H8	4.2	5.6	2.4	15.1
V1	6.3	12.8	3.2	7.1
V2	7.9	14.8	4.3	7.0
V3	3.3	5.8	1.7	3.9
V4	7.7	13.5	3.9	10.8
V5	10.2	19.9	5.3	18.8
V6	6.5	9.9	3.0	8.6
V7	7.7	10.7	4.4	2.4
V8	8.4	12.1	5.7	0.0
V9	7.2	10.7	5.3	2.2
V10	7.6	11.6	5.6	7.3
V11	7.8	14.8	4.3	27.1
V12	8.9	18.8	4.8	18.7
K1	17.9	31.1	10.5	4.0
T1	6.3	20.8	1.7	16.3
T2	5.9	20.9	1.4	19.2
P1	6.1	13.5	3.1	8.2
P2	5.1	11.8	2.5	2.2
P3	4.6	11.5	2.0	0.4
BC3	12.6	19.3	9.3	17.0
BC4	10.8	16.6	8.3	8.2
BC5	5.7	8.6	4.2	13.5
BC6	6.1	8.9	4.5	22.4

Table 6. Median modeled groundwater nitrate values for Basic Land Use, Basic Doubled, and Basic Halved scenarios, and the median measured nitrate+nitrite values at each well site.

Well Site	Modeled depth (ft)	Modeled concentration at original depth (mg/L)	Modified concentration at revised depth (mg/L)	Median measured concentration (mg/L)
V8	65	7.0	18.2	16.3
V9	65	7.2	18.7	19.2
V10	95	7.5	28.5	8.2

Table 7. Recalculated nitrate concentrations with revised well site depths.

well site	Basic Land Use (mg/L)	No N. in irrigation (mg/L)	Double N. in irrigation (mg/L)	Half N. in irrigation (mg/L)	Half irrigation rate (mg/L)	Double irrigation rate (mg/L)
H1	5.8	5.8	5.8	5.8	5.8	5.8
H2	7.4	7.4	7.4	6.9	7.4	7.4
H3	6.9	6.8	6.9	6.8	6.4	6.4
H4	11.5	11.4	11.5	11.4	11.4	11.5
H5	13.3	13.2	13.4	13.3	13.3	13.4
H6	12.5	12.4	12.6	12.4	12.4	12.5
H7	4.9	4.9	5.0	4.9	4.9	5.0
H8	4.2	4.1	4.2	4.2	4.2	4.2
V1	5.9	5.9	5.9	5.9	5.9	5.9
V2	7.6	7.6	7.6	7.6	7.6	7.6
V3	3.2	5.7	5.8	3.2	3.2	3.3
V4	7.6	7.6	7.6	7.6	7.6	7.6
V5	10.0	10.0	10.3	10.0	10.2	10.0
V6	6.5	6.5	6.6	6.5	6.5	6.5
V7	7.6	7.6	7.7	7.6	7.6	7.7
V8	8.4	8.3	8.5	8.3	8.4	8.4
V9	7.2	6.9	7.0	6.9	7.0	7.2
V10	7.6	7.5	7.7	7.6	7.6	7.6
V11	7.5	7.5	7.6	7.5	7.5	7.5
V12	8.9	8.6	8.7	8.6	8.6	8.7
K1	17.3	17.3	17.3	17.3	17.3	17.3
T1	6.1	6.1	6.1	6.1	6.1	6.1
T2	5.8	5.9	5.9	5.8	5.9	5.9
P1	5.8	5.8	5.9	5.8	5.8	5.9
P2	4.8	4.5	4.5	4.5	4.8	4.8
P3	4.3	4.3	4.3	4.3	4.3	4.3
BC3	12.6	12.4	12.7	12.5	12.6	12.6
BC4	10.8	10.6	10.9	10.7	10.8	11.2
BC5	5.7	5.2	5.7	5.6	5.2	5.7
BC6	6.1	5.8	5.9	5.8	5.8	5.8

Table 8. Median modeled groundwater nitrate values for Basic Land Use, the three scenarios with varying concentrations of all nitrogen species in irrigation water, and the two scenarios with double and half of the default irrigation rate.

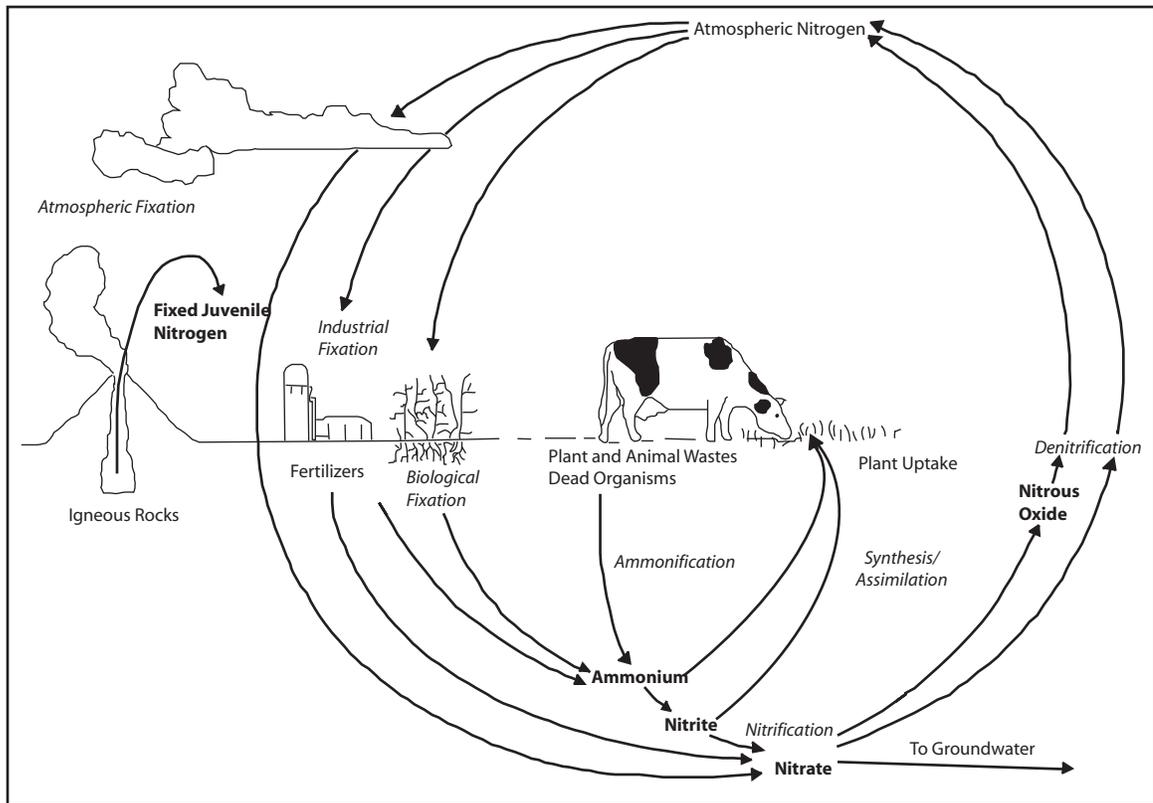


Figure 1. Transformations of nitrogen through the atmosphere, geology, soil, animals, plants, and water (adapted from Canter, 1997). Processes in the nitrogen cycle are italicized, and nitrogen compounds are in bold.

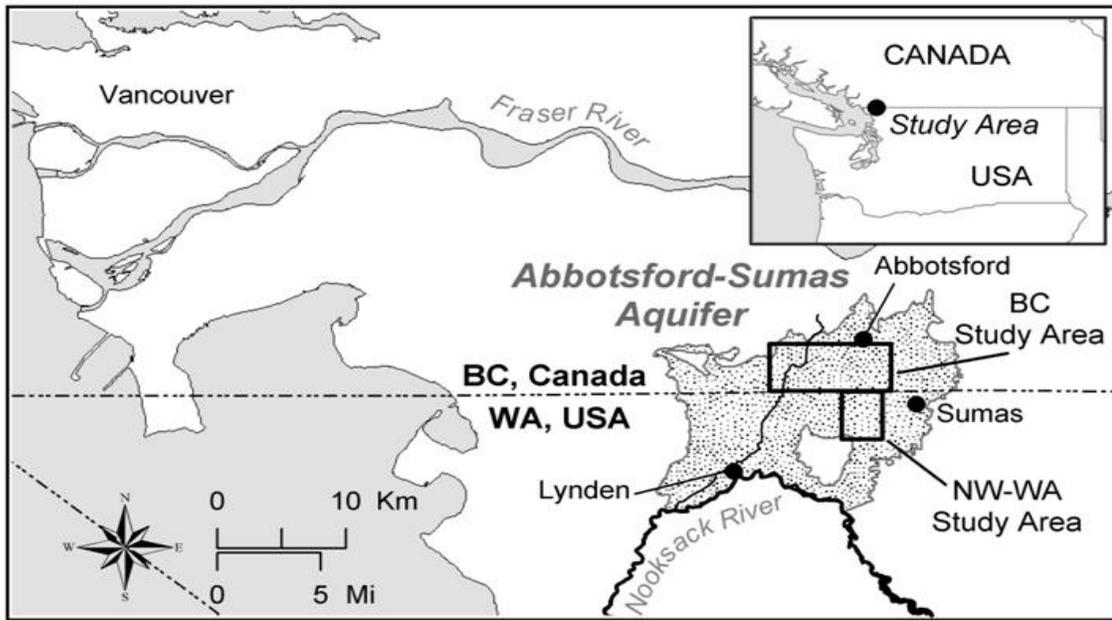


Figure 2. Location of Abbotsford-Sumas aquifer (from Mitchell *et al.*, 2003).

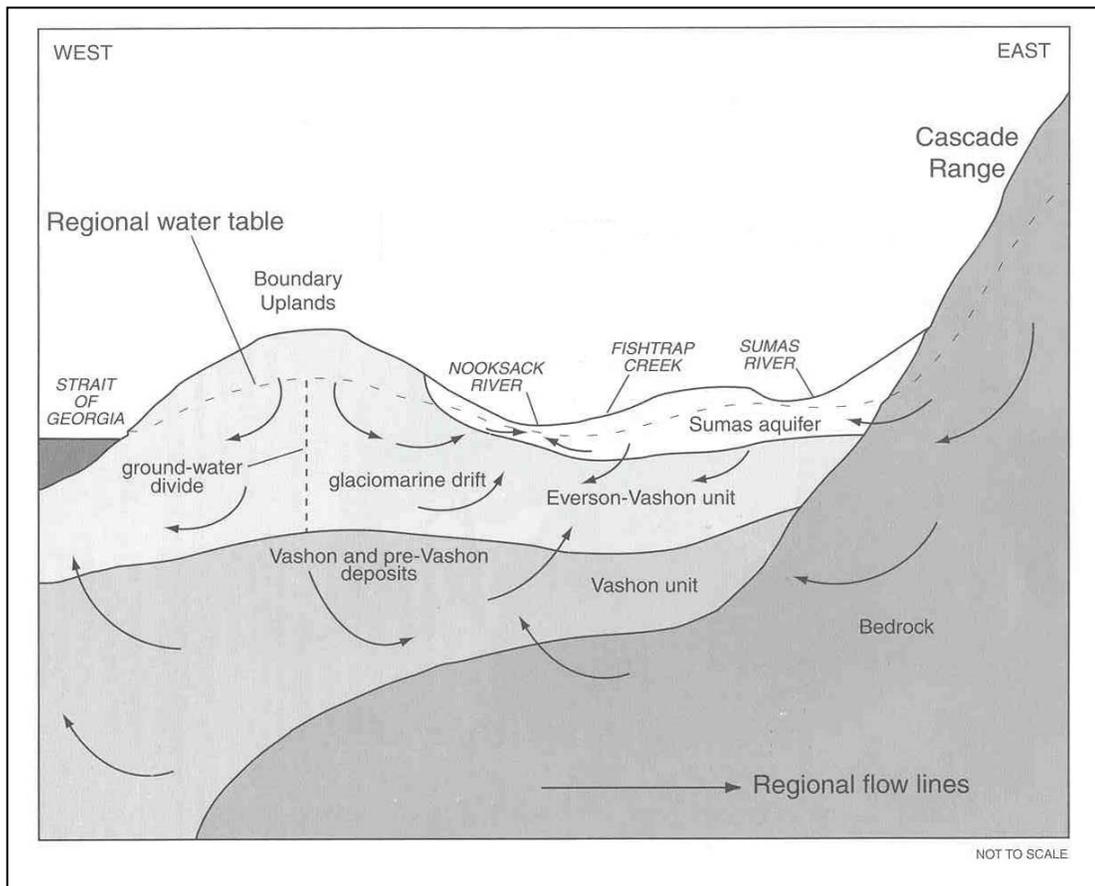


Figure 3. Generalized cross-section of hydrostratigraphy in the Abbotsford-Sumas aquifer. Arrows indicate generalized flow direction of groundwater. Adapted from Cox and Kahle, 1999.

