Summer 2004

Denitrification Along Pangborn Creek in the Abbotsford-Sumas Aquifer, Washington

Leslie B. (Leslie Braverman) McKee
Western Washington University

Follow this and additional works at: https://cedar.wwu.edu/wwuet

 Part of the Geology Commons

DENITRIFICATION ALONG PANGBORN CREEK
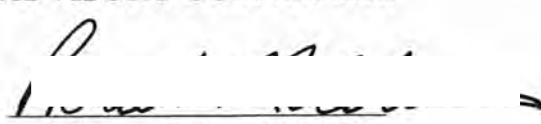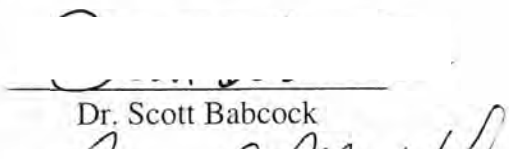IN THE ABBOTSFORD-SUMAS AQUIFER, WASHINGTON

by

Leslie B. McKee
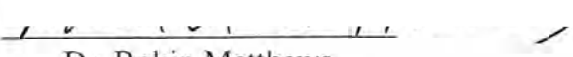
Accepted in Partial Completion

of the Requirements for the Degree

Master of Science

Moheb A. Ghali, Dean of the Graduate School

ADVISORY COMMITTEE

Chair, Dr. Robert Mitchell

Dr. Scott Babcock

Dr. Robin Matthews

MASTER'S THESIS

In presenting this thesis project in partial fulfillment of the requirements
for a master's degree at Western Washington University, I agree that the
Library shall make its copies freely available for inspection. I further
agree that copying this thesis project in whole or part is allowable only for
scholarly purposes. It is understood, however, that any copying or publication
of this thesis project for commercial purposes, or for financial gain, shall not
be allowed without my written permission.

Signature ~~~~~~~~~~~~~~~~

Date July 9, 2004

MASTER'S THESIS

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Western Washington University, I grant to Western Washington University the non-exclusive royalty-free right to archive, reproduce, distribute, and display the thesis in any and all forms, including electronic format, via any digital library mechanisms maintained by WWU.

I represent and warrant this is my original work and does not infringe or violate any rights of others. I warrant that I have obtained written permissions from the owner of any third party copyrighted material included in these files.

I acknowledge that I retain ownership rights to the copyright of this work, including but not limited to the right to use all or part of this work in future works, such as articles or books.

Library users are granted permission for individual, research and non-commercial reproduction of this work for educational purposes only. Any further digital posting of this document requires specific permission from the author.

Any copying or publication of this thesis for commercial purposes, or for financial gain, is not allowed without my written permission.

Name: _Leslie McKee_

Signature: _____

Date: _5/12/2018_

AN INVESTIGATION OF DENITRIFICATION EVENTS
ALONG PANGBORN CREEK IN THE
ABBOTSFORD-SUMAS AQUIFER, WASHINGTON

———————

A Thesis
Presented to
The Faculty of
Western Washington University

———————

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

———————

by
Leslie B. McKee
July 2004

Abstract

The Abbotsford-Sumas aquifer is a shallow, unconfined aquifer located in the agricultural regions of southwestern British Columbia and northwestern Washington and has a history of nitrate contamination. I monitored nitrate distributions in a study area bisected by a wide-scale peat deposit within a portion of the Whatcom County component of the aquifer to assess the current nitrate distribution, evaluate ground and surface water interactions in the peat, and determine the affect of peat on denitrification.

The water quality dataset and statistical analyses showed that nitrate contamination was heavily concentrated upgradient of the peatlands. In general, shallow wells (<10 m below the median water table) north of the peatlands had higher nitrate concentrations than deeper wells (>10 m below the median water table). Some upgradient wells showed low nitrate concentrations and data suggest they received denitrified ground water from unmapped peat deposits. Nitrogen isotope data ($\delta^{15}N$ on nitrate) indicated that nitrate sources included manure and inorganic commercial fertilizers. The contamination south of the peatlands was significantly lower than the contamination to the north and the median nitrate levels within the peatlands were near the detection limit. Nitrogen gas measurements and a combination of nitrogen ($\delta^{15}N$ on nitrate) and oxygen ($\delta^{18}O$ on water) isotopes confirmed that denitrification occurred in the peatlands and in much of the ground water south of the peatlands. In addition, the gas measurements suggested that iron, manganese, sulfate, and methane occurred throughout the peatlands and may have contributed to redox reductions.

The implication of these findings is that a natural means for nitrate reduction exists in this region. Hydrostratigraphic data suggest that peat deposits occur throughout Whatcom County at various unmapped depths. Identifying these peat deposits and quantifying the upgradient ground water nitrate contributions may help facilitate nutrient management in the region.

Acknowledgments

It is said that where there is no effort, there is no benefit.

Table of Contents

List of Tables, Figures, and Appendices

Tables

Figures

Appendices

1. Introduction

The Abbotsford-Sumas Aquifer is an unconfined aquifer located in southwestern British Columbia (B.C.), Canada and northwestern Washington (Figure 1). This transboundary aquifer lies within the Fraser Lowland and is comprised of glacial sands and gravels deposited during the Pleistocene epoch. The aquifer covers approximately 200 square km and serves as a water supply for approximately 110,000 people in the United States and Canada (Abbotsford/Sumas Aquifer 1996 Status Report). The aquifer is one of the most important in the region because of its productivity and heavy use (Carmichael et al., 1995). The combination of extensive agricultural activity, thin soil cover, high aquifer permeability, and high water table has caused water quality degradation in the region over at least the past 40 years (Mitchell et al., 2003). The most ubiquitous water contamination is in the form of excessive nitrate levels.

Nitrate is thought to be the most prevalent ground water contaminant in the world (Tesoriero et. al., 2000). Nitrate is a byproduct of fertilizer application, septic effluent, and natural processes. When found in excess, nitrate can negatively impact humans, livestock, and the environment (Starr and Gillham, 1993). Nitrates easily leach through the soil and into the water table, where they may reappear in wells, lakes, streams, and creeks (Stasney, 2000). Moreover, elevated nitrate concentrations may signal the presence of other agricultural pollutants (Liebscher et al., 1992). High levels of nitrate in drinking water have been linked to cancer, respiratory illness, and the blood disease methemglobinemia (Follett and Walker, 1989, Owens, 1994, Boeser, 2000). As such, the United States Environmental Protection Agency (EPA) and the Canadian Drinking Water Guidelines (CDWG) have set drinking water standards as 10 milligrams per liter nitrate as nitrogen (mg-N/L; State of Washington, 1992).

Numerous studies in distinct locations throughout the aquifer have documented nitrate concentrations consistently above 10 mg-N/L for both Whatcom County (Garland and Erickson, 1994, Cox and Kahle, 1999, Mitchell et al., 2003) and B.C. (Liebscher et al. 1992, Gartner-Lee, 1993). These findings support the need for continued ground water and surface water quality monitoring in order to assess nitrate magnitudes and to facilitate nutrient management in the region.

One such study was conducted by a team of graduate students and professors from Western Washington University (WWU; e.g., Stasney, 2000, Gelinas, 2000, Nanus, 2000, Mitchell et al., 2003). From April 1997 through February 1999, they quantified ground and surface water nitrate magnitudes and flow paths in the study area (1997-1999 studies). The studies analyzed hydrogeologic data, $\delta^{15}N$ signatures, water quality data, and statistics and concluded that a two-layered stratification of nitrate contamination existed in the study area. The shallow layer consisted of nitrate values greater than 20 mg-N/L and was considered a result of local agricultural practices. The deeper layer consisted of nitrate values greater than 10 mg-N/L and was considered a result of Canadian agricultural practices. Additionally, samples from many wells suggested denitrification signaled by a combination of low nitrate magnitudes, anoxic conditions, and the presence of metals.

The findings were consistent with reports of deep aquifer contamination in B.C. (Zebarth et al., 1998, Hii et al., 1999), despite the fact that the extent of vertical and horizontal mixing of ground water constituents in the study area was unknown (Mitchell et al., 2003). Authors of the 1997-1999 studies suggested monitoring water quality, confirming the occurrence of denitrification, and determining the extent of surface and ground water interactions in this study area. Based on these suggestions, my objective is to investigate how denitrification influences nitrate distributions in the study area.

Denitrification is a microbially- mediated process where nitrate is transformed into nitrogen gas. Once nitrate has leached into the saturated zone, denitrification is the only process that can serve as a permanent nitrogen sink (Korom, 1992, Wassenaar, 1995). Denitrification has been documented in regions of the Abbotsford-Sumas aquifer (e.g., Paul and Zebarth, 1997, Cox and Kahle, 1999, Gelinas, 2000, Tesoriero et al., 2000). Gelinas (2000) examined statistical data and suggested denitrification was responsible for the nitrate loss between two wells separated by peat deposits in the study area. Regionally, Cox and Kahle (1999) found that denitrifying bacteria reduced ground water nitrates in the aquifer near the Abbotsford Airport in B.C. Tesoriero et al. (2000) studied the Canadian portion of the aquifer and found denitrification occurring at various depths in a riparian zone along a creek. Paul and Zebarth (1997) investigated an agricultural region in B.C. outside of the

2

aquifer and found evidence of denitrification when a source of organic carbon such as manure was available.

Although there have been many nitrate-centered studies in the aquifer, the influence of peat on denitrification in the aquifer has not been fully explored. The majority of the peat in the study area is located along Pangborn Creek, which is additionally surrounded by a riparian zone, or vegetated buffer zone. Previous studies have shown that both riparian zones and low conductivity soils, such as peat are critical landscapes that can regulate the nitrate load of waters discharging into streams (e.g., Mengis et al., 1999 and Devito et al., 2000). However, due to hydrologic and biogeochemical complexities, the effect of peat and the role of riparian zones on nitrate removal are unclear.

A strong likelihood exists for denitrification in peat along Pangborn Creek in the study area. The peat is saturated, has high levels of nitrate created by a mixture of discharging ground water and agriculturally-impacted surface water runoff, is full of dissolved organic carbon provided by peatlands and vegetation in the riparian zone (Mitsch and Gosselink, 1993 and Bridgham et al., 2001), and finally, has documented anaerobic conditions, which provide a necessary environment for reduction potential (Gelinas, 2000). A simplified scenario depicting nitrate-laden ground water flowing from the north into the peaty riparian area of Pangborn Creek is portrayed in Figure 2. The combination of factors found along Pangborn Creek should provide a favorable setting for denitrification and possibly other types of nitrate loss.

2. Background

The following sections describe the biochemical aspects of nitrate and the qualities of the aquifer that are of fundamental importance to this study. The *nitrogen cycle* governs the formation and destruction of nitrate in the unsaturated and saturated zones. The *geology* of the region controls the structure of the subsurface, including the formation and distribution of peat in the aquifer. The *hydrostratigraphy* of the study area controls the direction of ground water flow and nitrate transport. The *climate, soils, and recharge* of the study area dictate the rates of precipitation, temperature, infiltration, recharge, and stream discharge. The *hydrology* describes the surface water of the study area. Finally, the *agriculture and nutrient loading* in the study area dictate the land use practices and, hence, control both surface and ground water nitrate sources.

2.1 The Nitrogen Cycle

The processes that produce nitrate are governed by the nitrogen cycle. The nitrogen cycle includes chemical, biological, and hydrological processes causing nitrogen to take different forms, one of which is nitrate (Figure 3). The processes can involve fixation, mineralization, synthesis, ammonification, volatilization, and nitrification (Canter, 1997), as well as two nitrate reduction processes, denitrification and dissimilatory nitrate reduction to ammonium (Korom, 1992).

The following nitrogen cycle processes are summarized from Canter (1997) and Kendall (1998). *Fixation* occurs when di-nitrogen gas (N_2) is converted into organic nitrogen. There are two types of fixation: atmospheric and biological. Atmospheric fixation results from industrial processes (i.e., combustion or fertilizer application) and biological fixation results from microbial processes. *Mineralization* is a biochemical process where bacteria alter organic nitrogen into ammonium (NH_4^+) during the decomposition of plants, animals, and fecal matter. *Synthesis* is a biochemical process, where plants take up either ammonium or nitrate (NO_3^-) to form proteins or other nitrogen containing compounds. This process does not involve permanent nitrogen loss because these compounds are re-released into the subsurface. *Nitrification* is a biological process by which ammonium ions become oxidized. Nitrification occurs in two steps: first, ammonium and oxygen combine to form

4

nitrite (NO_2^+) and oxygen, and second, nitrite and oxygen combine to form nitrate. Nitrite is an intermediate stage that is not often found in most environments. *Denitrification* is the biological and chemical reduction of nitrate into di-nitrogen gas and occurs in anaerobic environments. Denitrification is the only naturally occurring process that can reduce nitrate compounds (Wassenaar, 1995). *Dissimilatory nitrate reduction to ammonium* occurs in anaerobic environments when nitrate is temporarily converted to ammonium.

2.2 Geologic Setting

The study area is a 6.4 square kilometer region in the Fraser Lowland in northwest Whatcom County, Washington (Figure 4). The topography in the study area was predominantly formed during the retreat of the Cordilleran Ice Sheet during the Sumas Stade of the Fraser Glaciation (ca. 11,600 to 10,000 years B.P.; Kovanen and Easterbrook, 2002).

Kovanen and Easterbrook (2002) documented four phases (SI-SIV) of the Sumas Stade in the study area. Phase SIII (ca. 10,980-10,250 ^{14}C years B.P.) deposited the Sumas Outwash, the gravelly water-bearing portion of the aquifer. It includes recessional and advance glaciofluvial and glaciolacustrine deposits (Kovanen, 2002). The ice continued to retreat and in doing so, buried a block of ice approximately 1 km in diameter beneath glacial till. Phase SIV is marked by glacial readvance into the study area (ca. <10,250-10,000 ^{14}C years B.P.) and more deposits of sand and gravel. It is believed that concurrently, the block of ice melted forming kettles in what are now Pangborn and Judson Lakes. Conditions were then appropriate for peat formation (ca. 10,245 ±90 and 10,265 ±65 ^{14}C years B.P.; Kovanen and Easterbrook, 2002). It is believed that peat was deposited in various other locales and depths throughout the region and has not been mapped entirely (D. Easterbrook, personal communication, 2003).

The geology of the study area, along with the ground and surface water sampling sites, are illustrated in Figure 5. The figure shows surficial peat deposits extending from Pangborn Lake east to site V4. However, fieldwork and reports from landowners have indicated that east of site PB3 to site V4 the peat plunges to an undetermined depth. Surficial peat deposits are also shown to occur at site K1, however fieldwork and examination of well logs have suggested that the peat exists below the ground to unknown depths. The age and extent of

5

peat deposits in the region are important to this study because ground water flow and nitrate concentrations are altered by the presence of peat at depth and may explain previous observations of low nitrate in the study area (e.g., Gelinas, 2000, Mitchell et al., 2003).

Other geologic deposits occurred following the retreat of the Cordilleran ice sheet. The Fraser River coarse and fine-grained alluvium was deposited during the Holocene epoch (Cox and Kahle, 1999 and Kovanen, 2002). And currently, the surficial peat deposits near Pangborn Lake continue to be replenished by decaying organic material.

2.3 Hydrostratigraphy

Stasney (2000) examined the hydrostratigraphy of the study area from data collected during April 1997 to August 1998. He determined that within the study area, the aquifer ranges in thickness from 55 meters in the northeast corner to about 24 meters in the southeast corner. The aquifer in the study area is composed of heterogeneous mixture of Sumas Outwash gravel and sand, Sumas Outwash sand lenses, and scattered silt, clay, and peat deposits (Figure 5).

Stasney estimated the hydraulic characteristics of the aquifer in the study area. Using both field data and modeling techniques, he developed water table contour maps (Figure 6). Ground water moves perpendicular to flow lines and in a southerly direction. Using sediment-size analyses and empirical correlations, Stansey estimated the average hydraulic conductivity to be 283 meters per day, which falls within the range of values determined by Cox and Kahle (1999) of 2.1-2,377.4 meters per day. Stasney (2000) estimated an average hydraulic gradient of 0.0075 and an average horizontal flow velocity of 6.0 meters per day. These values differ some from those presented by Cox and Kahle (1999), which were 0.0028 and 0.8 meters per day, respectively. Cox and Kahle's (1999) values are for an area much greater than the study area, from the Nooksack River to the Sumas River, which may explain the discrepancies. Stasney (2000) estimated a residence time of 4 to 5 years for a distance of 10 km. The residence time based on Cox and Kahle's (1999) values is 34-35 years for the same distance.

The peat layers of the aquifer have drastically different hydrogeologic properties than the aquifer matrix. The peat covers about 430 acres and has an unknown thickness. The deepest

6

cores were collected at 7.3 meters but the peat is known to extend deeper (Figure 7; Rigg, 1958). The peatland is termed a quaking bog, one that progressively fills its basin from the margins inward (Mitsch and Gosselink, 1993), which explains the presence of a small amount of water in Pangborn Lake. The cross section reveals that the deepest part of the peat is composed of sedimentary peat, a peat formed in aquatic environments that contain aquatic plants, chitenous and siliceous aquatic animal remains, and their feces. The west and east parts of the peatland are composed of fibrous peats, which contain terrestrial sedges, other similar plants, and woody peat (Rigg, 1958).

Peat accumulates when primary productivity from vascular plants, algae, mosses, and lichen, exceed decomposition of organic matter (Mitsch and Gosselink, 1993 and Bridgham et al., 2001). Rigg (1958) measured accumulation rates in 151 Washington state soils and found the average accumulation rate is 16 years per centimeter of peat in both sedimentary and fibrous peats.

Peatlands have an inherent ability to change the hydrology of a region based on their hydraulic conductivity (Bridgham et al., 2001). The hydraulic conductivity of peat varies greatly depending on heterogeneities within its structure and the degree of decomposition and compaction. The accepted general values are 1.3 meters per day for poorly decomposed peat and <0.010 meters per day for mostly decomposed and well-compressed peat (Mitsch and Gosselink, 1993). A recent study has shown that hydraulic conductivity in peat can vary with depth (Beckwith et al., 2003), so it is likely that the upper, more loosely packed peat deposits have higher hydraulic conductivities than more buried deposits.

The southerly ground water flow pattern causes water to discharge through peatlands. Although the residence time was not measured in the peat, it can be surmised that it would be longer than that of the aquifer matrix as a result of the lower hydraulic conductivity found in peatlands. The long residence time coupled with the high organic content of the peat and the nitrate-laden ground water discharging into it provide a likely locale for progressive reduction of nitrate.

2.4 Climate, Soils, and Recharge

2.4.1 Climate

The climate of the study area is influenced by a combination of maritime air cells from the Pacific Ocean, which bring moisture-laden air into the region, and the mountainous air cells from the Cascade Mountains, which cause the moisture to condense into precipitation. With the exception of the Fraser River outflow, the Cascade Mountains keep out cold interior air during the winter causing mild, rainy winters and warm, dry summers. The mean annual air temperature for the region is 9.4°C (Cox and Kahle, 1999) and the thirty-year average precipitation value is approximately 81 cm (National Climatic Data Center, Clearbrook, WA).

Precipitation can significantly influence the input and movement of ground water nitrate into peatlands, hence monthly precipitation data were obtained from the Clearbrook Station and compared to the thirty-year average precipitation values for the region (Figure 8). The precipitation values document a sharply defined dry (<6.0 cm) and wet season (>6.0 cm) during the study. The dry season (July 2002-October 2002, June 2003) and most wet season (November 2002 to May 2003) values were significantly lower than the thirty-year average, with the exception of November, January, and March (Figure 8). Despite the low precipitation values in February 2003, this month was included with wet season data for convenience during data analysis.

2.4.2 Soils

Six major soil types are significant to this project based on where they lie in relation to sampling sites and land use practices (Figure 9, Table 1). For the purposes of this study, peat, muck, and histosols will be collectively referred to as peat or peatlands. The Kickerville Silt Loams are the most widespread soils in the study area and are primarily used as berry fields and pasture land. The Pangborn Peat is the next most widespread soil and is used primarily for berry fields. The Cagey Loamy Sand and the Hale Silt Loam make up a small portion of the study area and are used for dairy and berry production. The Briscot Silt Loam and Laxton Loam make up the remainder of major soils and include residential, berry,

8

and pasture use. Refer to the Soil Survey of Whatcom County (1992) for more information on these soils.

2.4.3 Recharge

Recharge is the amount of precipitation that infiltrates into the saturated zone less the amount of evapotranspiration and runoff. Factors controlling recharge include soil permeability, evapotranspiration, and precipitation rates. The Kickerville Silt Loam has a moderate permeability ranging from 1.52 to 5.08 centimeters per hour, while the Pangborn Peat has a moderate to slow permeability of 1.52 to 0.152 centimeters per hour. From climate data at the Clearbrook and Abbotsford stations, Cox and Kahle (1999) estimated the ground water recharge rates to be 66-76 centimeters per year, or approximately 60% of the average annual precipitation for the region. Furthermore, they determined that evapotranspiration was greater than precipitation from May to September and precipitation was greater than evapotranspiration from October to April. Irrigation occurs in the study area and data is provided by the Whatcom County Conservation District.

2.5 Surface Water

There are several bodies of water in the study area; among the most important are Pangborn Lake and its distributary, Pangborn Creek. Pangborn Creek flows eastward to the confluence with Johnson Creek, which flows northeast from its headwaters south of the study area near the town of Everson, to the confluence with the Sumas River (Figure 10). In 1954, the westernmost 0.64 kilometers of Pangborn Creek were channelized to connect the existing creek to Pangborn Lake, draining it and thereby increasing farm acreage (Rigg, 1958 and Overdorff, 1982). To provide better drainage for fields, drainage ditches were engineered west of the lake and north of the lake (Figure 11). Drainage ditches may increase nitrate and ammonium transport to Pangborn Lake and influence concentrations in Pangborn Creek. Currently, Pangborn and Johnson creeks drain through some of the most concentrated dairy land in Washington State (Wills, 1998).

Pangborn Creek is of primary importance to this study for a number of reasons. First, it is a discharge zone where upgradient ground water nitrate flows into peat layers and may be

undergoing denitrification processes. Second, it is a locale where ground and surface water interactions can be investigated. Third, a riparian zone envelops the creek and may attenuate or reduce nitrates from discharging ground water and agricultural surface water runoff.

Pangborn Creek bisects the study area and is a principal tributary to Johnson Creek. The average stream discharge of Pangborn Creek was most recently measured in 1996 and was determined to be about 12 cubic feet per second, but is greater in the winter and lower in the summer (Wills, 1998). Both natural and engineered riparian zones occur along Pangborn Creek. Studies have shown that the type of vegetation in a riparian zone may affect its ability to attenuate or reduce non-point source pollution (see Section 2.8). The natural zone contains established trees, shrubs, grasses, and sedges. Examples include Douglas Fir, Western Hemlock, Cascara, Red Alder, blackberries, and Reed Canary grass (Rigg, 1958 and Overdorff, 1982). The engineered zone contains Reed Canary grass and young remediation project trees such as Red Alder, Douglas Fir, Red Cedar, and Big Leaf Maple. The engineered buffer typically ranges in size from fifty to eighty feet and is monitored by the Conservation Reserve Program, a division of the Whatcom County Conservation District.

Johnson Creek is the main stream within the Johnson Creek Watershed. The average annual stream discharge is about 50 cubic feet per second; discharge is usually highest in mid winter and lowest in late summer resulting from variation in seasonal precipitation (Wills, 1998). The same type of vegetation found along the Pangborn Creek riparian area also dominates the middle part of the Johnson Creek buffer. Both creeks have been cited for excessive nitrate concentrations from anthropogenic sources (e.g., Overdorff, 1981 and 1982, Wills, 1998, Nanus, 2000).

2.6 Land Use and Nutrient Loading

The primary agricultural activities in both Whatcom County and B.C. affecting the aquifer include stockpiling and spreading animal manure, applying fertilizer, and spraying pesticides (Cox and Kahle, 1999, Mitchell et al., 2003). Most of the land use in the study area involves dairy production, pasturelands, raspberry, and blueberry fields, and corn crops. Lesser amounts of acreage are used for hazelnuts and other fruit trees, hydrangeas, rhubarb, and black currants. Non-agricultural uses include forests, a cemetery, and residential acreage

(including residential livestock). Land use data was provided by the Whatcom Conservation District in form of orthophotos taken during 2003. Due to the impact of dairy and berry farms determined by previous studies, land use was subdivided based on these farming practices (Figure 11). Dairy production includes dairy cow farms, grasses (pasture), and corn crops and uses manure for fertilizer. Berry indicates raspberry and blueberry production and primarily uses inorganic commercial fertilizers and may use manure during pre-planting. A guide to the fertilizer application time periods for each of the 4 crops and associated irrigation information is provided in Table 2a and 2b. In the study area, the manure application is cow manure and in B.C the source is poultry manure.

Land use in B.C. is primarily berry farming, poultry production, row crops, and pasture (Liebscher et al., 1992 and Wassenaar, 1995). Sumas City Planning provided Land use data, but poultry information was not available. According to the Whatcom County Conservation District, poultry manure has ten times the nitrogen of dairy manure (J. Gillies, personal communication, 2002). Hence the contribution of nitrate from B.C. poultry farms and fertilizer mixes applied to raspberry crops may affect ground water in the study area greatly.

In response to contamination issues cited in previous studies (e.g., Wills, 1998 and Mitchell et al., 2003) Washington State signed into law the Dairy Nutrient Management Act in 1998. The law required all dairy farmers to develop dairy nutrient management plans by July 2002 and implement the approved plans by December 2003. Monitoring water quality in the study area before, during, and after the implementation of the Dairy Nutrient Management Plan will help assess the law's effectiveness toward improving water quality.

2.7 Denitrification Processes

Denitrification in the saturated zone requires several environmental conditions, including a source of nitrate, denitrifying bacteria, suitable electron acceptors and donors, and anaerobic conditions (e.g., Korom, 1992, Starr and Gillham, 1993, Hill et al., 2000). The presence of nitrate has been established (e.g., Mitchell et al., 2003) and so this discussion will focus on the other three requirements.

Denitrifying bacteria are widespread and are assumed to occur in saturated soils; however, not all bacteria denitrify (Kendall, 1998). Most bacteria in the saturated zone are

heterotrophic facultative anaerobes, meaning that they can survive with or without oxygen (Korom, 1992 and Kendall, 1998). These bacteria obtain energy by oxidizing organic (carbon from organic matter) or inorganic (manganese (II), iron (II), or sulfides) compounds. These compounds are called electron donors and two classes can be designated based on the bacteria that oxidize them. When the electron donor is organic matter, the denitrifying bacteria are organotrophic, and when the electron donor is inorganic matter, the bacteria are lithotrophic. Both groups are a type of chemotroph, meaning that cellular energy is derived from chemical reactions rather than the sun (Korom, 1992). The reactions by which microbial respiration and cellular growth occur are called redox (reduction-oxidation) reactions. Compounds that change their valence state by gaining an electron are reduction reactions, and those that lose an electron are oxidation reactions. To complete the reaction, electron acceptors are necessary (Korom, 1992 and Fetter, 1999). A list of microbial respiratory processes, associated electron acceptors and donors, byproducts, and redox reactions is provided in Table 3 (Champ, 1979, Chapelle, 1995, and Vance, 2003).

Organic matter is composed of dissolved organic carbon and is found in agricultural areas as fertilizer and in inherently organic rich soils like peat (Starr and Gillham, 1993). Many studies have shown that dissolved organic carbon is a strong regulator in denitrification processes; in general, the greater the level of carbon, the larger the microbial population it can sustain by providing more electron donors for respiratory processes (e.g., Trudell et al., 1986, Hiscock et al., 1991, Starr and Gillham, 1993, Paul and Zebarth, 1997, Hill et al., 2000).

The electron acceptor that will create the most energy for the chemotroph by oxidizing carbon will be preferentially chosen, as listed in Table 3. Therefore, aerobic chemotrophs will use oxygen until it is limited. Once oxygen is removed from the system, it can be slowly replaced by diffusion from the unsaturated zone or via diffusion and advection from other oxidized regions in the aquifer. The oxygen depleted saturated zone allows facultative anaerobes to use other electron acceptors. Anaerobes switch to nitrate until it becomes limited (Korom, 1992). Denitrification is the result of an anaerobic process in which organotrophs use nitrate as an electron acceptor to oxidize dissolved organic carbon. Nitrate is reduced to one or both ionic nitrogen oxides (NO_3^- and NO_2^-) to gaseous oxides (NO and

12

N_2O), and further to di-nitrogen gas (N_2; Canter, 1997). According to Hiscock $et\ al.$ (1991), the overall process occurs as follows:

$$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
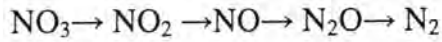
Once nitrate becomes limited, manganese (IV), iron (III), and sulfate are reduced in order of abundance. These elements are particularly important because when nitrate is introduced to regions where a plethora of any of these elements exists, nitrate becomes unstable- even in the absence of dissolved organic carbon (Korom, 1992). If the appropriate lithotrophic bacteria are present, progressive reduction of nitrate occurs using manganese and iron as electron donors; when iron is the electron donor, the process is referred to as iron corrosion and zero valent iron (Fe^0) is responsible. A suggested reaction for nitrate loss by iron corrosion in anaerobic conditions is:

(1)

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

The resultant iron serves as an electron donor for abiotic nitrate reduction. When iron and manganese compounds are exhausted, methanogenesis will occur where the organic compound carbon dioxide (CO_2) is reduced into methane (CH_4).

A second nitrate transformation process occurs under the same conditions as denitrification. The process is called dissimilatory nitrate reduction to ammonium and involves the conversion of nitrate to ammonium. Rather than serving as a permanent loss as in denitrification, dissimilatory nitrate reduction to ammonium only temporarily immobilizes nitrate. Dissimilatory nitrate reduction to ammonium is particularly important to consider because it may occur in the peat in tandem with denitrification (Korom, 1992).

Dissimilatory nitrate reduction to ammonium has been studied on a limited basis and is not completely understood. In a field study along a riparian zone, Ostrom $et\ al.$ (2002) found that dissimilatory nitrate reduction to ammonium is favored when nitrate is limited (approximately <3.0 mg-N/L) and abundant dissolved organic carbon or another electron donor exists. They determined that denitrification is favored when the electron donor (i.e., dissolved organic carbon) is limited. Tobias $et\ al.$ (2001) measured rates of dissimilatory nitrate reduction to ammonium and denitrification in a fringe marsh and found dissimilatory nitrate reduction to ammonium is favored where the nitrate load is small, whereas

13

denitrification is favored where large inputs of nitrate occur. In their study, only 30% of the nitrate reduction was due to dissimilatory nitrate reduction to ammonium, and 70% was due to denitrification. Hill (1996a) agrees that dissimilatory nitrate reduction to ammonium is uncommon in riparian zones and peaty marshes because ground water flows are variable due to seasonal fluctuations and because sediments become more oxidized due to ground water table fluctuations. These studies suggest that dissimilatory nitrate reduction to ammonium will not be a major pathway for nitrate in the Pangborn peatlands; nevertheless it is important to consider.

2.8 Denitrification Environments

2.8.1 Riparian Zones

Riparian zones are vegetated buffer zones between terrestrial and aquatic areas where discharging ground water encounters surface water. The riparian zone central to this study lies along Pangborn Creek. Many studies have shown that riparian zones mediate the effects of non-point source pollution by intercepting nutrients such as nitrogen and phosphorous (e.g., Hill 1996a, Correll et al., 1997, Tesoriero et al., 2000, Clement et al., 2003). These studies were conducted where nitrate was removed from the shallow subsurface by denitrification. Fewer studies have been conducted where nitrate is introduced deeper than vegetation in the riparian zone (e.g., Clement et al., 2003). The effectiveness of riparian zones in reducing nutrients is dependent on the width and type of vegetation, soil type (organic content and hydraulic conductivity), type of flowpath supplying nitrate, depth, and redox reactions (Vought et al., 1994 and Correll, 1996). Since the latter has been explored, my discussion will focus on the former four factors.

2.8.1.1 Vegetation

Leverett (2003) investigated how two types of vegetation, Red Alder and Reed Canary grass, both of which occur in the study area, affect nitrogen fluxes into a stream along a riparian zone. She found that total nitrogen fluxes to the stream were greater in Red Alder forests than in Reed Canary grasslands. Correll et al. (1997) also investigated a forested area versus a grass floodplain. Their results agreed that nitrate levels were lower in the grassland.

14

Despite these results, Leverett (2003) concluded that depth below the water table was a greater factor on nitrate than vegetation type (see below).

2.8.1.2 Soil Type

Hill *et al.* (2000) investigated subsurface denitrification in a forest riparian zone in southern Ontario. They used 3 sites, one composed of peat, one of sand, and one with a mixture of the two. They found that denitrification occurred when ground water nitrate was introduced into peat and peat + sand locales. The result was based on the presence of organic matter inherent in peat, which provided a substantial quantity of electron donors for denitrification to occur.

2.8.1.3 Flow Paths

Clement *et al.* (2003) investigated riparian flow paths along a fourth order stream to identify the processes of nitrate removal. They showed that nitrate loss was temporal and was caused by variable flow paths due to seasonality. During the high water of fall and winter, runoff (overland flow) was dominant and both denitrification and dissimilatory nitrate reduction to ammonium occurred. During the low water of summer, deep ground water flow was dominant, but was too deep for denitrification; hence, nitrate decreases were due to dilution. Other studies agree that denitrification rates vary according to depth below the water table (see below).

2.8.1.4 Depth Below the Water Table

Cey *et al.* (1998) monitored a small, agricultural watershed in Ontario for several geochemical parameters. They concluded that denitrification in the shallow organic-rich sediments of riparian zones was responsible for decreased levels of nitrate.

Tesoriero *et al.* (2000) conducted a study along the riparian zone enveloping Fishtrap Creek, a creek bisecting the B.C. portion of the aquifer. They determined that although denitrification was not widespread throughout the aquifer (in agreement with Wassenaar, 1995), it was occurring in riparian discharge zones along Fishtrap Creek. Denitrification caused decreased levels of nitrate in the shallow sediments of the riparian zone. Tesoriero *et al.* (2000) used N_2 gas measurements to quantify denitrification rates. They found the fastest

denitrification rates at the ground water discharge zone, slower rates in shallow ground water, and even slower rates in deep ground water. This finding is in agreement with Leverett's (2003) conclusion that denitrification magnitudes were greater in the shallow subsurface (20 cm) than in deeper subsoils (80 cm).

2.8.2 Streams

Nanus (2000) discovered that nitrate concentrations in Pangborn Creek were lowest in the vicinity of Pangborn Lake and steadily increased as distance from the lake increased. She determined that runoff was responsible for much of the nitrate in the creek. Her results suggested that the combination of extensive peatlands and the riparian area were responsible for removing the nitrate introduced to the creek.

Specific methods of stream nitrate removal were reviewed by Hill (1996b). He surmised that nitrate loss occurs via uptake by aquatic macrophytes and benthic algae, adsorption to sediment load, and denitrification. In a mass balance study, less than 10% of the nutrient load was removed by streams via biological processes, and 20-80% of the load was attenuated by sediments. Hill (1996b) concluded that denitrification is greatest in anaerobic zones during the spring and summer because microbes are dependent on temperatures ranging from 2-23°C, with 23°C supporting the greatest activity. Temperatures outside of this range cause a cessation in microbial respiration.

2.8.3 Peaty Soils

Peat is a soft and highly organic soil. It is further distinguished by having a substantial amount of decomposition, where plant remains are still recognizable (Bridgham et al., 2001). The general composition of peat is partially decomposed aquatic and terrestrial plant and microscopic animals (Rigg, 1958, Mitsch and Gosselink, 1993, Bridgham et al., 2001). The main elemental content of organics is carbon (~50%), with oxygen, nitrogen, and hydrogen making up the remainder (Yamaguchi, 1990). The peat in the study area contains deposits of iron-manganese nodules, and thus the elemental content also includes iron and manganese (R.S. Babcock, personal communication, 2004).

Peatlands store large amounts of carbon, compared to other soils (Bridgham et al., 2001). The carbon in peat is primarily *in situ* carbon and possibly labile carbon from allochtonous deposition and root decay (Sloan, 1999). In general, peat soils are highly saturated, very acidic, and nutrient poor. Because of nutrient limitations, denitrification is often concentrated in regions that are rich in nitrate (e.g., Cirmo and McDonnell, 1997, Hill et al., 2000, Starr and Gillham, 1993, and Trudell et al., 1986). For example, Cirmo and McDonnell (1997) found that introducing nitrate to peat soils can stimulate its own removal by "priming" the populations of microbial denitrifiers. In nitrate-depleted peat soils denitrification levels are low; however, with sufficient influx of nitrate the "priming" effect will occur, and denitrification levels will increase (Cirmo and McDonnell, 1997).

Research suggests that unlike most soils, microbial processes in peatlands are not limited by dissolved organic carbon because of its inherent water-saturated and organic- rich nature. Davidson and Stahl (2000) investigated the extent to which organic carbon affects nitrate removal in five different soil types. One of these soils was a peat much like that found in the study area. The peat soil removed five times more nitrate than the sandy loam (73.59% versus 13%, respectively) and exhibited the highest denitrification rates of all five soils. They found no indication of carbon limitations on denitrification.

In addition to carbon, iron and manganese can also be used as electron donors during nitrate reduction. These metals are easier to oxidize than carbon and because of their observed presence in the peatlands in the study area, may also cause nitrate loss (R.S. Babcock, personal communication, 2004).

2.9 Research Objectives

The purpose of my project is to determine how peat affects nitrate distributions in the study area. Most of the peat lies along Pangborn Creek and is part of a shallow riparian zone. The peat is saturated, rich in organic matter, and has high levels of ground water nitrate discharging into it. The site should have favorable conditions for nitrate loss. My four main questions are:

1) What is the general distribution of nitrate in the study area and what are the sources?

17

Task 1: measure and analyze nitrate, ammonium, total nitrogen, and nitrogen isotopes in domestic drinking water wells.

2) What are the nitrate magnitudes discharging into the Pangborn peat?

Task 2: measure and analyze the same chemical indicators detailed above as well as vertical gradients using piezometers.

3) How do peat, riparian zone dynamics, and ground and surface water interactions impact nitrate concentrations?

Task 3: measure and analyze nitrate, ammonium, pH, total phosphorous, chloride, iron, manganese, nitrogen isotopes, and fecal coliform from piezometers and Pangborn Creek.

4) What are the processes of nitrate removal in the peat?

Task 4: measure and analyze nitrate, ammonium, dissolved oxygen, iron, manganese, nitrogen and oxygen isotopes, and di-nitrogen gas from wells, piezometers, and Pangborn Creek.

3. Methods

The study area is located west of the city of Sumas and east of the city of Lynden. It was chosen because it is downgradient from the study area monitored by Environment Canada, which will make available information about B.C. nitrate distributions. It was also chosen because previous studies characterized aquifer properties, ground water flow directions, and nitrate distributions (e.g., Stasney, 2000, Gelinas, 2000, Nanus, 2000, Mitchell et al., 2003). The following Townships, Sections, and Ranges delineate the study area (Figure 4):

T41N, Sec. 36, R3E; T41N, Sec. 31 and 32, R4E;

T40N, Sec. 1 and 12, R3E; and T40N, Sec. 5, 6, 7, and 8, R4E.

In order to quantify the general distribution of nitrate in the study area and the possible magnitudes discharging into the Pangborn peat, 25 ground water wells located upgradient and down gradient of the peat were monitored over a twelve-month period from July 2002 to June 2003 (Figure 12). The water quality parameters and a description of why they were measured is discussed in Appendix A. The wells included shallow (<10 m) and deep wells (>10 m) and were designated based on median depth below the water table. The well identification letters were abbreviated based on the road names nearest the site, where H is for Halverstick Road, P is for Pangborn Road, V is for Van Buren Road, T is for Trap Line Road, and K is for Kraght Road. The shallow wells included: H1, H2, H5, H6, H8, K1, P3, T1, V1, V4, V5, V6, and V11. The deep wells included: H3, H4, H7, P1, P2, T2, V2, V3, V7, V8, V9, and V10. Three wells were an exception to the shallow and deep well designations, despite the depth below the water table. Wells V9 and V10 are considered deep because topography creates large vadose zones. Well H7, a deep well, was considered shallow because data indicate it is likely breached.

