Quality Assurance Project Plan

Monitoring for Nitrate Trends in the Central Sumas-Blaine Surficial Aquifer

by Denis Erickson, L.G.,L.HG.

Washington State Department of Ecology Environmental Assessment Program Olympia, Washington 98504-7710

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Approvals

Approved by:	March 14, 2003
Janet Burcham, Bellingham Field office	Date
Approved by:	March 13, 2003
Andrew Craig, Bellingham Field Office	Date
Approved by:	March 14, 2003
Richard Grout, Section Manager, Bellingham Field Office	Date
Approved by:	February 6, 2003
Denis Erickson, Principal Investigator, Watershed Ecology Section	Date
Approved by:	February 10, 2003
Darrel Anderson, Unit Supervisor, Nonpoint Studies Unit	Date
Approved by:	February 5, 2003
Will Kendra, Section Manager, Watershed Ecology Section	Date
Approved by:	February 5, 2003
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	February 6, 2003
Cliff Kirchmer, Ecology Quality Assurance Officer	Date

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Abstract

The purpose of this project is to design and implement a groundwater monitoring program to determine nitrate concentration trends in the central portions of the Sumas-Blaine Surficial Aquifer. The Sumas-Blaine Surficial Aquifer is the principal surficial aquifer in the Nooksack Watershed in northwestern Whatcom County. Studies over the last 12 years have documented extensive nitrate contamination of the central and northcentral portions of the Sumas-Blaine Surficial Aquifer.

The major sources of nitrate in the Sumas-Blaine Surficial Aquifer are the storage and application of dairy wastewater and manure, inorganic fertilizer application, and septic systems. Substantial effort has been made in recent years to improve the handling and storage of dairy wastewater and manure. The results from this project and subsequent long-term monitoring will document whether these improvements translate to decreased nitrate concentrations in groundwater.

The project proposes to sample the groundwater monitoring network of about 30 to 35 wells for nitrate every other month for two years. The variability of the data will be used to define the sample frequency for long-term monitoring. The data will be evaluated using the Seasonal Kendall or equivalent statistical test to identify statistically significant trends.

Background/Problem Statement

Sumas-Blaine Surficial Aquifer

The Sumas-Blaine Surficial Aquifer is the principal surficial aquifer in the Nooksack Watershed in northwestern Whatcom County (Tooley and Erickson, 1996). Its location is shown in Figure 1. It occupies an area of about 150 square miles and consists mostly of sand and gravel glacial outwash deposits as well as mixed gravel, sand, silt, and clay alluvial deposits of the Nooksack and Sumas rivers. The thickness of these deposits ranges from less than 25 feet near Blaine to greater than 75 feet near Sumas. The aquifer is unconfined and the water table is commonly less than 10 feet deep.

The Sumas-Blaine Surficial Aquifer readily interacts with rivers, streams, lakes, and ditches in the watershed. In general, groundwater flows toward the tributaries and main stems of the Nooksack River, Sumas River, and Dakota Creek. The aquifer is recharged predominately by infiltrated precipitation.

Nitrate Contamination

Nitrate is one of the most frequently identified contaminants found in groundwater (Miller and Canter, 1980). It is soluble in water and mobile in groundwater. The major sources of nitrate in the Sumas-Blaine Surficial Aquifer are the storage and application of dairy wastewater and manure, inorganic fertilizer application, and septic systems (Cox and Kahle, 1999). The Washington State Department of Health has established a 10 mg/L drinking water standard (Maximum Contaminant Level or MCL) for nitrate-N in public water supply systems (Chapter 246-290 WAC). The criterion for nitrate-N in the Washington State Water Quality Standards for Ground Waters (Chapter 173-200 WAC) is also 10 mg/L.