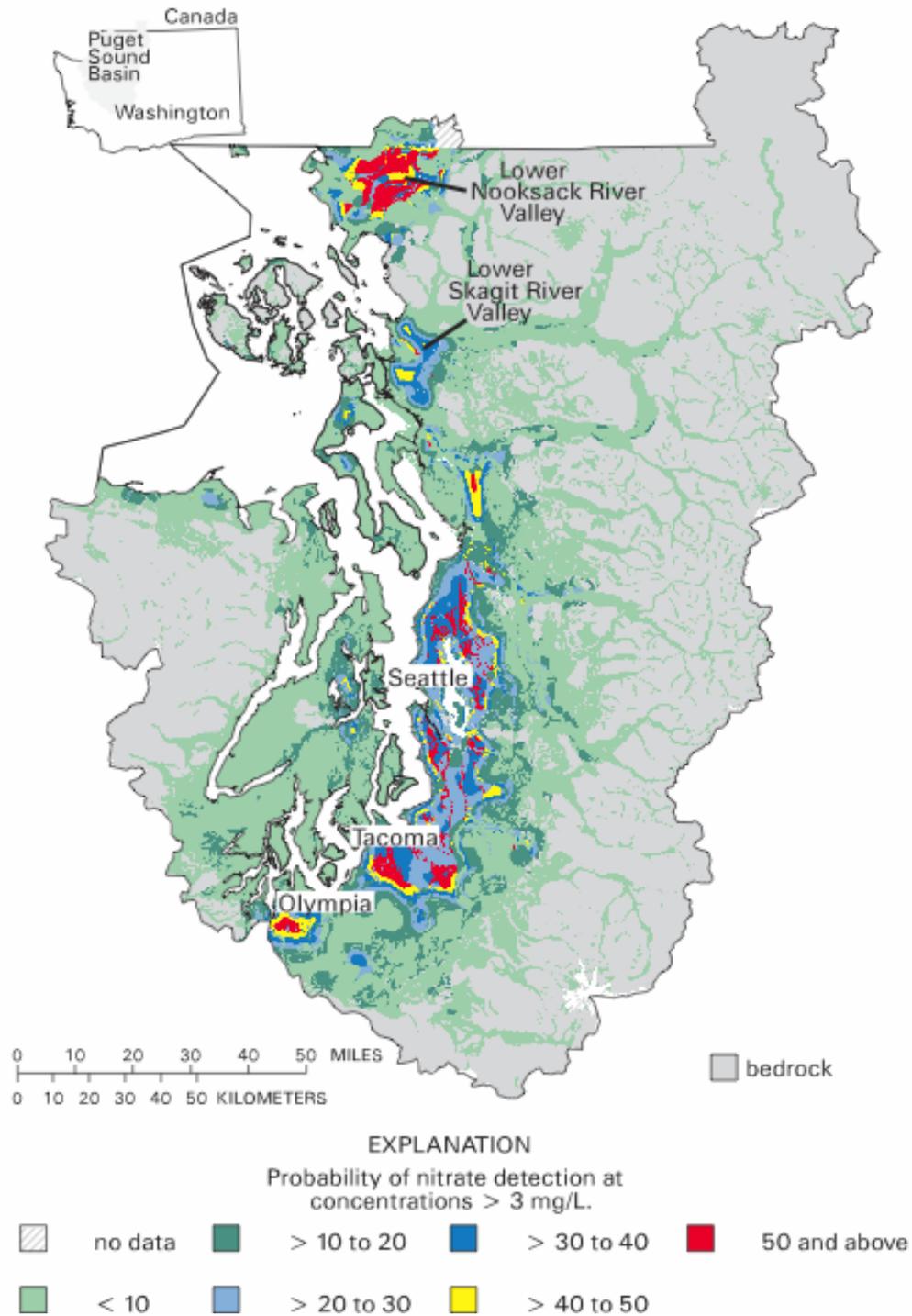


Figure 4. Nitrate vulnerability of Puget Sound Basin. Color indicates probability of nitrate concentrations in a 50 foot deep well exceeding 3.0 mg/L which indicates possible human influence (Tesoriero and Voss, 1997).

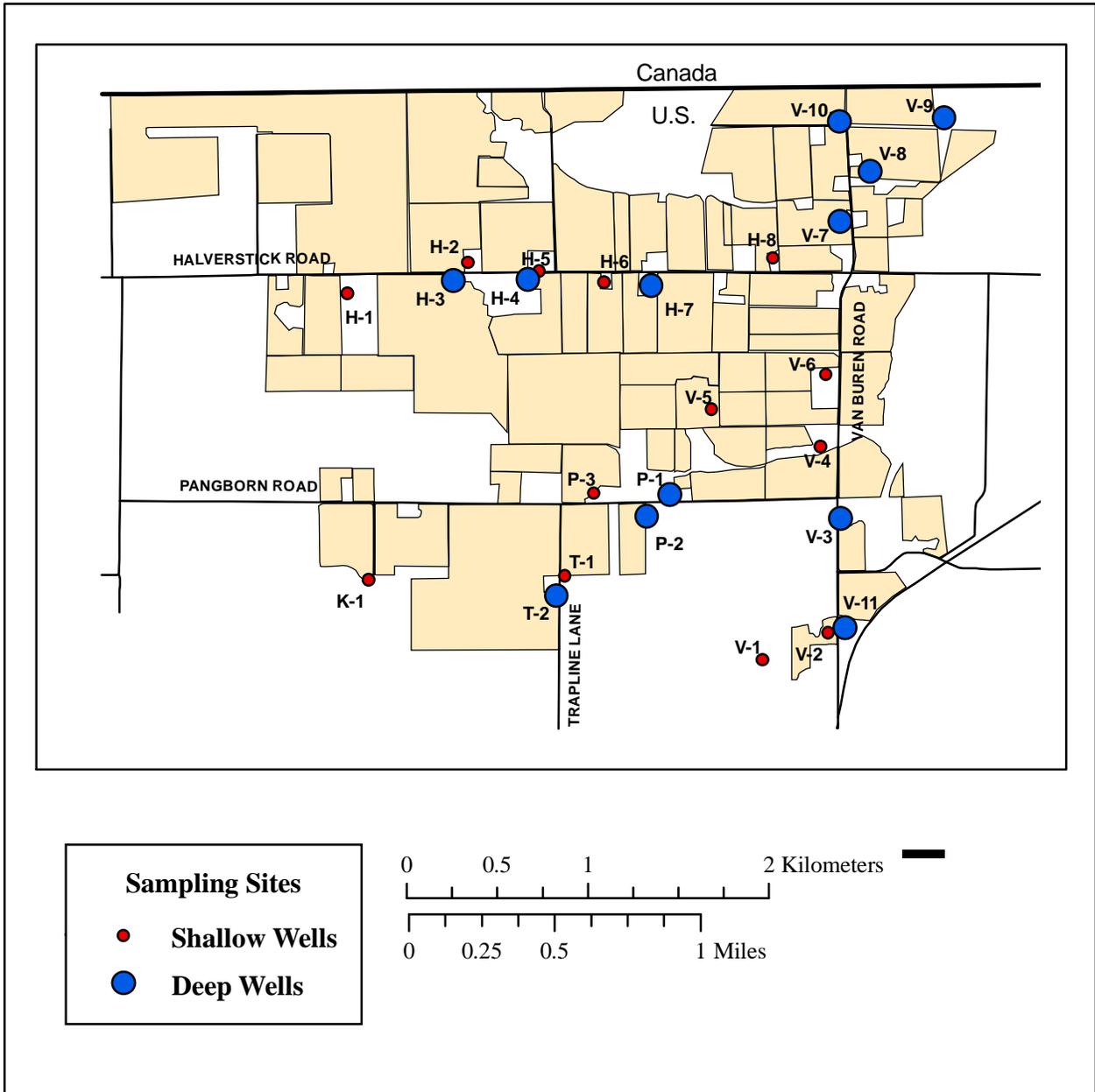


Figure 5. Location of well sampling sites used in WWU's water quality study. Wells are separated based on their finished depth. Shallow wells are finished <25 feet deep, and deep wells are finished >25 feet deep.

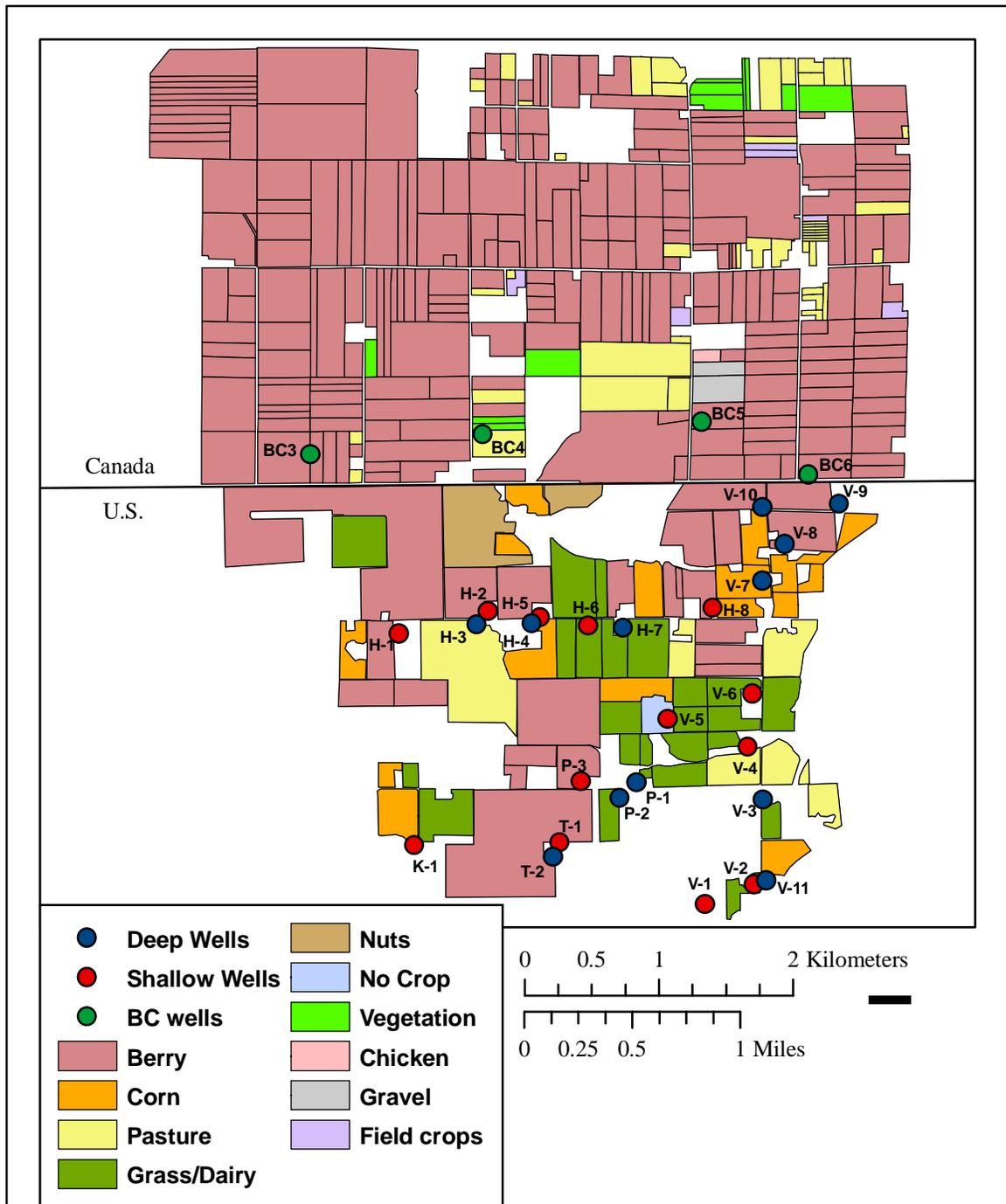


Figure 6. Land use in the WWU study area and southern British Columbia, with the locations of well sampling sites from the WWU study and Environment Canada's piezometers.