To quantify the extent of surface water nitrate, five sites in Pangborn Creek (PB1-PB5) and five sites in Johnson Creek (JN1- JN5) were monitored bimonthly from July 2002 to June 2003 (Figure 12). Processes of nitrate removal in peat were explored using three sets of nested piezometers completed in peat, labeled 1 through 3. Each set of piezometers was designated S for shallow (<1.37 m) and D for deep (>1.37 m), where the shallow well was the eastern-most and the deep well was the western-most. These sites were monitored monthly over a ten-month period from October 2002 to June 2003. The monitoring results

19

were used to analyze the influence of peat, riparian zone dynamics, and ground and surface water interactions on nitrate concentrations.

All site addresses, locations, well and piezometer depths, and screening intervals from this study, as well as a cross-reference for well identification numbers from the 1997-1999 studies, are provided in Appendix B.

3.1 Field Sampling

3.1.1 Ground Water Sampling

Ground water samples were extracted from a standpipe at 25 residential wells (H1-H8, T1, T2, K1, P1-P3, and V1-V11; Figure 12) every other month for a 12-month period, beginning in July 2002. Thirteen of the 25 wells were monitored monthly and were chosen based on high nitrate values (H1, H2, H3, H4, H5, H7, T1, T2, K1, V5, V6, V8, and V9; Figure 12). The criteria used to select ground water sampling locations were as follows:

1) Spatial distribution of wells,
2) Depth below the water table,
3) Road access,
4) Land owner agreement for access and participation in the study,
5) Existence of a well log,
6) Detection of nitrate levels from previous studies, and
7) Presence of hose-barb fittings for flow cell chamber.

The static water level was measured at accessible locations before water was collected using a depth-to-water meter with an electrical sounding probe. The standpipe closest to the well was purged for approximately ten minutes, until the dissolved oxygen, specific conductance, and temperature values were stable. Samples and measurements were extracted from a one-liter flow cell chamber in order to minimize atmospheric interactions. Dissolved oxygen, specific conductance, and temperature were measured using a YSI model 85 analyzer. Dissolved oxygen was calibrated at every site to the nearest 100 feet of elevation and within 95%-105% saturation. Before each day of sampling, conductivity was checked using a known standard and temperature was checked using a mercury thermometer.

Three bottles were used to collect samples at each site. The samples that were analyzed in the laboratory for nutrients, including nitrate, ammonium, total phosphorus, and total nitrogen, were collected in 500 ml 2 N hydrochloric acid-washed Nalgene bottles. The samples analyzed for chloride were collected in 500 ml soap- washed Nalgene bottles. Those analyzed for iron and manganese were collected in 60 ml 20% nitric acid-washed Nalgene bottles. The 500 ml bottles were rinsed three times with the sample prior to collection; the 60 ml bottles were not rinsed as they contained ultra pure nitric acid for metal preservation. All samples were packed on ice for transport.

Nitrate-nitrogen isotope analysis was performed in February and May on samples from sites with significant levels of nitrate from the previous month (all but site V2). Samples with nitrate ranging from 0.3-2.0 mg-N/L were collected in 2 N hydrochloric acid-washed 500 ml bottles; samples in excess of 2.0 mg-N/L were collected in 2 N hydrochloric acid-washed 250 ml bottles. After collection, samples were filtered in the lab with a 0.45-micron 2 N hydrochloric acid- soaked filter, preserved with sulfuric acid to a pH of 2, and shipped on ice to the Colorado Plateau Stable Isotopes Laboratory at Northern Arizona University for analysis (Appendix C).

Water-oxygen isotope analysis was performed at sites K-1, P1-P3, and V-4 during February and May in order to quantify suspected denitrification activity. Samples were collected in 60 ml 2 N hydrochloric acid-washed Nalgene bottles. After collection, samples were filtered in the lab with a 45-micron, 2N hydrochloric acid-soaked filter, and shipped overnight to INSTAAR Stable Isotope Laboratory at the University of Colorado, Boulder for analysis (Appendix C).

3.1.2 Surface Water Sampling

Surface water samples were collected at 5 sites along Pangborn Creek (PB1-PB5) and 5 sites along Johnson Creek (JN1-JN5) every other month for 12 months, beginning in July 2002 (Figure 12). The criteria used to determine surface water sampling locations were as follows:

1) Spatial location,
2) Land owner permission, and

3) Data from previous studies regarding particular locales (e.g., Wills, 1998 and Nanus, 2000).

Dissolved oxygen, specific conductance, and temperature were measured by placing the YSI model 85 analyzer probe in the center of the channel and the center of the water column (when possible). Dissolved oxygen was calibrated at every site to the nearest 30.5 m of elevation. Calibration checks for specific conductance and temperature were performed in the laboratory prior to sampling. Dissolved oxygen was calibrated in the laboratory before each day of sampling. The acceptable calibration range was 95%-105% saturation.

Four bottles were used to collect samples at each site to analyze pH, nutrients, chlorides, metals, and fecal coliform. Fecal coliform was collected in a 125 ml plastic container and placed on ice until transport to Avocet Environmental Laboratories in Bellingham (Appendix C). Sample bottles were rinsed with sample three times prior to collection (except for fecal coliform and metals). All water samples were collected facing upstream in the deepest part of the channel or the area with maximum flow velocity. When necessary, a reaching pole with sample-bottle at the end of it was used to create a minimum amount of disturbance to bottom sediments. When possible, samples were collected at elbow depth. All samples were packed on ice for transport.

Nitrate-nitrogen isotope analysis was performed on samples collected from sites PB1, PB3, PB4, PB5, JN1, and JN4 in February and April. Samples were collected according to the previous months nitrate concentrations: nitrate from 0.3-2.0 mg-N/L were collected in 2 N hydrochloric acid-washed 500 ml bottles and samples in excess of 2.0 mg-N/L were collected in 2 N hydrochloric acid-washed 250 ml bottles. After collection, samples were filtered in the lab with 0.45 micron 2 N hydrochloric acid-soaked filter, preserved with sulfuric acid to a pH of 2, and shipped on ice to the Colorado Plateau Stable Isotopes Laboratory at Northern Arizona University for nitrogen isotope analysis (Appendix C). Stable oxygen isotope analysis was not performed on stream samples.

3.1.3 Piezometer Sampling

Water samples were collected monthly from nested piezometers at three locations along the peaty banks of Pangborn Creek over a ten-month period, beginning in October 2002. The

piezometers were composed of 2-inch diameter PVC pipe that extended above the ground surface. The length of the screening was 0.05 meters coupled with a length of solid PVC pipe on top. The depths included one shallow (<1.37 m) and one deep piezometer (>1.37 m) per site. The piezometers were packed with sand at the bottom and a one-inch cap of bentonite clay used to decrease preferential pathways caused by drilling the hole.

Sites were numbered from west to east and piezometers were lettered according to depth, S for shallow and D for deep (S1, D1, S2, D2, S3, and D3). The piezometers ranged in depth from 0.61 meters to 2.64 meters below ground. Refer to Appendix B for a profile of the piezometers and depth specifications. The criteria used to determine sampling locations were as follows:

1) Spatial location,
2) Presence of peat deposit,
3) Land owner permission, and
4) Ability to install piezometers into the ground.

The static water level was measured at all locations using a depth-to-water meter with an electrical sounding probe before water was collected. Dissolved oxygen, specific conductance, and temperature were measured using a YSI model 85 analyzer. Dissolved oxygen was calibrated at every site to the nearest 100 feet of elevation. Specific conductance, dissolved oxygen, and temperature were calibrated in the laboratory before each day of sampling.

Samples were extracted using a peristaltic pump connected to a 12-volt battery. The piezometer was purged to a constant conductivity for approximately 10 seconds, before samples were collected. Water samples were collected as specified in Section 3.3.1. All samples were packed on ice for transport.

Nitrate- nitrogen isotope analysis was performed in November, February, and May on shallow piezometers (S1, S2, and S3). Samples were collected in two 1000 ml 10% hydrochloric acid-washed bottles, filtered in the lab with 45-micron 2N hydrochloric acid-soaked filters, and preserved with sulfuric acid to a pH of 2. The samples were sent to the Colorado Plateau Stable Isotopes Laboratory at Northern Arizona University for analysis (Appendix C).

Water-oxygen isotope analysis was performed at the same time as nitrate-nitrogen isotopes in order to correlate results. Samples were collected in 60 ml 2N hydrochloric acid-washed bottles, filtered in the lab with 45-micron 2N hydrochloric acid-soaked filters, and shipped overnight to INSTAAR Stable Isotope Laboratory at the University of Colorado, Boulder for analysis (Appendix C).

Nitrogen gas was measured from water in deep piezometers (D1, D2, and D3) and well sites V4, V5, and K1 in order to measure denitrification rates. Samples were extracted using a Sample Pro Portable MicroPurge® pump by QED Environmental Systems, Inc. The pump was operated using a MP15 controller attached to a CO_2 compressed gas tank. The pump bladder was purged with distilled water between sites to decrease contamination potential. The samples were collected using the USGS protocol for sampling dissolved gases in ground water (E. Busenberg, personal communication, 2002) (Appendix D). Samples were placed in 150 ml glass bottles and analyzed using head-space chromatography at the USGS Reston laboratory facility (Appendix C).

3.2 Laboratory Analysis

Nutrients, chlorides, pH, specific conductance, turbidity and dissolved oxygen were analyzed at the laboratory at the Institute for Watershed Studies (IWS) at WWU a Washington State Department of Ecology certified laboratory. Metal concentrations and sulfate peaks were measured at Scientific Technical Services (SCITECH) at WWU. Fecal coliform samples were analyzed at Avocet Laboratories. Nitrogen isotopes were analyzed at the Colorado Plateau Stable Isotopes Laboratory at Northern Arizona University and oxygen isotopes were analyzed at the INSTAAR Stable Isotope Laboratory at the University of Colorado, Boulder.

Quality control included field blanks (1 per day), field duplicates (10% of all samples collected), laboratory duplicates (10% of all samples run), check standards, and spikes (Appendix E). Field blanks were used to check bottle preparatory procedures. Duplicates were used to measure precision, expressed as relative standard deviation and the relative percent difference. Check standards were used to measure laboratory accuracy and spikes were used to measure laboratory recovery. The methods and detection limits for all IWS and SCITECH instruments are shown in Table 4.

3.3 Statistical Analysis

Exploratory and confirmatory statistical analyses were performed on all water quality data, isotope and nitrogen gas data, and monthly precipitation data. The variable types included continuous (quantitative) and categorical (both nominal and ordinal) variables. Continuous variables are defined as values within a continuum or interval, such as nitrate, temperature, and pH. Categorical variables are finite values that can be ordered (ordinal) or unordered (nominal), such as month, day, and year (Swinscow, 1997). I used the statistical program R® to perform the majority of statistical analyses (http://www.r-project.org/). The programs SPSS® and Excel® were also used.

3.3.1 Univariate Statistics

All continuous water quality data were examined using statistical summaries and notched boxplots. Statistical summaries, including, medians, standard deviations, and minimum and maximum ranges were used to describe the distribution of variables. Notched boxplots are a graphical tool that can determine if groups are significantly different. They also provide a way to assess symmetry and to check for outliers. When the notches of two notched boxplots overlap, the groups are not significantly different (Figure 13). Each notch has an upper and lower limb expressed as a confidence interval. Comparing the values of the confidence intervals is another way to distinguish between groups. Where confidence intervals overlap, the groups are not significantly different. Notched boxplots are conservative tools that can operate on the edge of statistical significance. For this reason, it is important to check these patterns using a different type of test (e.g. the Kruskal-Wallis test).

The Kruskal-Wallis non-parametric rank-sum testing technique was used as a confirmatory test for boxplots because it is a more powerful test. The Kruskal-Wallis test results are reported as Kruskal-Wallis chi-square and p-values. The test assesses whether the group means are statistically different. If the means are different, then the variables are not in the same order, and more than one group exists. The test does not assume that the data are normally distributed or homoskedastic, making it applicable to both normal and non-normal datasets.

25

3.3.2 Bivariate Statistics

Bivariate correlations were used to measure the relationship between two continuous variables. The non-parametric ranking technique, Kendall's τ, was used for correlation analysis. Kendall's τ represents the probability that the two variables are in the same order versus the probability that the two variables are in different orders. The test does not assume that the data are normally distributed or homoskedastic. This non-parametric technique was chosen because water quality data sets are often non-normally distributed and where there is normal distribution. Kendall's τ is a robust and effective test that alleviates the task of transforming non-normal data.

Bivariate linear regressions were applied to compare independent variables to dependent variables. The x-value served as a predictor and the y-value served as a response variable. A regression line was used to predict the value of y from a known value of x. The regression model measurement is R^2, where values closest to |1.0| (absolute value) show a strong regression. The linear regression residuals were plotted beside the linear model to show the distribution of the values about the line y = 0. The residuals show the difference between the measured y-value and the predicted y-value.

3.4 Other Data Analysis

3.4.1 Geographic Information System

ArcMap® Geographic Information System was employed to modify existing land use maps (from Nanus, 2000) with updated data (e.g., 2003) from the Whatcom County Conservation District. Monthly nitrate and isotope data from well, stream, and piezometer sites were overlayed onto the land use maps. The impacts of nutrient loading were analyzed using this spatial representation.

3.4.2 Precipitation and Agronomic Loading

Average monthly precipitation values were obtained from the National Climatic Data Center in Clearbrook, WA, throughout the duration of the study. These data were used to investigate seasonal effects of agronomic loading. The Whatcom Conservation District

provided agronomic loading and irrigation information (J. Gillies, personal communication, 2004).

3.4.3 Nitrogen and Oxygen Isotopes

The ratio of stable nitrogen isotopes from nitrate (nitrate-nitrogen isotopes) can be used to differentiate among commercial fertilizers, septic field leaks, and animal wastes versus *in-situ* soil nitrogen (Aravena et al., 1993, Wassenaar et al., 1995). Nitrogen is composed of two isotopes, the lighter ^{14}N, with a natural abundance of approximately 1% and the heavier ^{15}N, with a natural abundance of approximately 99%. The notation used to express the high abundance of ^{15}N is "delta N-15" ($\delta^{15}N$). Delta values are the relative differences between the sample ratio ($^{15}N/^{14}N_{sample}$) and the standard ratio ($^{15}N/^{14}N_{standard}$) (Kendall, 1998). Measurements are in per mil (‰) and the standard is atmospheric air, where:

$$\delta^{15}N = ((^{15}N/^{14}N_{sample} - {}^{15}N/^{14}N_{standard})/ ({}^{15}N/^{14}N_{standard})) (1000 ‰) \qquad (2)$$

A wide range of $\delta^{15}N$ values can occur from a single source because of soil microbial activities, such as ammonia volatilization and nitrification, cause values to be hard to interpret. Ranges presented by Wassenaar (1995) provide a guideline to determine source identification and serve as a basis for comparing results from this study to previous isotope work done by the 1997-1999 studies. In ground water, inorganic commercial fertilizers result in values ranging from 0 to –2 ‰. Animal wastes have delta values from +8 to +16 ‰. Values between +2 and +8 ‰ should then indicate a mixture of inorganic commercial and animal fertilizers. Human waste from septic tank effluent would fall in the category of animal waste, between +8 and +16 ‰. However, Cox and Kahle (1995) determined that <7% of nitrogen in the region is related to septic tanks.

The $\delta^{15}N$ technique is inaccurate where denitrification occurs because fractionation due to nitrate reduction causes enrichments in $\delta^{15}N$ from the original signature. To account for this, stable oxygen isotopes (water-oxygen isotopes) were coupled with $\delta^{15}N$ values to determine where denitrification took place (Wassenaar, 1995, Cey et al., 1999).

27

Oxygen is composed of three stable isotopes: the lightest is ^{16}O, with a natural abundance of 99.76%, the middle is ^{17}O with a natural abundance of 0.04%, and the heaviest is ^{18}O, with a natural abundance of 0.20%. The heavier isotope will preferentially remain in a liquid due to its mass and hence is most useful in water studies (Aravena et al., 1993, Wassenaar, 1995, Kendall, 1998). The measurement is in per mil and the standard is Standard Mean Ocean Water from Vienna (VSMOW) and is given as:

(3)

$$\delta^{18}O = (({}^{18}O/{}^{16}O_{(VSMOW)\ sample} - {}^{18}O/{}^{16}O_{(VSMOW)\ standard})/({}^{18}O/{}^{16}O_{(VSMOW)\ standard}))(10^3\text{‰})$$

The $\delta^{18}O$ values can be determined either as oxygen of nitrate or oxygen of water; the $\delta^{18}O$ values from this project are from water. When compared to $\delta^{15}N$ values, a linear relationship between $\delta^{15}N/\delta^{18}O$ will indicate denitrification (Bottcher et al., 1990, Cey et al., 1998).

3.4.4 Dissolved Gases

The USGS provided a Dissolved Gases spreadsheet to calculate denitrification magnitudes from the measured values of nitrogen and argon gas, excess air, and recharge temperature (Appendix F). Argon and nitrogen gas are incorporated into ground water during recharge via air-water equilibration processes. Air can also be trapped in the form of air bubbles and be transported with ground water causing argon and nitrogen gas concentrations to be in excess of equilibrium, thus creating excess air (Vogel et al., 1981, Blicher-Mathiesen, 1998, Tesoriero et al., 2000). Excess air and nitrogen gas (N_2) at standard temperature and pressure (STP) are equivalent and are calculated as:

(4)

$$N_{2\ (STP)}\ (cc) = [N_{2measured}\ (mg/L) - \textit{Excess}\ N_2\ (mg/L) - N_{2A\text{-}W\ T}\ (mg/L)]$$
$$/0.98\ mgL^{-1}/cc$$

Where $N_{2measured}$ is the amount of nitrogen gas measured from the ground water sample; *Excess N_2* represents the product created by denitrification and is in excess of atmospheric nitrogen gas; $N_{2A\text{-}W\ T}$ is the amount of nitrogen gas at the air-water equilibrium and is dependent on recharge temperature, T; and the constant value converts units from milligrams

28

per liter into cubic centimeters. Recharge temperature is equivalent to annual mean air and shallow ground water temperatures. Argon at standard temperature and pressure ($Ar_{(STP)}$) is calculated as:

$$Ar_{(STP)} (cc) = Ar_{measured} (mg/L) - Ar_{A-W\ T} (mg/L)/0.012 \qquad (5)$$

Where $Ar_{measured}$ is the amount of argon gas measured from the ground water sample; $Ar_{A-W\ T}$ is the amount of argon at the air-water equilibrium and is dependent on recharge temperature, T; and the constant value converts units from milligrams per liter into cubic centimeters (Tesoriero et al., 2000).

The calculations for *Excess* N_2 gas are determined by balancing N_2/Ar ratios. From balanced N_2/Ar ratios, the calculations are further constrained by *Excess* air and recharge temperatures. Excess air values are usually 0-3 cc but have been reported up to 10 cc in fractured rock. Tesoriero *et al.* (2000) reported values of 0-4 cc for the B.C. portion of the Abbotsford-Sumas aquifer. Recharge temperatures should be in range of mean annual air temperature, which is 9-11°C for the study area (in agreement with Tesoriero et al., 2000). Where excess air and recharge temperature are unrealistically high, significant levels of *Excess* N_2 gas exist. *Excess* N_2 gas values are then manually increased on the spreadsheet until excess air values and recharge temperatures return to within the acceptable range. Denitrification can only exist in low dissolved oxygen conditions. The presence of reduced methane and carbon dioxide provide further evidence for denitrification.

A large error factor can exist when determining *Excess* N_2 values, so it is extremely important to have accurate recharge temperatures, excess air values, and other gas values. In order to validate the interpretations of this study, results were confirmed by the USGS staff (A.J. Tesoriero and E. Busenberg, personal communication, 2003). The model does not account for gas stripping and degassing can skew results. Gas stripping occurs when the total pressure of the gas is greater than the hydrostatic pressure. Degassing is indicated by an unrealistically high recharge temperature, negative excess air values, and a decrease in argon concentrations when compared to replicate sample results.

3.4.5 Biochemical Processes and Redox Reactions

The biochemical processes and redox reactions responsible for nitrate loss were primarily determined from dissolved gas data, metal concentrations, and sulfate peaks. Isotopic signatures and water quality indicators were used as supplemental evidence to demonstrate the presence of nitrate loss.

4. Results and Discussion

Between July 2002 and June 2003, I collected and analyzed 230 samples from residential ground water wells, 65 surface water samples from sites along Pangborn and Johnson Creeks, and 54 ground water samples from piezometers completed in peatlands. The compiled dataset is listed in Appendix G. The strong positive correlation between well nitrate and well total nitrogen (τ =0.933, p-value <2.2e-16; Figure 14) indicates that the dominant form of nitrogen in the study area is nitrate and supports the nitrate-focus of the study. The water quality results were used to (1) describe the distribution of nitrate in the study area and identify nitrate sources, (2) distinguish ground water nitrate from surface water nitrate in order to understand how the peatlands and riparian zone dynamics affect nitrate concentrations, and (3) evaluate the processes of nitrate removal in the peatlands and their effect on water quality to the south of Pangborn Road.

4.1 Ground Water Nitrate North of Pangborn Creek

I monitored ground water nitrate in 15 wells north of Pangborn Creek in order to determine the spatial distribution of nitrate contamination and to estimate the magnitude of nitrate discharging into the peatlands. All of these wells had median nitrate values greater than 3 mg-N/L (Table 5a), indicating anthropogenic sources (Tesoriero and Voss, 1997). Furthermore, of the fifteen wells north of Pangborn Creek, 80% had median nitrate concentrations above the established drinking water limit of 10 mg-N/L. A spatial representation of median nitrate concentrations for both shallow and deep wells is shown with land use in Figure 15. The median nitrate magnitudes are represented by graduated circles and indicate that the higher ground water nitrate north of Pangborn Creek is concentrated south and east of Judson Lake and that a mixture of dairy and berry farming occurs upgradient of this region (see also Figure 11).

Mitchell *et al.*, (2003) indicated that stratification in nitrate contamination occurred in the study area, where shallow ground water-nitrate had higher magnitudes than deep ground water nitrate. Analysis of boxplot patterns for shallow and deep well nitrate north of the peatlands indicates that the groups are not significantly different (Figure 16). In addition to graphical measures, numerical comparisons can be obtained from the notched boxplots,

31

where the confidence interval provides values for the limbs of the notches. The confidence interval results show that the ranges between deep (D) and shallow (S) well nitrate overlap (D= 13.04-17.08 and S= 11.21-13.52), indicating there is no significant difference between the groups. When the more powerful rank-sum Kruskal-Wallis test is applied for the same comparison, the results indicate that at a 95% significance level, the groups are not the same (KW = 11.90 and p-value = 0.05e-02). The results of the Kruskal-Wallis test indicate that the power of the boxplot test is insufficient for distinguishing the group medians in this application and that a greater sampling size is necessary for this test to be effective. The results of the Kruskal-Wallis test further indicate that stratification in nitrate contamination still exists in the study area. For this reason, I consider shallow and deep ground water nitrate separately.

4.1.1 Shallow Ground Water Nitrate

Shallow ground water is the focus of this study because it is likely discharging into the peatlands; whereas, because the vertical extent of the peat deposits are unknown, it is unclear whether the deep ground water is flowing through the peat or bypassing it by flowing underneath.

The median nitrate values for shallow ground water located north of the peatlands (H1, H2, H5, H6, H7, H8, V4, V5, and V6) exceeded the EPA limit (10 mg-N/L) throughout the sampling period (Table 5a). Temporal and spatial relationships were tested to determine the reason behind these measurements. Based on nitrogen cycle dynamics and soil microbial activity, nitrification typically occurs in the spring and summer due to increased microbial activity and leaching occurs in the fall and winter due to increased precipitation. Hence, shallow wells will often show higher nitrate concentrations when precipitation is great, as precipitation will cause nitrate to leach into the water table. The effects of precipitation on wet season well nitrate (November 2002 to June 2003) and dry season well nitrate (July 2002 to October 2002) were investigated using univariate statistics, however, no significance was found in this study (KW = 0.08 and p-value = 0.772) or in the 1997-1999 studies (e.g., Nanus, 2000). The lack of relationship between precipitation and nitrate values for the well dataset is not unexpected for non-point source pollution. In this region, the prevalence of

ground water nitrate irrespective of season is mainly because of intensive agricultural practices in B.C. and Whatcom County coupled with recirculation by irrigation (Guimera, 1998) and mixing processes, which allow a substantial amount of ground water-nitrate to exist in the water table year round.

4.1.1.1 Wells H1, H2, H5, H6, and H8

Ground water measured from wells H1, H2, H5, and H8 have generally high nitrate concentrations with minor variations over the sampling period (Figure 17). Data at well H6 were collected sporadically due to problems with the onsite ground water pump (Figure 18). The wells had similar concentrations during the 1997-1999 studies (Nanus, 2000), but median nitrate values for wells H5 and H8 are higher in this study. Well H5 has a median value of 10.86 mg-N/L as opposed to the previously measured median value of 5.02 mg-N/L. Well H8 has a median value of 15.47 mg-N/L as opposed to the previously measured median value of 10.87 mg-N/L. A hypothesis to explain the nitrate increases is that between 1997 and 2003 an increase in berry farming and a concurrent decrease in dairy farming occurred. Such changes in local land use may have raised the median nitrate levels measured in this study. The median $\delta^{15}N$ signatures support this hypothesis, reflecting mixed sources for these wells according to Wassenaar (1995). The values include 6.05‰ for H1, 5.36‰ for H2, 4.69‰ for H5, and 4.51‰ for H8 (Table 5a). The upgradient land use consists of berry farming, which uses inorganic commercial fertilizers and may use manure during pre-planting, and dairy farming, which uses manure as fertilizer. The spatial distribution of upgradient land use, coupled with the median $\delta^{15}N$ results, indicate that mixed sources probably cause shallow ground water nitrate north of Pangborn Creek (Figure 19).

4.1.1.2 Well H7

Well H7 is a deep well that was grouped with shallow wells based on its recent and historic sensitivity to local upgradient manure loading. The temporal pattern at well H7 depicts a nitrate spike from December to March (Figure 18). Field notes indicate that manure loading occurred on the upgradient grass field at the corner of Holmquist and Halverstick roads during February and March, the months with the largest nitrate spikes. The Whatcom

Conservation District describes the farmer's loading practices as aggressive, where fertilizer is loaded deep into the thin soil cover and likely into the sand above the water table (J. Gillies, personal communication, 2004). Moreover, the Whatcom Conservation District states that manure loading to grass fields occurs in late winter to spring (Table 2a), the same months that the nitrate spikes were observed. Median $\delta^{15}N$ measurements confirm that manure is the cause of nitrate contamination in the ground water sampled from H7 (11.04‰; Table 5a).

Historic evidence of the response of the ground water in the vicinity of well H7 to upgradient agricultural practices is provided by data from an unpublished study by the Department of Ecology from 1994-1997. They measured ground water nitrate of approximately 40 mg-N/L in well H7 shortly after heavy manure loading to the same grass field occurred (D. Garland, personal communication, 2004). Within months after loading and during no loading intervals, the nitrate levels drop to approximately 10 mg-N/L, consistent with the other shallow wells.

The rapid response of nitrate to local land use practices at H7 is likely due to a breach in the well casing that allows local sources to influence the ground water quality sooner than is anticipated in this deep well. Hence, I am classifying H7 as shallow.

4.1.1.3 Wells V5 and V6

Ground water measured from V5 and V6 have higher and more variable nitrate trends over time, compared to the previously mentioned shallow wells (Figure 17). Median nitrate values for these wells are 28.07 mg-N/L at V5 and 23.59 mg-N/L at V6 (Table 5a). Historical trends for the two wells also show higher and variable nitrate levels, 27.12 mg-N/L and 11.57 mg-N/L, respectively (Nanus, 2000). These wells have rather steady concentrations until a decline in mid-winter. Both wells are located directly down gradient from dairy fields and median $\delta^{15}N$ measurements reflect manure usage (V5=10.9‰ and V6= 8.8‰; Figure 19). The nitrate drop in February may be a result of a decrease in microbial conversion rates due to low soil temperatures or due to decreased loading during the months prior to February. Fertilizer application activities take place from the early spring to the late fall. A combination of nitrification and precipitation may explain the higher nitrate values

34

during these months. The high and steady values measured during the summer months were also observed in some upgradient shallow wells in the Environment Canada study area (Hii et al., 1999). Hii *et al.* (1999) theorized that recirculation might have been the cause, where ground water is extracted for irrigation and is then returned to the aquifer enriched in nitrate (e.g., Guimera, 1998). Because the vadose zone is very thin near site V5 and only slightly thicker at site V6, recirculation may affect the ground water here. This theory is substantiated by irrigation data proved by the Whatcom Conservation District (Table 2a). The management-based data suggests that irrigation for the upgradient grasses from April to September ranges from 1.35-10.29 cm.

4.1.1.4 Well V4

The last shallow well north of Pangborn Creek, well V4, fell into the variable nitrate group (Figure 20). The trend for ground water at well V4 showed high nitrate concentrations during the summer and fall and lesser concentrations during the winter and spring, with a median value of 8.26 mg-N/L (Table 5a). This trend may be reflective of upgradient land use practices, where fertilizer is applied and nitrified in the spring when microbial conversion rates escalate in tandem with temperature, and nitrate is then leached in the fall when precipitation increases. One hypothesis for low winter nitrate values is that microbial conversion rates are low due to low soil temperatures and no loading occurs. A third hypothesis is that fall and early winter precipitation may flush most of the nitrate out of the thin vadose zone. The median $\delta^{15}N$ measurements for V4 (5.55‰) indicate a mixed source, which agrees with the median upgradient shallow well analysis (6.05‰). A second factor may be recirculation. Based on the thin vadose zone and irrigation that occurs during the summer in the vicinity of well V4 (Table 2a), recirculation may be enriching nitrates and flushing stored soil nitrate (e.g., Guimera, 1998).

In summary, shallow ground water nitrate north of Pangborn Creek is contaminated with concentrations greater than or equal to the EPA drinking water limit of 10 mg-N/L. Shallow ground water is more contaminated than both the deeper ground water in the northern region of the study area and the shallow ground water south of the peatlands. Median $\delta^{15}N$ results suggest a mixture of organic and inorganic fertilizers cause the contamination, likely due to

upgradient farming in Whatcom County and B.C. Shallow wells in the vicinity of berry fields have relatively steady nitrate concentrations, whereas, wells in the vicinity of dairy fields have variable concentrations that may relate to periods of fertilizer loading. For the most part, historical measurements of these wells are similar, with some current median concentrations measured at levels greater than in the 1997-1999 studies.

4.1.2 Deep Ground Water Nitrate

The deep ground water north of Pangborn Creek ranged in median nitrate concentrations from high (>10 mg-N/L) to intermediate (3-10 mg-N/L; Figure 19).

4.1.2.1 Wells H3, H4, V8, and V9

Ground water with high nitrate values was measured from wells H3, H4, V8, and V9. All four of these wells had constant nitrate concentrations over time (Figure 21). Mitchell *et al.* (2003) speculated that the source of deep ground water nitrate is loading in B.C. In order to investigate the implications of this finding on my study, I compared my data to that from the Environment Canada study area (Figure 11). Nitrate was measured at four wells located just north of the border from data collected from July 2002- June 2003, the same months as this study. The results indicate similar temporal trends as the shallow and deep wells north of Halverstick Road in my study area (Figure 22). Median nitrate magnitudes ranged from 10-15 mg-N/L for shallow wells 4 and 5 located near Judson Lake and 15-20 mg-N/L for deep wells 6 and 17 located east of Judson Lake. The study area wells were within range of these values, where wells H3 and H4, located near Judson Lake yielded a median nitrate concentration of 11.7 mg-N/L. Wells V8 and V9, located east of Judson Lake yielded a concentration of 16.7 mg-N/L. Variations in nitrate concentration among the B.C. sites and the study area sites are probably caused by mixing of nitrate along flow paths.

Median $\delta^{15}N$ values from wells H3 (7.2‰), H4 (7.0 ‰), and V8 (6.8‰) indicate that much of the nitrate contamination is due to a mix of inorganic commercial fertilizer and manure caused by ground water mixing. The source of nitrate measured in well V9 (8.5‰) is manure. Based on land use in B.C. and ground water flow direction, nitrate concentrations measured in B.C., and nitrate and $\delta^{15}N$ concentrations measured in the study area, the

constant trend observed in the deep ground water north of Pangborn Creek is likely due to berry and poultry farming in B.C.

4.1.2.2 Wells V7 and V10

Two wells fell into the intermediate ground water nitrate category (3-10 mg-N/L), including wells V7 and V10 (Figure 23). This range represents nitrate caused by anthropogenic sources with concentrations below the EPA limit (Tesoriero and Voss, 1997). The 1997-1999 studies measured similar nitrate values (Nanus, 2000). These wells may be in the vicinity of unmapped layers of peat where denitrification is occurring, which would explain their anomalously low nitrate values compared to other deep wells north of Pangborn Creek. Low dissolved oxygen values measured at site V7 support this hypothesis (Figure 23). The median $\delta^{15}N$ value at site V10 indicates mixed sources (6.6‰) and the value at site V7 (1.5‰) indicates inorganic commercial fertilizer is the source. However, neither value indicates any nitrogen isotopic fractionation, which would suggest denitrification.

In summary, the overall temporal trends observed in the deep wells north of Pangborn Creek are relatively steady over time. Most of the contaminated ground water is located immediately south of the U.S.-Canadian border and is similar in magnitude to measurements in B.C. wells along the border (B. Hii, personal communication, 2004). Two locations of lesser contamination occur to the east of Judson Lake, where localized peat may occur at an unknown depth. Nitrogen isotope measurements indicate that most of the nitrate is a result of mixed sources and based on the hypothesis of Mitchell *et al.*, (2003) and ranges determined by Wassenaar (1995), the contamination is due to a mixture of ground waters influenced by agricultural practices in B.C.

4.1.3 Ground Water Nitrate Fluxes to and from the Peatlands

The nitrate contamination north of the peatlands is mainly concentrated in shallow ground water just south of the U.S.-Canadian border. I compared nitrate values between shallow wells north of the peatlands (H1, H2, H5, H6, H7, H8, V4, V5, and V6) and shallow wells to the south (K1, P3, T1, V1, and V11). Boxplots and the Kruskal-Wallis rank-sum test indicate that the northern shallow ground water nitrate values are significantly higher than

the southern shallow ground water (Confidence intervals: N= 13.04-17.08 and S= 4.35-12.18; KW = 23.56 and p-value = 1.21e-06; Figure 24). This statistical relationship documents that nitrate loss is occurring between the northern and southern portions of the study area and likely in unmapped peat deposits.

Vertical gradients were measured in nested piezometers in order to validate that the peatlands surrounding Pangborn Creek are a zone of ground water-discharge (Table 6). Calculations for the vertical gradients are listed in Appendix H. The results show that a mixture of upward and downward flow occurs at different times of the year, however, the values at site 3 indicate that the stream is a discharge zone. This is validated by observations of increasing stream flow downstream, indicating that Pangborn Creek is a gaining stream. Although the values for sites 1 and 2 are mixed, I assume that the peatlands are also a discharge zone based on nitrate measurements and because water levels in the piezometers were typically above the ground surface during several months of the year.

A median nitrate value of 15.47 mg-N/L was calculated from wells H1, H2, H5, H6, H7, H8, V4, V5, and V6 (a range of 8.26-28.07 mg-N/L) and was used as a basis for estimating shallow ground water nitrate discharging into the peatlands. A boxplot of nitrate values for the nine shallow wells north of the peatlands shows the variability associated with this (Figure 25). The values are higher in the region between H6 and V5 (Figure 15). Season, crop type and fertilizer application process, hydraulic gradients, changes in hydraulic conductivity associated with changes in geology, and redox are some of the reasons that the flux of nitrate may be higher or lower in areas around the peat.

The output flux from the peatlands was estimated from the low nitrate piezometers (Table 5c) and values measured in well P3 (median of 6.99 mg-N/L). As nitrate-laden ground water discharges through the peatlands, it becomes greatly reduced, as measured by piezometers. It also acquires high ammonium concentrations (median of 1.52 mg-N/L), some of which becomes oxidized, and again increases the nitrate levels as measured by P3. The low shallow ground water nitrate output from the peatlands suggests that denitrification occurred.

4.2 Surface Water Nitrate

Water quality in both Pangborn and Johnson Creeks was monitored throughout the duration of the study, but due to its proximity to the peatlands, Pangborn Creek is the focus of the surface water results. Pangborn Creek water quality and stream morphology are considered in determining ground and surface water interactions in relation to the peat. Water quality analysis includes nitrate, nitrogen isotopes ($\delta^{15}N$), ammonium, chloride, and fecal coliform concentrations. Due to its extremely shallow nature and its proximity to Pangborn Creek, the water quality at shallow well V4 is used as a means to assess ground water discharge into the creek.

The morphology of Pangborn Creek also affects water interactions and contaminant contributions. The geology of the headwaters along with sites PB1 and PB2 is peat. Field observations indicate that surface peat deposits extend as far east as stream site PB3, creating a discrepancy with the USGS map in Figure 5 that illustrates deposits as far east as site PB4. As the creek flows eastward from site PB3, the geology changes to cobbles, gravels, sand, and silt up through site PB5.

Changes in stream morphology affect ground and surface water interactions and hence influence stream water quality. Based on these factors, the water quality at each site is examined by location relative to the peat and by time of year, due to upgradient agricultural practices.

4.2.1 Nitrate and Nitrogen Isotope Concentrations

Both the effect of peat on creek nitrate and the source of nitrate were explored using nitrate and nitrogen isotope ($\delta^{15}N$) magnitudes, respectively. Site PB1 has relatively low nitrate concentrations throughout the year, with an increase from February to June (Figure 26). Nitrate values here remain low over time, presumably because ground water nitrate is reduced by peat. In addition to low nitrate values, low dissolved oxygen values support nitrate loss in the vicinity of this site (median value of 2.61 mg/L; Table 5b). This time period corresponds with both increased precipitation (Figure 8) and increased fertilizer application activity for the upgradient raspberry field (Table 2a; J. Gillies and C. McConnell, personal communication, 2004). The combination of the two events would cause increased

39

volumes of recharge and surface runoff. Additionally, the nitrate increase in the creek at this time may indicate a failure in the ability of the riparian vegetation to reduce the entire nitrate load being introduced by surface runoff. This finding concurs with a nutrient-trapping study conducted by Correll *et al.* (1997), who found that the riparian zone was unable to capture all of the nitrogen and phosphorous running off agricultural fields into a nearby stream. One other consideration is that duckweed was observed in the spring and the summer. This macrophyte will take up nitrate and raise the pH of the water. However, the influence of biota here is likely minor because pH values tend to increase downstream (Table 5b).

The four other creek sites show a temporal pattern of high summer nitrate magnitudes and lower winter and spring magnitudes (in agreement with Wills, 1998). In addition, the latter trend was observed in Fishtrap Creek, located in the aquifer outside of the study area (J. Gillies, personal communication, 2003). A univariate comparison between dry season (June-October) nitrate values and wet season (November to May) nitrate values at sites PB1-PB5 is shown in Figure 27. The patterns and the confidence intervals ($D = 12.58-14.17$ and $W = 6.70-8.81$) show that the groups are different. Kruskal-Wallis analysis confirms that the two groups are different ($KW = 9.20$ and p-value $= 0.002$). As in other studies, the boxplot documents that higher stream nitrate values occur during the summer.

The high summer nitrate values measured at sites PB2-PB5 can be explained by two hypotheses. One factor is that ground water is influencing stream nitrate concentrations. The similar nitrate trend among the stream sites and shallow well V4 suggests that ground water is delivering nitrate to the creek in summer months (Figure 26). Ground water also was found to contribute to the high summer nitrates in Fishtrap Creek (J. Gillies, personal communication, 2004).