Studies over the last 12 years have documented extensive nitrate contamination of the central and northcentral portions of the Sumas-Blaine Surficial Aquifer largely from agricultural sources:

- Cox and Kahle (1999), based on sampling conducted in 1990 to 1992, reported that 27% of 236 wells sampled in the Sumas Aquifer (the eastern portion of the Sumas-Blaine Surficial Aquifer) showed concentrations exceeding 10 mg/L with a mean nitrate concentration of 6 mg/L.
- Erickson and Norton (1990) reported nitrate+nitrite-N concentrations for 27 wells in the Bertrand Creek drainage ranged from less than 0.01 to 24 mg/L with a mean of 6.7 mg/L.
- In a three square-mile area north of Lynden, Garland and Erickson (1994) reported nitrate+nitrite-N concentrations as high as 73 mg/L and a median concentration of 2.3 mg/L for 21 wells.
- Erickson (1998) defined the springtime distribution of nitrate+nitrite-N concentrations over the aquifer by sampling 248 wells and two springs. Nitrate+nitrite-N concentrations exceeded 10 mg/L at 53 wells located primarily in the central and northcentral portions of the aquifer.

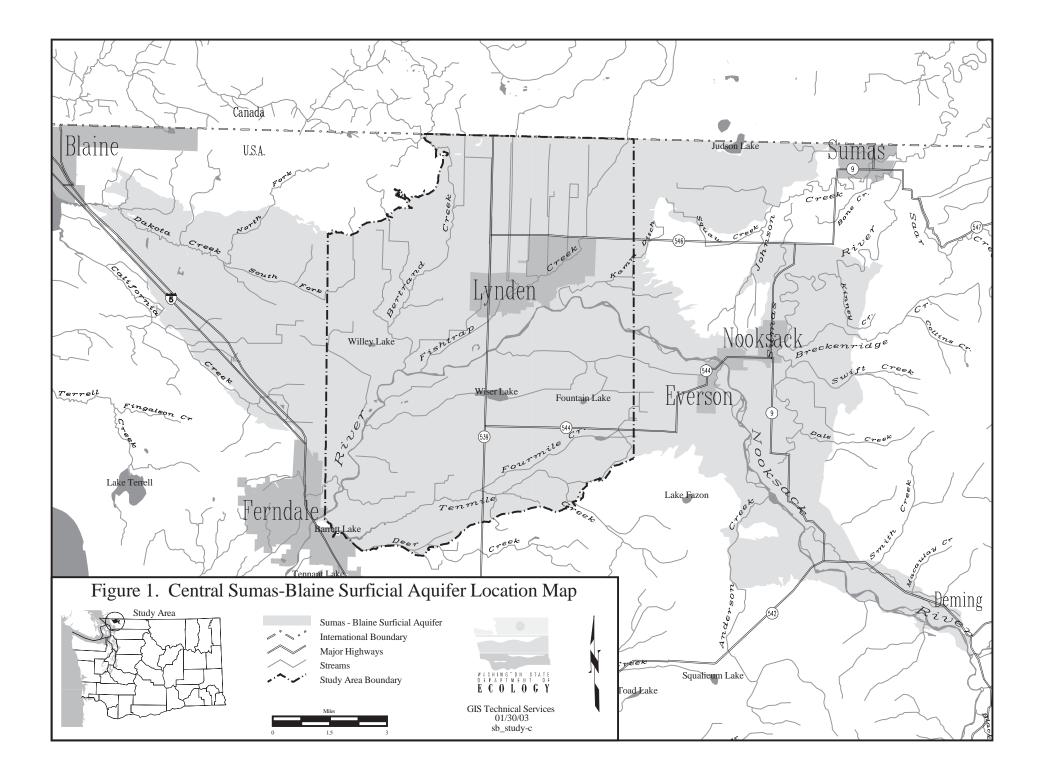
- Erickson (2000) reported nitrate+nitrite-N concentrations for 53 wells in the northcentral portion of the aquifer ranged from 0.012 to 22.1 mg/L with a median concentration of 10.3 mg/L.
- Mitchell et al. (2000) monitored 26 wells in 1997 and 1998 in the Judson Lake area. The median nitrate+nitrite-N concentration in 12 of the 26 wells exceeded 10 mg/L.