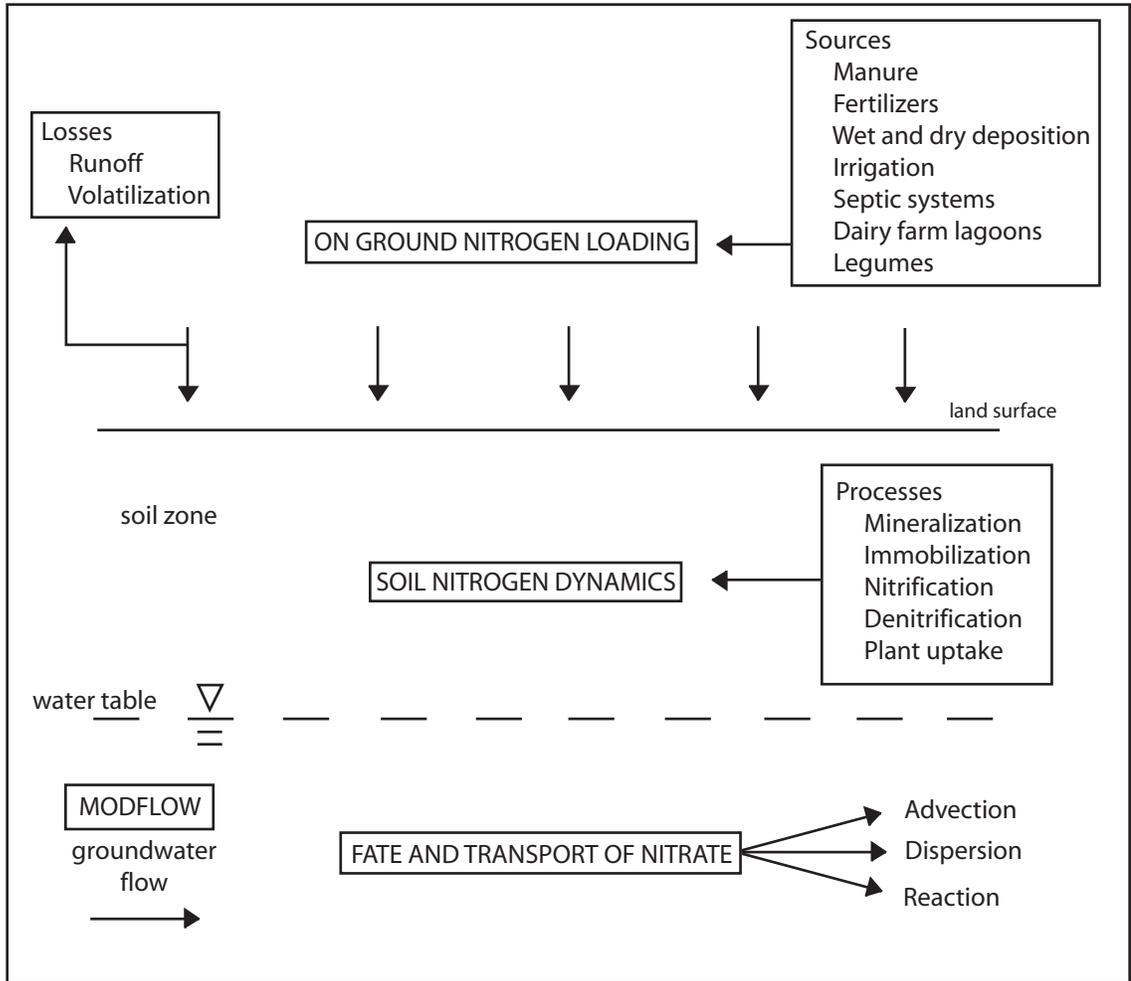


Figure 7. Spatial schematic of the A&K model. Sub-model names are in all caps. Adapted from Almasri and Kaluarachchi, 2004.

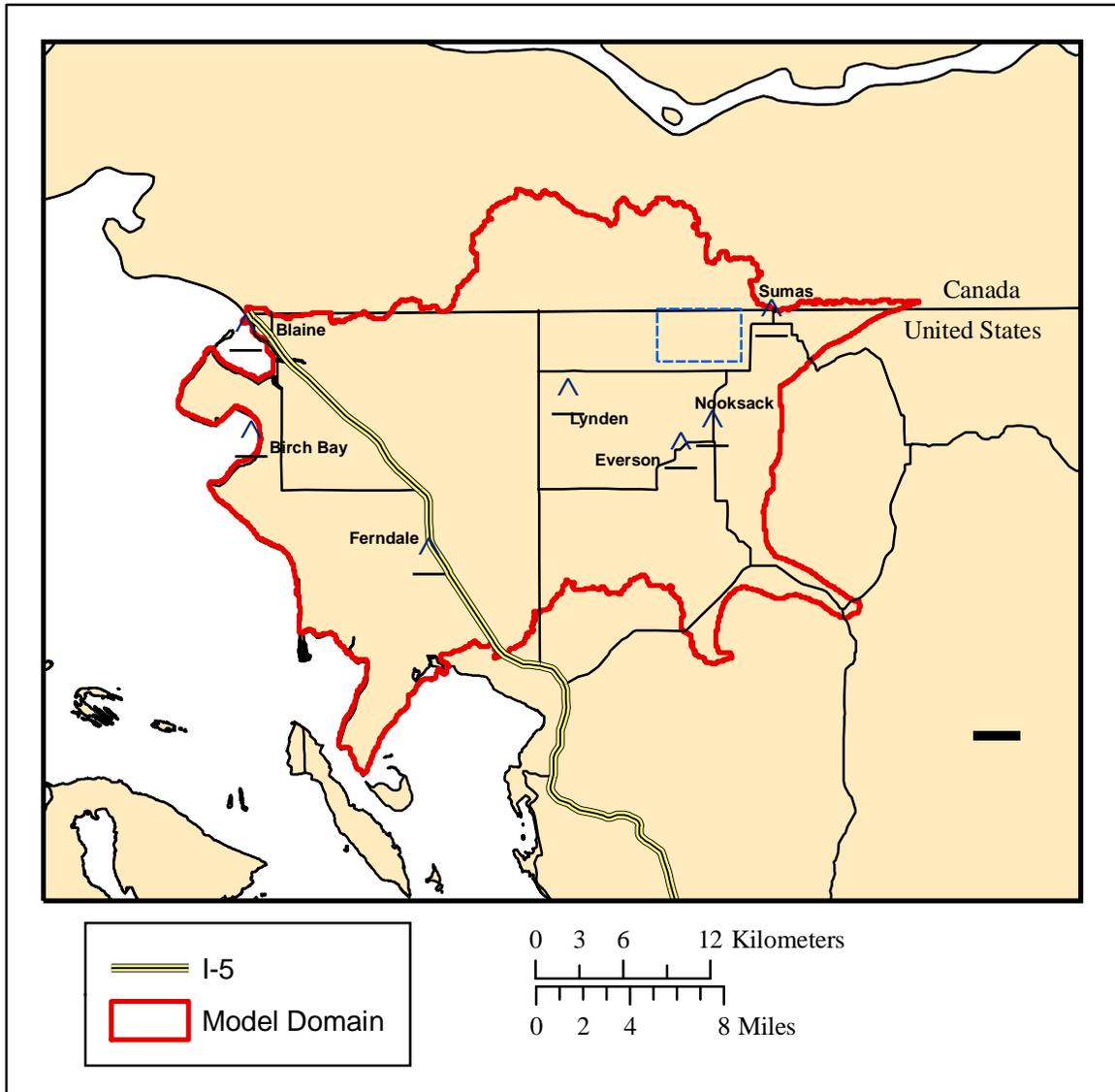
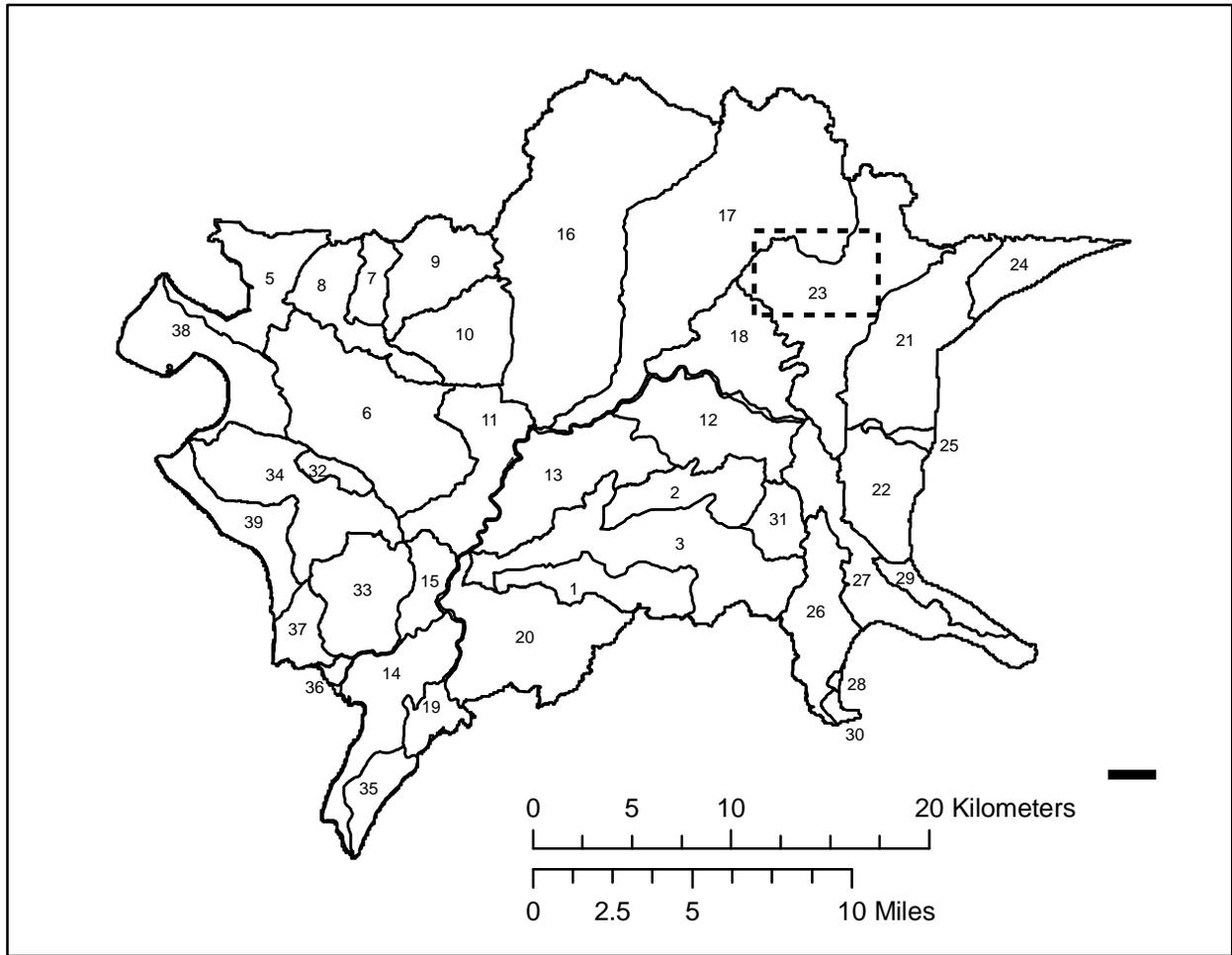


Figure 8. Location of model domain within Whatcom County. Blue dashed outline shows approximate location of WWU study area within the model domain.



ID	Drainage Name						
1	Deer	11	Schneider	21	Breckenridge	31	Fazon
2	Fourmile	12	Scott	22	Dale	32	Fingalson
3	Ten Mile	13	Wiser Lake/Cougar Creek	23	Johnson	33	Jordan
4	Nooksack Channel (water)	14	Lummi Peninsula West	24	Saar	34	Lake Terrell
5	Blaine	15	Schell	25	Swift	35	Lummi Peninsula East
6	California	16	Bertrand	26	Lower Anderson	36	Lummi River Delta
7	Haynie	17	Fishtrap	27	Nooksack Deming to Everson	37	Sandy Point
8	Lower Dakota	18	Kamm	28	North Fork Anderson	38	Semiahmoo
9	North Fork Dakota	19	Nooksack River Delta	29	Smith	39	Cherry Point
10	South Fork Dakota	20	Silver	30	South Fork Anderson		

Figure 9. Drainages in the model domain (adapted from Almasri and Kaluarachchi, 2004). Dashed box indicates approximate location of WWU study area.