A second hypothesis to explain the high nitrate trend for stream sites PB2-PB5 from July to September is that a combination of irrigation and precipitation may have transported nitrified fertilizer into the creek causing an increase in nitrate concentrations. This theory is substantiated by data from the Whatcom Conservation District (Table 2a; J. Gillies, personal communication, 2004). The data indicate that upgradient grass irrigation occurs from April to September on the order of 1.35-10.29 cm. Upgradient raspberry irrigation occurs from May to August on the order of 6.45-14.10 cm, with drip irrigation occurring with increased

frequency in July and August (C. McConnell, personal communication, 2004). Nanus (2000) found that precipitation and upgradient irrigation had a direct impact on the nitrate load in Pangborn Creek during summer months. The lower nitrate levels measured in winter, as depicted by Figure 26, are likely due to a combination of lower nitrification rates brought about by low soil temperatures, increased precipitation rates causing increased stream discharge and increased surface runoff, and diluted downstream nitrate loads caused by ground water contributions to the stream and increased rates of precipitation and surface runoff.

Median $\delta^{15}N$ results indicate that creek nitrate is a result of manure (10.90‰). Nanus's (2000) stream measurements yielded similar $\delta^{15}N$ values. On the other hand, the nitrate measured in upgradient shallow ground water (i.e., V4) is a result of mixed sources (5.55‰). The elevated stream nitrogen isotope values may be caused by mixing with enriched $\delta^{15}N$ values originating at the headwaters in the peatlands, as evidenced by piezometer $\delta^{15}N$ signatures (median of 16.2‰). This finding provides more evidence that the creek is partially recharged by ground water.

4.2.2 Ammonium Concentrations

Ammonium was measured to evaluate both the impact of the peatlands on stream water quality and to assess ground and surface water interactions. The main source of ammonium in the study area is un-nitrified fertilizer applied to crops in excess of the nutrients required. In general, the greater the distance from the field, the more complete the nitrification process. However, drainage ditches to the north of Pangborn Lake may allow for direct transport of ammonium from upgradient fields into the lake and possibly into Pangborn Creek (Figure 11). The drainage ditches force excess, un-nitrified fertilizer into the lake rather than along a shallow ground water flow path, where nitrification could occur. A secondary source of ammonium in the study area is inherent in peat deposits. The ammonium is a result of organic decomposition in an anoxic environment. A tertiary source of ammonium is via dissimilatory nitrate reduction to ammonium in the peatlands. Based on the work by Hill (1996a), this contribution is assumed to be minor.

41

Ammonium levels decrease downstream, with some months below the detection limit of 0.02 mg-N/L (Figure 28). Well V4 was not included in the figure because the ammonium concentrations are below detection. The high ammonium measured upstream at site PB1 is a result of organic matter inherent in the peat. The quantity of ammonium in peat is evidenced by the high values measured in piezometers (median value of 1.52 mg-N/L). The lower ammonium levels measured downstream may be caused by dilution, which occurs as ground water discharges into the stream, nitrification, or incomplete redox reactions, such as ammonium oxidizing to nitrite. Nanus (2000) attributed the downstream decrease in ammonium concentrations to nitrification in the more aerobic part of the stream. Nitrification would cause an increase in downstream nitrate, which was observed April, where nitrate concentrations increased from approximately 5 to 7 mg-N/L (Figure 26). Nanus's nitrate concentrations increased about 5 to 8 mg-N/L.

Temporally, site PB1 had high ammonium in August, December, and April (Figure 28). Similar ammonium patterns were observed in the piezometers during the months of December and April, the month of August was not measured (see Section 4.3). The ammonium magnitudes for the other sites are highest in July and April (Figure 28). The spikes occur due to agronomic loading mobilized by precipitation or irrigation. The low precipitation values measured during July (<6 cm) and the low ammonium measured at PB1 suggest that irrigation water may have transported ammonium to the creek via shallow ground water. This theory is substantiated by management-based data from the Whatcom Conservation District (Table 2a; J. Gillies, personal communication, 2004). Irrigation magnitudes for grasses in July reach an estimated value of 10.29 cm and 14.10 cm. The high creek ammonium measured in April was associated with precipitation (>6 cm). The undetected values in the shallow ground water at well V4 (Table 5a) suggest that surface runoff and/or extremely shallow ground water from irrigation and precipitation contributed ammonium to the creek. Another influence could be that ammonium was introduced at the headwaters from ground water flowing through peat and is diluted as distance downstream increases.

4.2.3 Chloride Concentrations

One means by which to investigate the contribution of surface runoff and ground water discharge to the creek is by measuring chloride. Chloride can indicate effluent from manure and can aid in identifying the impact of upgradient agriculture on stream water quality.

In Pangborn Creek, the chloride values increased downstream (Figure 29). The median upstream and downstream values are 7.70 mg/L and 10.30 mg/L, respectively (Table 5b). The median piezometer chloride value is 7.07 mg/L (Table 5c), which is similar to the PB1 value, as expected. Downstream, chloride concentrations at site PB4 and well V4 are similar in the summer months, which further supports that ground water contributes to the creek (Figure 29). The variability observed during the rest of the year, suggests that surface runoff and/or extremely shallow ground water contributes more chloride than does ground water. However, the chloride values measured at wells V5 and V6 (Appendix G) have a similar trend to the PB4 measurements, suggesting that despite the chloride decline from December to June 2002 at V4, ground water may be delivering chloride to the creek during this time (Figure 29).

The creek chloride trends are a result of upgradient land use, where as the occurrence of dairy farming increases downstream, chloride concentrations increase. Additionally, soil type may play a role, where as peat decreases downstream, chloride values increase.

4.2.4 Fecal Coliform Concentrations

A second way to determine the impact of upgradient agricultural activities on stream water quality is to analyze fecal coliform. Fecal coliform is a measure of bacterial colonies from the intestinal tracks of warm blooded animals and therefore indicates manure-based agricultural activities, as well as septic effluent. As in the chloride results, fecal colonies increase downstream (Figure 30). Fecal coliform concentrations are highest in the summer and lowest in the winter (in agreement with Wills, 1998). This trend is likely a result of manure spreading, which occurs from late winter to late summer coupled with low winter microbial conversion rates. One anomaly at site PB5 occurred in December and may indicate a unique effluent event. Although fecal coliform was not measured in wells and thus

cannot be used to assess ground and surface water interactions, fecal concentrations can help to justify the concentrations of chloride, ammonium, and nitrate measured in the creek.

4.2.5 Ground and Surface Water Interactions

The water quality indices detailed above provide insight to the question of ground and surface water interactions at the Pangborn Creek discharge zone. The results suggest that throughout the year, ground water and surface runoff contribute water volume to the creek. During fall, winter, and spring, surface runoff is a result of increased precipitation; during the summer, surface runoff and shallow ground water are generated by localized regions of irrigation. In general, nitrate, chloride, and fecal coliform increase as distance from the headwaters increases; ammonium concentrations decrease as distance from the headwaters increases (Figure 31). The nitrate reduced and ammonium enriched headwaters are a result of the peat layers, while water quality away from the peat is influenced by a combination of upgradient agricultural practices and oxidizing redox conditions.

4.3 Ground Water Nitrate South of Pangborn Creek- Evidence for Denitrification

The major identified location of peat in the study area lies at the west end of Pangborn Creek, enveloping Pangborn Lake. However, hydrostratigraphic data suggest that peat deposits occur throughout the study area at various unmapped depths (e.g., Rigg, 1958, Kovanen and Easterbrook, 2002, D. Easterbrook, personal communication, 2003). Reducing conditions and iron-rich regions within peat deposits offer conditions favorable to denitrification. Hence, ground water may be reduced locally in the vicinity of peat layers and independent of the peatlands along Pangborn Creek. A combination of physical and chemical indicators can document denitrification. These include low nitrate concentrations, low dissolved oxygen concentrations, presence of iron and manganese, enriched $\delta^{15}N$ signatures, a linear relationship between nitrogen and oxygen isotope values, and detection of di-nitrogen gas. Each indicator is explored in detail in the following subsections. Dissimilatory nitrate reduction to ammonium will also be discussed.

4.3.1 Low Ground Water Nitrate and Dissolved Oxygen

Temporal nitrate trends in wells P1, P2, V1, V2, V3, V11, P3, and K1 and all piezometers support nitrate loss in the region south of Pangborn Creek. Nitrate values from deep wells P1 and P2 fell into the lower end of the intermediate nitrate group (3-10 mg-N/L; Figure 23). These wells are of interest because they show a relationship to dissolved oxygen levels- both nitrate and dissolved oxygen concentrations are low. Although well logs indicate that neither of these wells are within peat, the proximity to the upgradient peatlands and the geologic history of the area support the existence of deeper unmapped peat layers upgradient of, or in the vicinity of the wells, causing denitrifying conditions.

A mix of shallow and deep wells south of Pangborn Creek have nitrate values less than 3 mg-N/L indicating no nitrate contamination. These wells include V1, V2, V3, and V11 (Figure 32). Based on the similar pattern between very low nitrate concentrations (median values <2.0) and very low dissolved oxygen levels (<2.0 mg/L), nitrate loss occurs upgradient or in the vicinity of the wells. Unlike the aerobic wells upgradient of Pangborn Creek, the anaerobic conditions measured here provide an environment where the nitrate-reduced ground water discharging from the peatlands can remain nitrate reduced due to redox conditions.

Wells P3 and K1 are shallow wells with variable ground water nitrate values over time (Figure 20). A similar pattern between nitrate and dissolved oxygen exists in both wells, where under anaerobic conditions nitrate concentrations are low, and under aerobic conditions nitrate concentrations increase. Evidence from well logs indicates that wells K1 and P3 are located adjacent to organic layers. The trends and the location show how redox conditions can control the speciation of nitrate in ground water and why low dissolved oxygen levels are mandatory for denitrification.

Another indicator for denitrification south of Pangborn Creek is the low nitrate and dissolved oxygen concentrations measured in the peatlands by piezometers. Nitrate and dissolved oxygen concentrations over time indicate that nitrate concentrations remain low (<1.0 mg-N/L) throughout the sampling duration, with the exception of D3 in February (2.47 mg-N/L) and site D1 in April (1.33 mg-N/L; Figure 33). These higher nitrate values are coincident with declines in piezometer ammonium (see Section 4.3.3) and indicate that

45

nitrification occurs as conditions become more aerobic. The nitrified ammonium is likely caused by the peat, but may also be due to farm practices. The February nitrate value in D3 may be attributed to manure loading to upgradient grasses (Table 2a). Temporal nitrate trends from V4 also show an increase in February nitrate values (Figure 20).

All shallow piezometers plus deep site D2 had low dissolved oxygen concentrations (<1.0 mg/L) during sampling. The quality control for dissolved oxygen in the field versus the laboratory shows a positive correlation, though variability did exist and differences would impact low magnitudes the most (Appendix E).

4.3.2 Low Ground Water Nitrate and Metals

Another condition that can enhance denitrification potential is the presence of desorbed metals. Well P2 had high median levels of iron and manganese (0.34 mg/L) and wells V1 and V2 had significant median levels of iron and manganese (0.13 mg/L and 0.21 mg/L, respectively; Table 5a). Additionally, field notes indicate that residents at site P1 complained of yellow water and clogged filters, which is a common result where high levels of iron occur (Kolle et al., 1985). To deal with their water quality complaints, the landowners installed a filtration system that would eradicate the metals in their drinking water. Nitrate, iron, and manganese can coexist only if the flux of nitrate is greater than the kinetic rate of reduction or if iron oxidation is occurring. Tesoriero *et al.* (2000) found that iron sulfide oxidation from pyrite occurred in an anaerobic riparian zone along Fishtrap Creek in the B.C. portion of the aquifer as indicated by low nitrate and dissolved oxygen and high sulfate and iron. A more likely source of iron and manganese in the peatlands is from iron-manganese nodules (R.S. Babcock, personal communication, 2004).

In a study done by Gu (2004) at a remediation site in Oak Ridge, Tennessee, *in situ* iron barriers were used to reduce nitrate contamination in ground water. Both microbially-mediated and abiotic denitrification were observed in the iron-barrier. Ground water measured down gradient remained nitrate-reduced. Based on the work of Gu (2004) and the findings of Tesoriero *et al.,* (2000), abiotic iron corrosion and microbial iron reduction are possible pathways for nitrate loss in the peatlands.

46

The nitrate loss potential associated with ground water measured in the wells listed above is associated with mineral constituents in the peat deposits. Wells P1 and P2 are located adjacent to the peatlands, and wells V1 and V2 have suspected peat deposits in the vicinity based on water quality indicators. Additionally, data from a newly measured well in a depression near well V5 indicates that a combination of low nitrate and dissolved oxygen values and high manganese values occur (H. Hirsch, personal communication, 2004). The well was completed in peat (J. Gillies, personal communication, 2004) and provides more evidence that nitrate loss is associated with the environmental conditions found in peat deposits.

The median iron and manganese concentration in piezometers (1.78 mg/L) is significantly greater than that measured in the wells (<0.10 mg/L; Tables 5a and c). The positive correlation among nitrate, iron, and manganese in the peat is strongest where nitrate values are smallest (<0.1 mg-N/L) and iron plus manganese values are increasing ($\tau=0.28$, p-value= 2.60 e-03; Figure 34). The influence of higher nitrate values on the nitrate-metal relationship is evident in Figure 34. The graph with higher nitrate values (outliers) appears to have a negative correlation versus the clearly positive correlation shown by the graph with low nitrate values. The positive correlations provide evidence that redox rates are sufficient for nitrate loss.

Iron is present in greater quantities in the shallow piezometers than in the deep piezometers (Table 5c) indicating heterogeneities within the peat matrix. The data suggest that along shallow flow paths, iron-bearing minerals play a role in reducing nitrate concentrations.

4.3.3 Ground Water Nitrate and Ammonium

Dissimilatory nitrate reduction to ammonium may explain the low nitrate values measured in ground water south of Pangborn Creek. Were dissimilatory nitrate reduction to ammonium to occur instead of denitrification, ammonium concentrations would be high. The data show that of 230 ammonium samples measured in wells, all but four values were below detection. Hence, statistical evidence supports denitrification as the major pathway for nitrate loss in wells, not dissimilatory nitrate reduction to ammonium.

The lack of correlation between piezometer nitrate and total nitrogen indicates that nitrogen exists in the peatlands but not in the form of nitrate ($\tau = 0.138$, p-value = 0.142). The same relationship is true for nitrate and ammonium, where ammonium is the preferred species of nitrogen in the peatlands ($\tau = -0.163$, p-value=0.081). The median ammonium value was 1.57 mg/L (Table 5c). There was minimal variability in ammonium levels from month to month within each site, but some variability from location to location (Figure 35). Tesoriero et al. (2000) observed that when ammonium variability was low, denitrification was responsible for nitrate loss, not dissimilatory nitrate reduction to ammonium. In the months where variability does exist, such as May at site S1, April at site D1, and February at site D3, ammonium converts into nitrate. Dissimilatory nitrate reduction to ammonium was not observed during this study, and hence the majority of ammonium is a result of redox conditions in peat where nitrogen from decomposing organic matter is preferentially speciated to ammonium in the anaerobic environment. The variability is due to nitrification of ammonium to nitrate during aerobic conditions.

Under the right geochemical conditions, ammonium may volatilize to ammonia (Figure 3). One way to determine whether this pathway occurs is by measuring pH. At a pH greater than 7.3, ammonium begins to volatilize and change the nitrogen budget (Oklahoma State University, 2004). The maximum pH value measured in piezometers was 6.9 (Appendix G). Based on pH, ammonia volatilization did not occur during the study.

4.3.4 Isotope Indicators for Denitrification

Median $\delta^{15}N$ signatures for wells downgradient of the peatlands reflected mixed sources (7.19‰). However, the accuracy of the $\delta^{15}N$ values may be compromised due to enrichment caused by denitrification or ammonia volatilization. All piezometers show enrichment, as evidenced by median values (16.2 ‰; Table 5c). The wells that may show enrichment include P1 (15.42‰), P2 (14.74‰), K1 (11.86‰), and V1 (11.72‰) based on high median $\delta^{15}N$ signatures. Analyzing nitrogen and oxygen isotopes together can distinguish denitrification from high values resulting from manure and ammonium volatilization.

As denitrification occurs along a flowpath, a linear relationship should occur between $\delta^{15}N$ and $\delta^{18}O$ caused by isotopic fractionation during denitrification (Bottcher et al., 1990,

Aravena et al., 1998, Devito et al., 2000). The measured wells included piezometers S1, S2, and S3, and wells K1, V4, P1, P2, and P3. The linear relationship between $\delta^{15}N$ and $\delta^{18}O$ in Figure 36 confirms the enrichment trend, where as $\delta^{15}N$ values increase, so do $\delta^{18}O$ values ($R^2 = 0.34$). The fitted residuals curve depicts large departures from the y = 0 line and an unbiased fit, confirming the appropriate use of the linear model.

The magnitude of $\delta^{15}N$ enrichment measured during the winter and spring can be used as an indicator for the strength of denitrification at each site. The range of $\delta^{15}N$ values shown as boxplots in Figure 37 indicates that some sites had more complete denitrification than others. Based on Wassenaar's (1995) values, sites with $\delta^{15}N$ values >16‰ indicate isotopic enrichment. Sites P1, S2, and S3 have the most complete denitrification, with site S2 showing the greatest variability between sampling periods. Sites K1, P2, P3, and V4 have incomplete denitrification or possibly no denitrification occurring based on the lower magnitudes. Site S1 has the most variable $\delta^{15}N$ magnitude and may indicate that it water from different sources in winter and spring causing the $\delta^{15}N$ signature to fluctuate.

The univariate and bivariate methods employed in this section can only provide qualitative thresholds for levels of denitrification. In order to quantitatively compare the various denitrification events in ground water, gaseous byproducts of denitrification must be explored.

4.3.5 Gas Indicators for Denitrification

The metabolic gaseous byproducts from progressive reduction of nitrate were measured during winter and spring in deep piezometers (D1, D2, and D3) and three shallow wells (K1, V4, and H5). Sites V4 and H5 served as control sites because of their aerobic nature. From the di-nitrogen/argon ratios, the atmospheric component of di-nitrogen in ground water was calculated (Equation 4 in Section 3.4.4).

The relationship between argon and di-nitrogen in February and May is shown in Figure 38. The air-saturated water (ASW) line shows concentrations of di-nitrogen and argon for varying recharge temperatures (4-12°C). The air-saturated water plus excess air (ASWEA) line assumes an equilibration temperature of 10°C (mean air temperature) and includes various amounts of excess air (up to 4 cc, in agreement with Tesoriero et al., 2000). The

horizontal distance of an anaerobic point from the ASWEA is the amount of *Excess* N_2 created by denitrification (Vogel et al., 1981 and Tesoriero et al., 2000). Wells K1 and D1 had the greatest amount of *Excess* N_2, piezometer sites D2 and D3 had a lesser amount for both sampling months, and control wells V4 and H5 had no *Excess* N_2. A few samples degassed during both months. In each case, the samples were collected at site D3 and were recognized by low argon concentrations, negative excess air values, and great variation from the other D3 samples.

A sensitivity analysis was performed on recharge temperatures at 9, 10, and 11°C. The chosen temperatures reflect mean air temperature at the study site over the past several years (A.J. Tesoriero, personal communication, 2003). For each temperature, the median *Excess* N_2 values for replicate samples were recorded. Next, all the *Excess* N_2 values for all three temperatures were averaged, excluding degassed samples. These median values are listed Table 7.

The results indicate that *Excess* N_2 varies from February to May. Based on microbial temperature responses, the *Excess* N_2 quantities should be greater in May than in February (Sawyer, 2001). Sampling sites D3 and K1 followed this trend; but site D1 showed lower values in May. The variance at D1 (-0.30) may have been caused by an increase in dissolved oxygen levels in May (Figure 33) allowing lower rates of denitrification.

The resultant gases from biochemical processes and redox reactions in both February and May are listed in Table 7. When dissolved oxygen values are low and nitrate values are undetectable, the type of redox reaction that occurs is dependent on the presence of iron and manganese, methane, di-nitrogen, and sulfate. Specific values of sulfate were not determined for this study, but sulfate peaks were measured at SCITECH so that when compared to one another, the relative amounts of sulfate could be extrapolated (Figure 39). These relative amounts cannot be used outside of this study, as the peaks are unique to the particular instrument settings, water matrix, and standards.

4.3.5.1 Aerobic Sites

As expected, shallow ground water from aerobic sites V4 and H5 show large amounts of oxygen and some carbon dioxide (Table 7). Due to redox chemistry, methane and *Excess* N_2

cannot occur here and the results show their absence. Shallow ground water from well K1 shows dissolved oxygen levels of approximately 4 mg/L during both months. Despite the aerobic nature of this well, *Excess* N_2 levels at this site are the largest of all those measured, signifying that denitrification occurs in the vicinity or upgradient. Metals, sulfate, and methane concentrations are insignificant, however (Table 5a and 7). Well K1 is located at the interface between sand and peat (Figure 5; J. Gillies, personal communication, 2002) and studies have shown that denitrification occurs at such interfaces (Hill et al., 2000). The presence of nitrate signifies that the redox potential is insufficient for complete consumption of the nitrate load.

4.3.5.2 Anaerobic Sites

Ground water measured from anaerobic sites D1, D2, and D3 are oxygen-depleted, have carbon dioxide, and have varying amounts of other gases and metals (Tables 5c and 7). Carbon dioxide is a result of all metabolic processes. The ground water in the vicinity of site D1 has a median iron + manganese value of 0.80 mg/L, a median methane value of 0.13 mg/L, and a substantial amount of *Excess* N_2 (Tables 5c and 7). A relatively large amount of sulfate also exists in both February and May. Based on these data, complete denitrification occurs at D1 and manganese, iron, and sulfate may participate in redox reactions.

Ground water measured at site D2 has a median iron + manganese concentration of 1.04 mg/L, a median methane value of 3.82 mg/L, and a small amount of *Excess* N_2 (Tables 5c and 7). An insubstantial amount of sulfate was measured in May, but larger quantities were found in February (Figure 39). The results indicate that incomplete denitrification occurs at D2 and redox reactions are subsequently influenced by manganese, iron, and methane. The lack of sulfate present in May is interesting, both because of the decline in quantities between February and May and also because methane was measured. Microbes use electron acceptors in the order outlined in Table 3, and so based on the presence of methane, one would infer that sulfate oxidation or reduction should occur. Chapelle (1995) found that a lack of sulfate does not necessarily mean that sulfate reduction is not occurring because dissolved sulfate will precipitate in the presence of metals. This finding may explain the lack of sulfate at site

D2. Field notes indicate that a sulfurous odor was detected throughout the sampling duration and substantiates the finding that sulfate precipitates at site D2.

Ground water measured at site D3 has a median iron + manganese concentration of 0.83 mg/L, a median methane value of approximately 0.17 mg/L, and a small amount of *Excess* N_2 (Tables 5c and 7). Ground water in the vicinity of site D3 has the largest amount of sulfate in the study area, relative to 25 ground water wells and 5 other piezometers. Based on these data, incomplete denitrification occurs at site D3 and redox reactions are subsequently influenced by manganese, iron, and sulfate.

4.3.6 Summary of Denitrification Findings in the Peatlands

A summary of the denitrification findings for all six piezometers in the peatlands is illustrated in Figure 40. The kite diagrams present multivariate data in a two dimensional fashion. By comparing the shapes of the kites from one piezometer to another, the relative amount of each variable is evident. The variables for shallow piezometers include $\delta^{18}O$ (‰), $\delta^{15}N$ (‰), nitrate (mg-N/L), ammonium (mg-N/L), dissolved oxygen (mg/L) and iron plus manganese (mg/L). Variables for deep piezometers include the above with the exception of *Excess* N_2 (mg/L) to replace the isotopes. All variables are median results.

Several observations are apparent from the kites. First, a large amount of variability exists from one piezometer to another. The variability reflects the heterogeneities within the peatlands. Second, nitrate levels are virtually non-existent and ammonium concentrations are high as a result of redox reactions reflected by the low dissolved oxygen values. Third, denitrification occurs at each piezometer, though with variable magnitudes. Shallow peat denitrification is illustrated by the linear relationship between $\delta^{18}O$ and $\delta^{15}N$ at the three shallow sites. Deep peat denitrification is measured by *Excess* N_2 magnitudes. The most complete denitrification occurs in the vicinity of site D1, evident by the large kite arm. The kites at sites D2 and D3 show lower levels of *Excess* N_2 indicating incomplete denitrification. Finally, the kites show high levels of iron and manganese throughout the peatlands and tend to be higher in the shallow subsurface than at depth.

4.4 High Ground Water Nitrate Concentrations South of Pangborn Creek

Shallow well T1 and deep well T2, located down gradient from the peatlands, have high median nitrate concentrations (21.47 mg-N/L and 9.09 mg-N/L, respectively). Nitrate trends over time show that the wells are consistently high in nitrate (>10mg-N/L; Figure 20). The shallow well is more contaminated than the deep well, following the trend of other wells in the study area upgradient of the peatlands. The land use directly upgradient from these wells is berry production. Based on Wassenaar's source ranges, the $\delta^{15}N$ results indicate that mixed sources are responsible for the nitrate contamination in ground water around wells T1 (4.41‰) and T2 (3.62‰). Additionally, well T2 had very high levels of chloride (median value of 18.43 mg/L). Pinpointing the exact source of the nitrates in the vicinity of these wells is beyond the scope of this study, however, one hypothesis is that the majority of the contamination measured in shallow well T1 was a result of the farming practices directly upgradient. The $\delta^{15}N$ values support this hypothesis, since both raspberry and blueberry farming can involve a combination of manure and inorganic commercial fertilizer application. The contamination in deep well T2 is likely caused by upgradient deep ground water bypassing the peat layers and contaminating the well. Based on the high concentration of chloride detected here, the farm practices may be dairy (local) and poultry (B.C.) related.

Both well T1 and T2 were aerobic throughout the sampling duration. The median values include 7.11 mg/L for T1 and 5.02 mg/L for T2. The wells also have undetectable levels of iron and manganese (<0.10 mg/L). Like the wells upgradient of the peatlands, this combination of physical parameters plus the nature of the upgradient land use makes ground water susceptible to nitrate contamination.

5. Conclusions

5.1 Nitrate Distributions

The distribution of nitrate in the study area is heavily concentrated north of the Pangborn Creek peatlands. In general, the greatest contamination occurs in shallow wells (<10 m) north of the peatlands, with a median value of 15.5 mg-N/L. The deep well (>10 m) contamination is lower in magnitude, with a median value of 12.0 mg-N/L. This stratification in nitrate contamination is in agreement with historical nitrate measurements in the study area (e.g., Mitchell et al., 2003). Some wells reflect low nitrate concentrations, which may be related to denitrification in unmapped peat layers in the vicinity of these wells.

Vertical gradients and hydrostratigraphy support the hypothesis that shallow ground water nitrate is discharging into the peatlands. Nitrate-nitrogen isotope data show that the prevalence of nitrates in the study area a result of inorganic commercial fertilizers and manure; the corresponding land use for these fertilizers are raspberry, blueberry, dairy, and poultry production.

Analysis of water quality in Pangborn Creek indicates that discharging ground water contributes water volume throughout the year. Surface runoff provides additional water volume and serves as another mechanism for contaminant transport during months of high precipitation or localized irrigation. Measurements show that the headwaters, which originate in peat, are enriched in ammonium from the peat and depleted in nitrate presumably due to denitrification. Minor contributions of ammonium from dissimilatory nitrate reduction to ammonium may also occur. Nitrate, chloride, and fecal coliform magnitudes increase as distance from the headwaters increases, concordant with an increase in farming density. The nitrate magnitudes are lower in Pangborn Creek than in most upgradient wells, indicating that processes such as denitrification, dilution, and possibly nutrient attenuation occur in the peatlands and possibly in the riparian zone.

South of Pangborn Creek, the ground water nitrate concentrations as measured by wells and piezometers are lower than the northern region. The combination of anaerobic conditions and the presence of metals detected in much of the ground water in the southern part of the study area, including the peatlands themselves, produce redox conditions supporting denitrification.

5.2 Denitrification

The processes of nitrate removal in the peat were examined from chemical analyses of piezometer samples, wells in close proximity to the peatlands, and from one well located at a sand and peat interface (K1). Three different methods were used to investigate nitrate loss, including water chemistry, isotopic signatures, and dissolved gas measurements. Of the three methods, isotopic ratios and dissolved gas analysis are the most robust and conclusive. The results show that ground water in the vicinity of sites S1, D1, P1, and K1 has the most complete denitrification; ground water in the vicinity of sites S2, D2, S3, D3, P2, and P3 has incomplete denitrification. A detectable seasonal effect between the months of February and May influenced the magnitude of denitrification at K1, which increased in *Excess* N_2 from 6.65 mg/L to 9.70 mg/L. The increase in soil temperature associated with climate changes from February to May would increase microbial respiration and explain the increase of denitrification magnitudes at this time. The increase in microbial conversion was only evident at K1.

5.3 Other Redox Reactions

In addition to denitrification, dissolved gas analysis provided information that may affect redox reactions. To the west of Pangborn Lake and immediately to the east, redox reactions may have been influenced by high levels of iron and manganese and some sulfate and methane. Reduction reactions may include manganese-iron reduction, sulfate reduction, and methanogenesis, where organic carbon is the electron donor. Oxidation reactions may include iron-sulfide oxidation, where iron is the electron donor. Both redox end products result in nitrate loss. Farther east of the lake, iron, manganese, and sulfate were measured, with lesser amounts of methane. The variability in nitrate loss processes is a result of heterogeneities within the peat matrix.

5.4 Regional Implications

Although nitrate is still widespread throughout the study area, this investigation confirms that peat soils can form a natural nitrate sink when provided with the right conditions. Such natural remediation techniques are of great significance in areas of heavy agriculture. The

extent and depth of peat in western Whatcom County has not been fully explored at this point; however, glacial and stratigraphic studies suggest that peat may be prevalent at various unmapped depths throughout the region (e.g., Kovanen and Easterbrook, 2001, Kovanen, 2002, and Kovanen and Easterbrook, 2002). Determining the distribution of this peat may help facilitate nutrient management in the region.

6. Recommendations for Future Studies

The results of this study indicate the importance of the Pangborn peat in providing an environment for natural nitrate loss in the study area. Future studies would improve the knowledge of such processes and could include the following:

1) Use well logs and stratigraphy data to determine the regional extent of peat in Whatcom County and assess the potential of this peat to reduce agricultural pollution at a wider scale.

2) Continue to assess the impacts of nutrient loading by monitoring wells and streams in the study area for nitrogen compounds, water quality indicators, and nitrogen and oxygen isotopes.

3) Determine biochemical processes other than denitrification occurring in peat by measuring electron milliequivalents and chemical indicators such as nitrogen gas (denitrification), sulfate concentrations (sulfate oxidation and reduction), and hydrogen gas (dissimilatory nitrate reduction to ammonium) along both shallow and deep flow paths.

4) Measure rates of denitrification in winter and spring using soil cores and the acetylene block technique.

References

Abbotsford-Sumas Aquifer Status Report, 1996. [Online]: http://www.elp.gov.bc.ca/wat/aquifers/absumas.html.

Aravena, R. and W.D. Robertson. 1998. Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic system plume. Ground Water 36(6):975-982.

Aravena, R., M.L. Evans, and J.A. Cherry. 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. Ground Water 31(2):180-186.

Beckwith, C.W., A.J. Baird, and A.L. Heathwaite, 2003. Aniostropy and depth-related heterogeneity of hydraulic conductivity in a peat bog. II: Modeling the effects on ground water flow. Hydrological Processes 17:103-113.

Blicher-Mathiesen, G., G.W. McCarty, and L.P. Nielson. 1998. Denitrification and degassing in groundwater estimated from dissolved di-nitrogen and argon. Journal of Hydrology 208:16-24.

Boeser, S. M. 2000. Exploring the Spatial Distribution of Breast Cancer Incidence and Environmental Risks in Whatcom County, Washington. M.S. Thesis, Western Washington University, Bellingham, WA.

Bottcher, J., O. Strebel, S. Voerkelius, and H.-L., Schmidt. 1990. Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. Journal of Hydrology 114:413-424.

Bridgham, S.D., C.L Ping, J.L. Richardson, K. Updegraff. 2001. Soils of Northern Peatlands: Histosols and Gelisols. In Wetland Soils, ed. J.L Richarson and M.J. Vepraskas, 343-353, Boca Raton: Lewis Publishers.

Canter, L.W. 1997. Nitrates in Groundwater. Boca Raton: CRC Lewis.

Carmichael, V., M. Wei, L. Ringham. October 1995. Fraser Valley Groundwater Monitoring Program Final Report. British Columbia, Canada: Ministry of Health, Ministry of Environment, Lands and Parks, and Ministry of Agriculture, Fisheries and Food.

Cey, E.E, D.L. Rudolph, R. Aravena, and G. Parkin. 1998. Role of Riparian Zone in Controlling the Distribution and Fate of Agricultural Nitrogen Near a Small Stream in Southern Ontario. Journal of Contaminant Hydrology 37:45-67.

Champ, D.R., J.Gulens, and R.E. Jackson. 1979. Oxidation-reduction sequences in ground water flow systems. Canadian Journal of Earth Science 16:12-23.

Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A.Vroblesky. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. <u>Water Resources Research</u> 30(2):359-371.

Cirmo, C.P. and J.J. McDonnell. 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate- forested catchments: a review. <u>Journal of Hydrology</u> 199:88-120.

Clement, J.-C., L.Aquilina, O. Bour, K. Plaine, T.P. Burt, and G. Pinay. 2003. Hydrological flow paths and nitrate removal rates within a riparian floodplain along a fourth-order stream in Brittany (France). <u>Hydrologic Processes</u> 17:1177-1195.

Clesceri, L.S., A.E. Greenberg, A.D. Eaton. 1998. <u>Standard Methods for the Examination of Water and Wastewater.</u> 20th ed. Baltimore: United Book Press.

Correll, D.L., T.E. Jordan, and D.E. Weller. 1997. Failure of agricultural riparian buffers to protect surface waters from groundwater nitrate contamination. Chap. in <u>Groundwater/surface water ecotones : biological and hydrological interactions and management options</u>, ed. J. Gibert, J. Mathieu, F. Fournier, 162-165. [Paris, France]: Unesco, Cambridge, New York: Cambridge University Press.

Correll, D.L. September 1996. Buffer zones and water quality protection: general principles. Chap. in <u>Buffer Zones: Their Processes and Potential in Water Protection: Proceedings of the International Conference on Buffer Zones</u>, edited by N. Haycock, T. Burt, K. Goulding, and G. Pinay, 7-20. Hertfordshire, UK: Quest Environmental.

Cox, S., and Kahle, S. 1999. Hydrogeology, Ground-Water Quality, and Sources of Nitrate in Lowland glacial Aquifers of Whatcom County, Washington, and British Columbia, Canada. Water Resources Investigations Report 98-4195. U.S. Geological Survey, Reston, VA.

"Dairy Nutrient Management Act" (RCW 90.64, April 1, 1998). [Online]: www.leg.wa.gov/rcw/index.cfm?fuseaction=chapter&chapter=90.64&RequestTimeout=500#rcw90.64.028.

Davidsson, T.E. and M. Stahl, 2000. The Influence of Organic Carbon and Nitrogen Transformations in Five Wetland Soils. <u>Soil Science of America Journal</u> 64:1129-1136.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a riparian zone. <u>Journal of Environmental Quality</u> 29:1075-1084.

Fetter, C.W. 1999. <u>Applied Hydrogeology</u>. 4th ed. New Jersey: Prentice Hall.

Follett, R.F. and D.J. Walker. 1989. Ground water quality concerns about nitrogen. In: Nitrogen Management and Ground Water Protection, edited by R.F. Follett, 1-22. Amsterdam, Oxford, New York, Tokyo: Elsevier.

Garland, D.P., and D. Erickson. 1994. Groundwater Quality Survey near Edaleen Dairy, Whatcom County Washington: January 1990 to April 1993. Washington State Department of Ecology.

Gartner-Lee, Ltd. 1993. Fraser Valley Groundwater/Drinking Water Study. B.C. Ministry of Health, Ministry of Agriculture, Fisheries and Food, Ministry of Environment Lands and Parks: March 1993.

Gelinas, S. 2000. An Exploratory Statistical Analysis of the Ground Water in the Abbotsford-Sumas Aquifer, Whatcom County, Washington. M.S. Thesis, Western Washington University, Bellingham, WA

Gu, B. 2004. Iron reactive barrier at the Oak Ridge Y-12 site. [Online]: http://www.esd.ornl.gov/~b26/barrier-geochem.htm.

Guimera, J. 1998. Anomalously high nitrate concentrations in ground water. Ground Water 36:275-282.

Hii, B., H. Liebscher, M. Mazallek, and T. Tuominen. 1999. Ground Water quality and flow rates in the Abbotsford aquifer, British Columbia. Aquatic and Atmospheric Science Division, Environmental Conservation Branch, Environment Canada, Pacific and Yukon Region, Vancouver, B.C.

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51:193-223.

Hill, A.R. 1996a. Nitrate removal in stream riparian zones. Journal of Environmental Quality 25:743-755.

Hill, A.R. 1996b. The potential of in-stream and hyporheic environments as buffer zones. In Buffer Zones: Their Processes and Potential in Water Protection: Proceedings of the International Conference on Buffer Zones, September 1996, edited by N. Haycock, T. Burt, K. Goulding, and G. Pinay, 115-127. Hertfordshire, UK: Quest Environmental.

Hiscock, K.M, J.W. Lloyd, and D.N. Lerner. 1991. Review of natural and Artificial Denitrification of Groundwater. Water Resources 25(9):1099-1111.

Kendall, C. 1998. Tracing nitrogen sources and cycling in catchments. In Isotope Tracers in Catchment Hydrology, ed. C. Kendall and J.J. McDonnell, 519-576. Amsterdam, Lausanne, New York, Oxford, Shannon, Singapore, Tokyo: Elsevier.

Kolle, W., O. Strebel, and J. Bottcher. 1985. Formation of sulfate by microbial denitrification in a reducing aquifer. Water Supply 3:35-40.

Korom, S. 1992. Natural denitrification in the saturated zone: A Review. Water Resources Research 28(6):1657-1668.

Kovanen, D.J. 2002. Morphologic and stratigraphic evidence for Allerod and Younger Dryas age glacier fluctuations of the Cordilleran Ice Sheet, British Columbia, Canada and Northwest Washington, U.S.A. Boreas 31:1643-184.

Kovanen, D.J. and D.J. Easterbrook. 2002. Timing and extent of the Allerod and Younger Dryas Age (ca. 12,500-10,000 14C yr B.P.) Ocillations of the Cordilleran Ice Sheet in the Fraser Lowland, Western North America. Quaternary Research 57:208-224.

Leverett, C. 2003. Groundwater nitrogen and carbon dynamics under riparian reed canarygrass and red alder. M.S. Thesis, Western Washington University, Bellingham, WA.

Liebscher, H., B. Hii, and D. McNaughton. 1992. Nitrates and pesticides in the Abbotsford Aquifer, southwestern British Colombia. Inland Waters Directorate, Environment Canada, North Vancouver, B.C.

Mengis, M., S.L. Schiff, M.Harris, M.C. English, R.Aravena, R.J. Elgood, and A. MacLean. 1999. Multiple geochemical and isotopic approaches for assessing ground water NO_3^- elimination in a riparian zone. Ground Water 37(3):448-457.

Mitchell, R.J., R.S. Babcock, S. Gelinas, L. Nanus, and D. Stasney. 2003. Nitrate distributions and source identification in the Abbotsford-Sumas Aquifer, northwestern Washington State. Journal of Environmental Quality 32(3):789-800.

Mitsch, W.J. and J.G. Gosselink. 1993. Wetlands. 2^d ed. New York: Van Nostrand Reinhold.