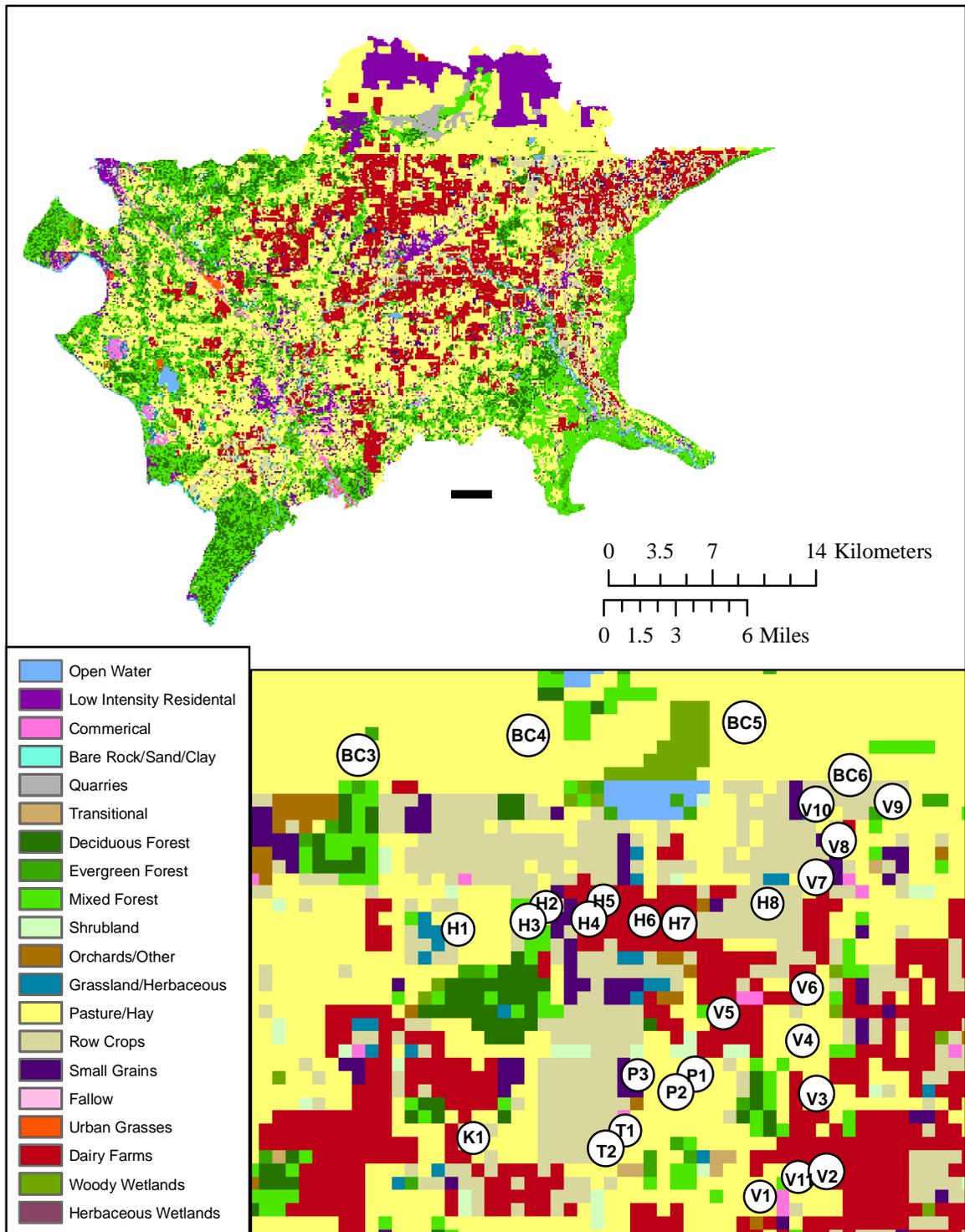


Figure 10. Land use in the A&K model domain. Enlarged area shows land use in the WWU study area. Land use is classified using the USGS National Land Cover Data. Adapted from Almasri and Kakuarachchi, 2004.

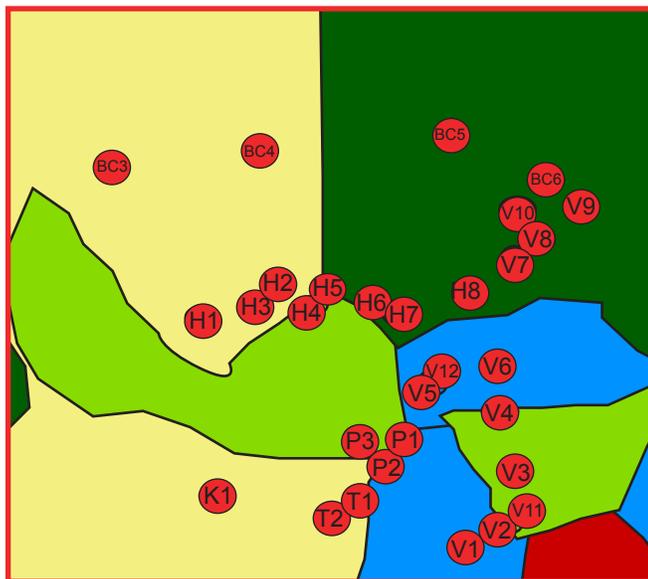
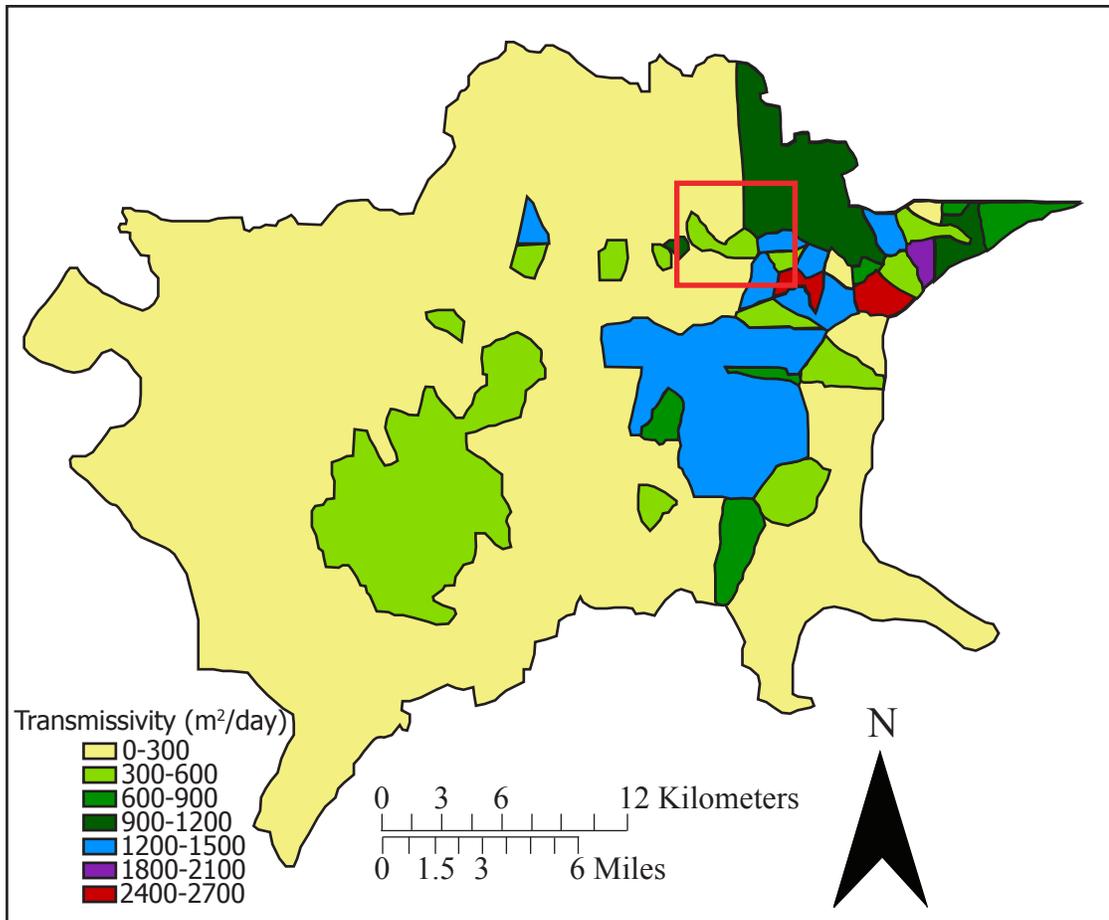


Figure 11. Transmissivity ( $m^2/day$ ) within the model domain (adapted from Almasri and Kaluarachchi, 2004). These transmissivity values were used within the groundwater flow model to calculate groundwater velocity. Red outline shows highlighted area with location of well sites.

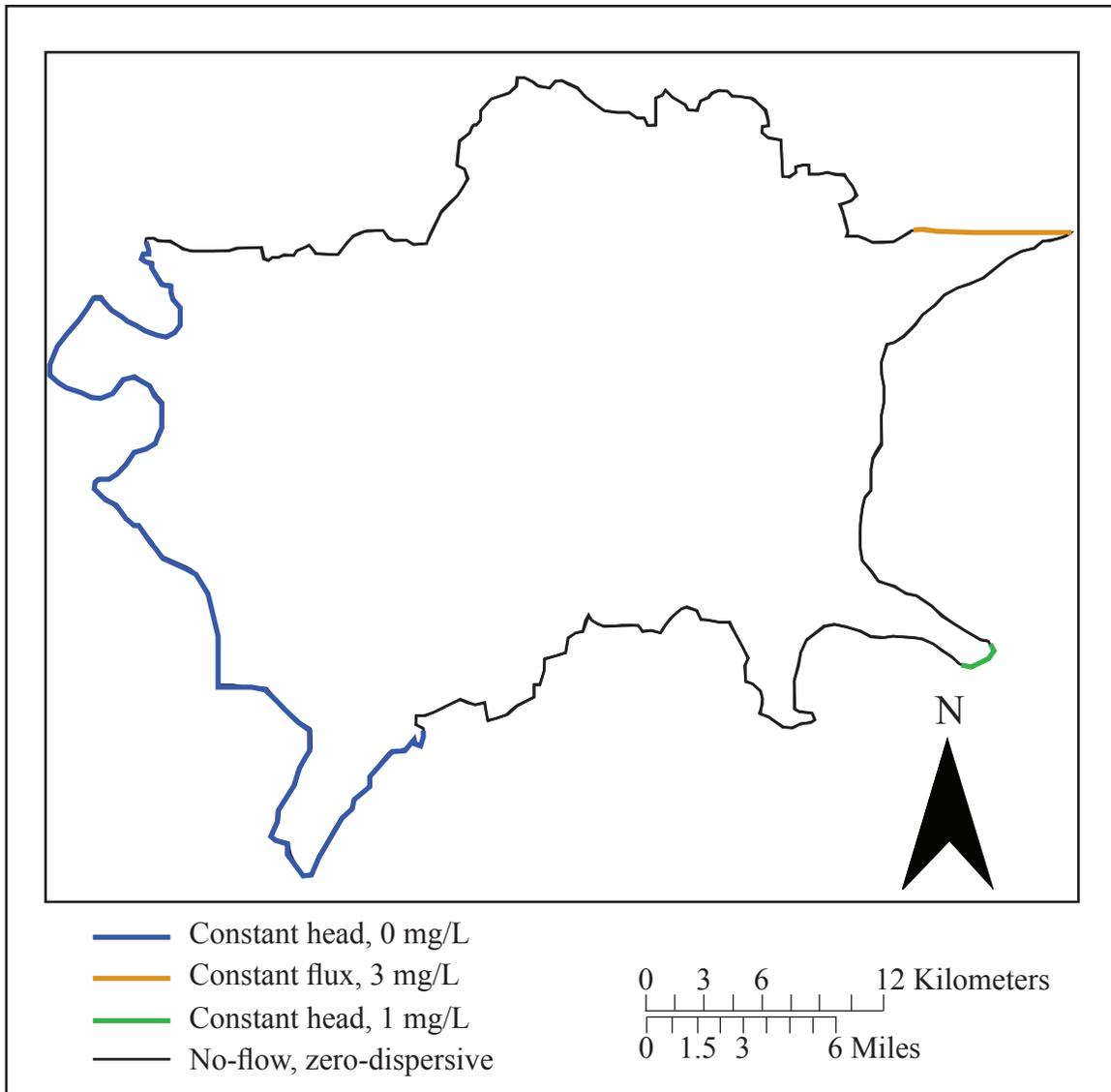


Figure 12. Boundary conditions for fate and transport component of model (adapted from Almasri and Kaluarachchi, 2004). These boundary conditions were used within the fourth sub-model of the A&K model to simulate nitrate transport in groundwater.

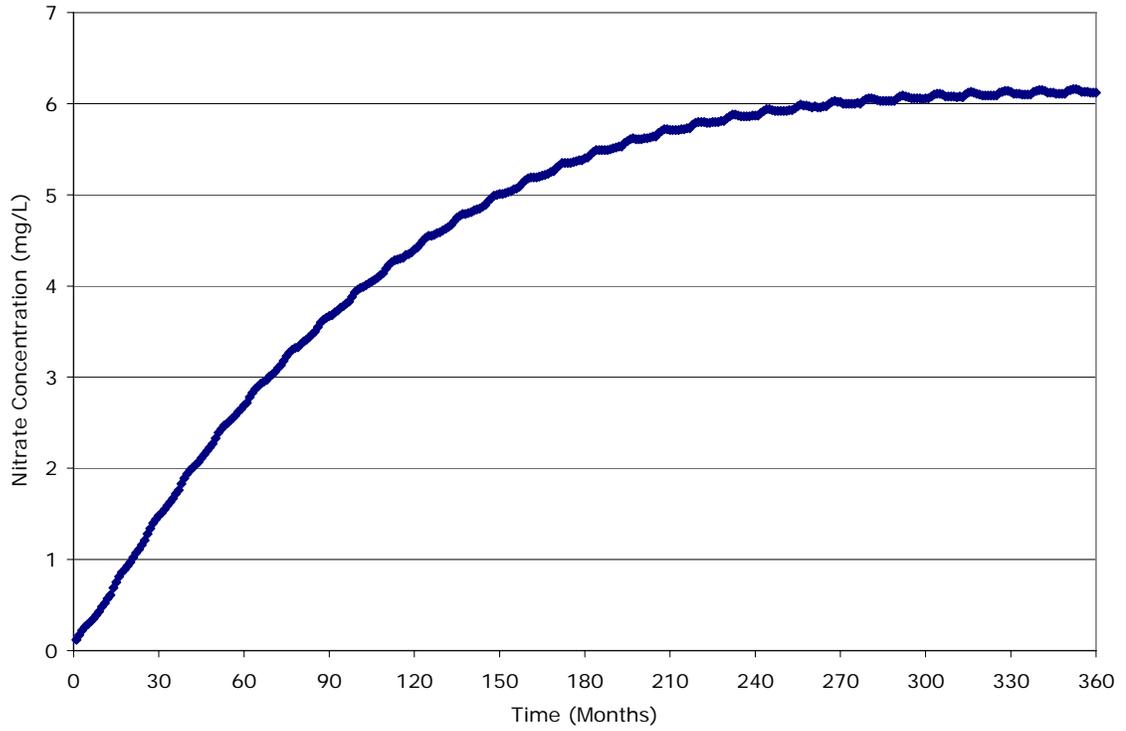


Figure 13. Modeled nitrate concentrations for 360 months at well site H1 from the Basic Land Use scenario. Scenarios were run until nitrate reached a steady-state within the aquifer.

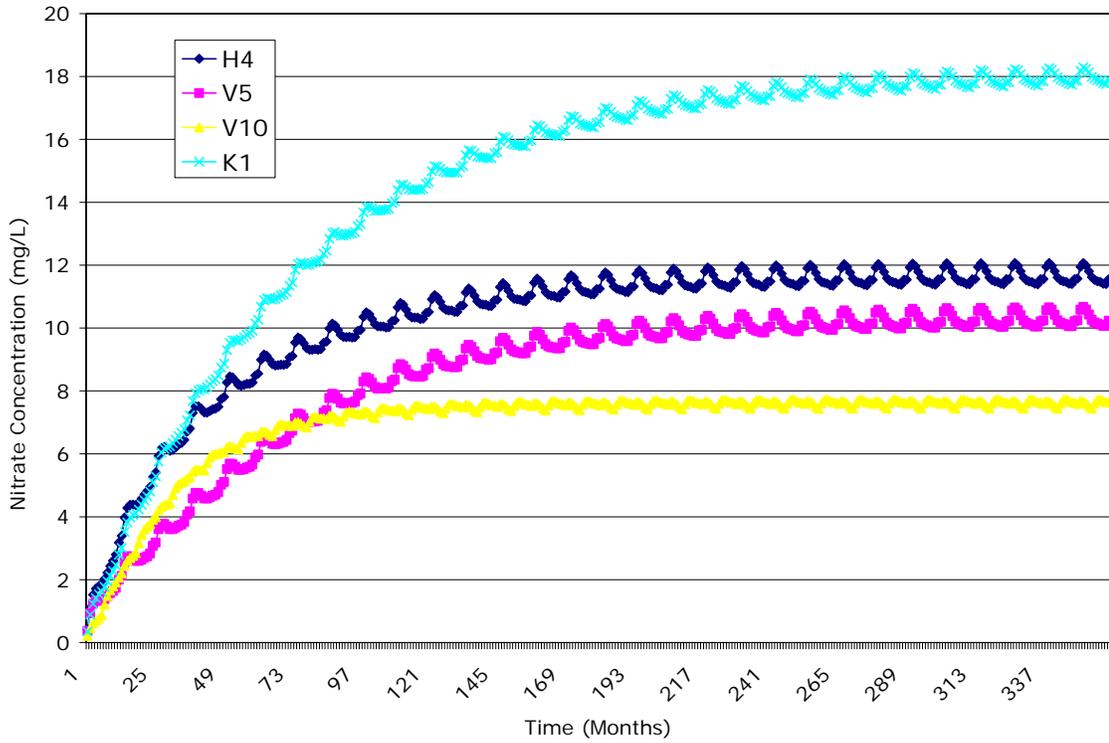


Figure 14. Time series of H4, V5, V10, and K1 for the basic land use scenario. The varying slopes of these time series shows the time needed for each well site to reach steady-state conditions. The time to reach steady-state conditions is a combination of the degree of up-gradient nitrogen loading, transmissivity of the aquifer at the well site, and depth of the well site.

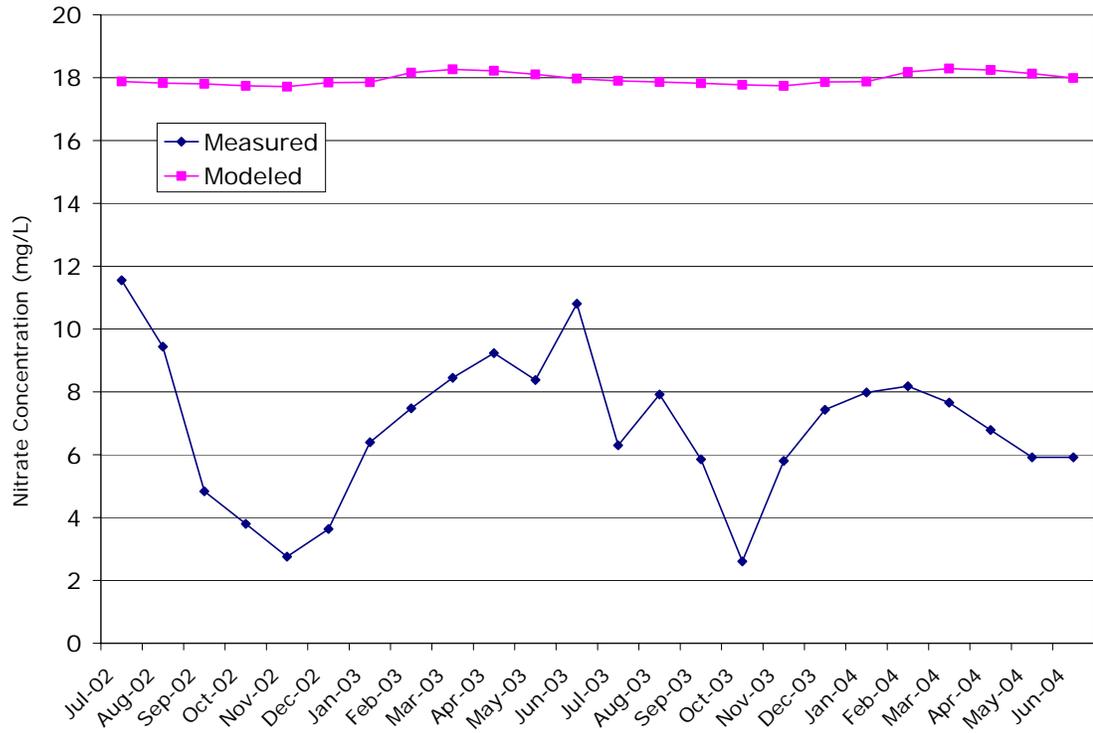


Figure 15. Comparison of time series data at well site K1. The bottom line shows measured nitrate concentrations from the WWU 2002-2004 water quality study, and the top line shows modeled nitrate concentrations for that well site over the same time period.

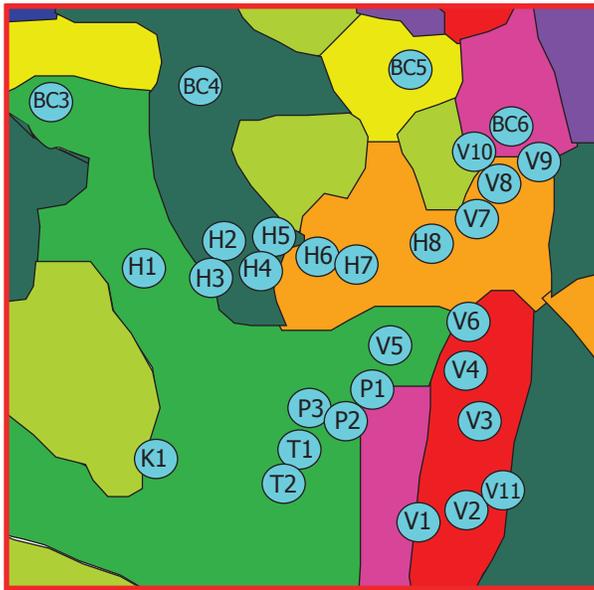
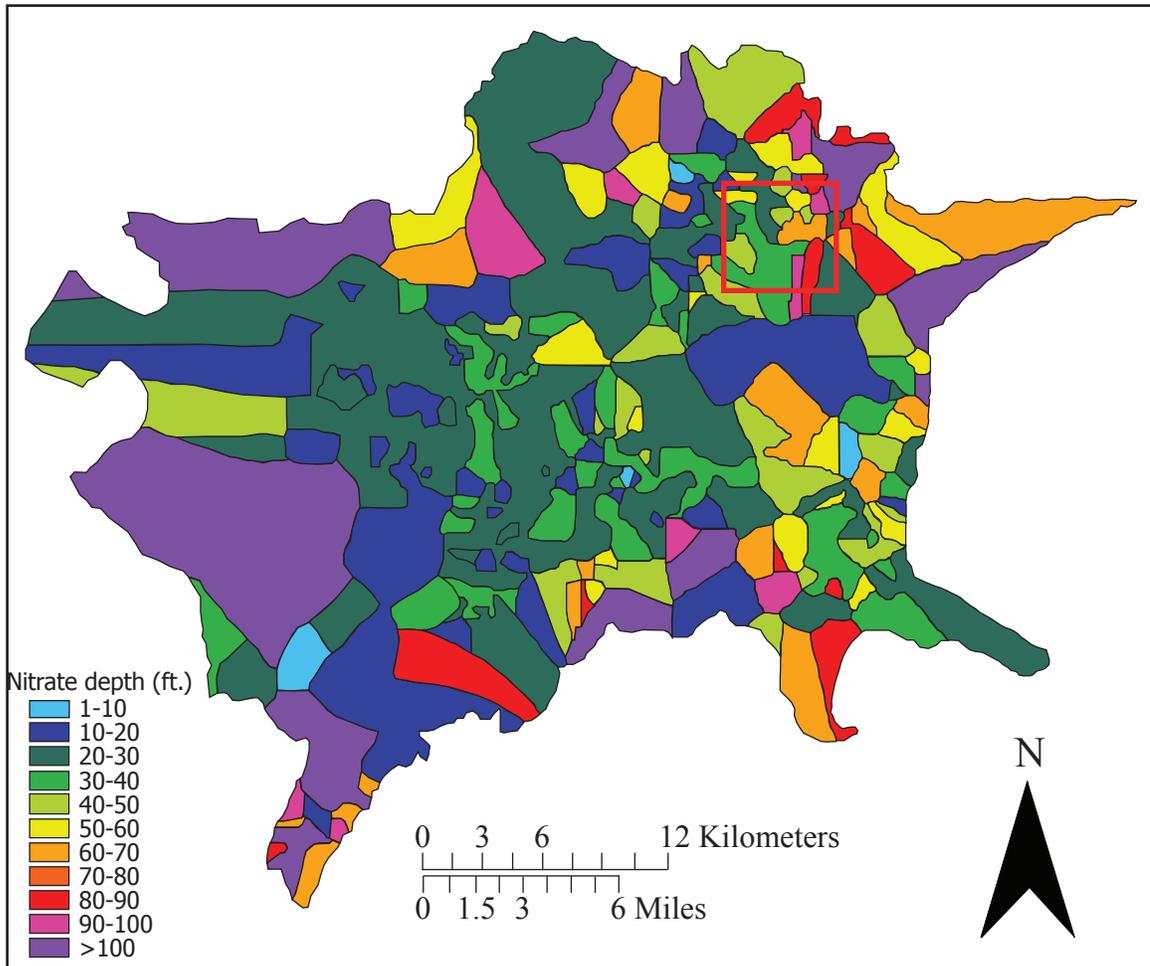


Figure 16. Modeled depth to a nitrate concentration of 1 mg/L (adapted from Almasri and Kaluarachchi, 2004). Red outline shows highlighted area. Highlighted area shows location of well sites.