Nanus, L. 2000. Spatial and Temporal Variability of Nitrate Contamination in the Abbotsford-Sumas Aquifer, Whatcom County, Washington. M.S. Thesis, Western Washington University, Bellingham, WA.

National Climate Data Center. July 2003. [Online]: http://www.ncdc.noaa.gov/ol/climate/climatedata.html.

Oklahoma State University. 2004. Ammonia Volatilization. [Online]: www.dasnr.okstate.edu/nitrogen_use/ammonia.pdf.

Ostrom, N.E., L.O. Hedin, J.C. von Fischer, and G.P. Robertson. 2002. Nitrogen transformations and NO_3^- removal at soil-stream interface: A stable isotope approach. Ecological Applications 12(4):1027-1043.

Overdorff, D.L. 1982. Some effects of dredging on fish communities in the Johnson Creek Watershed, Whatcom County, Washington. M.S. Thesis, Western Washington University, Bellingham, WA.

Overdorff, D.L. 1981. Final Report: Water Quality Monitoring Evaluation Program: Johnson Creek Watershed. Whatcom County Conservation District.

Owens, L. 1994. Impacts of soil nitrogen management on the quality of surface and subsurface water. Chap. in Soil Processes and Water Quality. Boca Raton: Lewis Publishers, 137-162.

Paul, J.W. and B.J. Zebarth. 1997. Denitrification during the growing season following dairy cattle slurry and fertilizer application for silage corn. Canadian Journal of Soil Science 77:241-248.

Rigg, G.B. 1958. Peat Resources of Washington. Olympia, Washington: Department of Conservation Division of Mines and Geology. Bulletin 44.

Sawyer, J.E. 2001. Why 50 degrees Fairenheit? [Online]: www.ipm.iastate.edu/ipm/icm/2001/10-22-2001/why50.html.

Sloan, A. 1999. In Situ Measurement of Denitrification in a Managed Riparian Wetland. M.S. Thesis, North Carolina State University, Raleigh, NC.

Soil Survey of Whatcom County Area, Washington. 1992. U.S. Department of Natural Resources and Washington State Agricultural Research Center.

Starr, R.C. and R.W. Gillham. 1993. Denitrification and Organic Carbon Availability in Two Aquifers. Ground Water 31(6):934-947.

Stasney, D. 2000. The Impacts of Hydrostratigraphy and Groundwater Flow on Nitrate Concentrations Within the Abbotsford-Sumas Aquifer, Whatcom County, Washington. M.S. Thesis, Western Washington University, Bellingham, WA.

State of Washington Department of Health, Environmental Health. 1992. Office of Toxic Substances Fact Sheet, Nitrate in Drinking Water.

Swinscow, T.D.V. 1997. Statistics at Square One. [Online]: http://bmj.com/collections/statsbk/1.shtml.

Tesoriero, A.J., H. Liebscher, and S. Cox. 2000. Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along ground water flow paths. <u>Water Resources Research</u> 36(6):1545-1559.

Tesoriero, A. J. and F. D. Voss. 1997. Predicting the probability of elevated nitrate concentrations in the Puget Sound Basin: Implications for aquifer susceptibility and vulnerability. <u>Ground Water</u> 35(6):1029-1039.

Tobias, C.R., S.A. Macko, I.C. Anderson, E.A. Canuel, and J.W. Harvey. 2001. Tracking the fate of a high concentration groundwater nitrate plume through a fringing marsh: A combined groundwater tracer and in situ isotope enrichment study. <u>Limnology and Oceanography</u> 46(8):1977-1989.

Trudell, M.R, R.W. Gillham, and J.A. Cherry. 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. <u>Journal of Hydrology</u> 83:251-268.

Vance, D. 2003. 2 The 4 Technical Solutions: Ground Water and Redox Potential. [Online]: http://2the4.net/redox.htm.

Vogel, J.C., A.S. Talma, and T.H.E. Heaton. 1981. Gaseous nitrogen as evidence for denitrification in groundwater. <u>Journal of Hydrology</u> 50:191-200.

Vought, L.B.-M., J. Dahl, C.L. Pedersen, and J.O. Lacoursiere. 1994. Nutrient retention in riparian ecotones. <u>Ambio</u> (September) 23(6):342-348.

Walker, Steven J. 1995. A Hydrologic Model for the Lake Whatcom Watershed: Development, Implementation, and Assessment. M.S. Thesis, Huxley College, Western Washington University, Bellingham, WA.

Wassenaar, L. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes of ^{15}N and ^{18}O in NO_3^-. <u>Applied Geochemistry</u> 10:391-405.

Western Regional Climate Center. 2002. [Online]: http://www.wrcc.dri.edu.

Whatcom County Conservation District. 2002. [Online]: http://whatcomcd.org.

Wills, M. 1998. Dairy farming and the effects of agricultural, nonpoint-source pollution on stream water quality, Johnson Creek watershed, Whatcom County, Washington. M.S. Thesis, Western Washington University, Bellingham, WA.

Yamaguchi, H. 1990. Physico-chemical and mechanical properties of peats and peaty ground. <u>Proceedings of the Sixth International Congress, International Association of Engineering Geology</u> 1:521-526.

Zebarth, B.J., B. Hii, H. Liebscher, K. Chipperfield, J.W. Paul, G. Grove, and S.Y. Szeto. 1998. Agricultural land use practices and nitrate contamination in the Abbotsford aquifer, British Columbia, Canada. Agriculture, Ecosystem, and Environment 69:99-112.

Table 1. The six major soils and associated permeabilities for the Abbotsford-Sumas study area. †

Soil Type	Description	Composition	Permeability	Land Use	Sampling Sites
Kickerville Silt Loam	loess and volcanic ash overlying glacial outwash	very gravelly to extremely gravelly sand	moderate (upper) and very rapid (lower)	berry fields and dairy production (corn and pasture)	most well sites
Pangborn Peat	deep, poorly drained soil deposited in swamps, floodplains, and perimeter of bodies of water	mixture of organic material and mineral matter	moderate to slow	Pangborn and Judson Lakes and berry fields	stream sites PB1-PB3 and all piezometers
Cagey Loamy Sand (Birchbay Silt Loam)	deep, moderately well drained soil formed of loess and volcanic ash overlaying glacialfluvial deposits	coarse-loamy to sandy soils laying on wave-reworked glaciomarine drift plains	moderate (upper) and rapid (lower)	berry fields and dairy production (corn and pasture)	well site V6
Hale Silt Loam	poorly drained soil composed of loess and volcanic ash overlying glacial outwash	subangular and blocky silt loam to fine sandy loam with very fine roots	moderate (upper) and rapid (lower)	berry fields and dairy production (corn and pasture)	well site K1 and stream site PB5
Briscot Silt Loam	formed in alluivium: very deep, poorly drained coarse-loamy silt loam	stratified silt loam with an irregular distribution of organic matter with increasing depth	moderate	residential, berry fields, and pasture	stream sites JN1, JN4, and JN5
Laxton Loam	very deep, moderately well drained soil formed in volcanic ash and loess overlying glacial outwash	subangular blocky structure ranging from a silt loam to a loamy sand with increasing depth	moderate (upper) and rapid (lower)	residential, berry fields, and pasture	steam sites JN2 and JN3

† Descriptions, compositions, and permeabilities are from the Soil Survey of Whatcom County (1992). Permeability is based on water movement downward through a saturated soil in inches per hour. Slow is 0.15 to 0.51 cm; moderate is 1.52 to 5.08 cm; rapid is 15.24 to 50.8 cm; and very rapid is >50.8 cm. The sampling sites are listed with their corresponding soil types and include wells, streams, and piezometers locales used in this study.

Table 2a. Monthly raspberry and grass crop loading and irrigation activities. Management-based data for irrigation was provided by the Whatcom County Conservation District for Kickerville Loam soil (J. Gillies, personal communication, 2004). Loading information was provided by J. Gillies and C. McConnell (personal communication, 2004).

Raspberries †

Month	Activity	Loading Type	Monthly Net Irrigation Requirement (cm)	Application Method
January	x	x	0.00	x
February	preplant	manure	0.00	x
March	bulb-break	synthetic fertilizer	0.00	x
April	growth	x	0.00	x
May	growth	x	5.69	big-gun sprinkler
June	growth	x	9.73	big-gun sprinkler
July	harvest	x	14.10	big-gun sprinkler
August	x	x	8.89	big-gun sprinkler
September	x	x	1.17	big-gun sprinkler
October	x	x	0.00	x
November	x	x	0.00	x
December	x	x	0.00	x

† Some raspberry crops receive drip irrigation, which is 35% more efficient than big-gun sprinkler systems. Fields are irrigated more frequently, but with less water use due to increased efficiency.

Grasses †

Month	Activity	Loading Type	Monthly Net Irrigation Requirement (cm)	Application Method
January	x	x	0.00	x
February	nutrient up-take	manure	0.00	x
March	growth	manure	0.00	big-gun sprinkler
April	growth	manure	1.35	big-gun sprinkler
May	growth	manure	4.72	big-gun sprinkler
June	growth	manure	6.45	big-gun sprinkler
July	dormancy	manure	10.29	big-gun sprinkler
August	dormancy	manure	7.42	big-gun sprinkler
September	growth	manure	2.26	big-gun sprinkler
October	growth	manure	0.00	big-gun sprinkler
November	x	x	0.00	x
December	x	x	0.00	x

† Grasses (pastures) are used by dairy farmers for feed purposes

Table 2b. Monthly blueberry and corn crop loading activities (J. Gillies and
C. McConnell, personal communication, 2004).

Blueberries

Month	Activity	Loading Type
January	x	x
February	preplant	manure or synthetic fertilizer
March	bulb-break	synthetic fertilzer
April	growth	x
May	growth	x
June	growth	x
July	growth	x
August	harvest	x
September	harvest	x
October	x	x
November	x	x
December	x	x

Corn †

Month	Loading Activity	Loading Type
January	x	X
February	x	X
March	pre-plant application	manure
April	x	x
May	starter fertilizer application	manure
June	x	x
July	fertilizer application	manure
August	x	x
September	Harvest	x
October	x	X
November	x	X
December	x	X

† Corn is used by dairy farmers for feed purposes

Table 3. Biochemical process, electron acceptor, and associated metabolic processes in soils and ground water listed in order of preference due to availability. The electron donor is dissolved organic carbon. From Champ, 1979, Chapelle, 1995, and Vance 2003.

Zone	Process	Electron Acceptor	Metabolic Product	Redox Reactions
Aerobic	Aerobic Respiration	O_2	CO_2, H_2O	$CH_2O + O_2 = CO_2 + H_2O$
Anaerobic	Denitrification	NO_3^-	N_2, CO_2	$3CH_2O + 4NO_3 = 2N_2 + 3HCO_3 + H^+ + 2H_2O$
Anaerobic	Manganese Reduction	Mn^{4+}	CO_2, Mn^{2+}	$CH_2O + 2MnO_2 + 3H^+ = 2Mn^{2+} + HCO_3 + 2H_2O$
Anaerobic	Iron Reduction	Fe^{3+}	CO_2, Fe^{2+}	$CH_2O + 4Fe(OH)_3 + 7H^+ = 4Fe^{2+} + HCO_3 + 10H_2O$
Anaerobic	Sulfate Reduction	SO_4^{2-}	CO_2, H_2S	$2CH_2O + SO_4^{2-} = HS^- + HCO_3 + H^+$
Anaerobic	Methanogenesis	CO_2	CO_2, CH_4	$2CH_2O + H_2O = CH_4 + HCO_3 + H^+$

68

Table 4. Instrument detection limits used by the Institute for Watershed Studies and Scientific Technical Services at Western Washington University.

Parameter	APHA Method	Description	Detection Limit
Ammonia	4500 NH_3 G.	Automated Phenate Method	0.021 mg-N/L
Nitrate	4500 NO_3 I.	Automated Cd Red.	0.006 mg-N/L
Total Nitrogen	4500-N C.	Persulfate Digested automated Cd Red.	0.100 mg-N/L
Total Phosphorus	4500-P E.	Persulfate Digested Ascorbic Acid	5 ug/L
Chloride	4110	Ion chromatography	NA
Iron	3500 Fe	Atomic Absorption Spectrometer	0.1 ppm
Manganese	3500- Mn	Atomic Absorption Spectrometer	0.1 ppm
Conductivity-Field	2510	YSI 85 meter	2 uS/cm
Conductivity-Lab	2510	ORION 162 Conductivity meter	2 uS/cm
Dissolved Oxygen-Field	4500-O C.	YSI 85 meter	0.1 mg/L
Dissolved Oxygen-Lab	4500-O C.	Winkler Sodium Thiosulfate Titration	0.1 mg/L
pH	4500-H^+	ORION 250A meter	NA

Table 5a. Well depth and analyte values measured between July 2002 and June 2003 in the northwestern Washington study area.†

	Well	Estimated Depth Below the Median Water Table (m)	Location Relative to Peatlands	Median Nitrate (mg-N/L)	Median Dissolved Oxygen (mg/L)	Median Chloride (mg/L)	Median Temperature (deg C)	Median Iron + Manganese (mg/L)	δ15N (‰)
Shallow (<10 m)	H-1	3.0	upgradient	**11.94**	7.49	5.83	11.90	<0.10	6.05
	H-2	4.1	upgradient	**12.21**	8.62	8.22	10.20	<0.10	5.36
	H-5	2.7	upgradient	**10.86**	9.02	4.58	10.30	<0.10	4.69
	H-6	0.7	upgradient	**16.43**	7.10	7.75	10.40	<0.10	8.52
	H-7	11.7	upgradient	**19.83**	3.15	11.75	11.95	<0.10	11.04
	H-8	5.3	upgradient	**15.47**	5.45	7.84	10.65	<0.10	4.51
	K-1	8.8	downgradient	7.93	1.76	21.30	12.00	<0.10	11.86
	P-3	0.2	downgradient	6.99	2.97	7.05	10.20	<0.10	4.61
	T-1	4.1	downgradient	**21.47**	7.11	7.71	10.90	<0.10	4.41
	V-1	2.9	downgradient	2.23	1.15	7.86	10.95	0.13	11.72
	V-4	2.4	upgradient	8.26	5.60	3.70	11.10	<0.10	5.55
	V-5	1.9	upgradient	**28.07**	4.34	16.90	11.00	<0.10	10.88
	V-6	1.5	upgradient	**23.59**	5.57	22.90	10.50	<0.10	8.83
	V-11	9.3	downgradient	2.03	7.48	1.69	10.75	<0.10	-0.51
Deep (>10 m)	H-3	15.3	upgradient	**11.43**	4.34	7.75	10.35	<0.10	7.17
	H-4	10.6	upgradient	**11.95**	5.70	8.16	10.30	<0.10	6.99
	P-1	11.4	downgradient	5.92	3.30	8.33	8.80	<0.10	15.42
	P-2	11.5	downgradient	3.63	0.60	5.65	11.00	0.34	14.74
	T-2	15.5	downgradient	9.09	5.02	18.43	10.65	0.10	3.62
	V-2	31.7	downgradient	<0.02	0.11	10.55	11.00	0.21	NA
	V-3	18.0	downgradient	2.55	2.31	9.81	10.90	<0.10	5.12
	V-7	10.1	upgradient	3.65	1.71	4.04	10.35	<0.10	1.51
	V-8	11.2	upgradient	**16.76**	5.65	10.40	10.55	<0.10	6.75
	V-9	5.5*	upgradient	**16.74**	7.59	7.42	11.25	<0.10	8.52
	V-10	5.2*	upgradient	8.97	3.77	11.75	10.20	0.11	6.60

			Median Nitrate	Median Dissolved Oxygen	Median Chloride	Median Temperature	Median Iron + Manganese	δ15N
Upgradient	x	x	**12.08**	5.68	7.79	10.38	<0.10	6.05
Downgradient	x	x	7.46	3.3	8.33	10.9	<0.10	7.19
N-samples	160	x	229	229	229	229	229	33

† Values include estimated depth below the water table, location relative to peatlands, median nitrate, median dissolved oxygen, median chloride, median temperature, median iron and manganese, and median nitrogen isotope values. Location relative to the peatlands and number of samples are also provided. Values that are below detection are listed as <detection limit. Nitrate values greater than the EPA standard are listed in bold.
* These values are estimated.

Table 5b. Stream analyte values measured between July 2002 and June 2003 in the northwestern Washington study area.†

Steam Site	Median Nitrate (mg-N/L)	Median Ammonium (mg-N/L)	Median Chloride (mg/L)	Median Dissolved Oxygen (mg/L)	Median pH	Median Fecal Coliform (col/100ml)	δ15N (‰)
PB1	3.75	0.17	7.70	2.61	6.60	54.00	11.11
PB2	9.02	0.04	9.90	4.29	6.50	68.00	NA
PB3	8.77	0.02	10.00	5.50	6.60	33.00	10.68
PB4	8.88	0.19	10.00	8.65	7.10	240.00	9.80
PB5	9.74	0.12	10.30	10.20	7.50	340.00	11.11
Total Median	8.88	0.12	10.00	5.50	6.60	68.00	10.90
N-samples	35	35	35	35	35	35	4

† Median surface water nitrate, ammonium, chloride, dissolved oxygen, pH, fecal coliform, and nitrogen isotope concentrations.

Table 5c. Piezometer analyte values measured between October 2002 and June 2003 in the northwestern Washington study area.†

Piezometer Site	Depth Below Ground (cm)	Median Nitrate (mg-N/L)	Median Ammonium (mg-N/L)	Median Dissolved Oxygen (mg/L)	δ15N (‰)	Median Iron + Manganese (mg/L)
S1	24	<0.02	1.74	0.49	12.68	3.88
D1	54	0.02	1.31	1.80	NA	0.80
S2	44	0.02	2.62	0.32	16.20	2.52
D2	104	<0.02	3.70	0.30	NA	1.04
S3	68	0.07	0.98	0.26	17.25	6.53
D3	104	<0.02	0.77	0.34	NA	0.89
Total Median	x	0.02	1.52	0.33	16.20	1.78
N-samples	x	54	54	54	8	54

† Median ground water nitrate, ammonium, dissolved oxygen, iron and manganese, and nitrogen isotope concentrations.

Table 6. Monthly vertical gradient values for piezometers sampled from October 2002 to June 2003. Positive values indicate upward flow and negative values indicate downward flow.

Site #	October	November	December	January	February	March	April	May	June
S1	-0.16	-0.14	0.03	0.06	-0.07	0.08	-1.33	0.08	0.91
S2	-0.92	-0.21	-0.12	-0.16	-0.57	-0.30	-0.18	-0.22	-0.13
S3	0.28	0.04	0.25	-0.41	0.87	0.28	0.23	0.34	0.20

† Calculations are provided in Appendix H.

Table 7. Median dissolved gas results for piezometers and wells measured using nitrogen gas headspace chromatography in February and May 2003. †

FEB Site	mg/L O2	mg/L CO2	mg/L CH4	mg/L N2	mg/L Ar	mg/L excess N2
D1	0.06	37.13	0.13	24.53	0.68	5.95
D2	0.01	82.35	3.82	18.73	0.67	2.00
D3	0.07	77.90	0.18	21.42	0.72	1.50
K1	3.25	24.43	0.00	28.60	0.75	6.65
V4	6.99	21.85	0.00	25.88	0.81	0.00
H5	0	0	0	0	0	0

H5* not sampled this month

MAY Site	mg/L O2	mg/L CO2	mg/L CH4	mg/L N2	mg/L Ar	mg/L excess N2
D1	0.06	37.13	0.13	24.50	0.68	5.50
D2	0.01	82.35	3.82	18.73	0.66	2.00
D3	0.07	43.99	0.15	20.27	0.66	1.80
K1	3.25	25.23	0.00	29.54	0.75	9.70
V4	6.99	21.94	0.00	19.72	0.71	0.00
H5	10.61	38.60	0.00	22.26	0.71	0.00

†The gases oxygen (O2), methane (CH_4), nitrogen (N2), and argon (Ar) were measured directly by the USGS. The median Excess N_2 gas values were calculated using a USGS spreadsheet. N = 3 for D1-D3 and N = 2 for K1, V4, and H5 in February and in May.
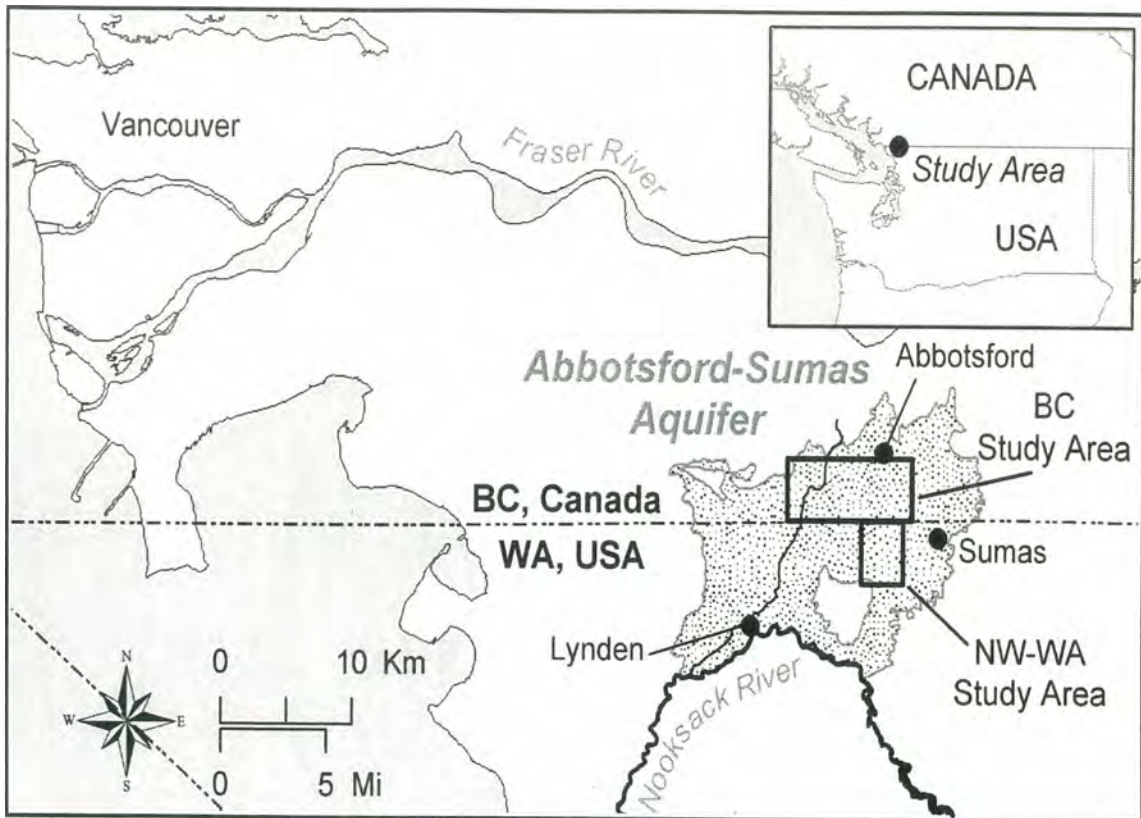
Figure 1. The Abbotsford-Sumas aquifer boundaries with designations for the Western Washington University study area in northwestern Whatcom County and the Canadian study area to the north in British Columbia (modified from Mitchell et al., 2003).
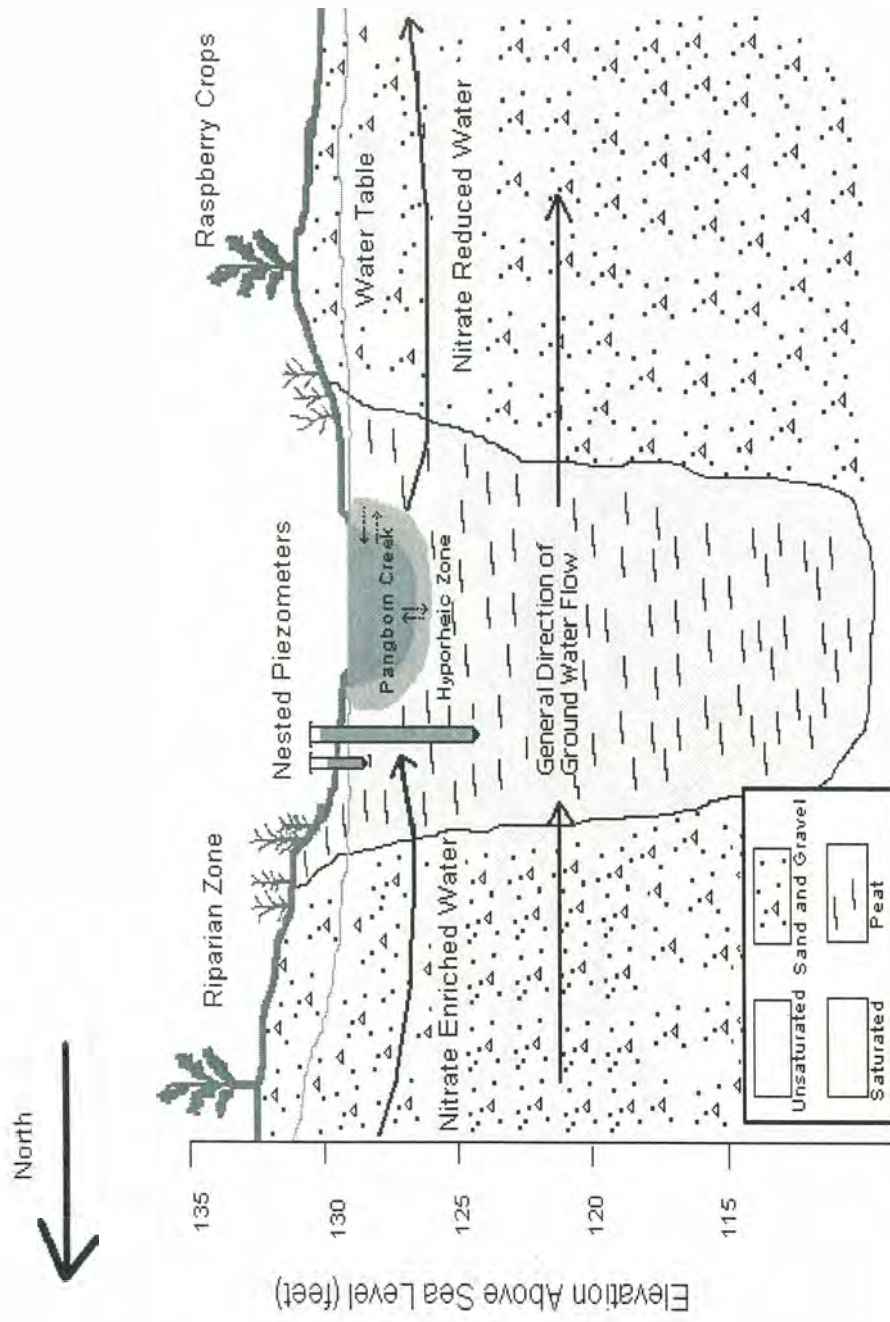
Figure 2. A conceptual picture of enriched ground water nitrate discharging through peat layers and along the riparian area of Pangborn Creek in the Abbotsford-Sumas aquifer. Elevation data were provided by Stasney (2000).

75
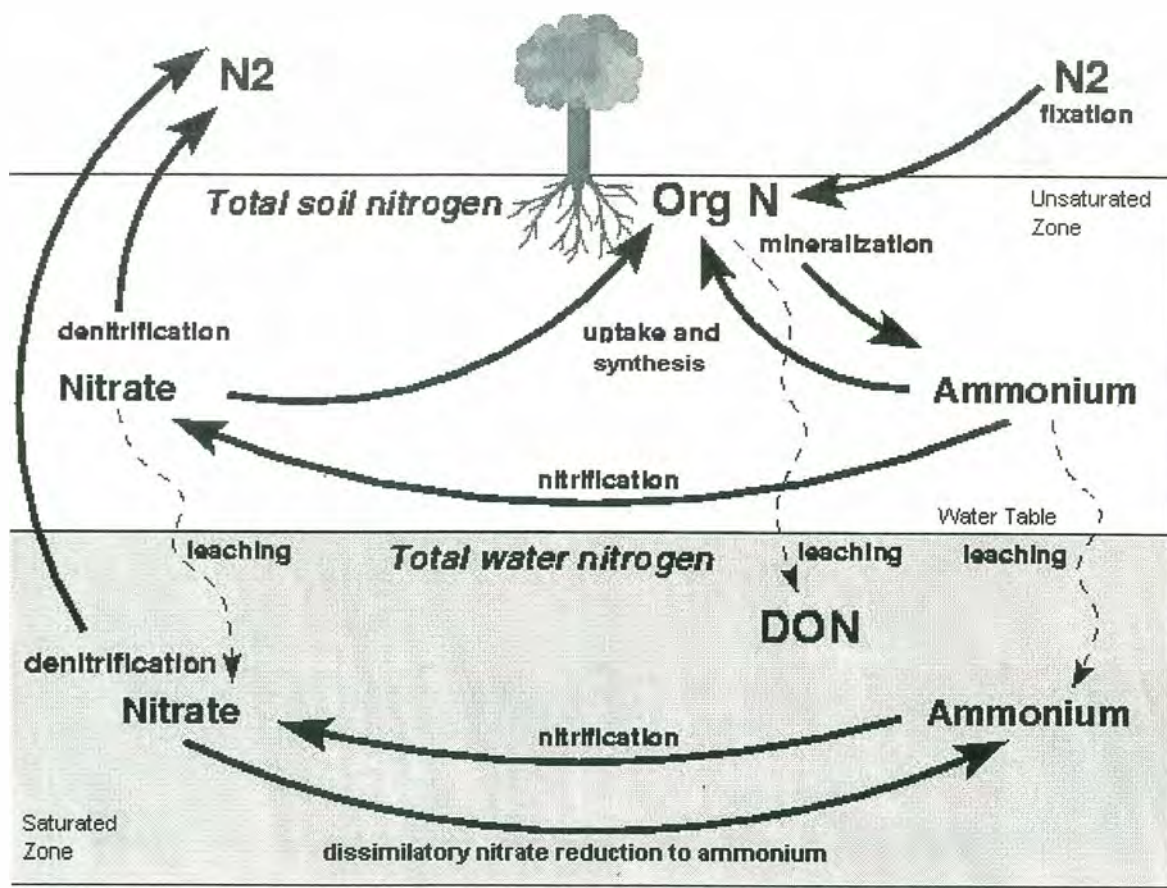
Figure 3. The nitrogen cycle (courtesy of Robin Matthews). Abbreviations include: organic nitrogen as Org N, dissolved organic nitrogen as DON, and di-nitrogen gas as N2.
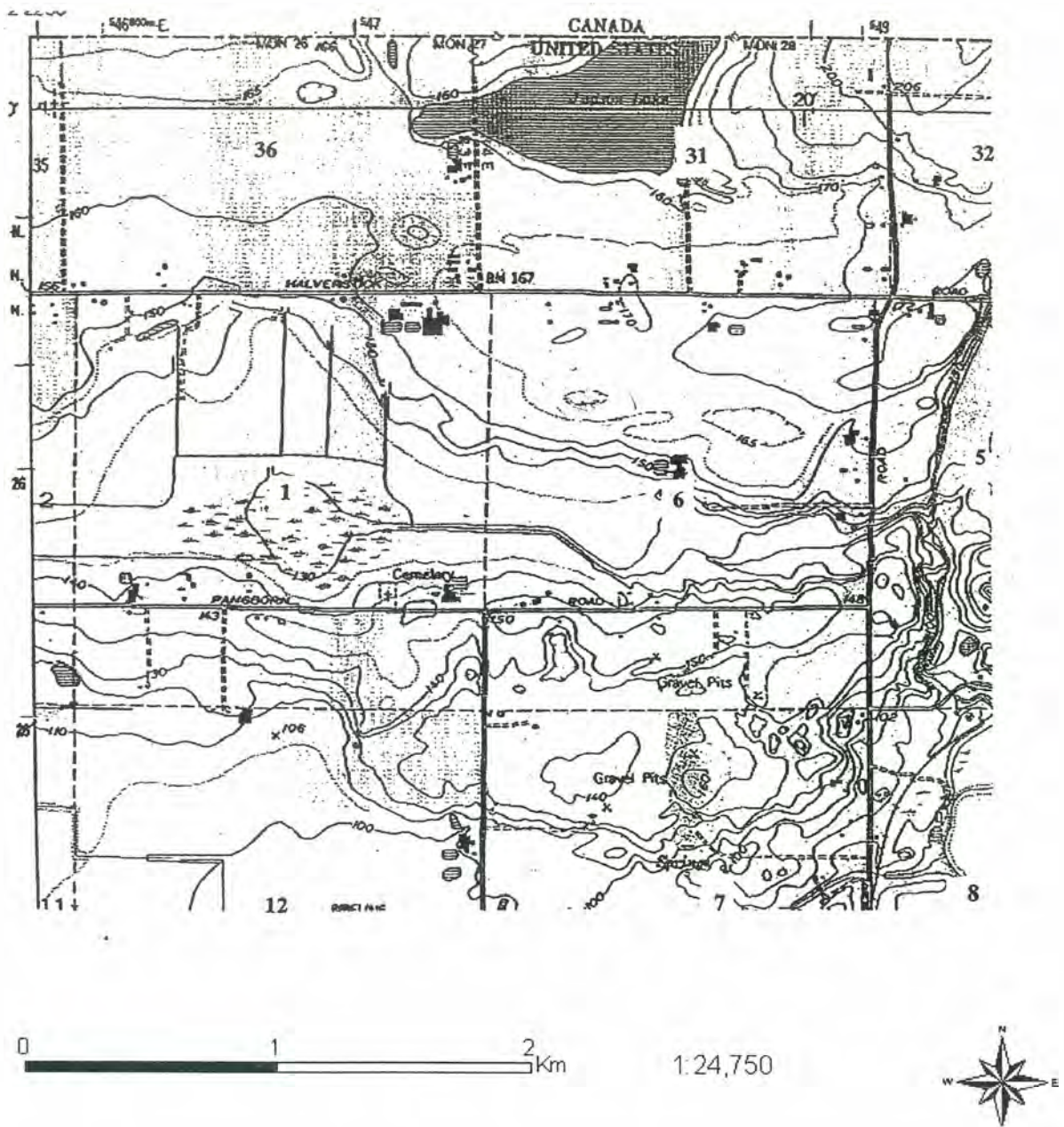
Figure 4. Topography map of the Western Washington University study area in the
Abbotsford-Sumas aquifer (from portions of the United States Geological Survey Sumas 7.5
minute quadrangle).
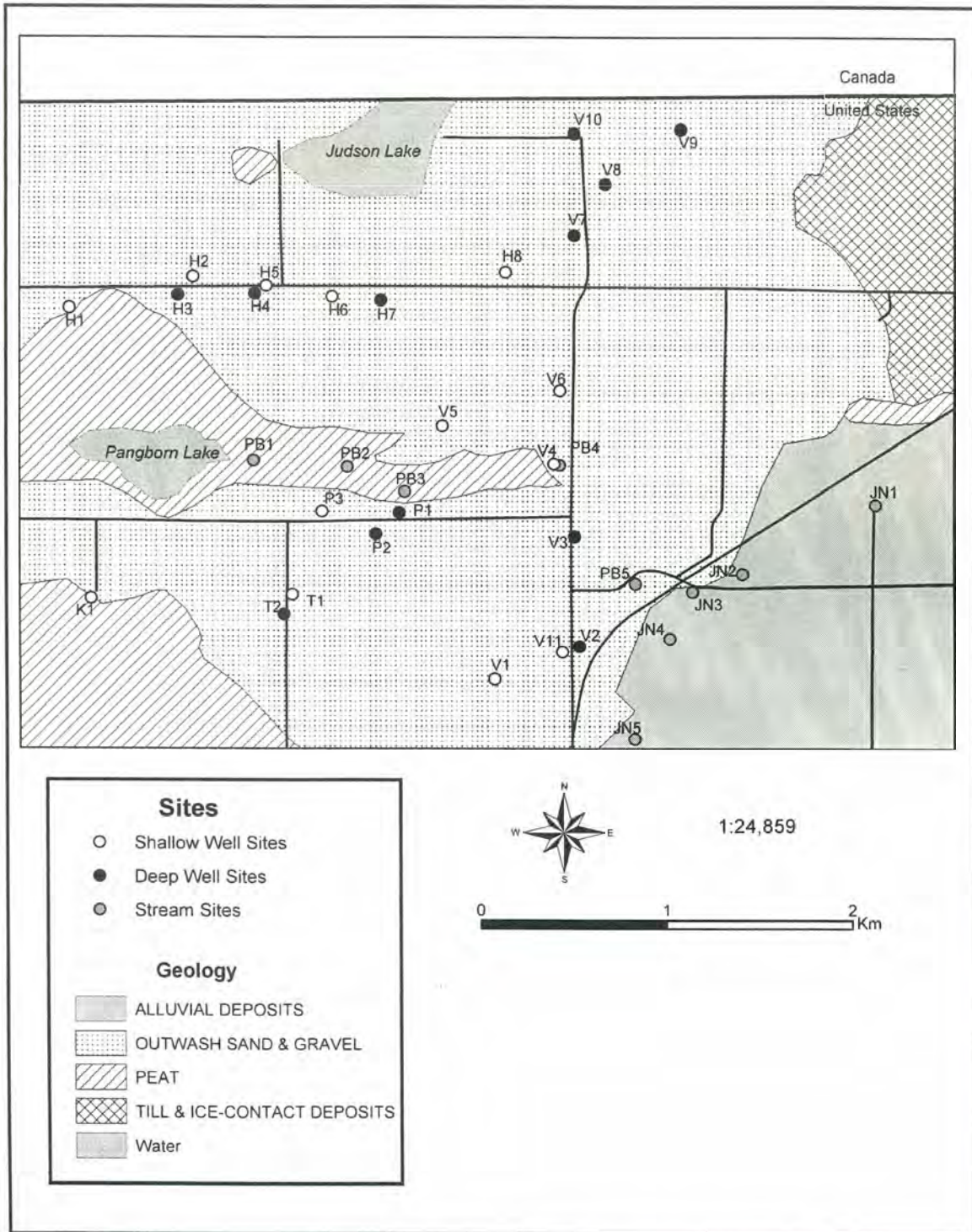
Figure 5. Geology layers and the 2002-2003 well and stream sites of the Western Washington University study area in the Abbotsford-Sumas aquifer (from the United States Geological Survey).

Figure 6. Direction of ground water flow and water table contours from the summer of 1998 (adapted from Stasney, 2000) for the Western Washington University study area in the Abbotsford-Sumas aquifer.

79
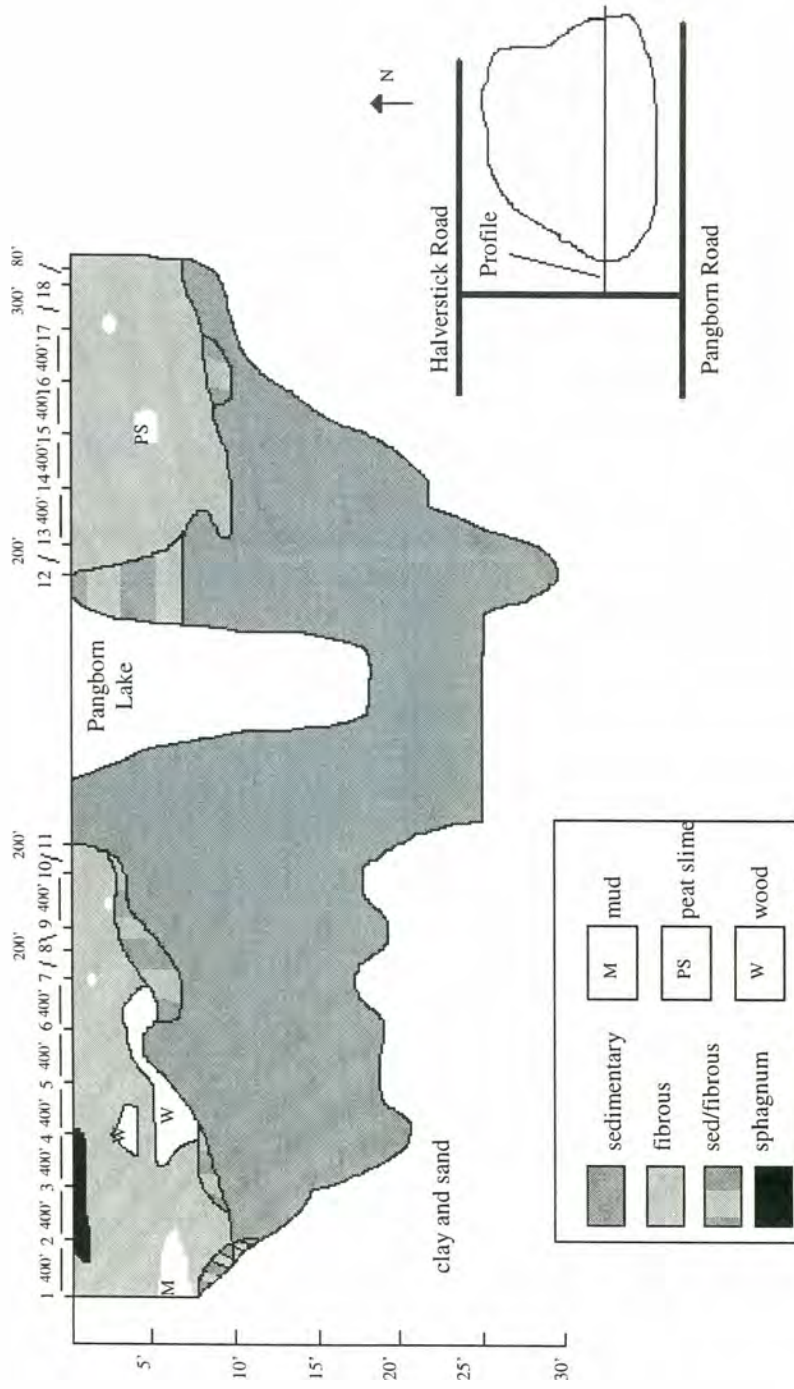
Figure 7. Cross section of Pangborn peat near Pangborn Lake in the Abbotsford-Sumas aquifer (adapted from Rigg, 1958). Distance and depth are in feet.

80
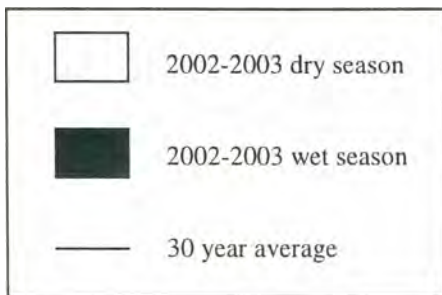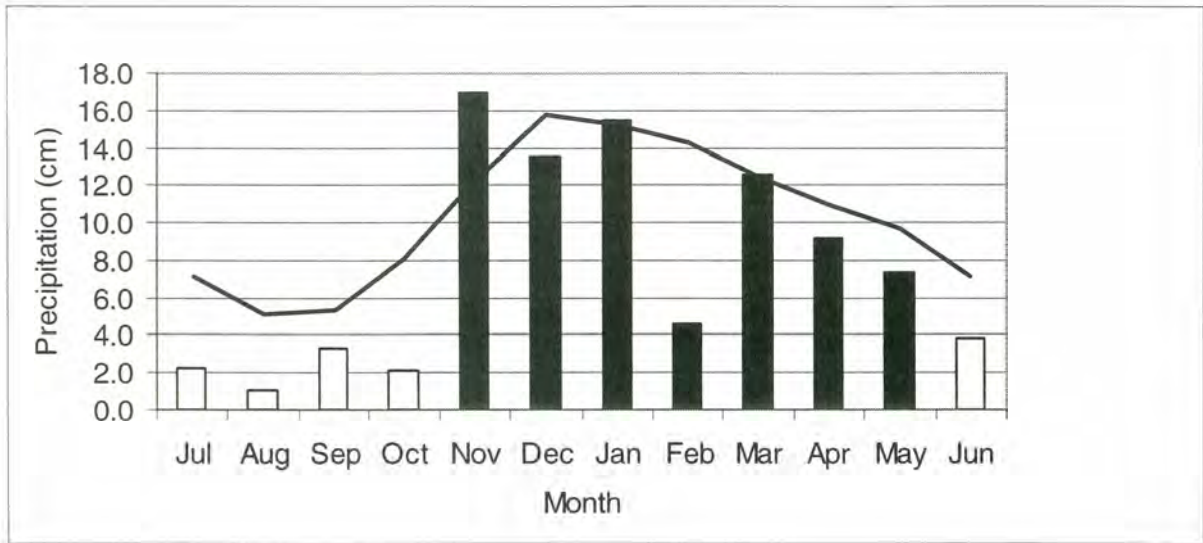
Figure 8. Monthly precipitation averages for the 2002-2003 data set and the thirty year average (Clearbrook Weather Station in Whatcom County, Washington). The dry season (<6 cm) includes July, August, September, and October of 2002, as well as June of 2003. The wet season (>6 cm) includes November 2002 through May 2003. Note that the month of February was included in the wet season data set despite the low magnitude of precipitation.
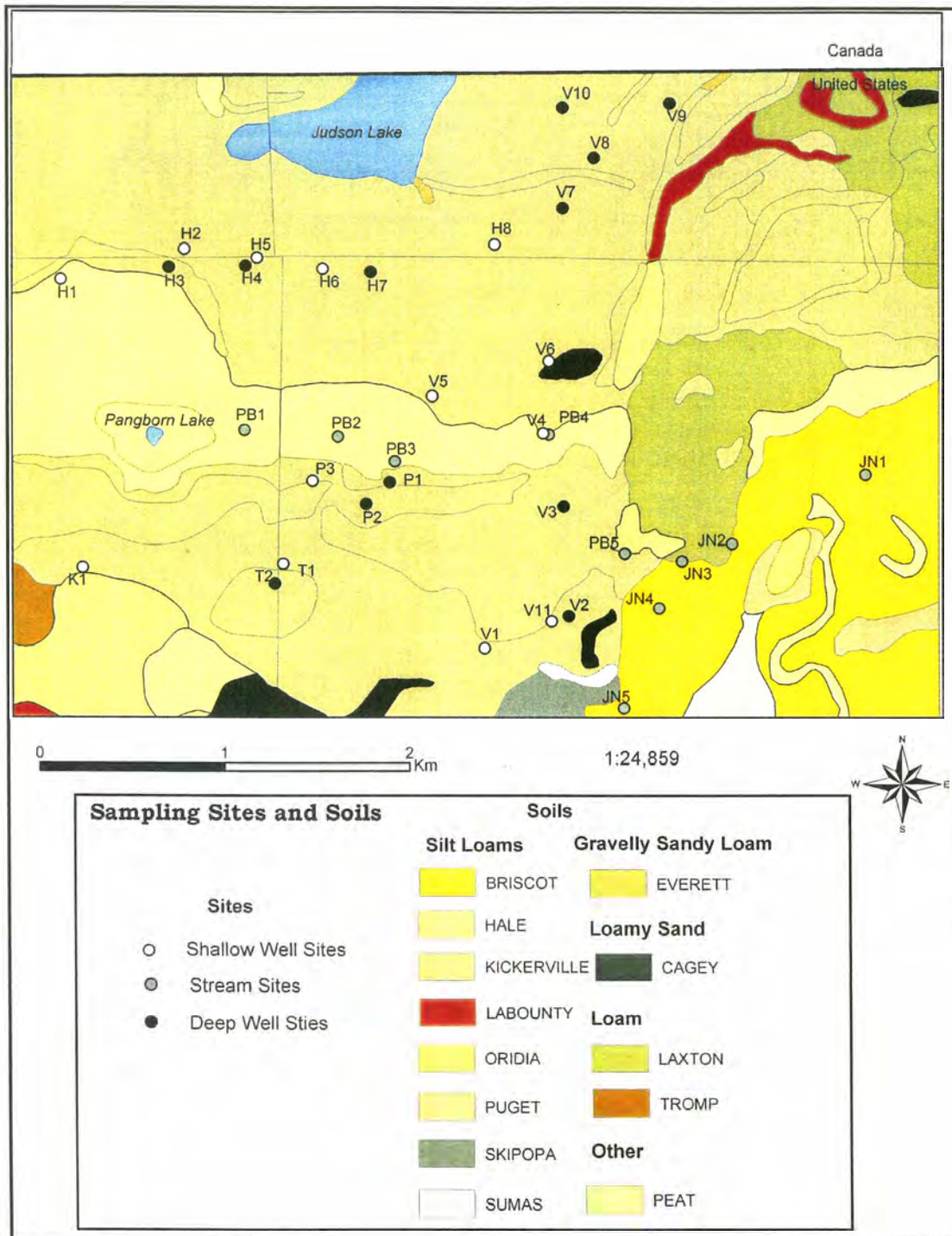
Figure 9. Soil layers in the Western Washington University study area in the Abbotsford-Sumas aquifer shown with the 2002-2003 well and stream sites (from the Washington State Department of Natural Resources Soil Survey, 1992). Histosols, Pangborn Variant, and Pangborn peat have been collectively grouped as Peat.
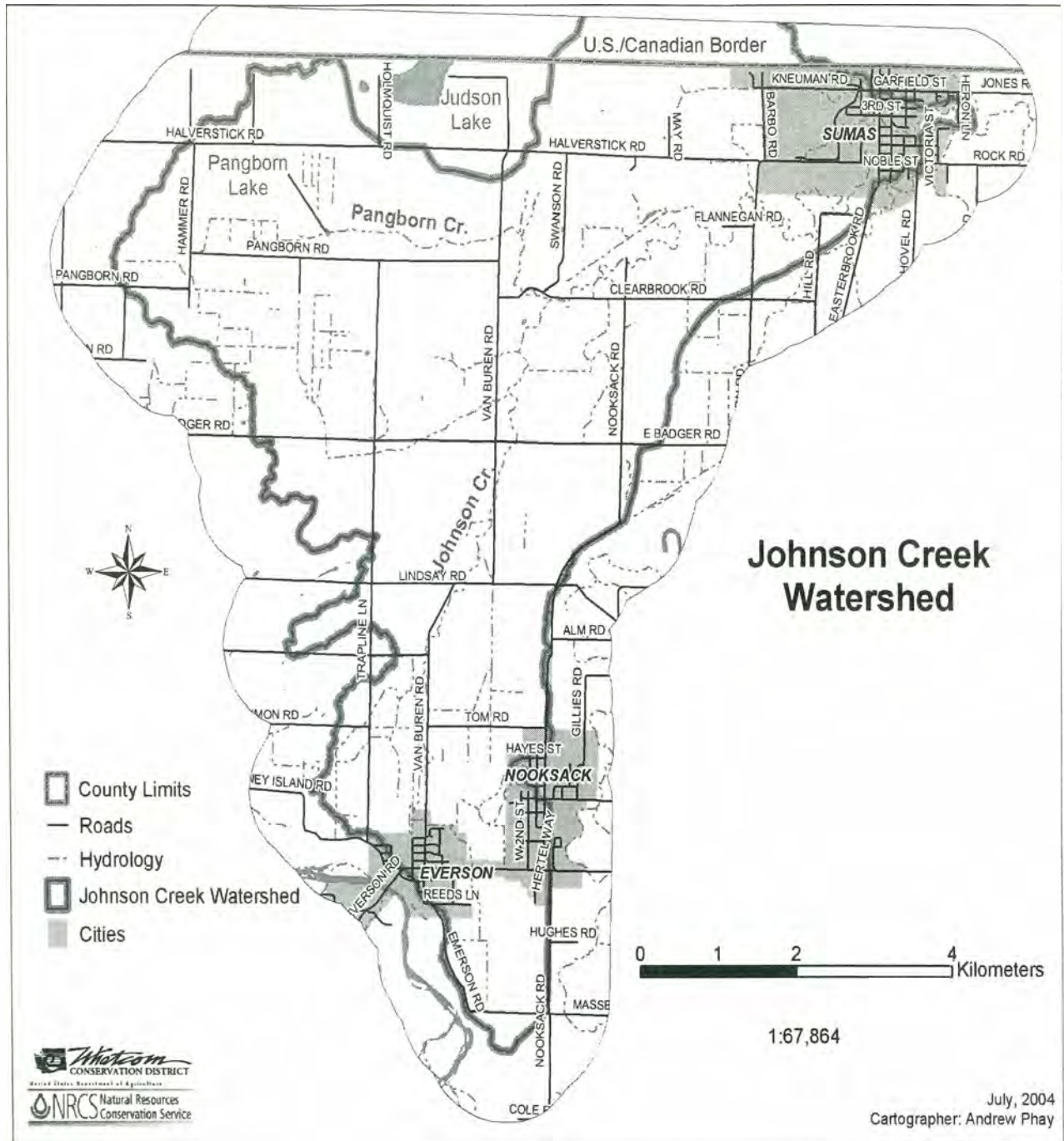
Figure 10. The Johnson Creek watershed in the Abbotsford-Sumas aquifer (courtesy of A. Phay, Whatcom Conservation District, 2004).
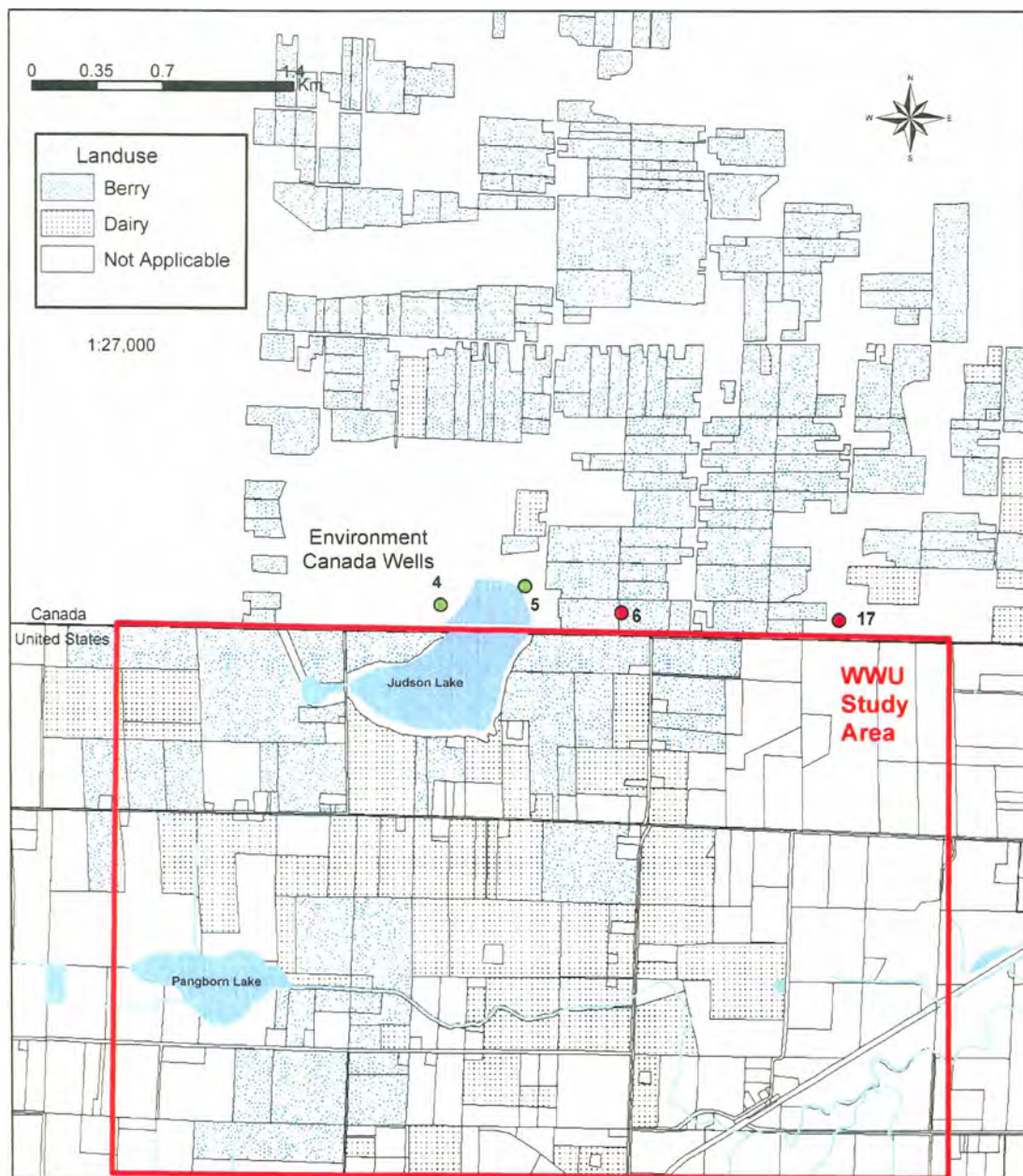
Figure 11. Land use in the Western Washington University study area and Environment Canada sites in the Abbotsford-Sumas aquifer. Land use is designated as Berry for raspberry and blueberry farms, Dairy for pasture and corn crops, and Not Applicable for residential dwellings, forests, and other. Note that only berry farming information is included for Canada, no information regarding poultry farming versus the designation of Not Applicable was provided. Land use data for Washington was provided by the Whatcom Conservation District and by Sumas City Planning for Canada. In addition to land use, four Environment Canada wells are shown. Wells 4 and 5 are shown in green indicating shallow depths (<10 m) and wells 6 and 17 are shown in red indicating deep depths (>10 m).
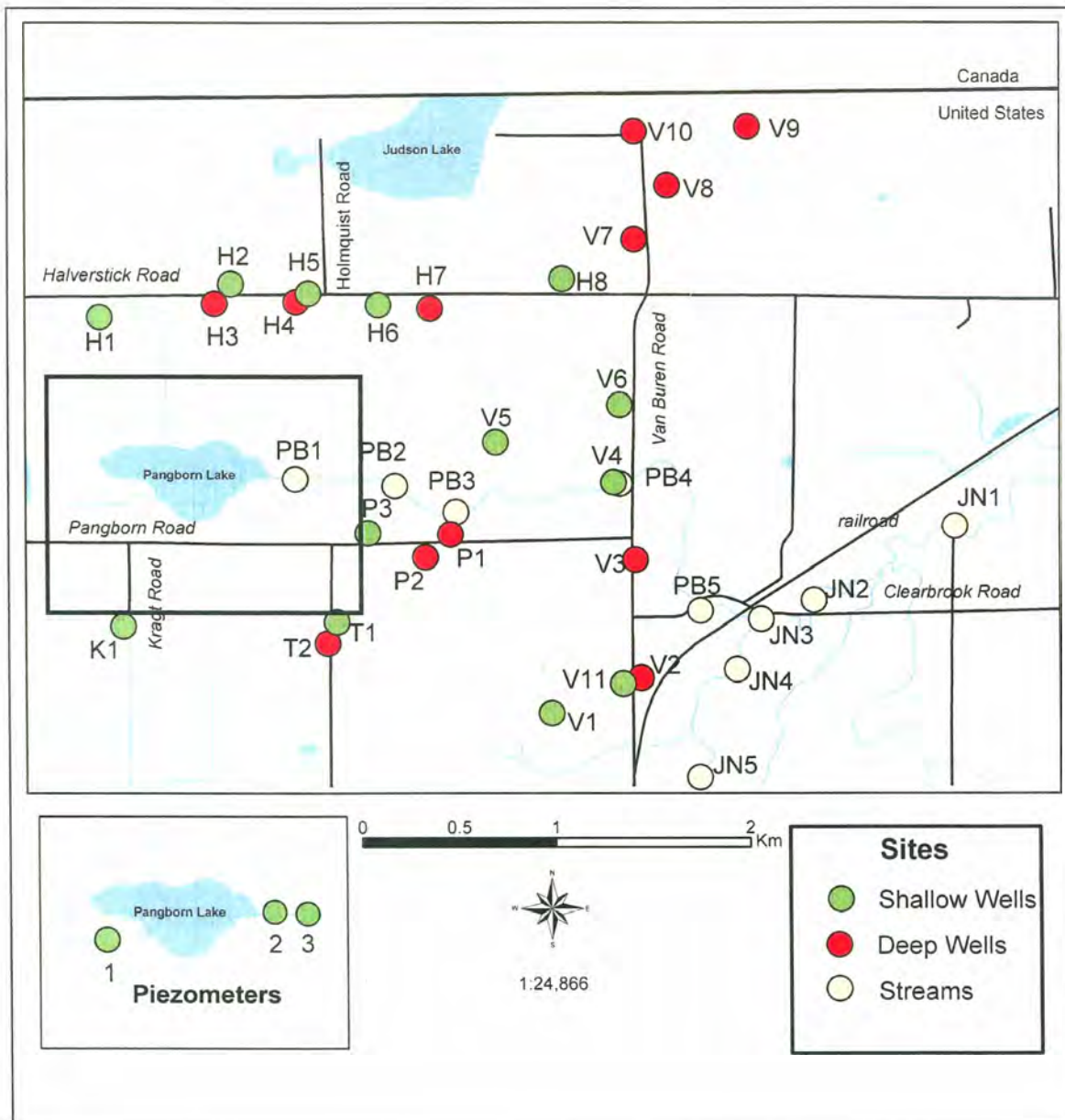
Figure 12. Sampling locations in the Western Washington University study area in the Abbotsford-Sumas aquifer.
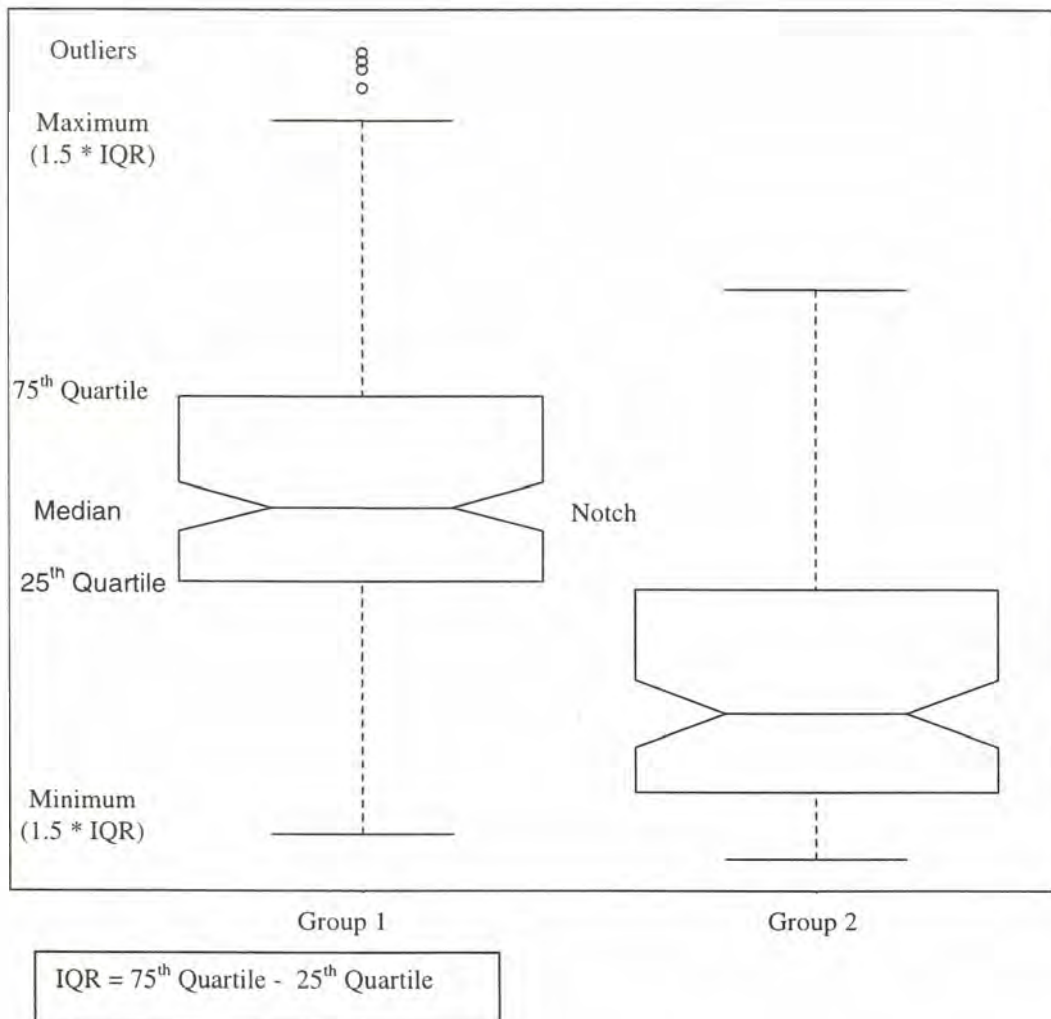
Figure 13. Description of notched boxplots. When notches overlap, the two groups are not significantly different. Group significance can also be measured by comparing the range of the notch for each group, or the confidence interval. Where overlap exists between the confidence intervals, overlap between notches will also occur, signifying that the groups are not significantly different. This diagram shows that Group 1 is significantly different from Group 2 because the notches do not overlap.
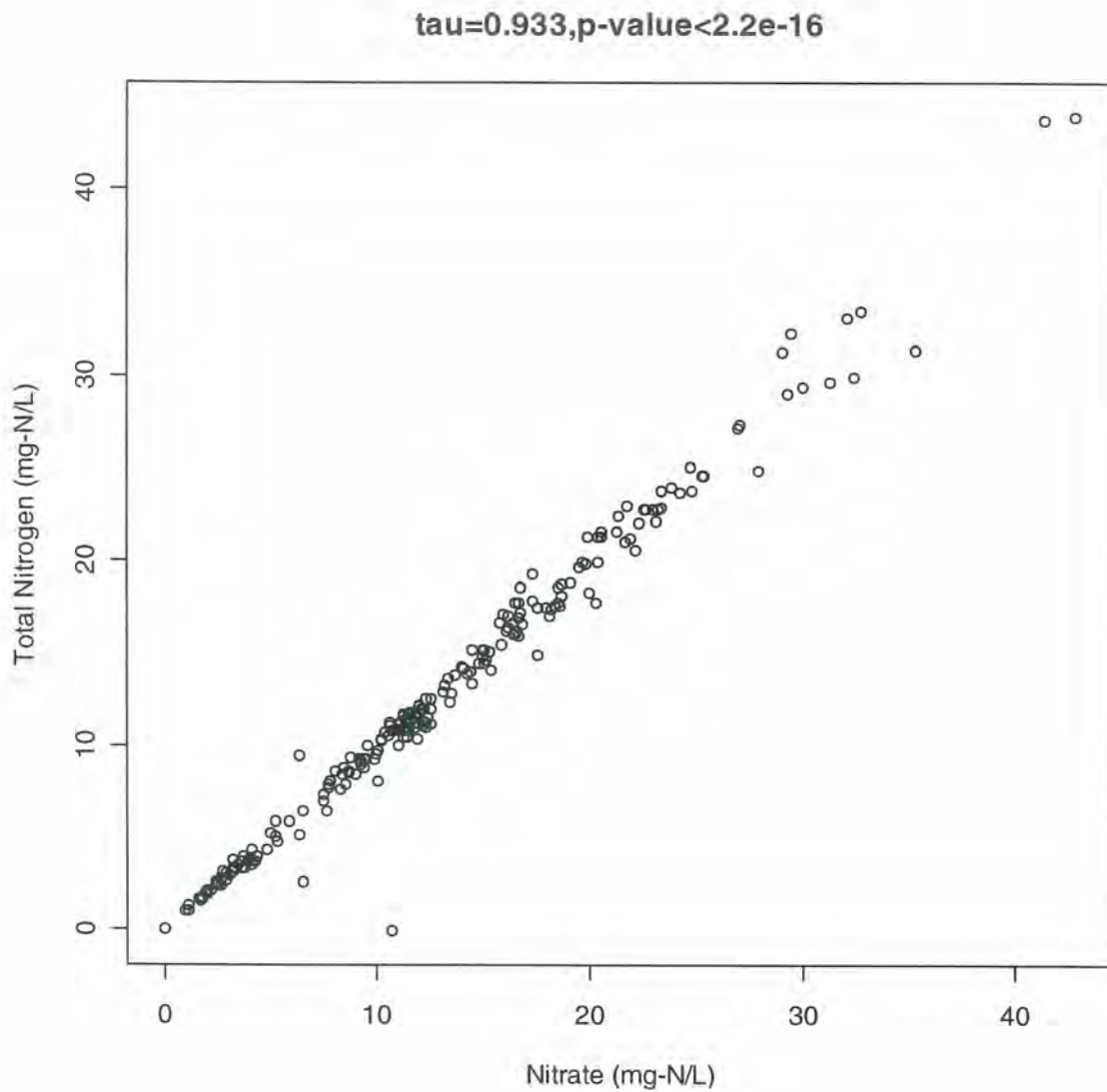
Figure 14. Correlation between well nitrate and well total nitrogen for the sampling period of July 2002 to June 2003. Kendall's tau correlation analysis indicates significance at a 95% level (Kendall's tau = 0.933 and p-value = 2.2e-16).
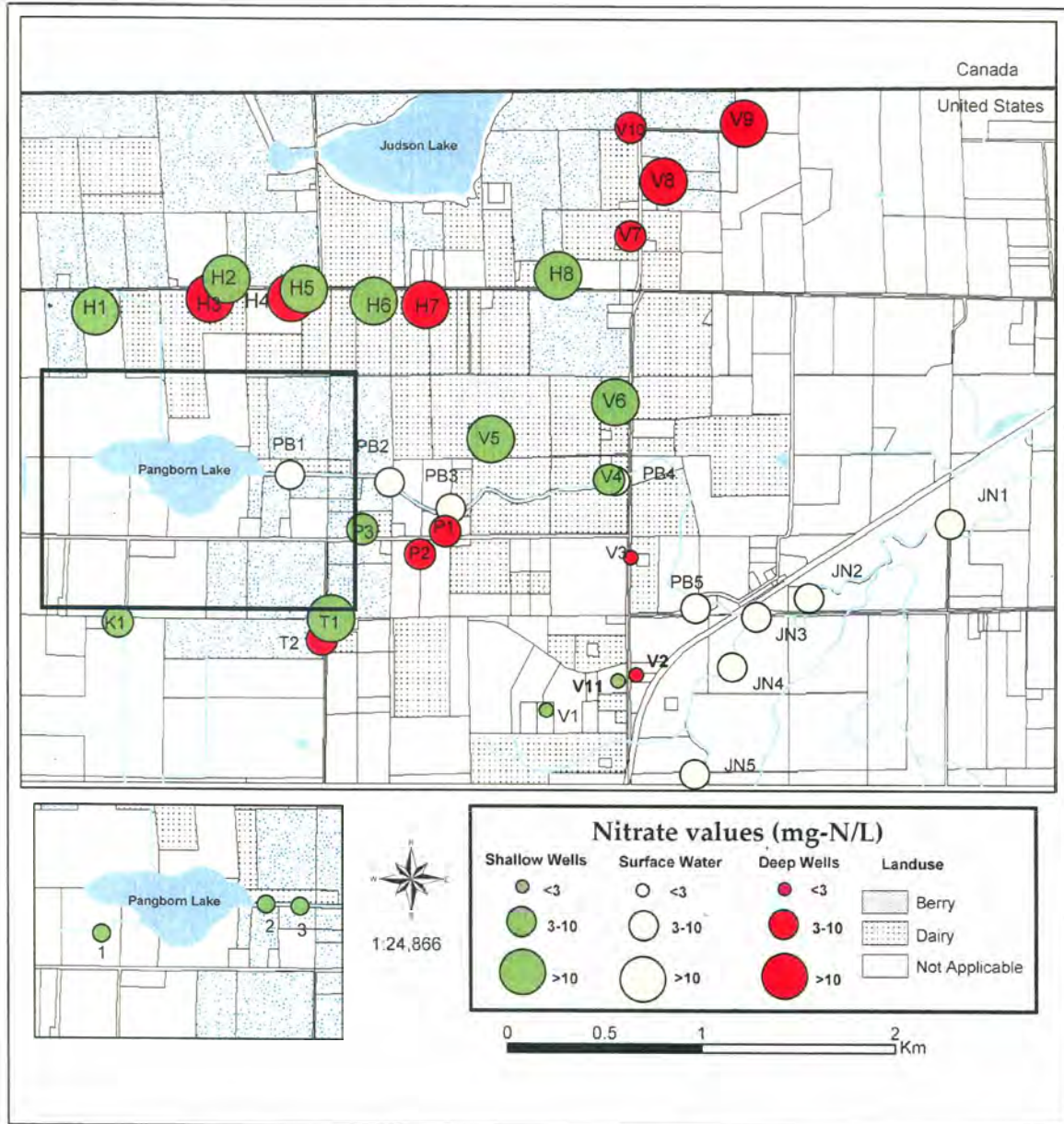
Figure 15. Land use and median nitrate magnitudes in the Western Washington University study area during the July 2002-June 2003 sampling period. Land use is designated as Berry for raspberry and blueberry farms, Dairy for pasture and corn crops, and Not Applicable for residential dwellings, forests, and other. Nitrate magnitudes are shown as graduated circles where values <3 mg-N/L are considered uncontaminated, values ranging from 3-10 mg-N/L have anthropogenic contamination, and values >10 mg-N/L exceed the EPA drinking water limit. Note that well H7 is assumed as a shallow well.
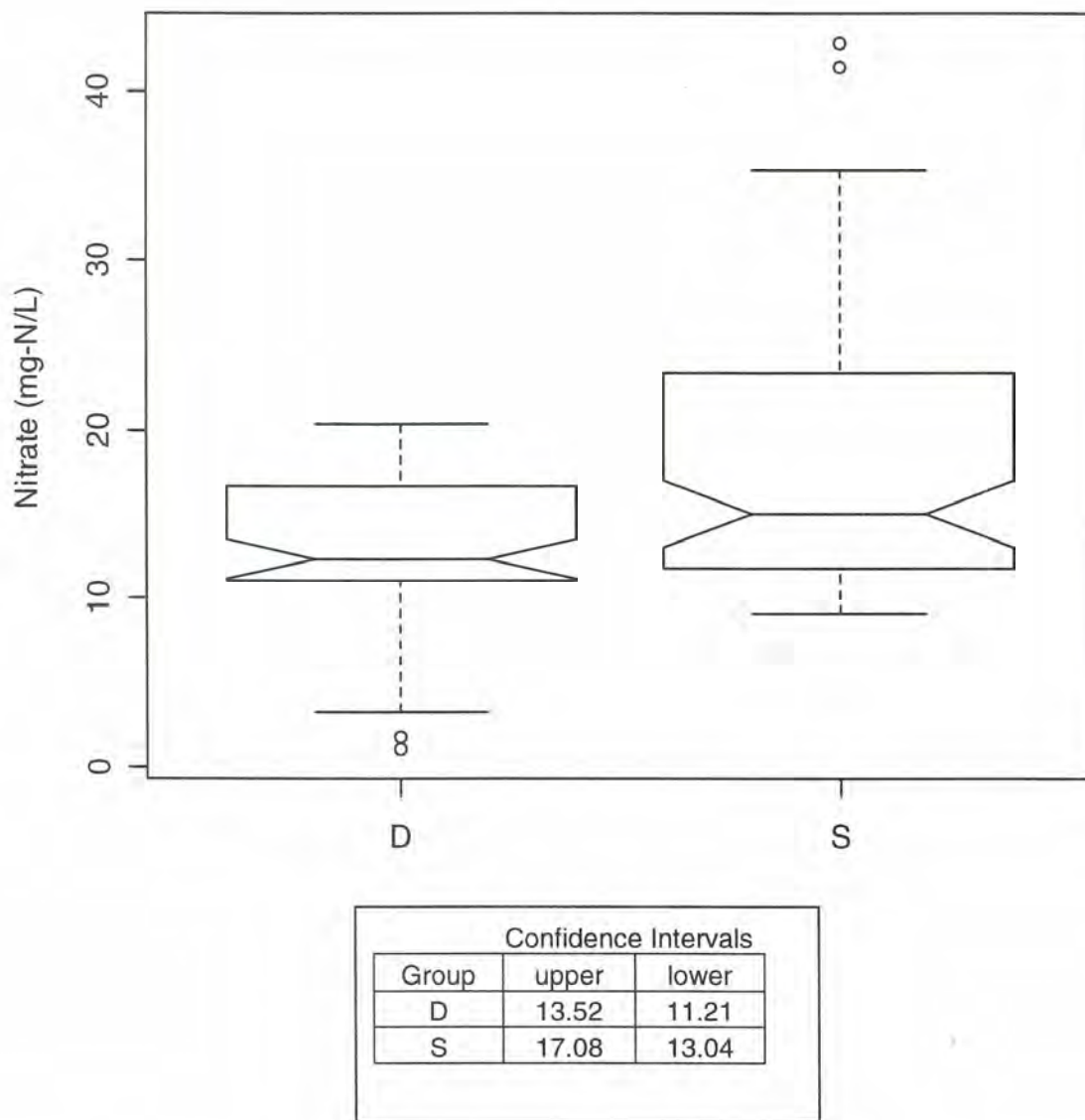
Figure 16. Shallow well versus deep well nitrate north of Pangborn Creek in the Abbotsford-Sumas study area. The confidence intervals for the notches indicate that the groups not are significantly.
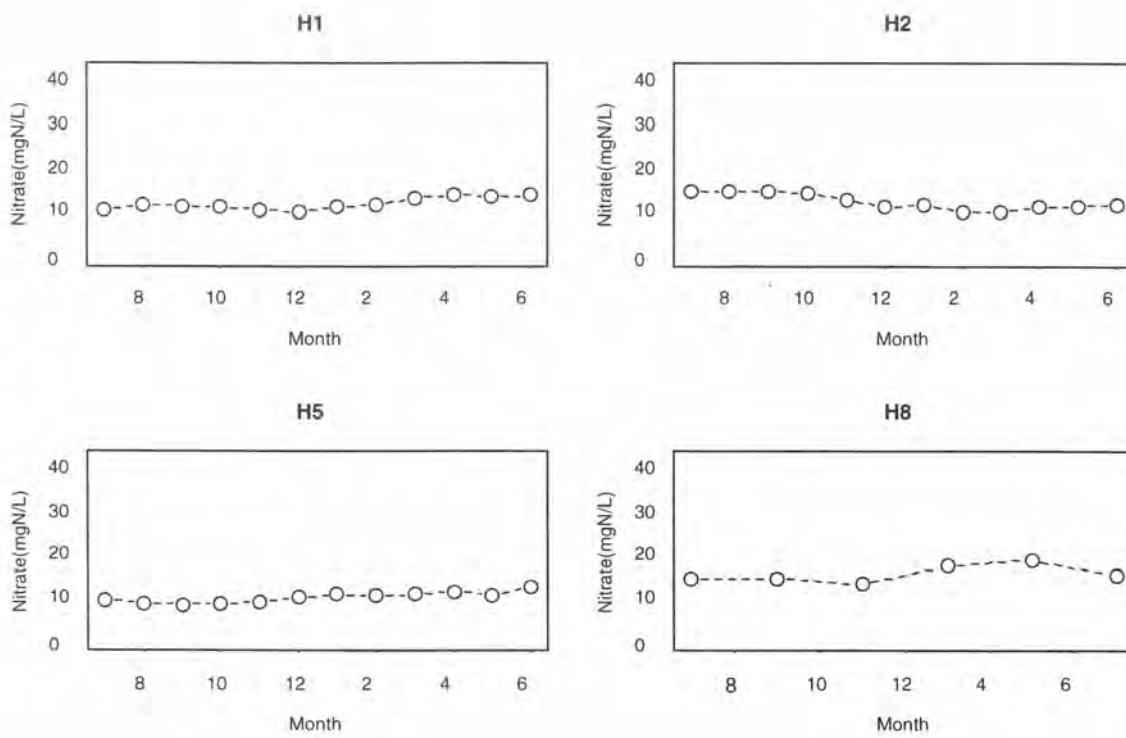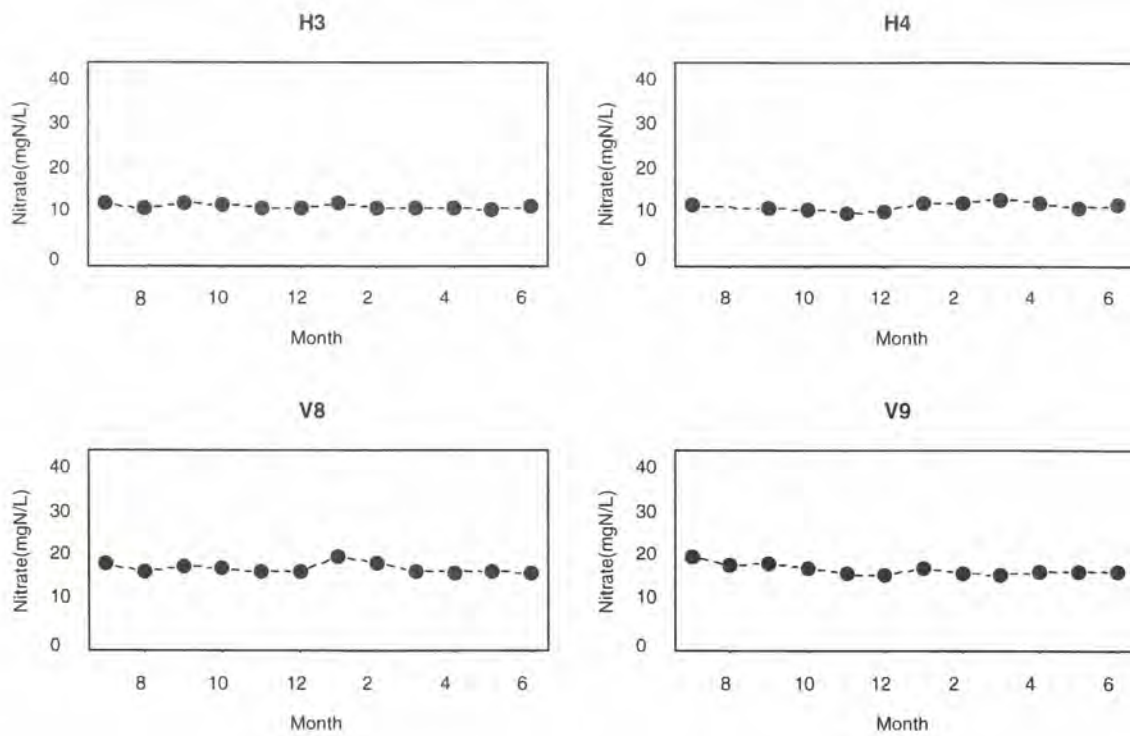
Figure 17. Shallow well nitrate >10 mg-N/L located north of the peatlands from July 2002 through June 2003.
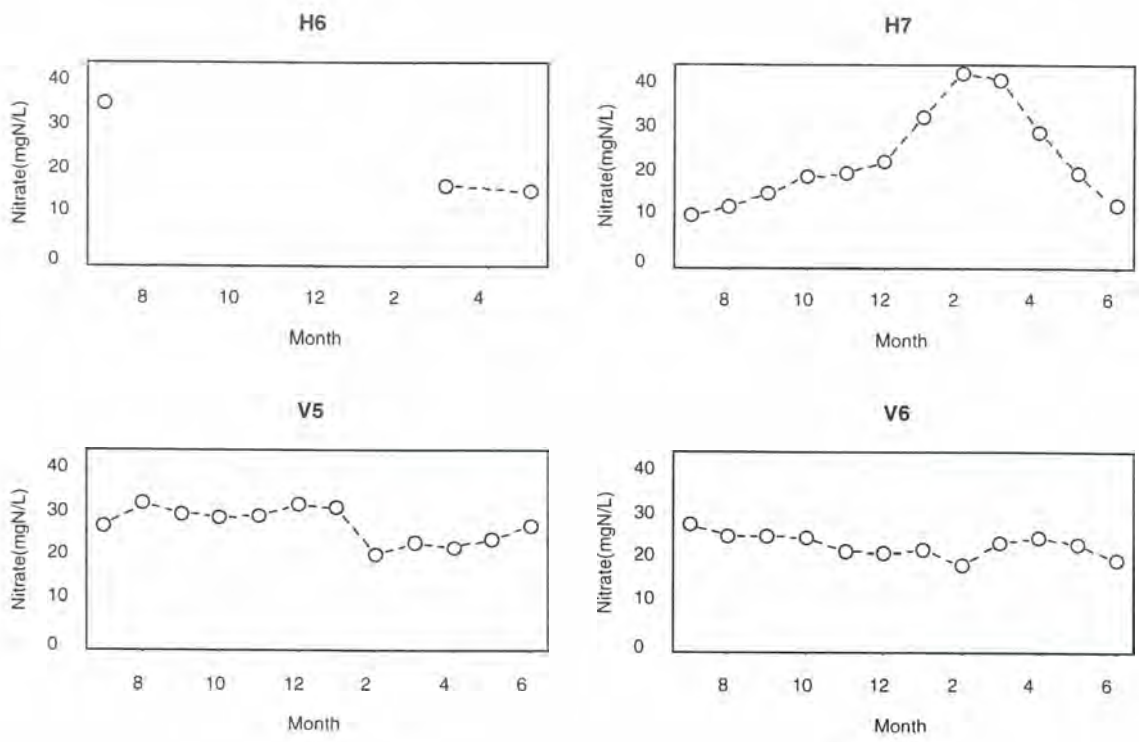
Figure 18. Shallow wells located north of the peatlands with nitrate >10 mg-N/L and temporal variation from July 2002 through June 2003. Well H6 had limited data collection.
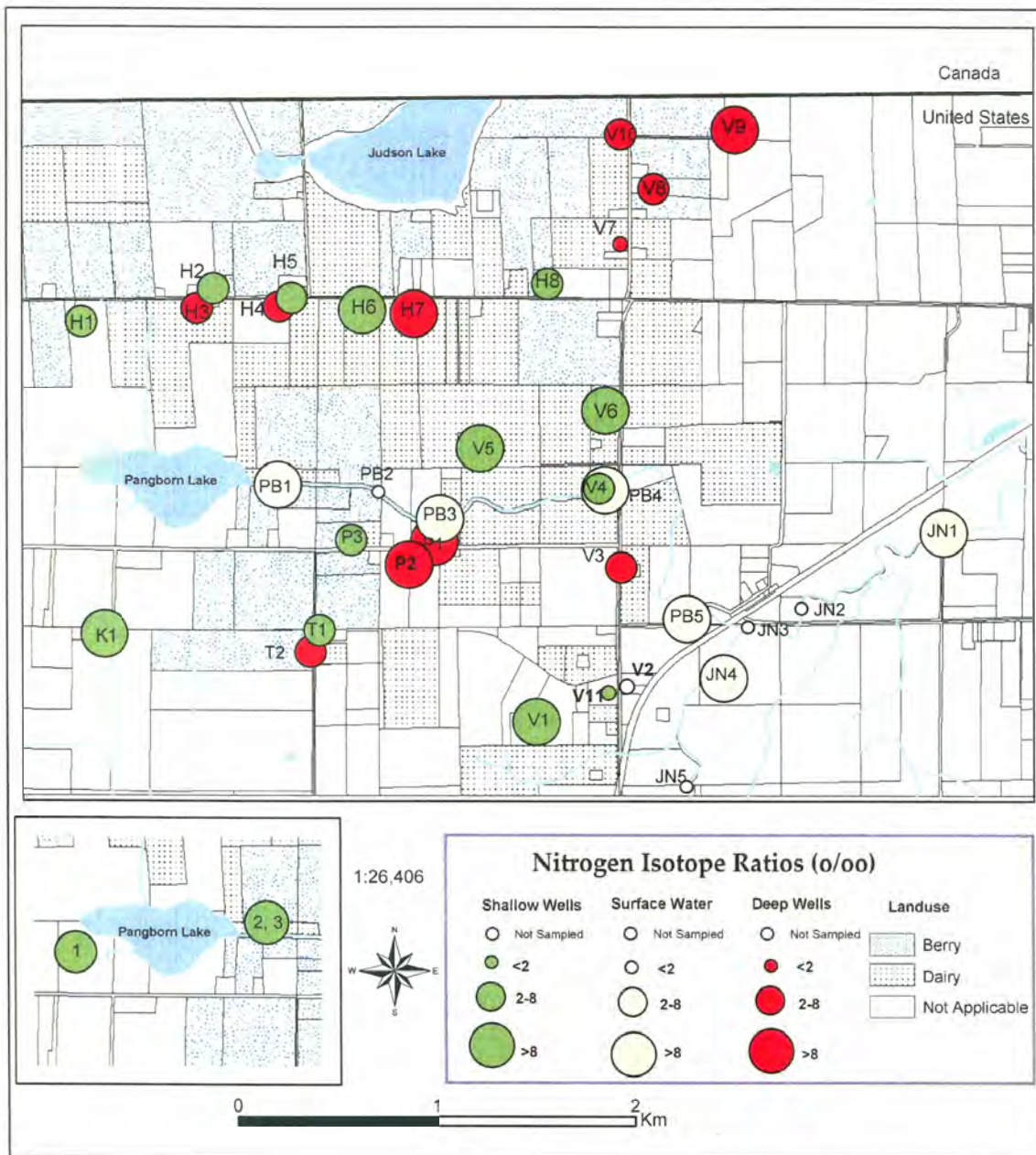
Figure 19. Land use and median nitrogen isotope ratios in the Western Washington University study area during the July 2002-June 2003 sampling period. Land use is designated as Berry for raspberry and blueberry farms, Dairy for pasture and corn crops, and Not Applicable for residential dwellings, forests, and other. Isotope ranges include <2 ‰ for inorganic commercial fertilizer, 2-8 ‰ for mixed fertilizer, and >8 ‰ for manure. Note that well H7 is assumed as shallow.
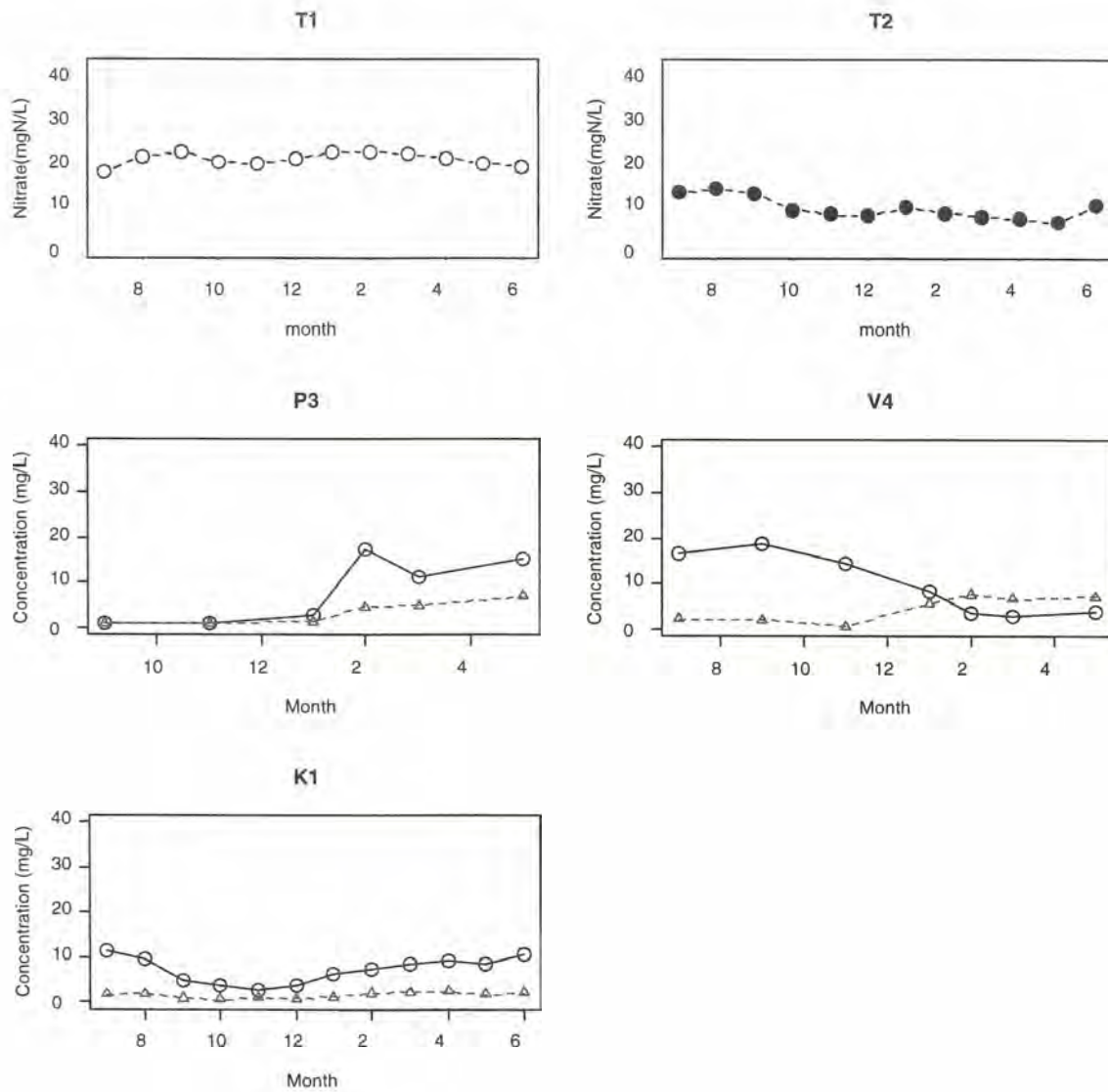
Figure 20. Two high nitrate wells, T1 and T2, south of the peatlands and three variable ground water nitrate wells both north and south of the peatlands from July 2002 through June 2003. The variable nitrate figures include well nitrate (circles) and dissolved oxygen (triangles) concentrations. Shallow well nitrate is depicted by open circles and deep well nitrate is depicted by closed circles.