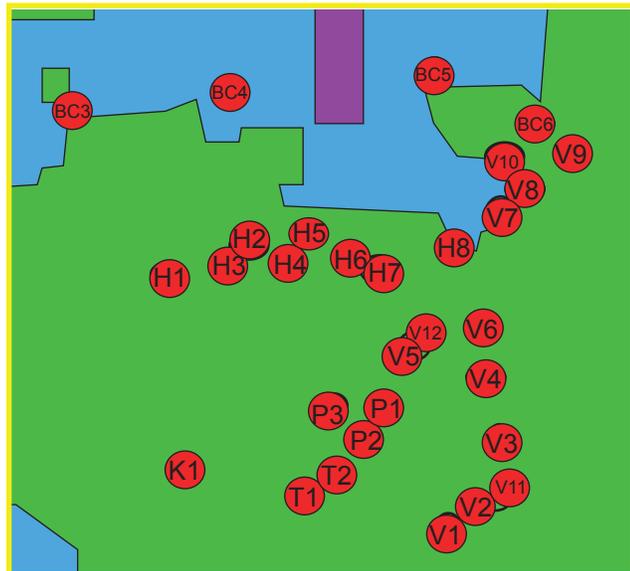
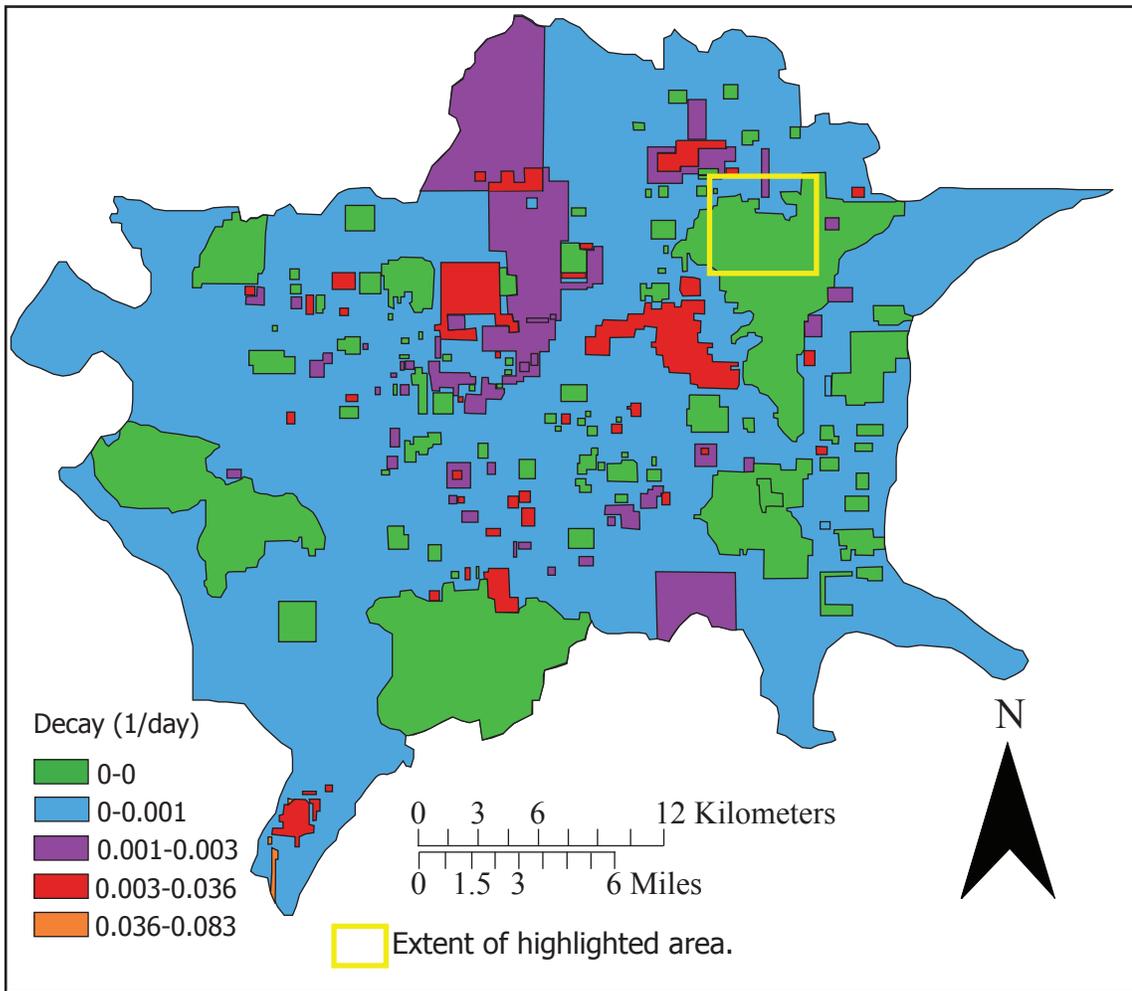


Figure 17. Spatial distribution of calibrated denitrification rates within the model domain (Adapted from Almasri and Kaluarachchi, 2004). Yellow outline shows highlighted area with location of well sites.

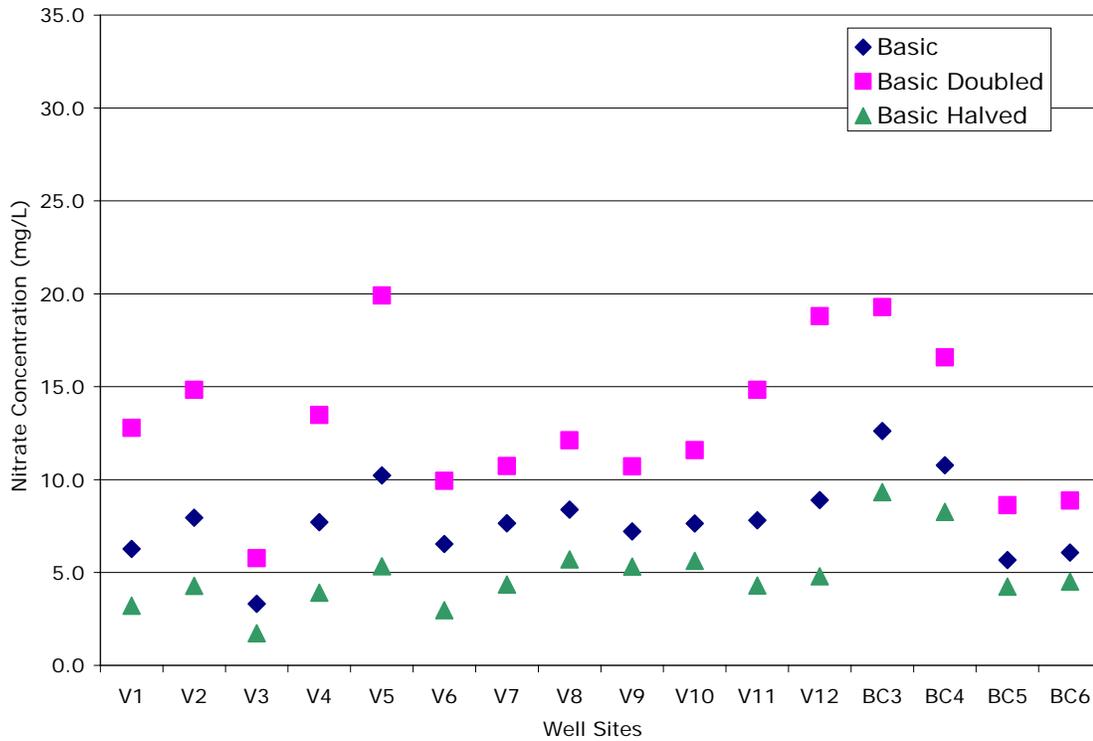
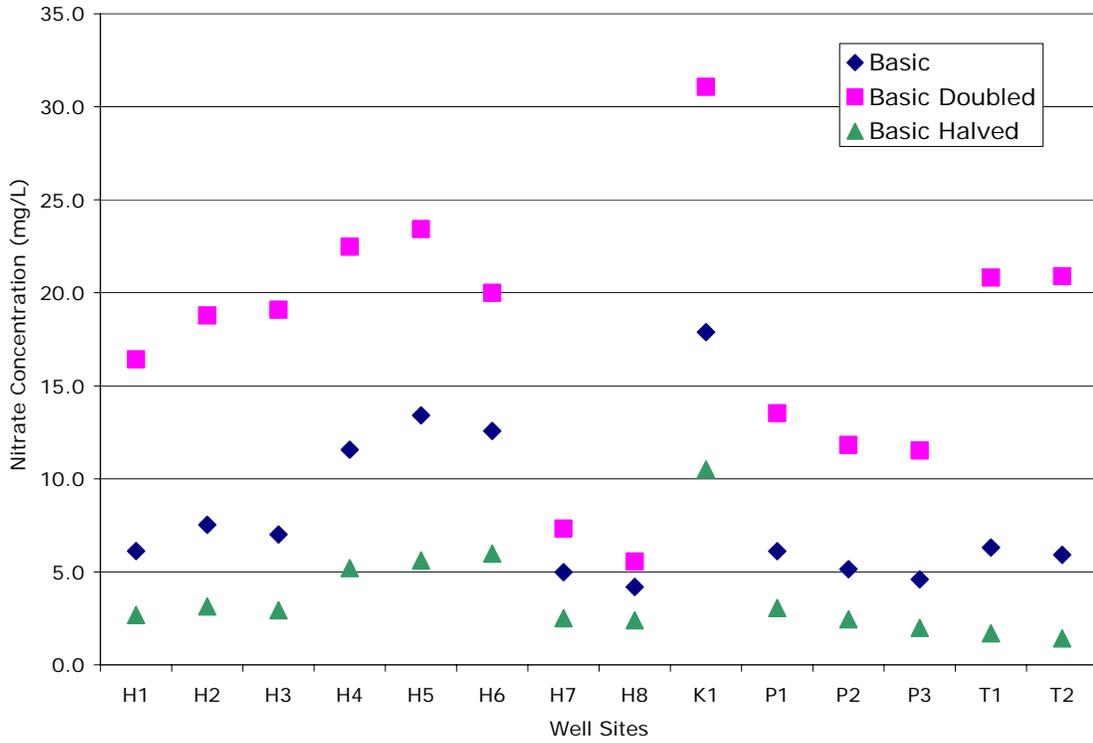


Figure 18. Comparison of median modeled values for the Basic Land Use, Basic Doubled, and Basic Halved scenarios, in which fertilizer loading and manure loading is doubled and halved from original values.

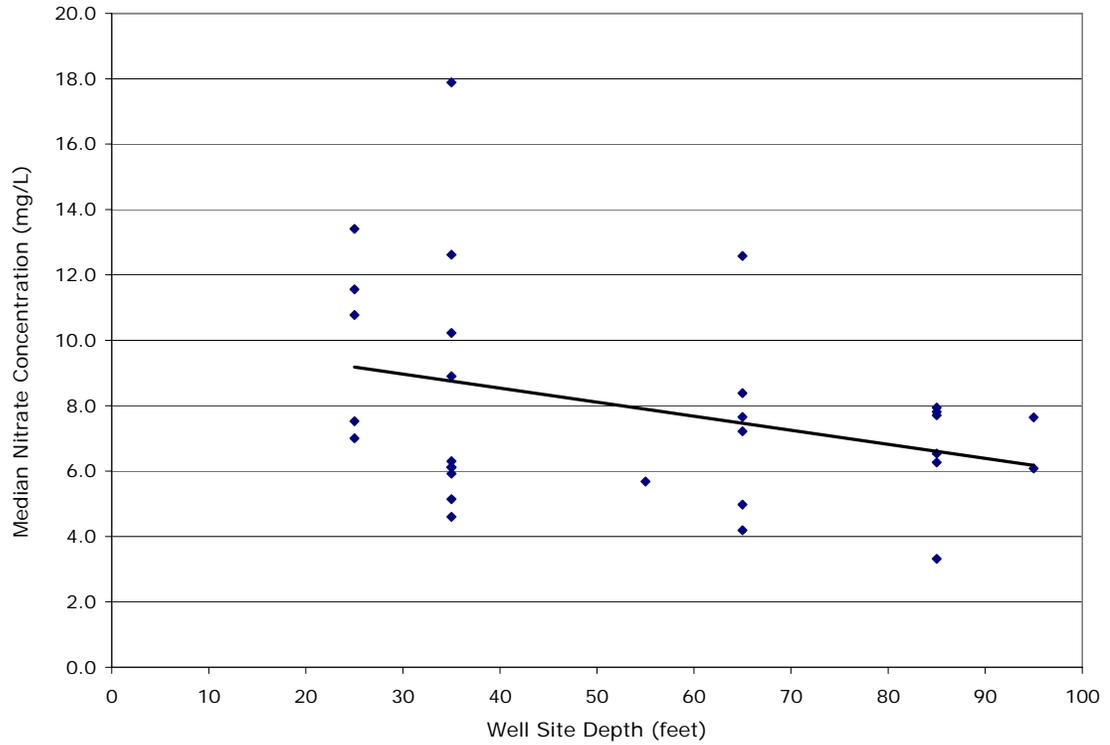


Figure 19. Differences between Basic Doubled and Basic Land Use median nitrate concentrations plotted by well site depth. A negative correlation exists between difference and well site depth, with greater well site depths showing less of a change in median nitrate concentration. The correlation value is  $-0.53$  with a p-value of  $0.000143$ . A p-value of  $<0.05$  is considered significant.