93

Figure 21. Deep well nitrate >10 mg-N/L located north of the peatlands from July 2002 through June 2003.
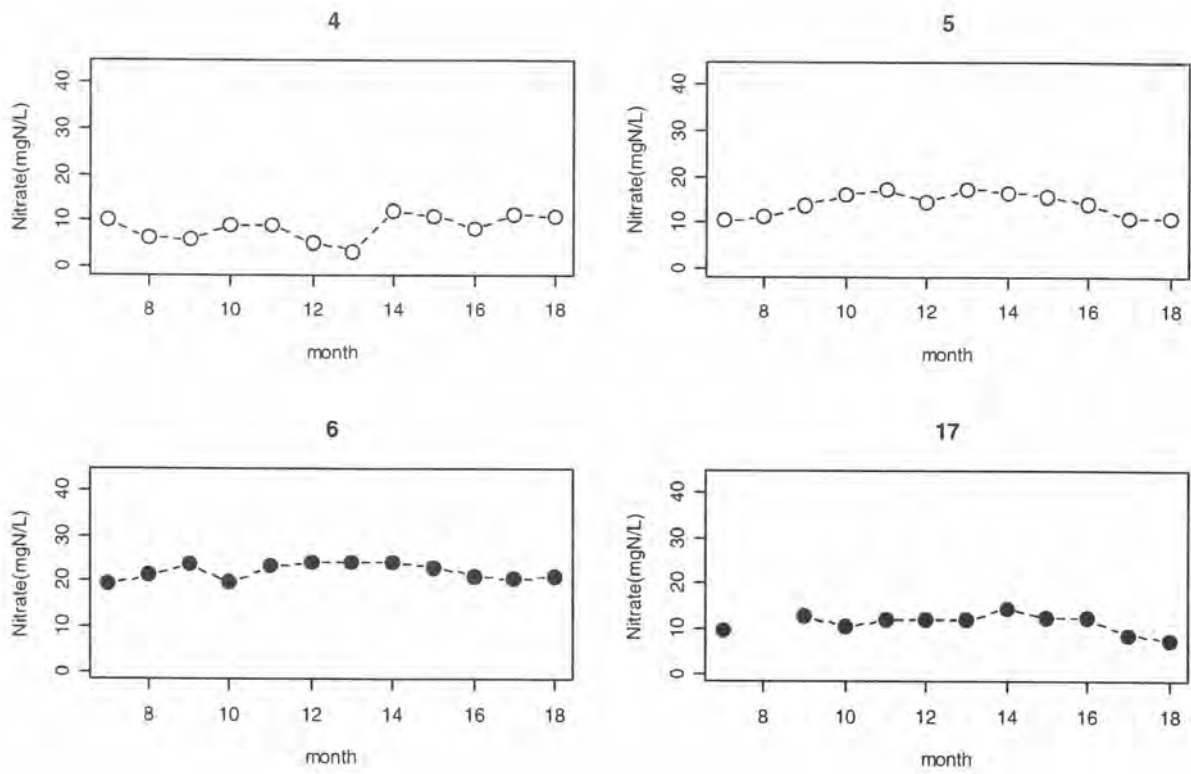
Figure 22. Temporal shallow (open circles) and deep (closed circles) well nitrate from four Canadian wells located north of the study area. See Figure 11 for spatial location. Data was provided by Hii *et al.*, 1999.

95
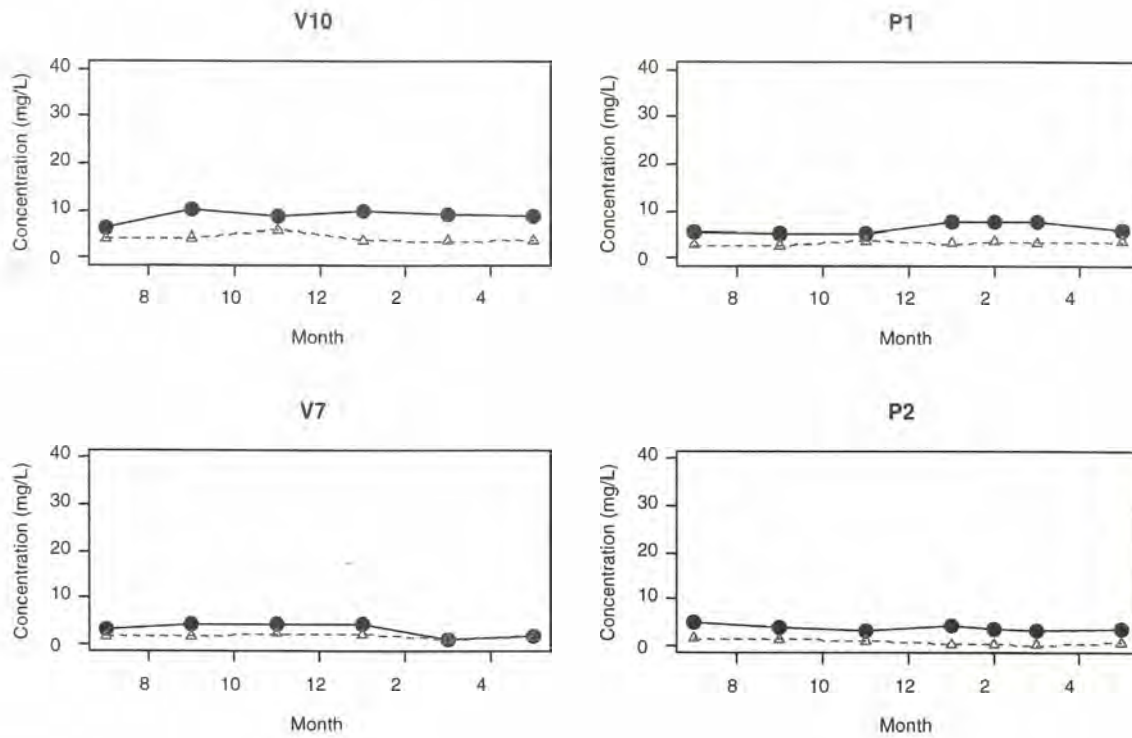
Figure 23. Four deep wells located both north (V10 and V7) and south (P1 and P2) of the
peatlands with ground water-nitrate ranging from 3-10mg-N/L. Each diagram includes well
nitrate (circles) and dissolved oxygen (triangles) trends from July 2002 through June 2003.

Confidence Intervals		
Group	upper	lower
N	17.08	13.04
S	12.18	4.35
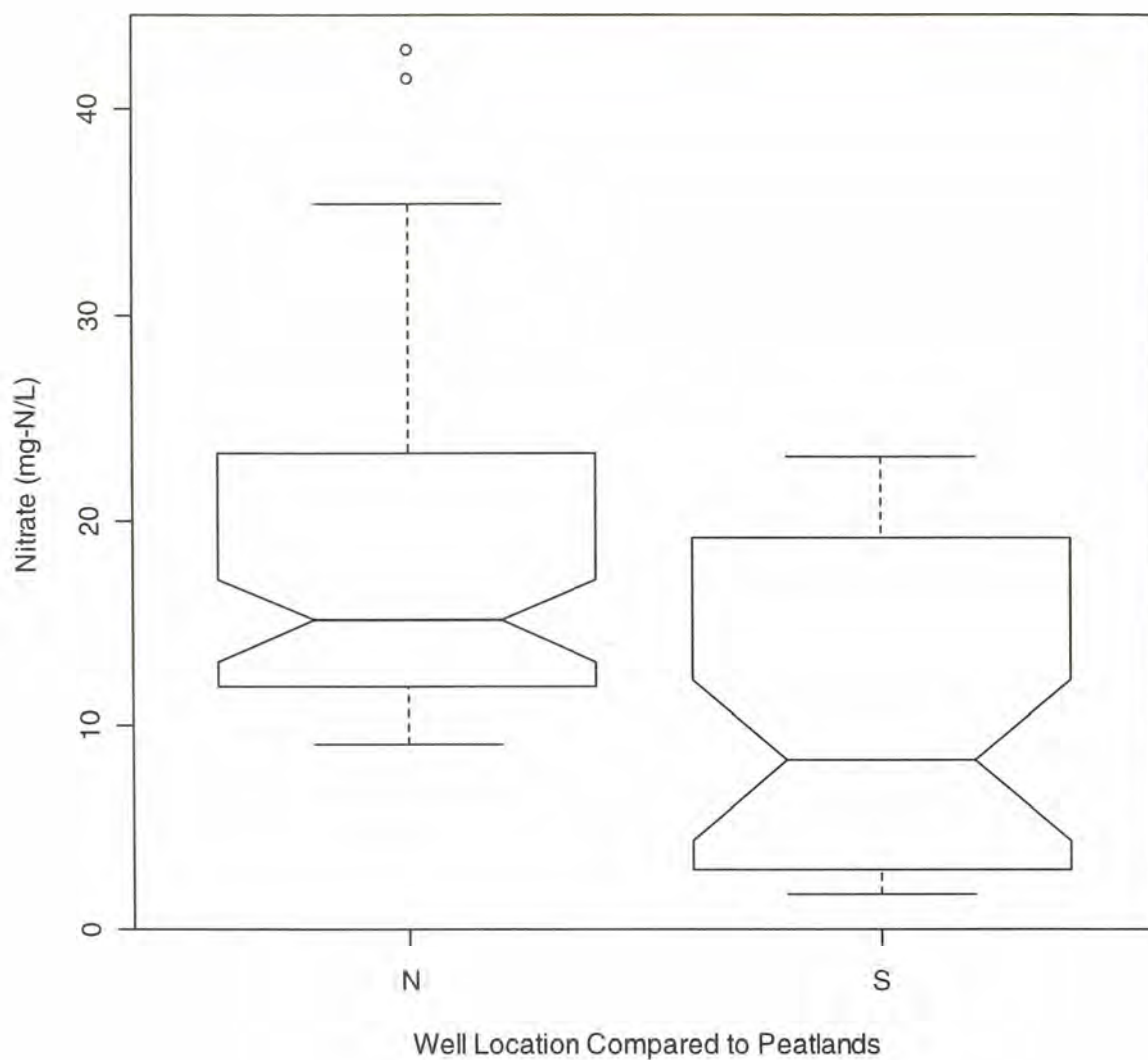
Figure 24. Shallow well nitrate for wells located north of the peatlands (N) and south of the peatlands (S). The confidence interval (CI) for the notches indicates that the groups are significantly different. The outliers are from well H7.
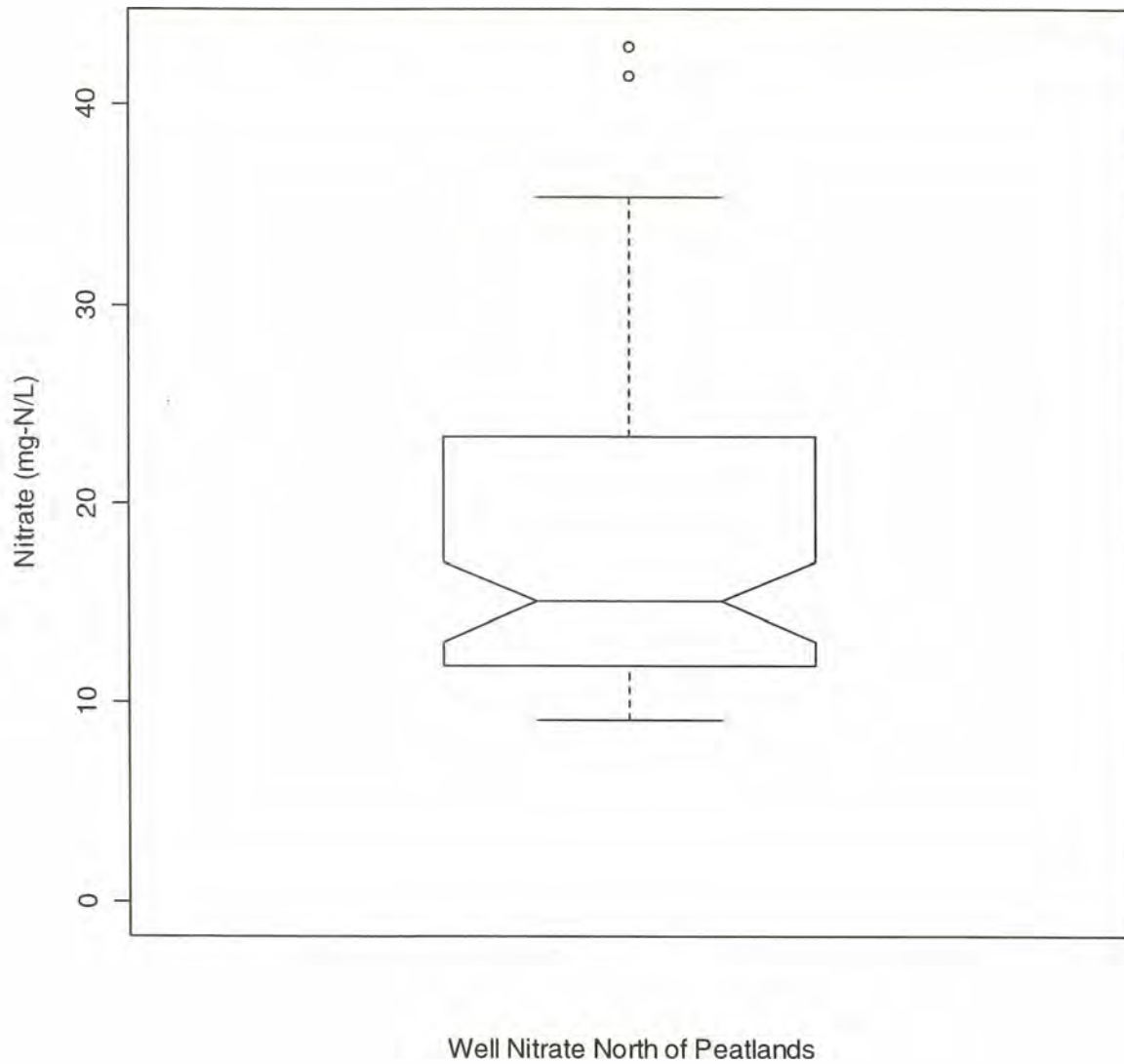
Figure 25. Variability for shallow well nitrate north of the peatlands from samples collected from July 2002 to June 2003. The median value is 15.47 mg-N/L.
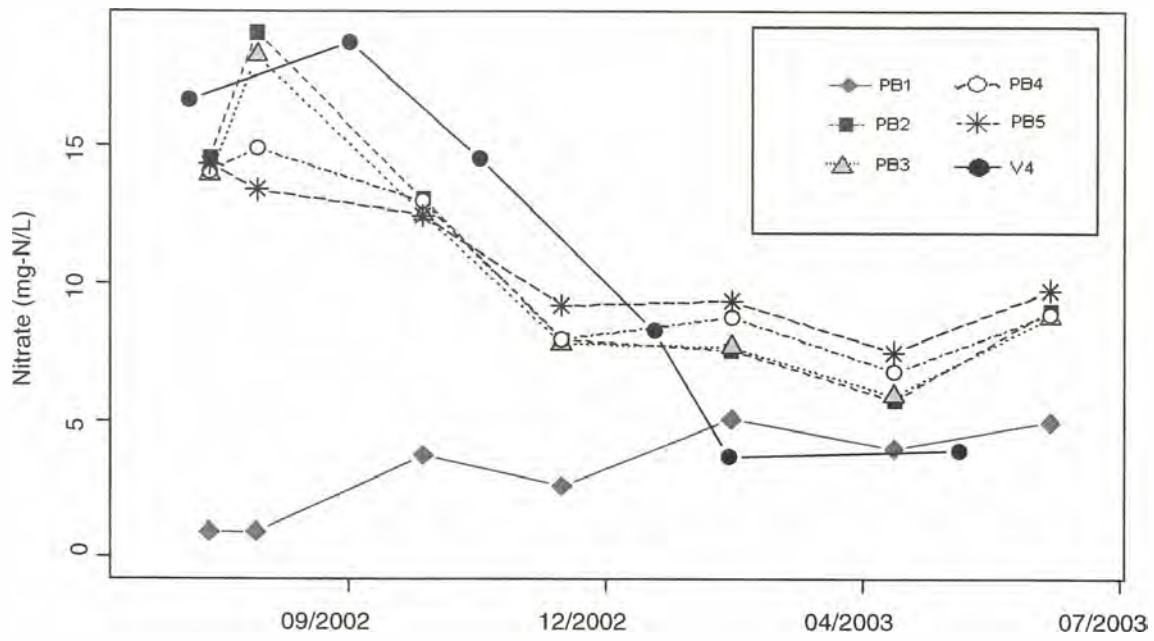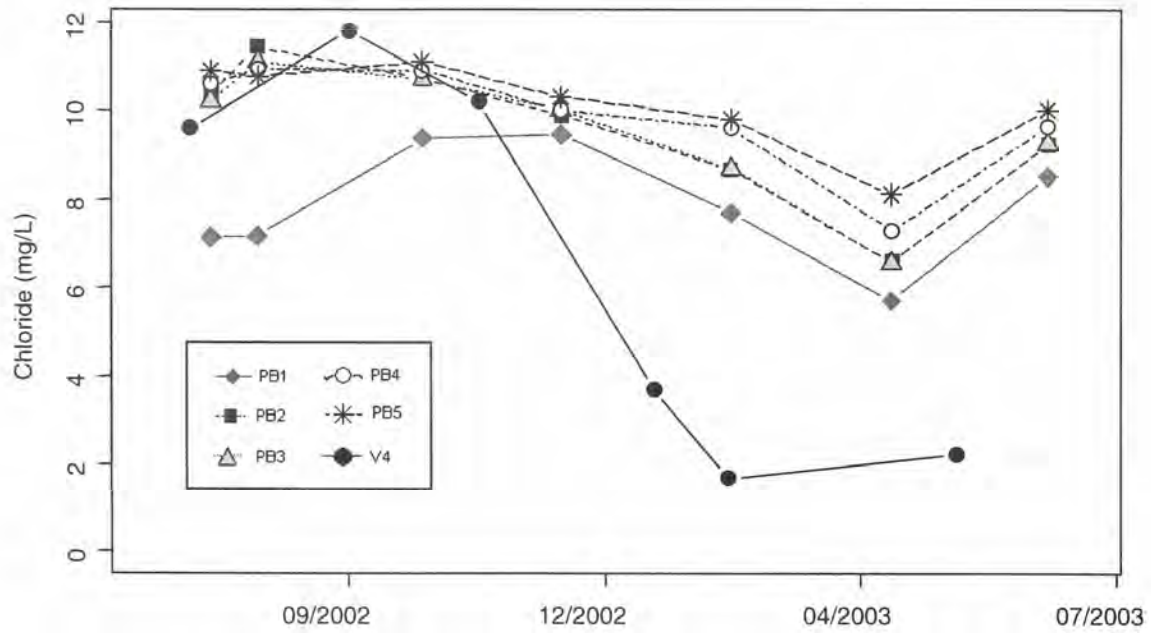
Figure 26. Temporal nitrate trends for stream sites along Pangborn Creek (PB1-PB5) and shallow well site V4 from July 2002 through June 2003.
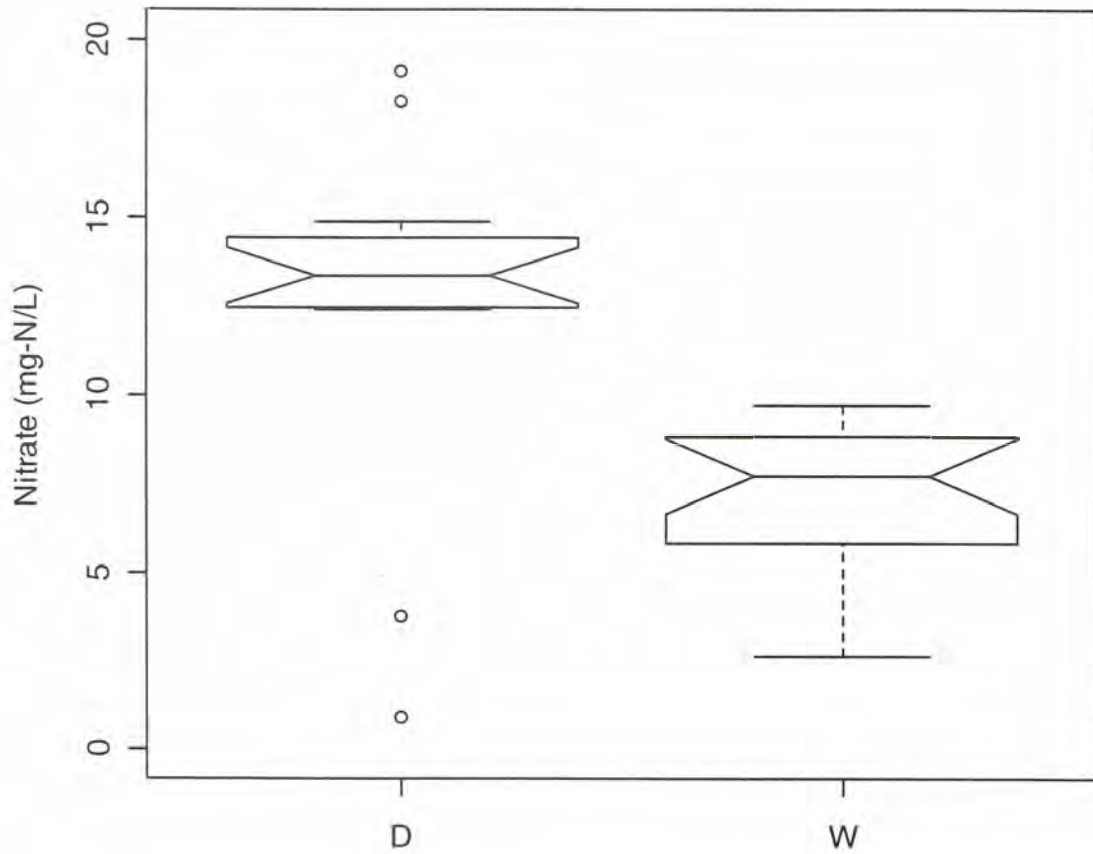
Confidence Intervals		
Group	upper	lower
D	14.17	12.58
W	8.81	6.70

Figure 27. Pangborn Creek nitrate during the dry (June-October 2002) and wet (November-June 2003) seasons. The confidence intervals for the notches indicate that the groups are significantly different.
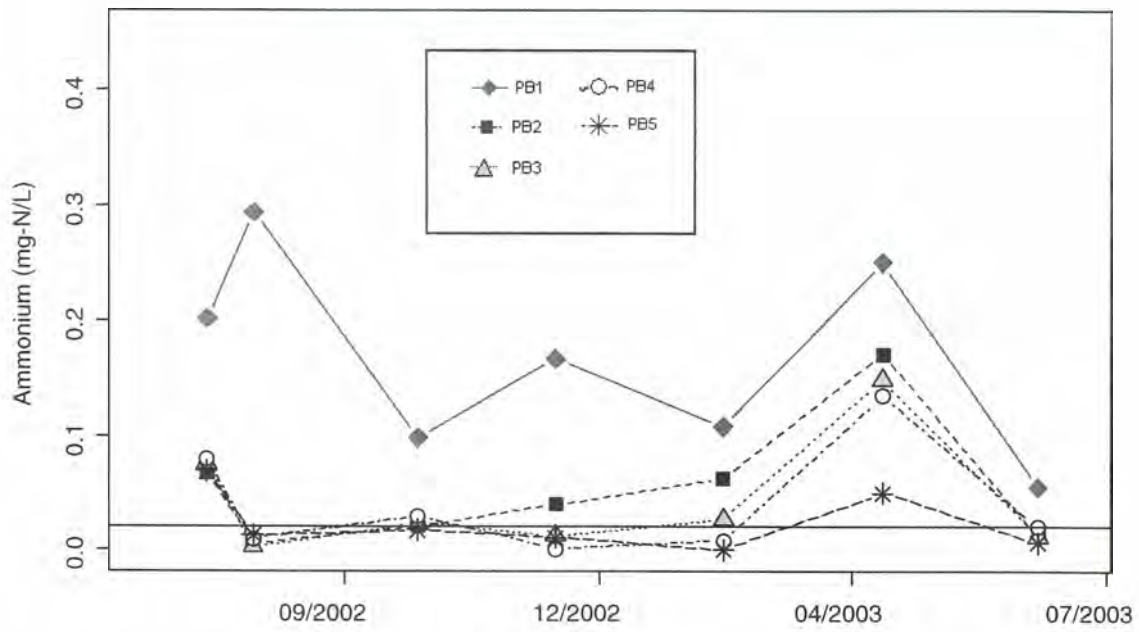
Figure 28. Temporal ammonium trends for stream sites along Pangborn Creek (PB1-PB5) from July 2002 through June 2003. Some values were below the detection limit (0.02 mg-N/L).

Figure 29. Temporal chloride trends for stream sites along Pangborn Creek (PB1-PB5) and shallow well V4 from July 2002 through June 2003.
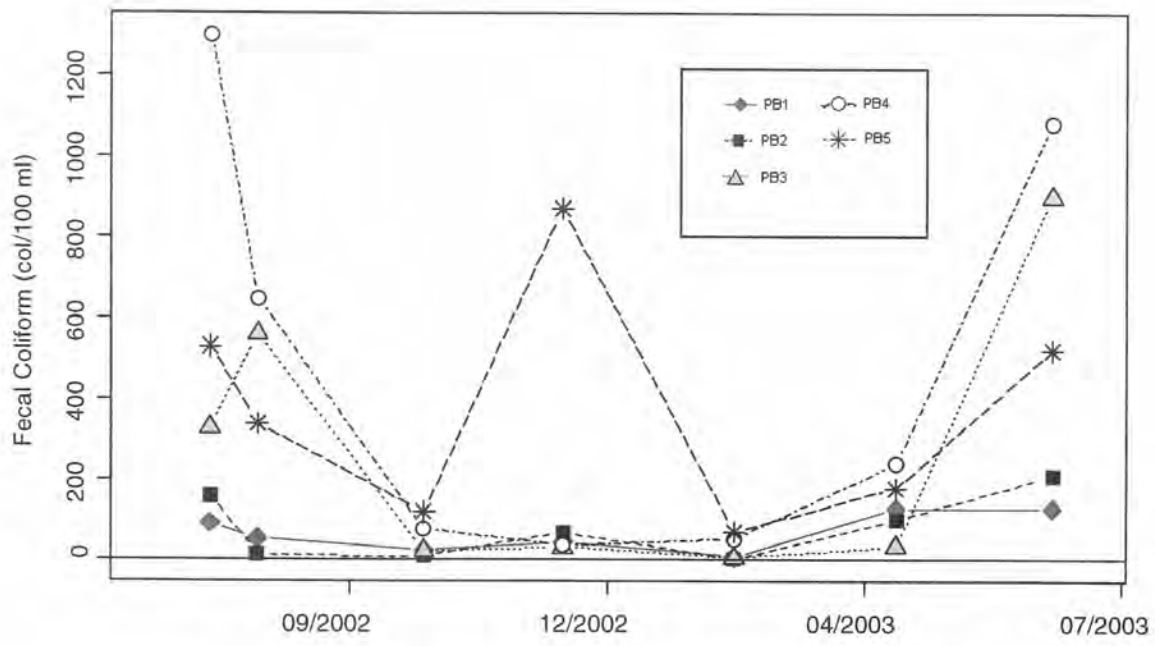
Figure 30. Temporal fecal coliform trends for stream sites along Pangborn Creek (PB1-PB5) from July 2002 through June 2003.
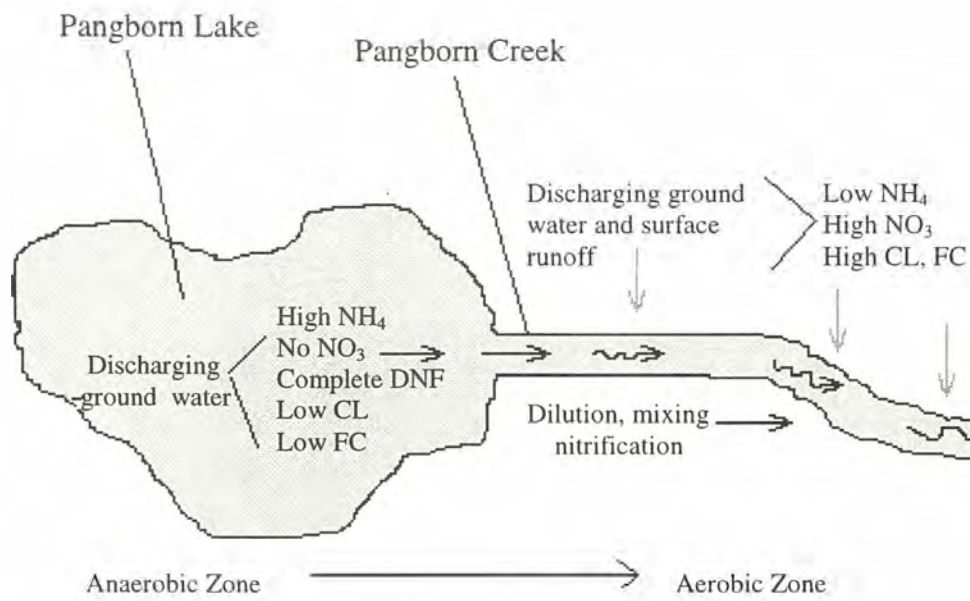
Figure 31. A top view of Pangborn Lake and Pangborn Creek. Ammonium is abbreviated as NH4, nitrate as NO3, denitrification DNF, chloride as CL, and fecal coliform as FC.
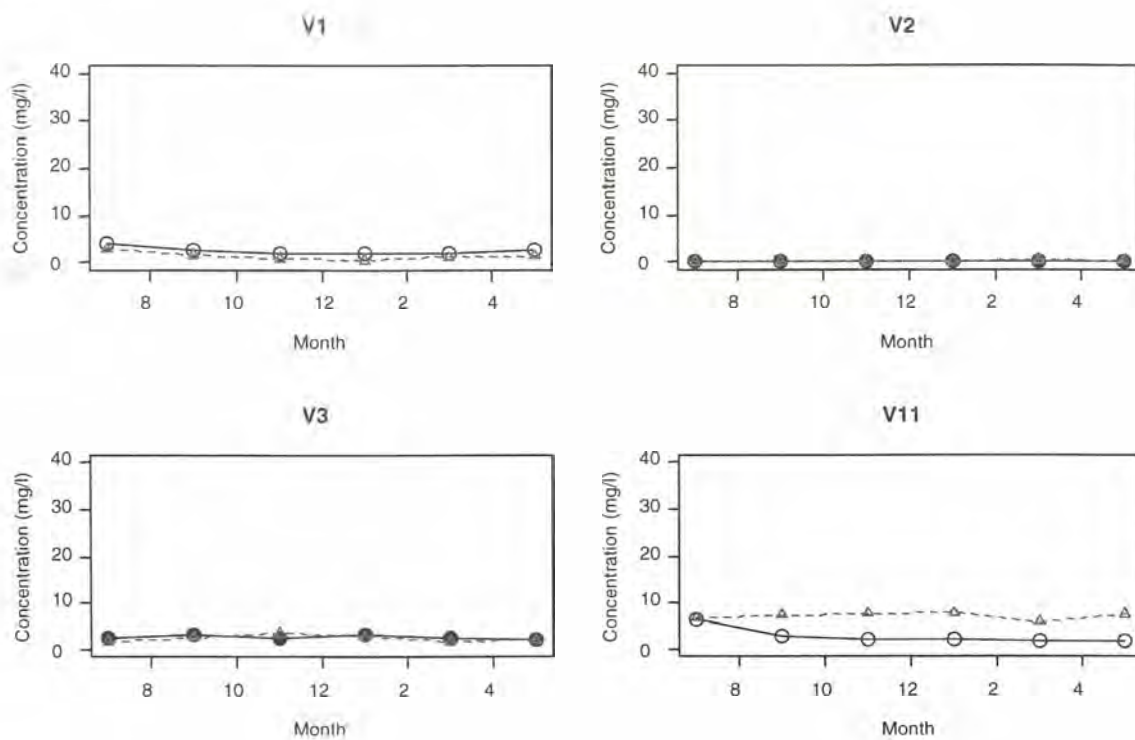
Figure 32. Four shallow (V1 and V11) and deep (V2 and V3) wells with nitrate values <3 mg-N/L over time located south of the peatlands. Each diagram includes well nitrate (circles) and dissolved oxygen (triangles) trends from July 2002 through June 2003.
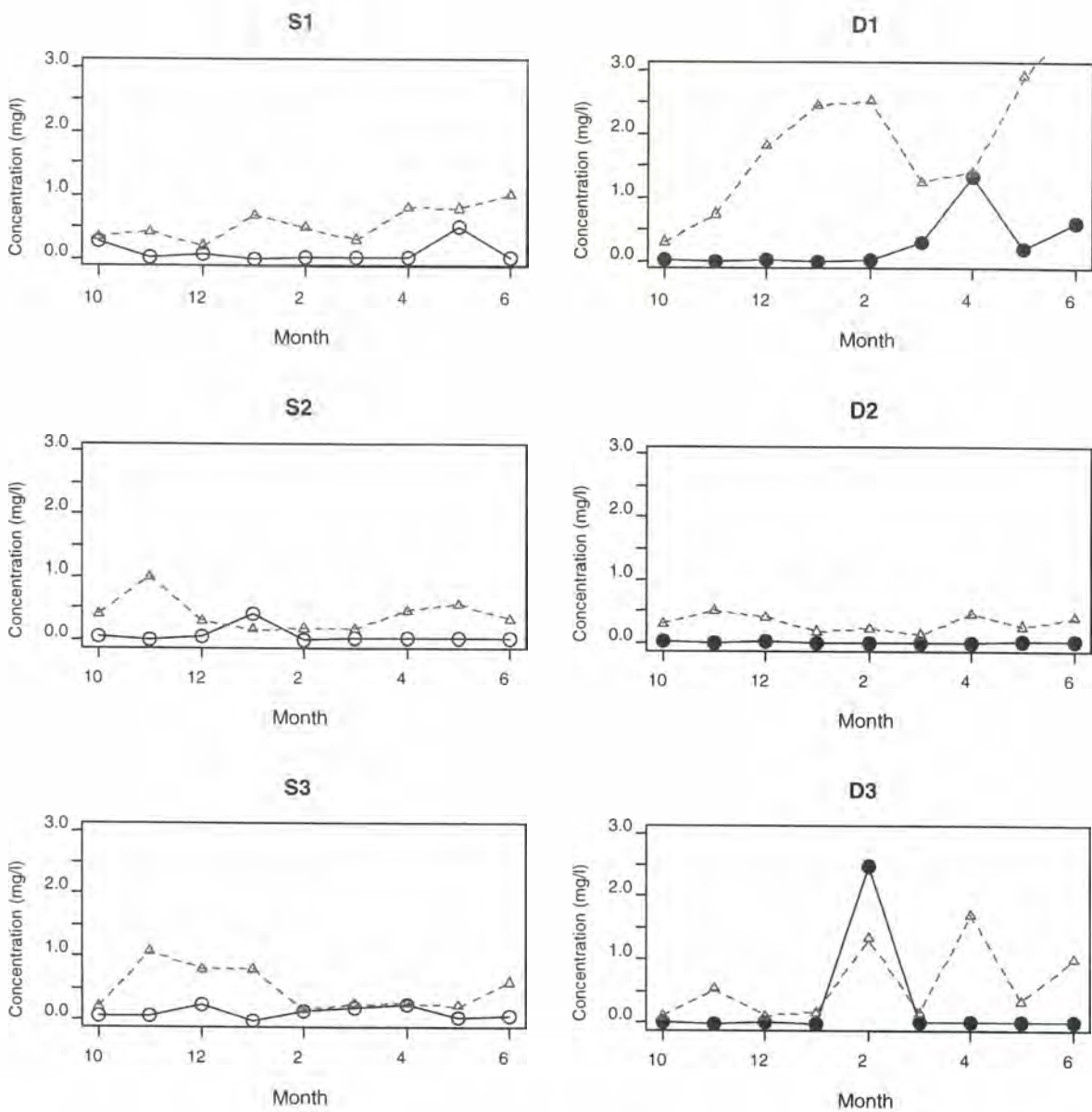
Figure 33. Piezometer nitrate and dissolved oxygen trends over time for both shallow and deep piezometers from October 2002 through June 2003. Nitrate is depicted by circles and dissolved oxygen by triangles.
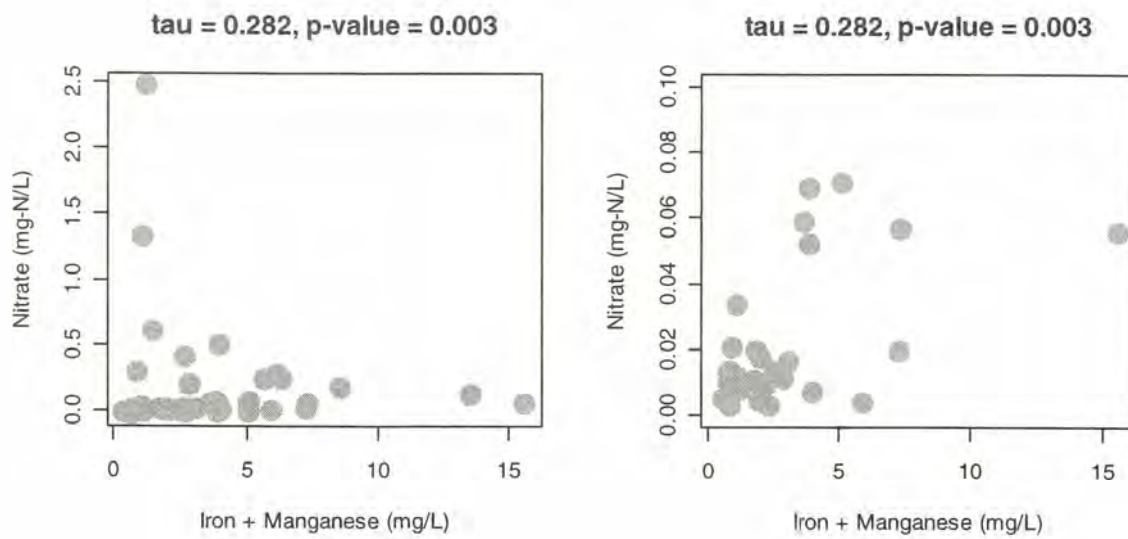
106

Figure 34. Correlation among piezometer nitrate, iron, and manganese. The diagram on the left is shown with outliers and the one on the right is without outliers. Kendall's tau correlation analysis indicates significance at a 95% level (Kendall's tau=0.282 and p-value=0.003).
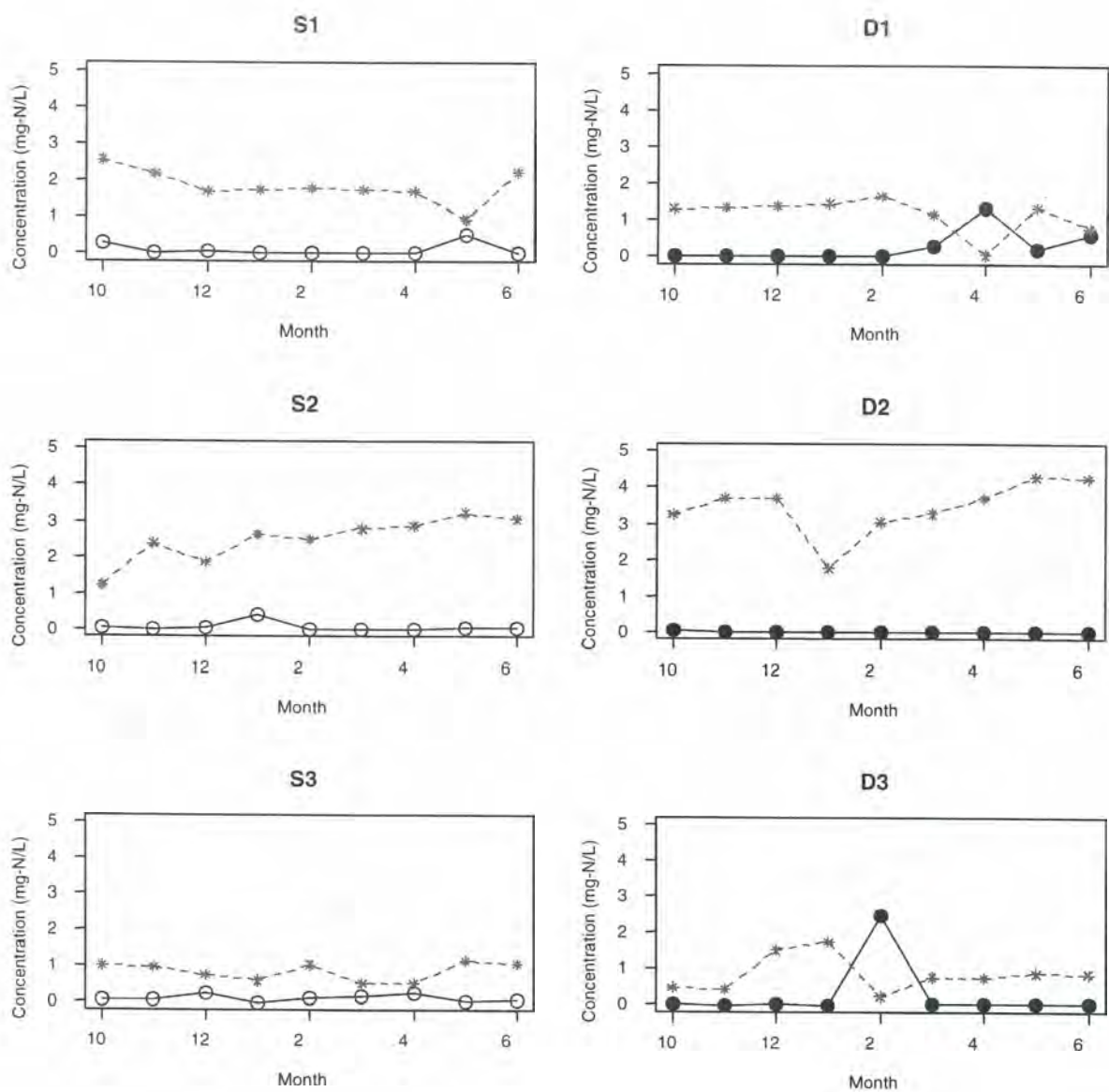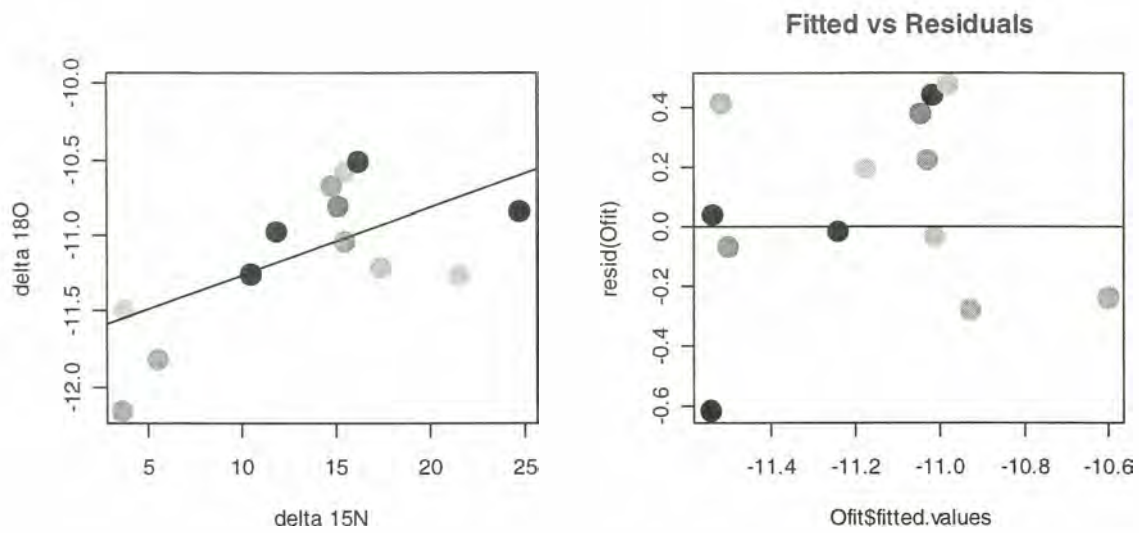
Figure 35. Piezometer ammonium (stars) and nitrate (circles) over time from October 2002 through June 2003.

Data	Regression Equation	X Value	p-value	R squared value	Error Bars
Delta 18O	Y=0.045X - 11.71	Delta 15N	0.0088	0.3776	± 0.06

Figure 36. Linear regression and fitted versus residuals plot for δ^{15}N and δ^{18}O for sites S1, S2, S3, P1, P2, P3, and V4. The values for each site are colored differently. Measurements are in per mil (‰).
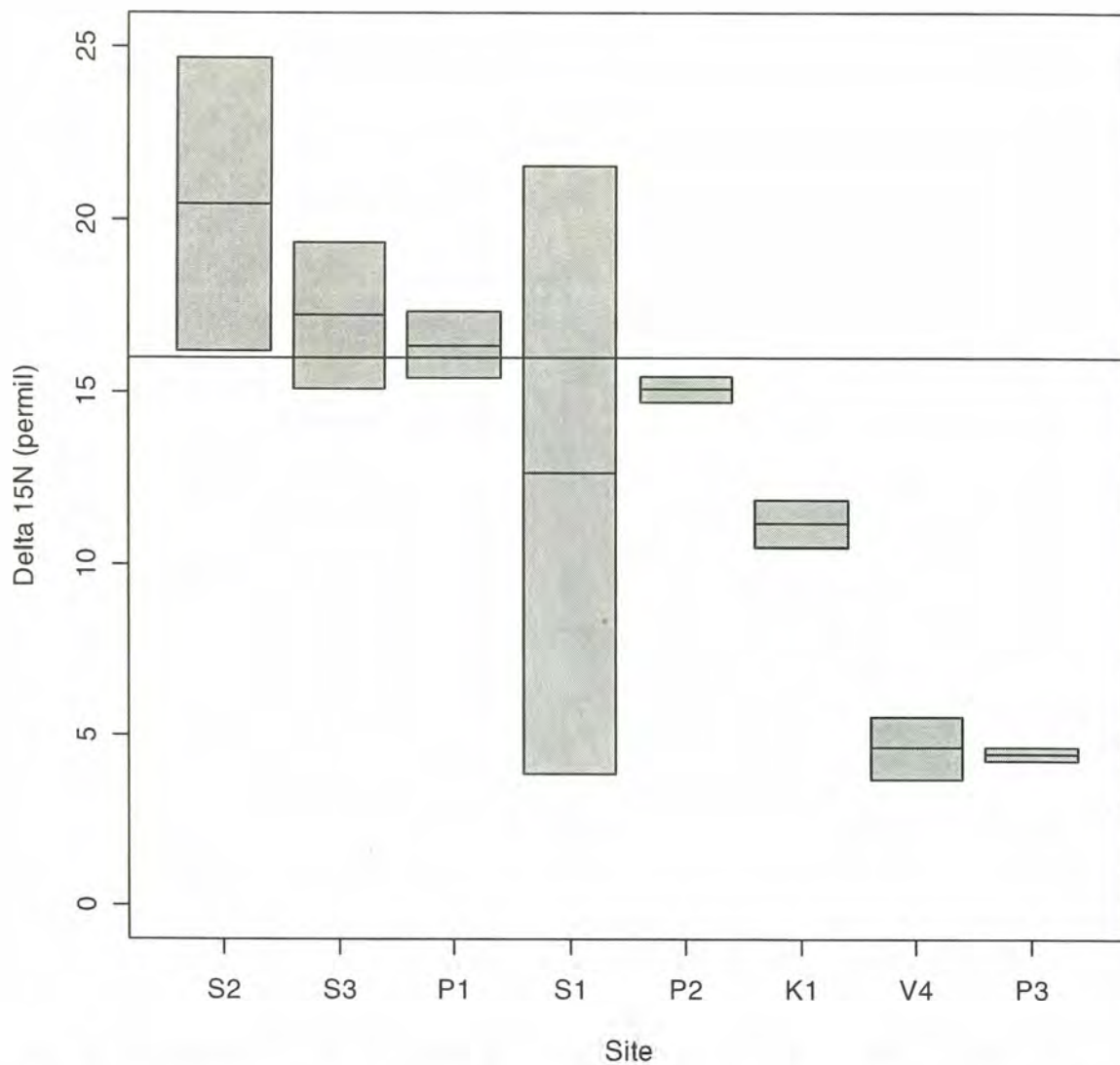
Figure 37. Boxplots of $\delta^{15}N$ values at well and piezometer sites. The magnitudes indicate the strength of denitrification at each site and the size of the box hinges indicates the variability between winter and spring measurements. The line at $\delta^{15}N=16\%o$ indicates that values above the line show denitrification (based on ranges by Wassenaar, 1995).
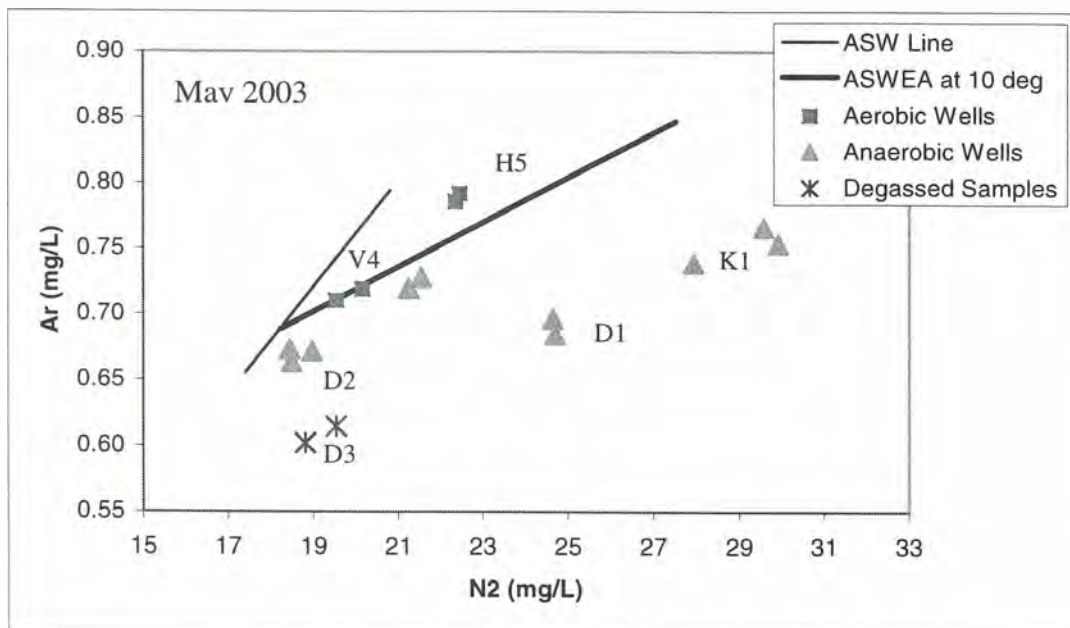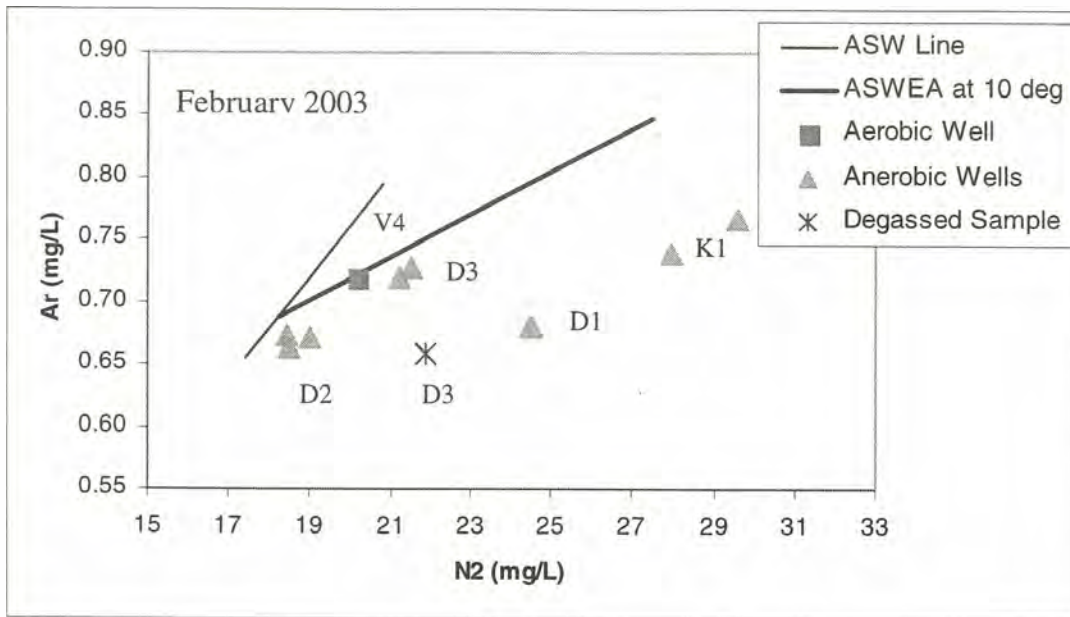
Figure 38. Ar-N_2 graph including the Air Saturated Water line (ASW), the Air Saturated Water plus Excess Air line (ASWEA), and data collected in February and May 2003 (listed in Table 6). The data are divided into aerobic, anaerobic, and degassed samples. The ASW line indicates the concentration of N_2 and Ar derived from air-water equilibration from 4-12 °C. The ASWEA line is the ASW line at 10 °C plus excess air ranging from 0 to 4 cc. The horizontal distance between each anaerobic data point and the ASWEA indicates the amount of non-atmospheric N_2 (Tesoriero et al., 2000).

111
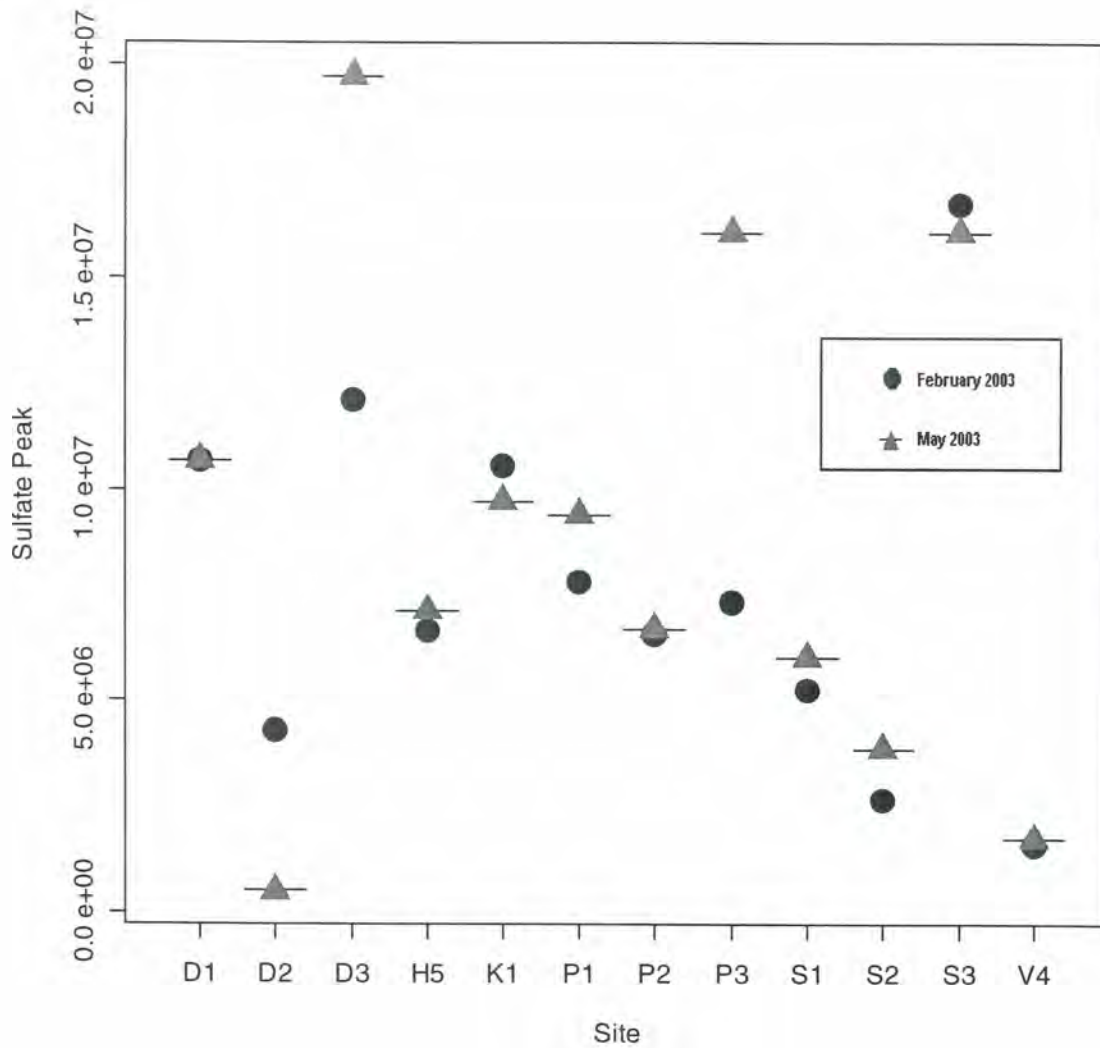
Figure 39. Sulfate peak values from well and piezometer samples in February (circle) and May (triangle). Note that the peak values represent relative concentrations and magnitudes can only be compared to one another and not to established values from other studies or laboratories. Where sulfate peak values are large, sulfate occurs in abundance and where sulfate peak values are small, little to no sulfate occurs.

Figure 40. Kite diagrams for shallow (S) and deep (D) piezometers along Pangborn Lake. Kite arms include median 18O and 15N isotopes (o/oo), nitrate and ammonium (mg-N/L), dissolved oxygen (mg/L), and iron plus manganese (mg/L), and Excess N2 (mg/L).

113

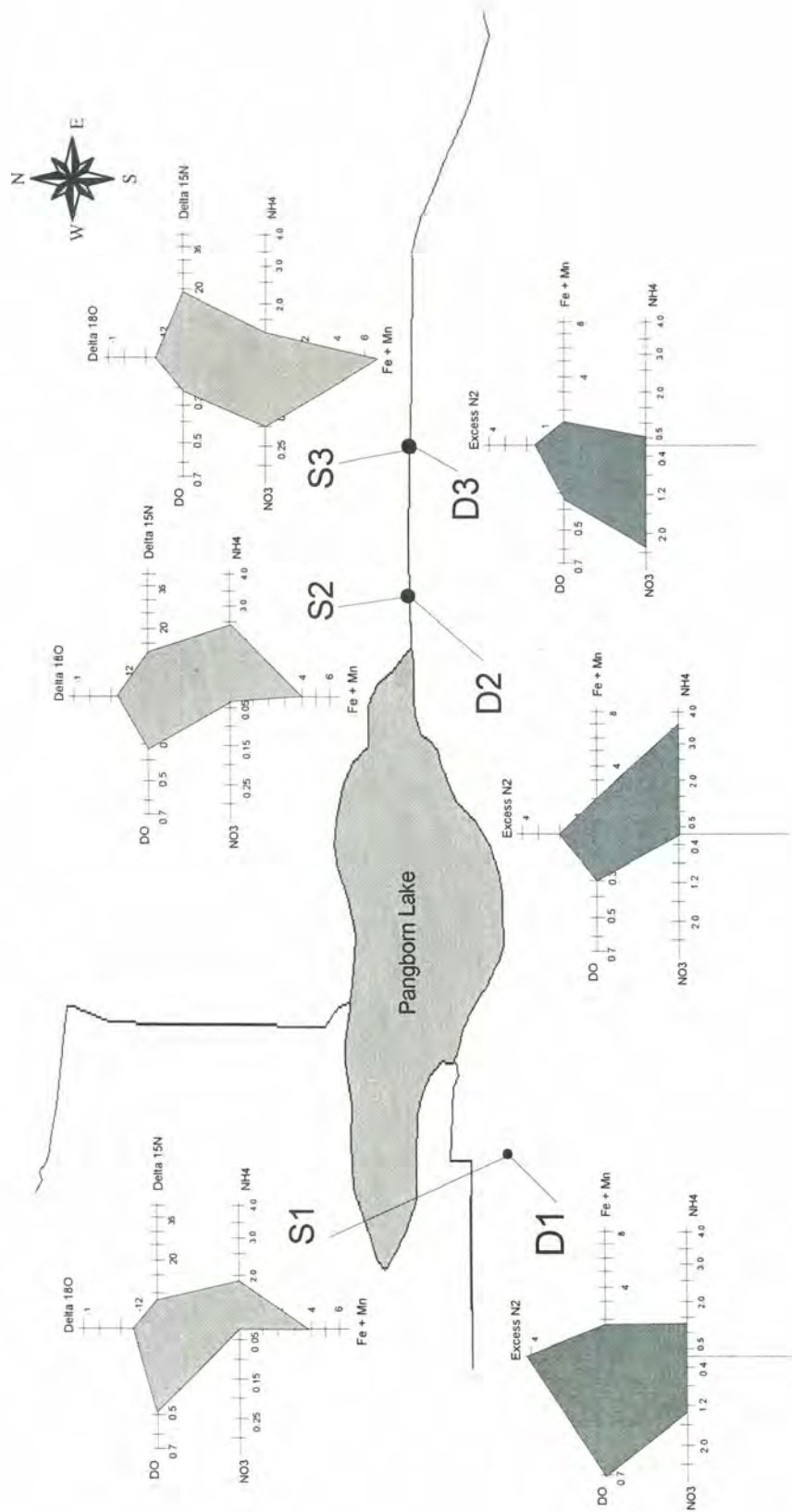Appendix A: Water Quality Indicators

Several water quality parameters were measured at well, stream, and piezometer sampling sites, including dissolved oxygen, pH, specific conductance, temperature, chloride, nitrate, ammonium, total nitrogen, total phosphorus, iron, and manganese. In addition to these parameters, turbidity was measured in piezometer samples, and fecal coliform in surface water samples. Although specific values of sulfate were not measured in this study, relative amounts of sulfate were examined.

Physical and Chemical Parameters

Dissolved oxygen defines where aerobic and anaerobic zones exist. High dissolved oxygen values indicate oxidizing reactions and low dissolved oxygen values indicate reducing reactions. Temperature in surface water governs the type of aquatic life that will exist and hence represents the health of a stream. In ground water, it governs the success of microbial respiration. Specific conductance indicates the concentration of dissolved ions in water as a function of temperature. High specific conductance may indicate elevated levels of chloride and nitrate. Cox and Kahle (1999) found values ranging from 70-4025 uS/cm in the Abbotsford-Sumas region versus 113-950 uS/cm in other Puget Sound counties (Tesoriero and Voss, 1997). Turbidity is a measure of suspended material in water. Turbidity was measured in piezometer samples because suspended particles can serve as sites onto which nutrients can adsorb.

The presence of chloride can indicate land use influences from manure slurries, septic tank effluent, and application of inorganic commercial fertilizers, or it can indicate sea salt carried on shore by wind and rain (Nanus, 2000). Nitrate is a very mobile ion and is prevalent in the study area in abundances greater than the EPA drinking water standard. Ammonium is a species of nitrogen that occurs in reducing environments and wherever fresh animal waste exists. Total nitrogen is a measurement of all nitrogen species, including ammonium, nitrate, nitrite, and organic nitrogen. Total phosphorus is the measurement of the nutrient phosphorus, found in fertilizers and manures. Phosphorus is much less mobile than nitrate and hence lower levels are expected. Iron, manganese, and sulfide will help

115

identify a reducing environment. Their concentrations specify which metabolic process is responsible for reducing nitrate (refer to Table 2 for biochemical processes). Finally, fecal coliform indicates the presence of bacteria that are associated with septic tank effluent, manure slurry, or other animal waste. Although they are not necessarily agents of disease, they indicate the presence of disease-carrying organisms.

Nitrate Sources and Denitrification as Indicated by Isotopes

See text Section 3.4.3.

Nitrate Reduction as Indicated by Dissolved Gases

Five dissolved gases, including nitrogen, argon, oxygen, carbon dioxide, and methane, were analyzed using headspace chromatography by the United States Geologic Survey (USGS). The gas samples were collected to directly measure the byproducts of denitrification and to determine which other biochemical processes were occurring. Refer to Table 2 for redox reactions and metabolic products associated with different biochemical processes.

Appendix B: Well, stream, and piezometer locations, depth, and property owners

Well	Address	Town, Zip Code	Owner Name
Halverstick Road Wells			
H-1	2207 Halverstick	Lynden, 98264	Amarjit Brar
H-2	2366 Halverstick	Lynden, 98264	Darryl and Louise Ehlers
H-3	2373 Halverstick	Lynden, 98264	Joe Kooi
H-4	2457 Halverstick	Lynden, 98264	Martin & Gerrilyn Vande Hoef
H-5	2480 Halverstick	Lynden, 98264	Tom Wiegand
H-6	2565 Halverstick	Lynden, 98264	Martin & Gerrilyn Vande Hoef
H-7	2633 Halverstick	Lynden, 98264	Connie Hogue
H-8	2804 Halverstick	Lynden, 98264	Lidia Rivera /Esquivel
Van Buren Road Wells			
V-1	9155 Van Buren	Everson, 98247	Jody & Darren Tjoelker
V-2	9244 Van Buren	Everson, 98247	Duane & Nolva Bouma
V-3	9383 Van Buren	Lynden, 98264	John Vanderveen (home)
V-4	9489 Van Buren	Lynden, 98264	Curt and Joy Hawley
V-5	9501 Van Buren	Lynden, 98264	John Vanderveen (farm)
V-6	9563 Van Buren	Lynden, 98264	Rolf Veening
V-7	9765 Van Buren	Lynden, 98264	Cynthia and Robert Bateman
V-8	9856 Van Buren	Lynden, 98264	Mark and Kathleen Iblings
V-9	9898 Van Buren	Lynden, 98264	Tim Vandermulen
V-10	9907 Van Buren	Lynden, 98264	unknown
V-11	9264 Van Buren	Everson, 98247	Kyle Stremler
Pangborn Road Wells			
P-1	2656 Pangborn	Lynden, 98264	Robert and Dorothy Bronkema
P-2	2629 Pangborn	Lynden, 98264	Cheetah and Virgil Stremler
P-3	2544 Pangborn	Lynden, 98264	Cheryl and Mark Vandyken
Trap Line Road Wells			
T-1	9294 Trap Line	Lynden, 98264	Bert McMurray
T-2	9295 Trap Line	Lynden, 98264	Gill
Kraght Road Wells			
K-1	9305 Kraght	Lynden, 98264	Associated Well (Visser)

Table B-1. Well address and owner name for the WWU Abbotsford-Sumas 2002-2003 sampling season.