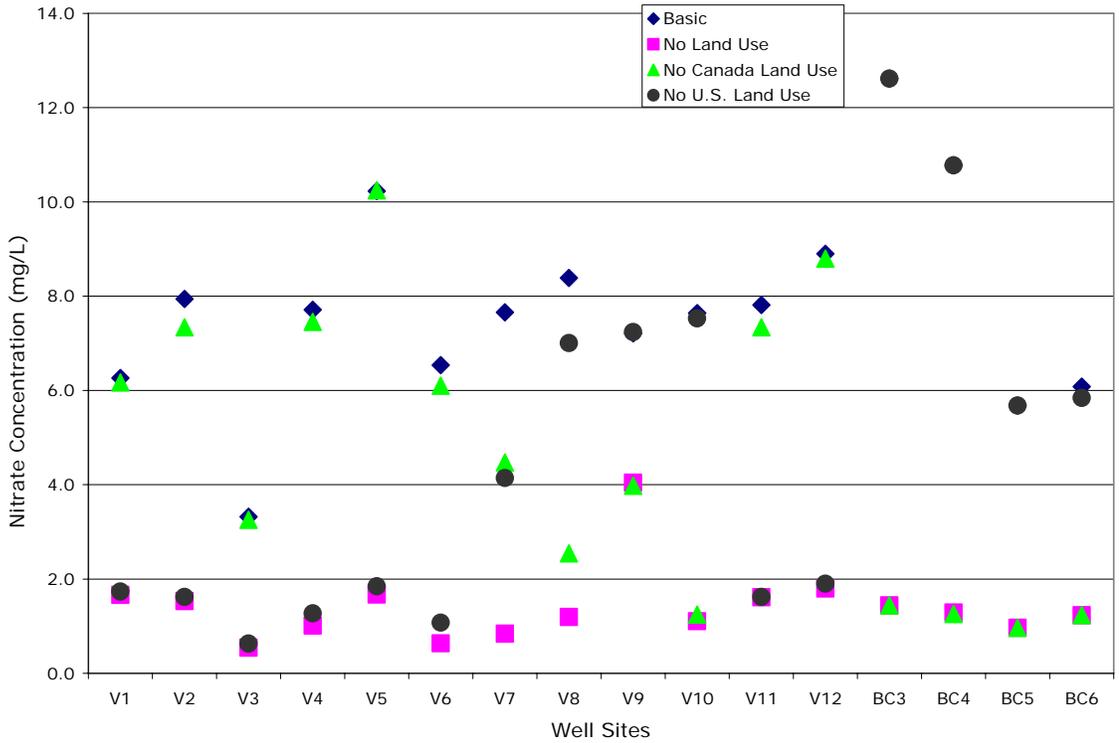
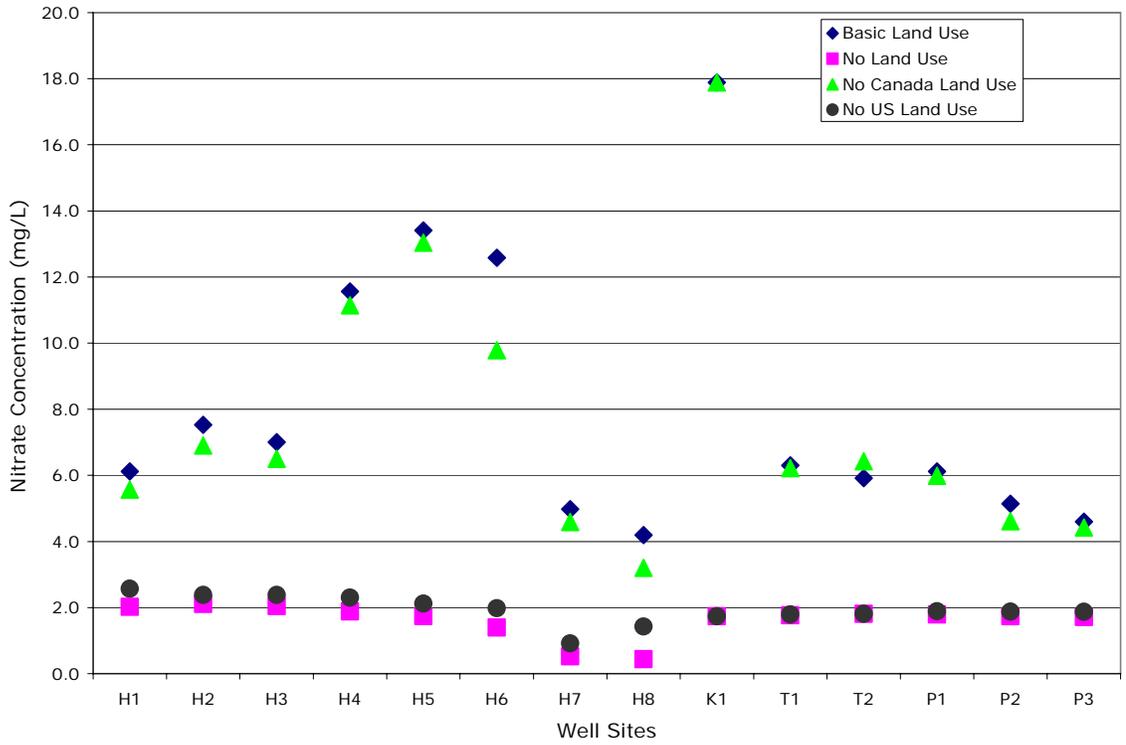


Figure 20. Comparison of median modeled values for Basic Land Use, No Land Use, No Canada Land Use, and No U.S. Land Use scenarios.

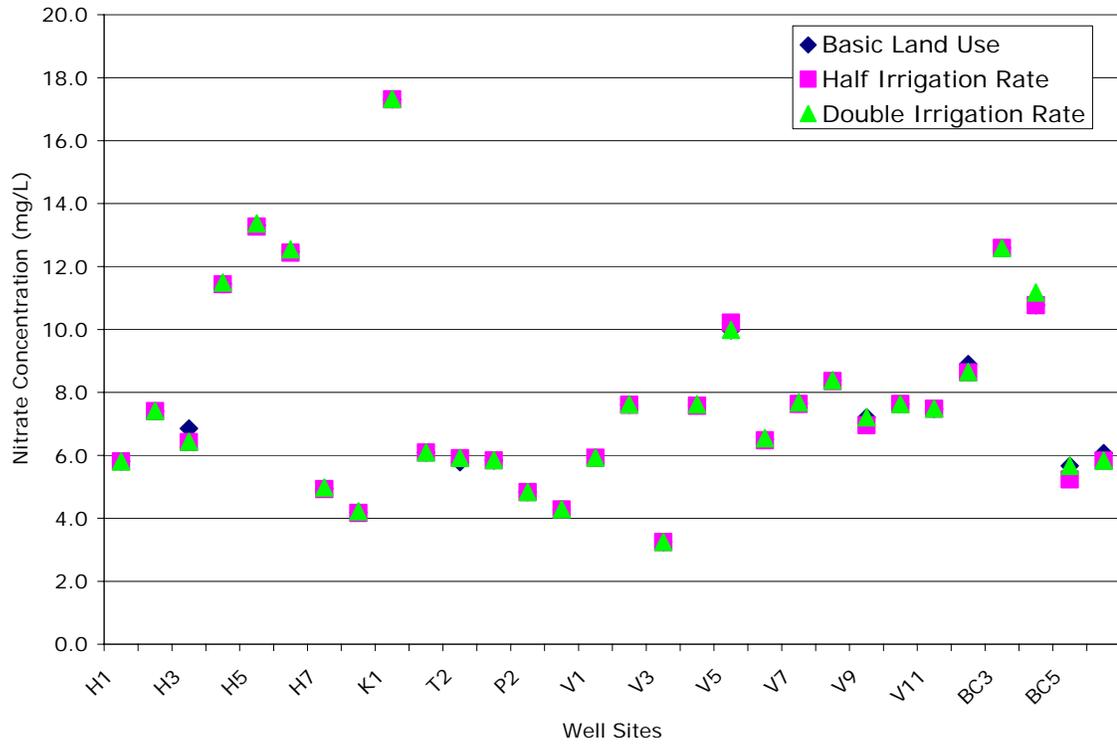


Figure 21. Nitrate concentration in groundwater (mg/L) for each well site in the Basic Land Use, Double Irrigation Rate, and Half Irrigation Rate scenarios.

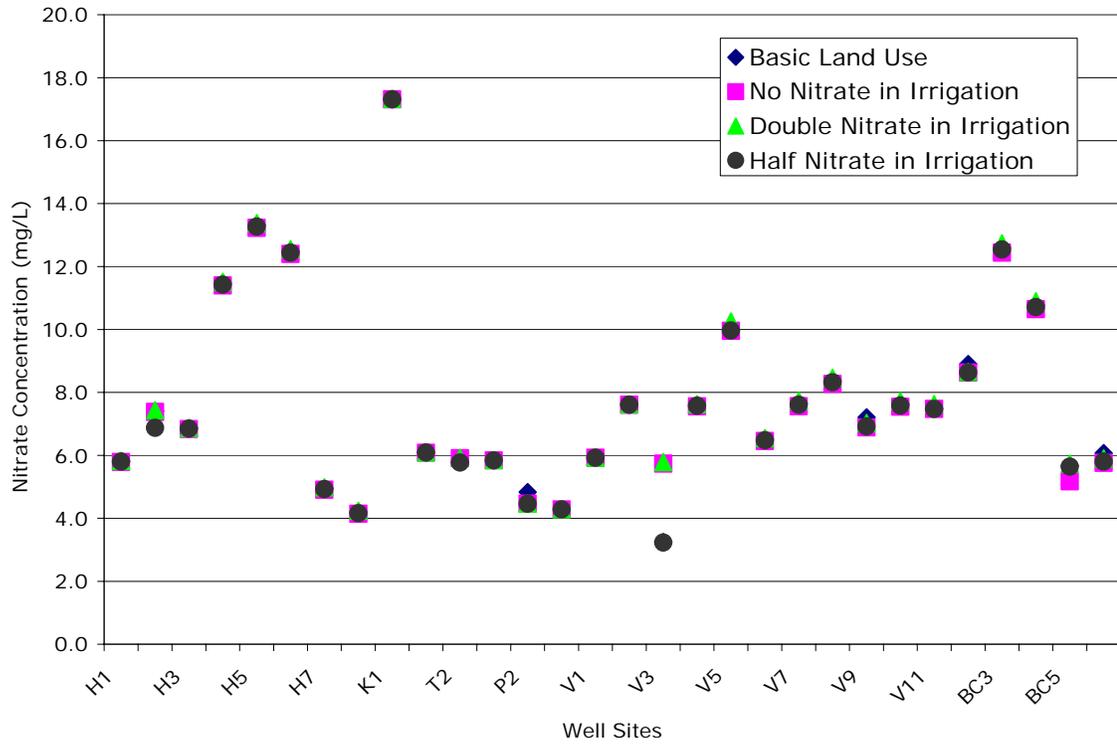


Figure 22. Nitrate concentration in groundwater (mg/L) for each well site in the Basic Land Use, No Irrigation Concentration, Half Irrigation Concentration, and Double Irrigation Concentration scenarios.