1997-1999 wells	2002-2003 wells	Well Log	Well Screen Length	Well Depth Below Ground (ft)†	Estimated Elevation (ft)	Median Depth to Water Table (ft)	Estimated Well Depth Below the Water Table (ft)	Estimated Well Depth Below the Water Table (m)
1	H-1	no	no data	30 (R)	145	20*	10	3.0
2	H-2	yes	26-34 feet	34 (A)	155-10	20.55	13.45	4.1
new	H-3	no	no data	75 (R)	150	24.8	50.2	15.3
new	H-4	yes	60-65 feet	65 (A)	165	30.35	34.65	10.6
22	H-5	no	no screen	34 (R)	165-10	25.2	8.8	2.7
24	H-6	yes	no screen	35 (A)	165	32.6	2.4	0.7
9	H-7	yes	66-71 feet	71 (A)	165	32.6*	38.4	11.7
10	H-8	yes	42-50 feet	50 (A)	165	32.6*	17.4	5.3
new	K-1	yes	39-49 feet	49 (A)	120	20*	29	8.8
new	P-1	yes	50-55 feet	65 (A)	140	27.75	37.25	11.4
new	P-2	yes	no screen	67 (A)	150	29.2*	37.8	11.5
new	P-3	no	no data	30 (R)	150	29.2	0.8	0.2
18	T-1	no	no data	42 (R)	130	28.4	13.6	4.1
26	T-2	yes	70-80 feet	80 (A)	130	29.1	50.9	15.5
new	V-1	no	no data	28 (R)	100	18.4	9.6	2.9
new	V-2	yes	117-122 feet	122 (A)	70	18	104	31.7
new	V-3	yes	no screen	86 (A)	140	27*	59	18.0
new	V-4	no	no data	12 (R)	115	4.25	7.75	2.4
14	V-5	yes	12-20 feet	25 (A)	150-15	18.8	6.2	1.9
13	V-6	no	no data	40 (R)	160	35*	5	1.5
7	V-7	yes	no screen	77 (A)	170	44.6	33	10.1
6	V-8	yes	no screen	95 (A)	200	58.3	36.7	11.2
new	V-9	yes	87-91 feet	91 (A)	210	72.9*	18.1	5.5
5	V-10	no	no data	90 (E)	200	72.9	17.1	5.2
19	V-11	no	no screen	45 (E)	80	14.5	30.5	9.3

† (R) = Reported Well Depth (A) = Actual Well Depth (E) = Estimated Well Depth * = Not able to survey/ static water levels not taken

Table B-2. Well screening and well depth below the ground for wells common to the 1997-1999 and 2002-2003 studies were provided by Stasney (2000). Data for the 2002-2003 study were calculated from well logs from the Washington State Department of Ecology (M. Snowberger, personal communication, 2002).

119

ID #	Property Owner	Address	Town, Zip Code	Phone #
PB-1	Bob Vandyken	2450 Pangborn Rd	Lynden, 98264	988-2988
PB-2	Bob Vandyken	2451 Pangborn Rd	Lynden, 98264	988-2989
PB-3	Jon Harvey	2686 Pangborn Rd	Lynden, 98264	988-6112
PB-4	Curt and Joy Hawley	9489 Van Buren Rd	Lynden, 98264	988-7044
PB-5	Frank Steiner	3011 Clearbrook Rd	Sumas, 98295	988-5202
JN-1	Weyhart Farm	9402 Nooksack Rd.	unknown	unknown
JN-2	Vanderveen	3114 Clearbrook Rd.	Sumas, 98295	988-7477
JN-3	unknown	access road on Clearbrook	unknown	unknown
JN-4	unknown	access road on Clearbrook	unknown	unknown
JN-5	Bob Kirkmans	9078 Van Buren Rd.	Everson, 98247	966-4270
or	Ken and Annette Kirkmans	9090 Van Buren Rd.	Everson, 98247	966-4111

Table B-3. Stream address and owner name for the WWU Abbotsford- Sumas 2002-2003 sampling period.

120

Piezometer	Address	Town, Zip Code	Owner Name	Height Above Ground (in)	Depth Below Ground (in)	Length of Screening (in)
S1	2274 Pangborn Road	Lynden, WA 98264	Karen Wraght	32	24	12
D1	2274 Pangborn Road	Lynden, WA 98264	Karen Wraght	30	54	24
S2	2450 Pangborn Road	Lynden, WA 98264	Bob Vandyken	40	44	24
D2	2450 Pangborn Road	Lynden, WA 98264	Bob Vandyken	37	104	24
S3	2450 Pangborn Road	Lynden, WA 98264	Bob Vandyken	14	68	48
D3	2450 Pangborn Road	Lynden, WA 98264	Bob Vandyken	16	104	24

Table B-4. Piezometer address and owner name for the WWU Abbotsford-Sumas 2002-2003 sampling period.

121

Appendix C: List of Contacts Used for Laboratory Analysis

List of websites for laboratories used in the Abbotsford-Sumas 2002-2003 project.

For fecal coliform analysis:
Avocet Laboratories reference page, provided by the Department of Ecology:
http://www.ecy.wa.gov/programs/eap/labs/a.html

For nitrogen isotope analysis:
Colorado Plateau Stable Isotopes Laboratory at Northern Arizona University
Homepage:
http://www2.nau.edu/~bah/cpsil.html

For oxygen isotope analysis:
INSTAAR homepage:
http://instaar.colorado.edu/sil/

For nitrogen analysis:
Institute for Watershed Studies at Western Washington University:
http://odonata.ietc.wwu.edu

For metals and chloride analysis:
SCITECH at Western Washington University:
http://www.wwu.edu/depts/scitech/scitechdesc.html

For nitrogen gas analysis:
USGS homepage for dissolved gas analysis:
http://water.usgs.gov/lab/cfc/

Appendix D: United States Geological Society Dissolved Gas Protocol

Sampling for Dissolved Gases in Ground Waters

1. Insert a needle into the rubber stopper until the tip slightly exits through the stopper.

2. Fill a bucket with well water.

3. Fill the 150 mL sample bottle with water and place it in the bottom of the water filled bucket. The water should be flowing into the bottle when it is put in the bucket. **Do not filter the sample, use raw sample.**

4. Make sure that no bubbles are adhering to the sides of the bottle. Insert the stopper in the bottle while the bottle is submerged in the water. Make sure that you push the stopper all the way down. **Take duplicates of all samples. Do not put any grease on the stopper.**

5. Remove the needle from the stopper while the bottle is still submerged in the water. **Properly dispose of all needles or return the used needles with the samples.**

6. Record the (a) sample name, (b) date & time, (c) water temperature, (d) estimated recharge altitude, and (e) submitter's name on the label attached to the foam sleeve.

7. Keep samples cool or about the temperature of the ground water. This will keep the stoppers from popping up as samples warm up. Store sample bottles upside down.

8. Ship samplers in cooler overnight express to:
   Peggy Widman / USGS
   M.S. 432, Room 5B-353
   12201 Sunrise Valley Dr.
   Reston, VA 20192

   Phone: 703-648-5347
   Email: pkwidman@usgs.gov
   Website: http://water.usgs.gov/lab/dissolved-gas/

9. Upon completion of sample collection, an electronic copy of the sample submission form **must** be submitted.

Do Not ship samples on a Friday. The samples will not be delivered here until Monday and may heat up in storage.

125
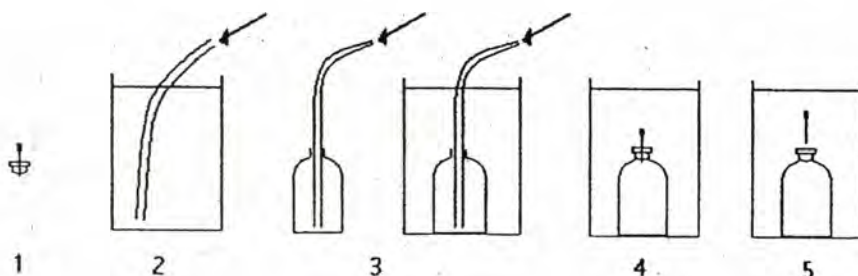
Appendix E: Quality Control

Quality Control

The laboratory quality control samples associated with water quality data collected from July 2002 to June 2003 include: laboratory duplicates (QC), check standards, and spikes. All data were analyzed using the following data quality control objectives:

- Laboratory Duplicates

  Ten percent laboratory duplicates measure the laboratory precision for each analyte. Precision is the degree of agreement among replicate analyses of a sample (Clesceri et al., 1998). The duplicates were analyzed using control charts, where ± 2 standard deviation from the mean served as the warning limits and ± 3 standard deviations from the mean served as the action limits.

- Check Standards

  Check standards were made for each sample run and indicate the accuracy of the measured analyte. Accuracy is the difference between a measured value and a known (true) value (Clesceri et al., 1998). Check standards were analyzed using control charts.

- Spikes

  Spikes are laboratory-fortified samples used to determine when a sample matrix is interfering with the analyzation method. Spikes were analyzed using control charts and calculated as percent recovery:

$$\% \text{ Recovery} = \{[(\text{sample} + \text{spike}) - \text{sample}] / \text{spike}\} * 100$$

The percent recovery must lie within the control chart limits.

The three quality control methods were graphed with control charts by analyte on the following pages. The analytes included total nitrogen, nitrate, ammonium, iron, and manganese. The Winkler titration laboratory dissolved oxygen measurements and the field meter dissolved oxygen measurements were evaluated using correlation analysis rather than control charts.
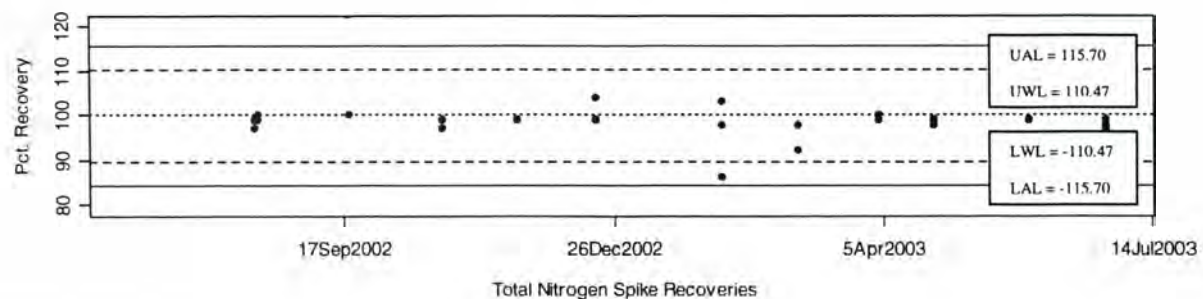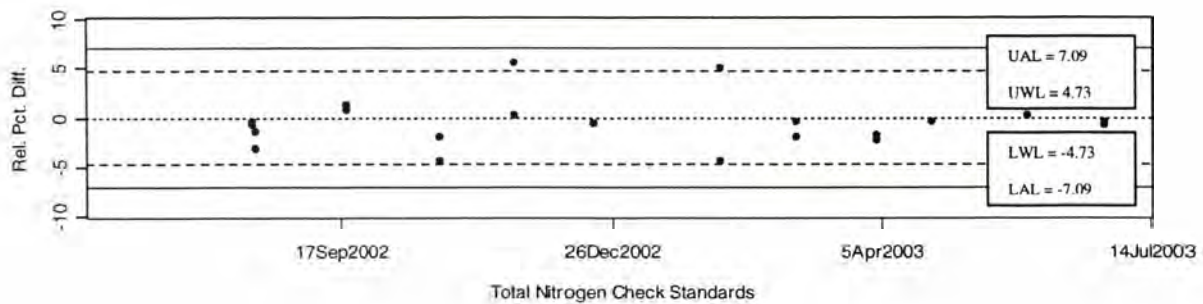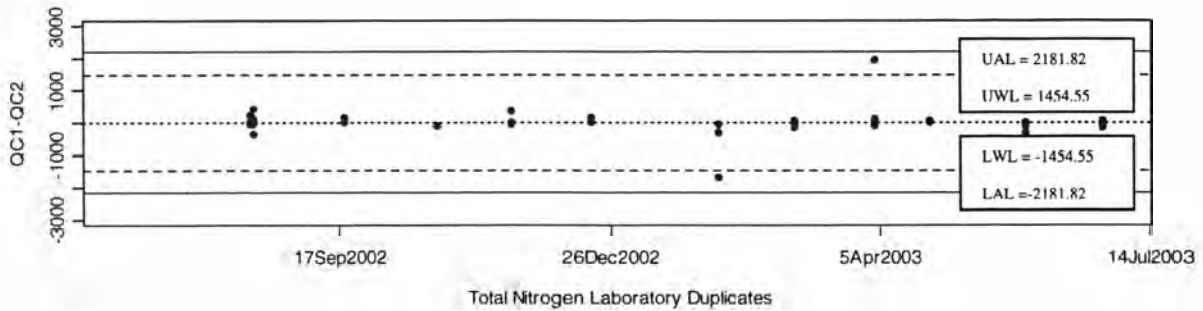
127

Figure D1. Control charts of total nitrogen laboratory duplicates, check standards, and spikes. The upper and lower action limits (± 2 std. dev. from mean pair difference) and upper and lower warning limits (± 3 std. dev. from mean pair difference) were calculated based on data from July 2002-June 2003. The majority of the data show acceptable precision, accuracy, and recovery.
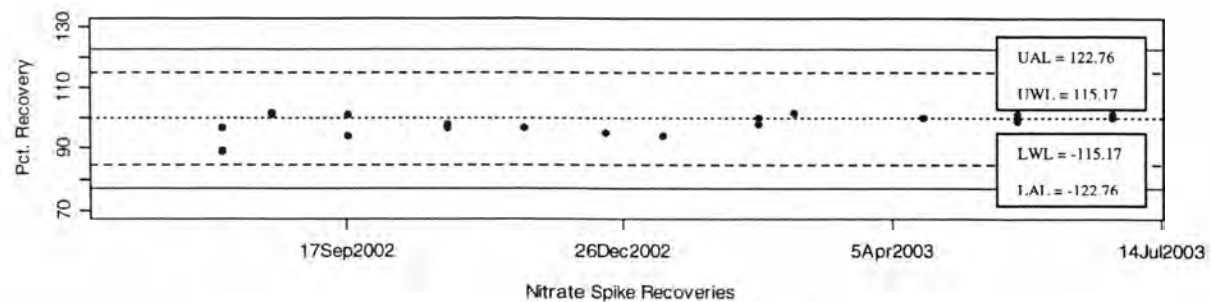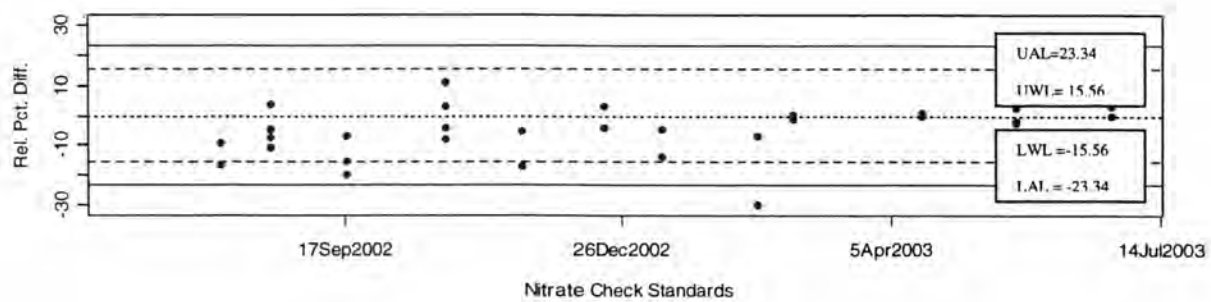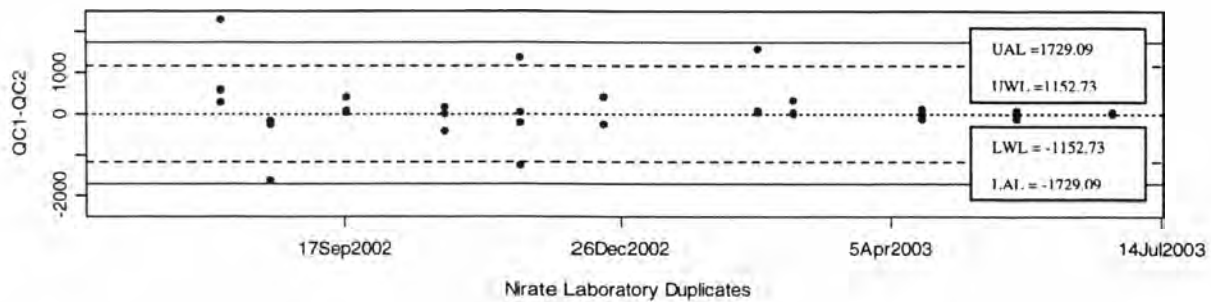
128

Figure D2. Control charts of nitrate laboratory duplicates, check standards, and spikes. The upper and lower action limits (± 2 std. dev. from mean pair difference) and upper and lower warning limits (± 3 std. dev. from mean pair difference) were calculated based on data from July 2002-June 2003. With the exception of one data point, the nitrate laboratory duplicates show acceptable precision and the check standards show acceptable accuracy. All spikes show acceptable recovery.
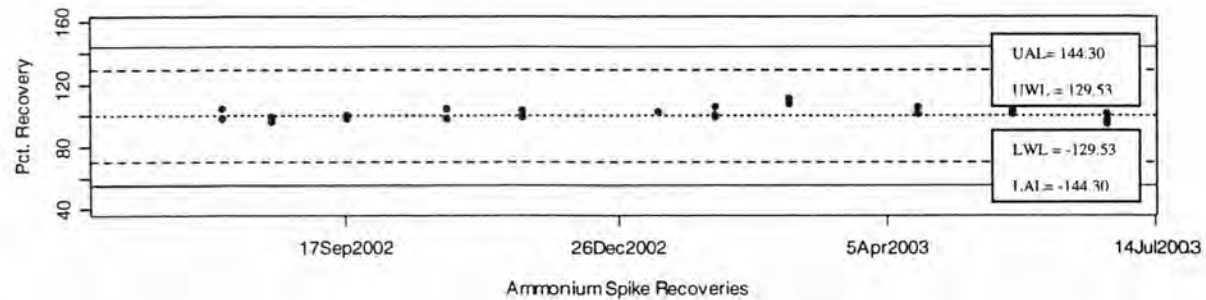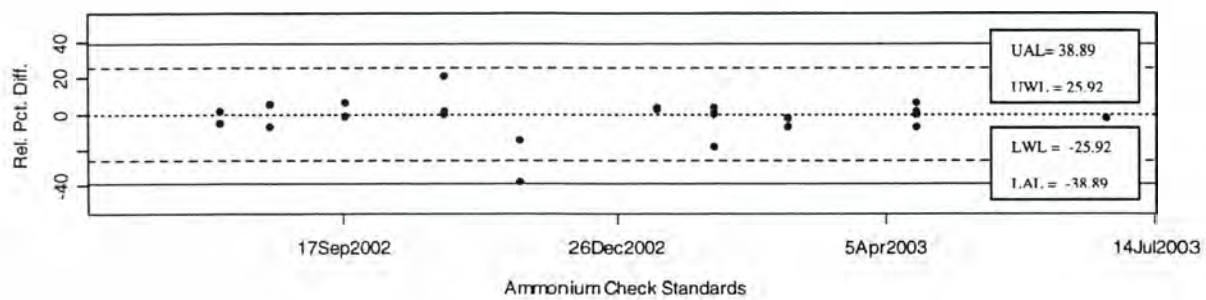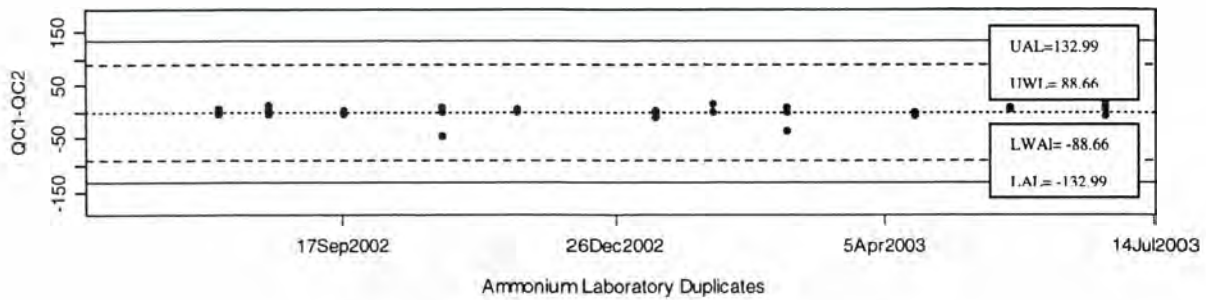
129

Figure D3. Control charts of ammonium laboratory duplicates, check standards, and spikes. The upper and lower action limits (± 2 std. dev. from mean pair difference) and upper and lower warning limits (± 3 std. dev. from mean pair difference) were calculated based on data from July 2002-June 2003. All duplicates, check standards, and spikes show acceptable precision, accuracy, and recovery, respectively.
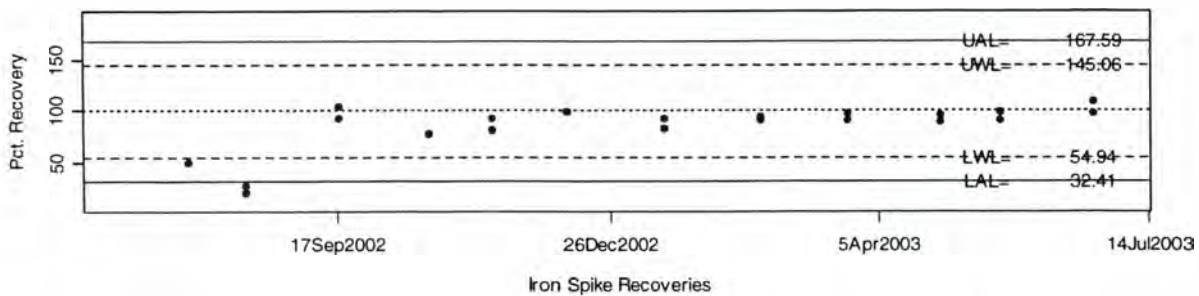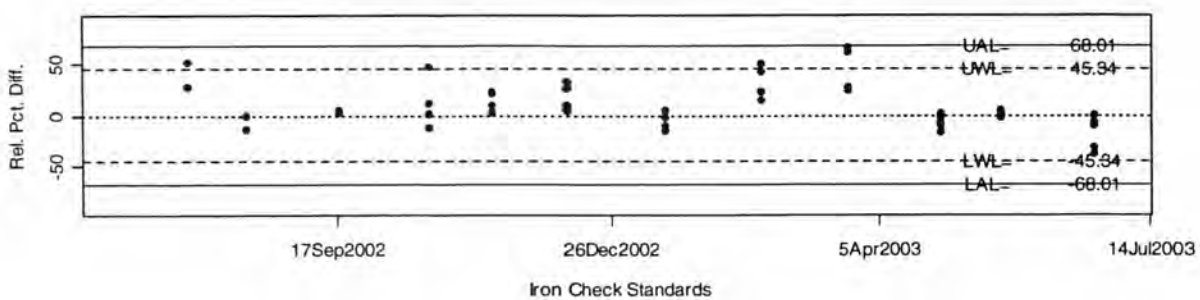
Figure D4. Control charts of iron laboratory duplicates, check standards, and spikes. The upper and lower action limits (± 2 std. dev. from mean pair difference) and upper and lower warning limits (± 3 std. dev. from mean pair difference) were calculated based on data from July 2002-June 2003. The iron laboratory duplicates show acceptable precision and the check standards show acceptable accuracy. The spikes show two data points early in the sampling period that fall outside of the control chart limits. Most of the spikes show acceptable recovery.
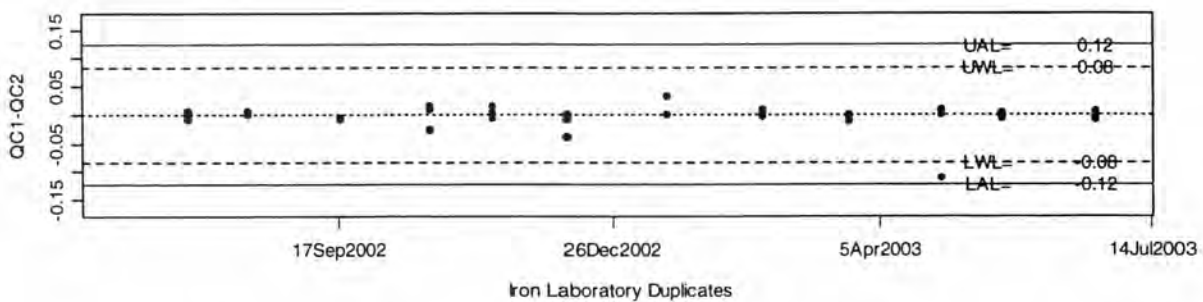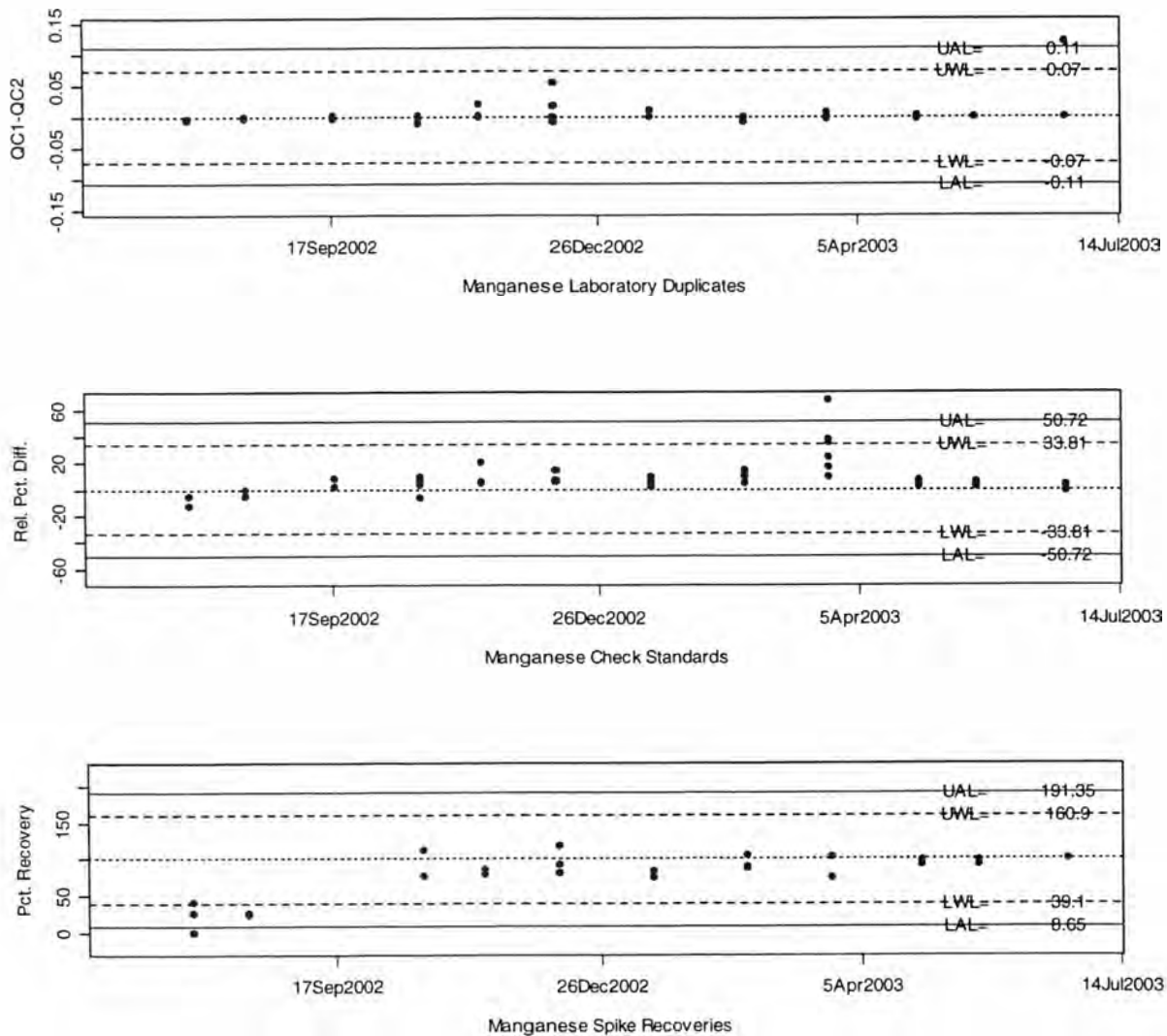
Figure D5. Control charts of manganese laboratory duplicates, check standards, and spikes. The upper and lower action limits (± 2 std. dev. from mean pair difference) and upper and lower warning limits (± 3 std. dev. from mean pair difference) were calculated based on data from July 2002-June 2003. With the exception of one data point each, the duplicates, check standards, and spike fall within the acceptable range of precision, accuracy, and recovery, respectively.

132

Dissolved Oxygen (mg/L)
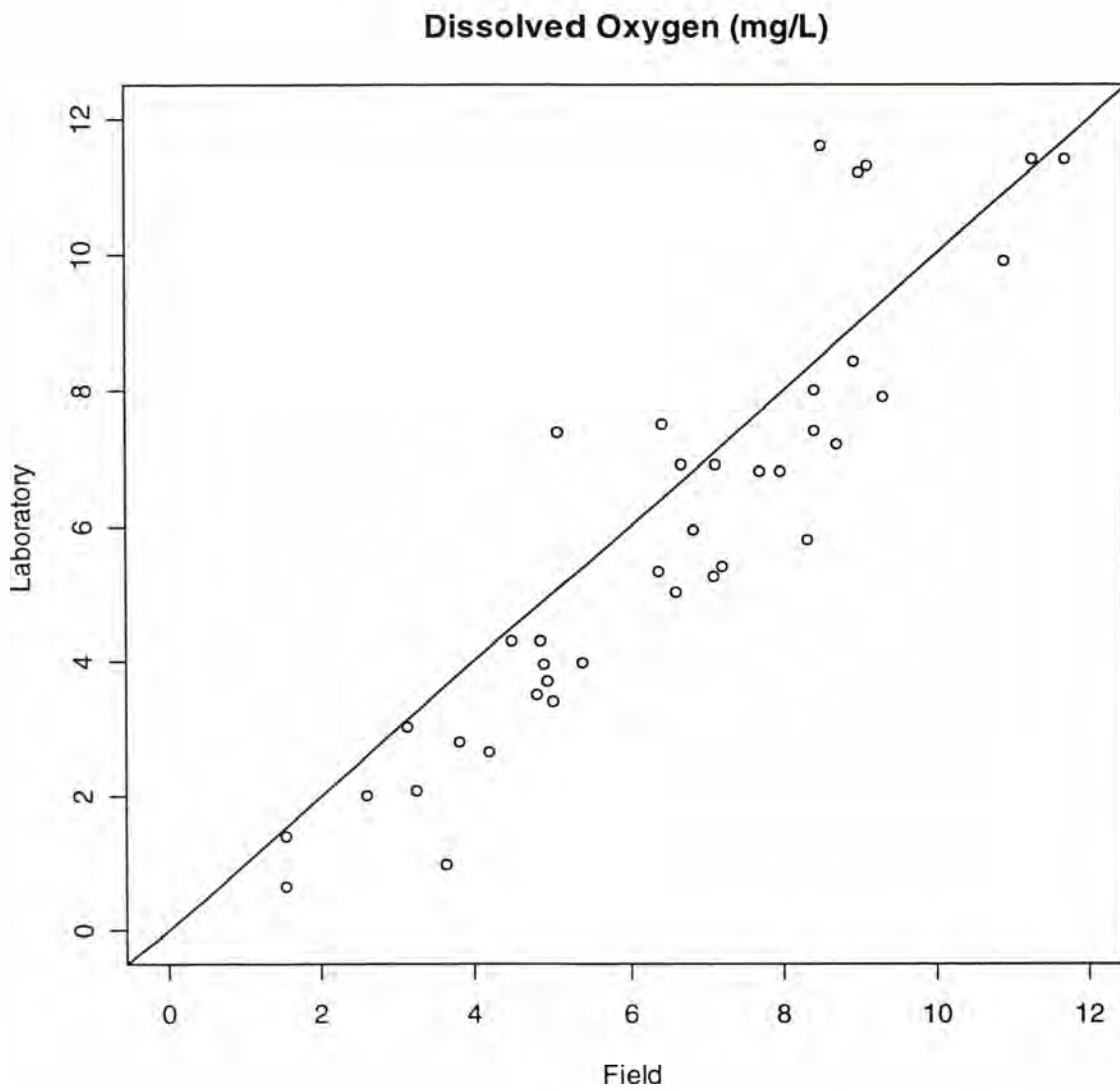
Figure D6. Dissolved oxygen measured in the field versus that measured in the laboratory from samples collected during the period of July 2002-June 2003. The line provides a reference for where exact overlap in values would occur. Some scatter away from the line does exist, but in general, the data show acceptable deviations.

133

Appendix F: Nitrogen Gas Results **(See Pocket Attachment)**

This section includes:

- February Results
- May Results
- Sensitivity Analysis: February Results for 9 degrees Celsius
- Sensitivity Analysis: February Results for 10 degrees Celsius
- Sensitivity Analysis: February Results for 11 degrees Celsius
- Sensitivity Analysis: May Results for 9 degrees Celsius
- Sensitivity Analysis: May Results for 10 degrees Celsius

Sensitivity Analysis: May Results for 11 degrees Appendix F: Data

Appendix G: Data **(See Pocket Attachment)**

Appendix H: Calculations for Piezometer Vertical Gradients
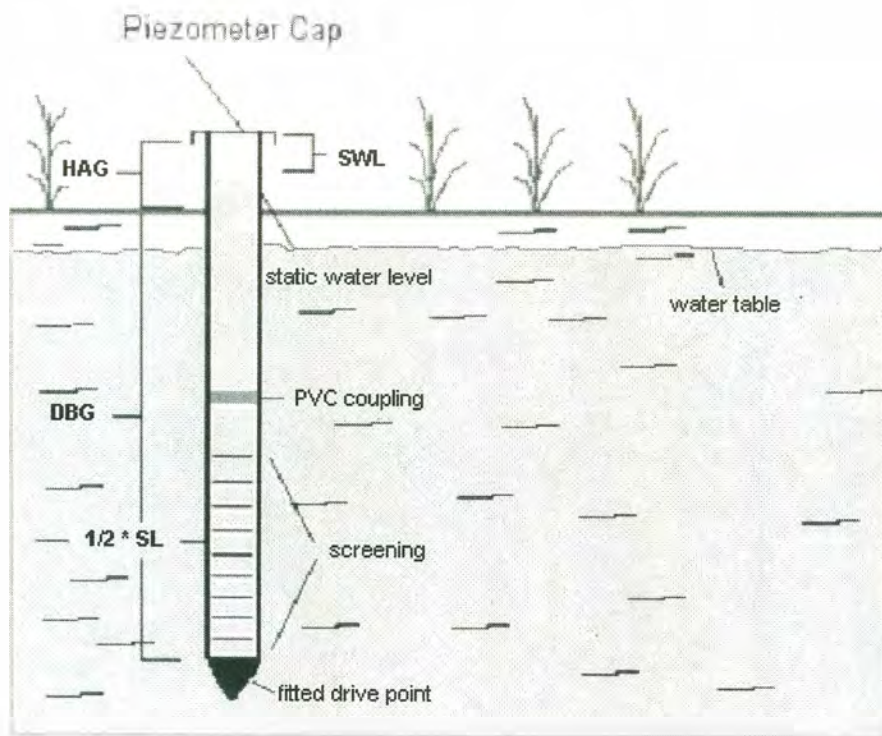
Calculations for Piezometer Vertical Gradients

HAG = Height Above Ground   DBG = Depth Below Ground

SWL = Static Water Level   SL = Screen Length

Site	Length (in)	Screening (in)	HAG (in)	DBG (in)	ΔL (in)
S1	56	24	32	24	30
D1	84	24	30	54	
S2	84	24	40	44	60
D2	141	24	37	104	
S3	82	48	14	68	48
D3	120	24	16	104	

Difference in length between deep and shallow piezometers (ΔL):

$$\Delta L = DBG_{deep} - DBG_{shallow}$$

185

Monthly Static Water Level (in) (measured from the top of the casing)

Site	October	November	December	January	February	March	April	May	June
S1	34.92	35.04	28.08	23.76	26.40	26.76	24.48	27.00	57.72
D1	37.80	37.20	25.20	19.80	26.40	22.32	62.40	22.68	28.32
S2	35.52	37.68	35.40	28.80	27.60	29.88	31.20	31.92	37.80
D2	87.60	47.40	39.60	35.16	58.80	45.00	38.88	42.12	42.60
S3	30.00	32.76	31.56	27.48	69.60	30.36	28.20	33.60	34.44
D3	18.60	32.88	21.60	49.20	30.00	18.96	19.32	19.20	26.88

Water level above ground (WAG):

WAG = HAG − SWL

Below ground water level above the midpoint of the screening (BGWAS):

BGWAS = DBG − 0.5 * SL

Monthly Pressure Head (in)

Site	October	November	December	January	February	March	April	May	June
S1	9.08	8.96	15.92	20.24	17.60	17.24	19.52	17.00	-13.72
D1	34.20	34.80	46.80	52.20	45.60	49.68	9.60	49.32	43.68
S2	36.48	34.32	36.60	43.20	44.40	42.12	40.80	40.08	34.20
D2	41.40	81.60	89.40	93.84	70.20	84.00	90.12	86.88	86.40
S3	28.00	25.24	26.44	30.52	-11.60	27.64	29.80	24.40	23.56
D3	89.40	75.12	86.40	58.80	78.00	89.04	88.68	88.80	81.12

Pressure head (ψ):

$$\psi = (HAG - SWL) + (DBG - 0.5*SL)$$

Monthly Water Height in the Column									
Site	October	November	December	January	February	March	April	May	June
S1	39.08	38.96	45.92	50.24	47.60	47.24	49.52	47.00	16.28
D1	34.20	34.80	46.80	52.20	45.60	49.68	9.60	49.32	43.68
S2	96.48	94.32	96.60	103.20	104.40	102.12	100.80	100.08	94.20
D2	41.40	81.60	89.40	93.84	70.20	84.00	90.12	86.88	86.40
S3	76.00	73.24	74.44	78.52	36.40	75.64	77.80	72.40	71.56
D3	89.40	75.12	86.40	58.80	78.00	89.04	88.68	88.80	81.12

Height of water in the column (h):

$$h = \psi + \Delta L$$

Monthly Vertical Gradients †									
Site	October	November	December	January	February	March	April	May	June
S1	-0.16	-0.14	0.03	0.07	-0.07	0.08	-1.33	0.08	0.91
S2	-0.92	-0.21	-0.12	-0.16	-0.57	-0.30	-0.18	-0.22	-0.13
S3	0.28	0.04	0.25	-0.41	0.87	0.28	0.23	0.34	0.20

† Positive values indicate upward flow and negative values indicate downward flow from the deep to the shallow piezometer.

Vertical Gradient (grad):

$$grad = (h_{deep} - h_{shallow}) / \Delta L$$