## APPENDIX A: Explanation of terms in A&K model

## 1.0 Nitrogen Loading Sub-Model

### *Dairy Manure*

The manure produced by cows in the model domain is used within the dairy farm. There was assumed to be no import or export of manure within the model domain. The total amount of nitrogen from manure was calculated by multiplying the number of milking and dry cows, heifers and calves by their corresponding rates of nitrogen production. This resulting amount was assumed to be deposited within the dairy farm area during the months of the year that the animals would be grazed outside.

$$\Sigma_{\text{type}}(\# \text{ of cows}) \times (\text{lbs of N produced})$$

### *Fertilizer*

Average fertilizer rates and timing of application for crops grown within the model domain were obtained from the Cooperative Extension Service of Washington State University. The fertilizer application rate was multiplied by the acreage of that crop within the drainage.

$$\Sigma(\text{NLCD class area}) \times (\text{fertilizer application rate})$$

### *Septic systems*

Septic systems are treated as point sources of nitrogen within the model domain. Septic systems are estimated to leach into the soil 10 pounds(lbs) of nitrogen per bedroom served within each drainage. The total sum is deposited in equal amounts throughout the year.

$$(\# \text{ of bedrooms}) \times (10 \text{ lbs})$$

### *Dairy farm lagoons*

Diary lagoons are used to store manure throughout winter months when the

potential for runoff from nutrient application is high. Lagoons are treated as point sources that are estimated to leach 1880 lbs of nitrogen each year. In the model domain, lagoons are assumed to be full from November to March and leaching of nitrogen only occurs during those months.

$$(\# \text{ of lagoons}) \times (1880 \text{ lbs N leached})$$

#### *Wet deposition*

Wet deposition occurs with nitrogen dissolved in precipitation. Average dissolved concentrations were assumed for the U.S and Canadian portion of the model domain. An average precipitation rate was assumed monthly for each drainage.

$$(\text{Precipitation rate}) \times (\text{drainage area}) \times (\text{concentration of NO}_3, \text{NH}_4, \text{organic N})$$

#### *Dry deposition*

Dry atmospheric deposition consists of particulate fallout and the adsorption of nitrous gas. The regional average dry deposition in Western Washington is estimated at 1 lb NO<sub>3</sub>/year. For dairy farms, the average dry deposition is 15 lbs NO<sub>3</sub>/year due to the re-adsorption of volatilized nitrogen.

$$(\text{Dairy area} \times 15 \text{ lbs N/acre}) + (\text{drainage area} \times 1 \text{ lbs N/acre})$$

#### *Lawns and gardens*

The total use of fertilizers on personal gardens and lawns per year is estimated to be 135 lbs/acre. This application is assumed to occur in equal amounts from April to September.

$$(\text{Lawn area}) \times (135 \text{ lbs N/acre})$$

#### *Irrigation*

Since groundwater in the drainage is the source for irrigation, an average nitrate

concentration was assumed for the groundwater within each drainage. An average irrigation rate was estimated monthly for each drainage.

$$(\text{Area}) \times (\text{irrigation rate}) \times (\text{concentration of NO}_3, \text{NH}_4 \text{ or organic N})$$

### *Legumes*

Legumes are nitrogen fixers; bacteria in their roots convert N<sub>2</sub> gas in the atmosphere into NO<sub>3</sub>. An acre of legumes is estimated to contribute 5 lbs NO<sub>3</sub> each year.

$$(\text{Acres of legumes}) \times (5 \text{ lbs/acre NO}_3)$$

## **2.0 Soil-Nitrogen Dynamics Sub-model**

### *Fixation*

Nitrogen fixation is the conversion of nitrogen gas to a form of ammonia that organisms can more readily use.

### *Mineralization*

Mineralization is the process by which organic material in the soil undergoes biological decomposition to inorganic material. Nitrogen in the organic material is converted to ammonia and ammonium salts, a process called ammonification. In the model, mineralization was considered for organic nitrogen and crop residues, and soil organic matter.

### Organic nitrogen and crop residues

Shaffer (*et al.*, 1991) developed the following equation for calculating the mineralization of crop residues and organic nitrogen:

$$\text{CRESR} = K_{\text{resr}}(\text{CRES})(T_{\text{fac}})(W_{\text{fac}})(\text{ITIME})$$

Where CRESR is the residue metabolized (lbs), Kresr is the first-order rate coefficient (1/d), Wfac is the soil water stress factor which is a function of the percent water-filled pore space (WFP), CRES is the carbon content of the residue (lbs) and ITIME is the time step being modeled (days).

The net mineralization/immobilization (NRESR in lbs/acre) is determined by the following equation (Shaffer *et al.*, 1991):

$$\text{NRESR} = (\text{CRESR})(1/\text{CN} - 0.042)$$

Where CN is the C/N ratio of the residues. Values used in the model calculation are CN of 18 for manure and 10 for crop residue, Kresr of 0.001 (1/d) for manure and 0.06 (1/d) for crop residues, ITIME of 30 days and WFP of 20 (Kaluarachchi and Almasri, 2004).

### Soil organic matter

Mineralization of soil organic matter (Nmn) is determined by the following relationship:

$$\text{Nmn} = \text{Komr} \times \text{OMR} \times T_{\text{fac}} \times W_{\text{fac}} \times \text{ITIME}$$

Where Nmn is the mineralized NH<sub>4</sub> (lbs/acre), Komr is the rate coefficient of mineralization (1/d), and OMR is the mass of soil organic matter (lbs/acre). The value for Komr was obtained from the NLEAP manual and is 0.000074. Cox and Kahle (1999) estimated the mass of soil organic matter in the Blaine-Sumas aquifer to be 7400 lbs/acre.

### *Immobilization*

The immobilization process is opposite to the process of mineralization. During the process of immobilization, organisms convert ammonium and nitrate into organic forms of nitrogen.

### *Nitrification*

Nitrification is the process in which ammonium ions are first converted to nitrite and then to nitrate (Canter, 1997). The process of nitrification is done by microbes, and happens quickly in warm, moist and well-aerated soils. The rate of nitrification is dependent on several variables, such as NH<sub>4</sub> content, pH, oxygen content, moisture, soil temperature, organic matter, carbon dioxide content, cation exchange capacity, tillage depth, season and soil treatment (Kaluarachchi and Almasri, 2004).

In the model, nitrification is estimated using the following relationship (Shaffer *et al.*, 1991):

$$\text{NO}_3\text{N} = \text{K}_n \times \text{area} \times \text{W}_{\text{fac}} \times \text{T}_{\text{fac}} \times \text{ITIME}$$

Where NO<sub>3</sub>N is the amount of nitrate from nitrification (lbs), and K<sub>n</sub> is the zero-order rate coefficient of nitrification (lb/acre-day). The value of K<sub>n</sub> used was 30 lb/day which is the default value used in the NLEAP model (Almasri and Kaluarachchi, 2004).

The equation above is limited by the amount of NH<sub>4</sub> available for nitrification (NAF). Therefore, NO<sub>3</sub>N must be less than NAF. NAF is determined by:

$$\text{NAF} = \sum \text{NAF}_S - \sum \text{NAF}_L + \text{N}_{\text{mn}} + \text{N}_{\text{RESR}}$$

Where NAF<sub>S</sub> and NAF<sub>L</sub> represent the total of all NH<sub>4</sub> sources and sinks (Almasri and Kaluarachchi, 2004).

### *Denitrification*

Denitrification is a biological process in which bacteria reduce nitrate to nitrogen gas (Cantor, 1997). The N<sub>2</sub> gas will then diffuse into the atmosphere. If denitrification occurs, it can be a major source of loss of nitrate in a system. Anoxic conditions are necessary for denitrification, therefore denitrification is more likely to occur as soils

become more saturated. K&A adapted an equation from Shaffer *et al.* (1991) to use when calculating amount of nitrate lost to denitrification,  $\text{NO}_3\text{T}$  (lb/month):

$$\text{NO}_3\text{T} = \text{Kdet} \times \text{MNO}_3 \times \text{Tfac} \times [\text{Nwet} + \text{Wfac} \times (\text{ITIME} - \text{Nwet})]$$

Where  $\text{Kdet}$  is the rate constant for denitrification,  $\text{MNO}_3$  is the mass of nitrate (lbs),  $\text{Nwet}$  is the number of days with precipitation and irrigation in each month. The authors assumed irrigation to occur every day from June to September, and gathered average days of precipitation from 50 years of data from the Blaine weather station. The above equation was constrained by  $\text{NO}_3\text{T} \leq \text{MNO}_3$  (Shaffer *et al.*, 1991).

### *Plant Uptake*

Plant uptake was assumed to be a fraction of the nitrogen fertilizer applied (Kaluarachchi and Almasri, 2004). The authors assumed that a fraction of 0.75 of the fertilizer applied was taken up by the plants. This value is comparable to estimates made by Cox and Kahle (1999). The uptake by plants occurred during the timing of application.

### **3.0 Groundwater Velocity Sub-model**

The following conceptual equation represents groundwater flow:

$$\frac{\partial}{\partial x} \left( K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial h}{\partial y} \right) = S_s \frac{\partial h}{\partial t} - R$$

Where  $K_x$  and  $K_y$  are components of the hydraulic conductivity in the x- and y-directions,  $h$  is head,  $S_s$  is specific storage,  $t$  is time, and  $R$  defines the volume of inflow into the aquifer per unit volume of aquifer per unit of time. The hydraulic conductivity of the aquifer is a function of the transmissivity and thickness of the aquifer. A distribution of

potentiometric head contour data was available from Erickson (1998) for use within the submodel. Time is the number of time steps (months) entered into the model.

#### 4.0 Fate and Transport Sub-model

The following conceptual equation represents the fate and transport of nitrate in groundwater:

$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + \frac{q_s}{\theta} C_s - \lambda \left( C + \frac{\rho_b}{\theta} C_a \right) + M$$

The terms of this equation are described below.

##### *Retardation*

Since nitrate is a highly mobile species, there is very little sorption of nitrate during its transport in groundwater. Therefore the retardation factor is considered negligible and:

$$R = 1$$

$$C_a = 0$$

##### *Advection*

Advection is used to describe the transport of contaminant by the average pore water velocity. The pore water velocity for the study area is equal to:

$$V = (K/n) * (\Delta h / \Delta L)$$

Where:

K = hydraulic conductivity

n<sub>e</sub> = effective porosity

Δh/ΔL = hydraulic gradient.

##### *Mechanical dispersion and diffusion*

Mechanical dispersion is the process by which variations in groundwater velocity at the pore-level of the aquifer will cause mixing of the contaminant with the surrounding groundwater. The amount of mechanical dispersion ( $D^*$ ) is quantified by:

$$D^* = \alpha \cdot v$$

Where:

$\alpha$  = characteristic length of pores in the aquifer

$v$  = average velocity

The majority of mechanical dispersion is longitudinal, and occurs along the flow path. A fraction of the dispersion is transverse which occurs off of the main flow path and is a result of the tortuous flow path of groundwater through the aquifer. The authors assumed transverse dispersion to be 1/10<sup>th</sup> the amount of longitudinal dispersion.

Diffusion is the spreading of molecules throughout the groundwater from an initial location. The rate of diffusion is driven by the concentration gradient, the number of molecules involved, and the diffusion coefficient of the molecule in liquid ( $D_l$ ). The effective diffusion coefficient ( $D_p$ ) for the system in question is quantified by

$$D_p = D_l \cdot w \cdot \theta$$

Where:

$w$  = tortuosity factor

$\theta$  = effective porosity

Dispersivity and diffusion are considered together in the model because of the similarity in process and units. However, the effects of diffusion are negligible when compared to mechanical dispersion. The hydrodynamic dispersion coefficient tensor ( $D_{ij}$ ) represents the combination of these two terms when determining dispersion

and diffusion for a longitudinal and transverse system.

### *Sink/Source*

This term represents the mass of nitrate that enters and exits the model domain via sources or sinks. The mass of solute gain or lost is determined by:

$$q_s * C_s$$

Where:

$Q_s$  = volumetric flow rate, represents fluid source (+) or loss (-)

$C_s$  = concentration of source/sink fluid

Sources or sinks can be distributed over a certain area or act as point sources or sinks.

An example of an areally distributed source is the mass of nitrate that leaches to the groundwater each month. Examples of point sinks or sources would be rivers, wells or drains.

### *Decay*

The half-life of nitrate is estimated as 1-2.3 years. The rate of half-life decay is represented as:

$$\lambda = 0.693/t_{1/2}$$

Where:

$t_{1/2}$  = half-life of nitrate (years)

This is the base-line value of decay estimated for the model domain. In some places in the aquifer, decay is greater because denitrification is taking place. In order for denitrification to occur, anaerobic conditions with electron donors and suitable bacteria must be present. In their work, the authors found that the values for decay/denitrification had the greatest impact on sensitivity testing. Therefore, when calibrating the model, the

authors used a trial-and-error method to determine in what parts of the aquifer the denitrification constant needed to change in order to accurately determine groundwater nitrate concentrations. Decay values were then changed accordingly throughout the model domain.