Substantial effort has been made in recent years to improve storage and application of wastewater and manure at a number of dairies. The Bellingham Field Office requested that the Environmental Assessment Program design and implement a monitoring program to define nitrate trends in groundwater. The purpose of the monitoring is to document whether improvements in the storage and application of wastewater and manure translate to decreased nitrate concentrations in groundwater.

Study Area

The study area consists of the central portion of the Sumas-Blaine Surficial Aquifer (Figure 1). The study area includes the major occurrences of elevated nitrate concentrations identified in Erickson (1998) with the exception of the Judson Lake area (Figure 2). A two-year study, including sampling and testing for nitrate in 25 wells, is ongoing in the Judson Lake area (Mitchell et al, 2002).

Agriculture is the dominant land use in the study area. Major crops include grass, corn, raspberries, strawberries, and seed potatoes. The density of dairies is among the highest in the state (Washington State Department of Ecology, 1996).



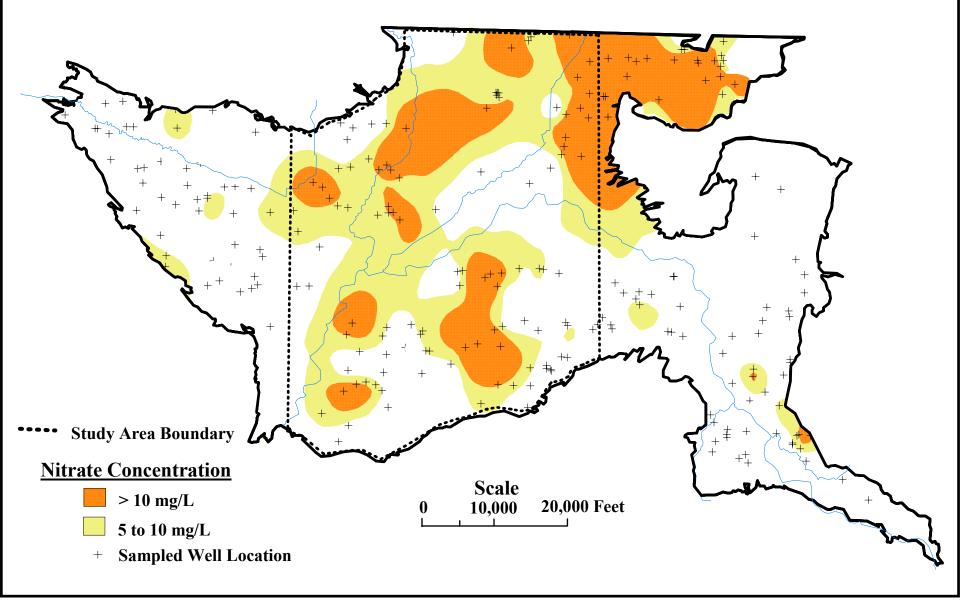


Figure 2. Areas of Elevated Nitrate+Nitrite-N in the Sumas-Blaine Surficial Aquifer, February-April 1997, and Proposed Study Area Boundary.

Project Description

A monitoring program will be designed and implemented to define nitrate concentration trends in the central portion of the Sumas-Blaine Surficial Aquifer. The network will consist of about 30 to 35 wells, most of which will be existing domestic water-supply wells.

Spatial and temporal variability of nitrate concentrations in shallow groundwater in an agricultural setting poses a challenge for identifying long-term trends. Because this project will rely on existing water-supply wells that are varying distances from nitrate sources and obtain water from varying depths in the aquifer, the magnitude and timing of nitrate variability is likely to be different from well to well. To define the nitrate variability at each well, the network will be sampled bimonthly (every other month) for two years. The observed variability will serve as a basis for determining the long-term sampling frequency for the network. The bi-monthly results will be evaluated for statistical trends using the Seasonal Kendall or equivalent statistical test to identify trends.

Responsibilities

Name	Duties	Phone
Denis Erickson	Project Lead	(360)407-6767
Janet Burcham	Quality Assurance (QA) Project Plan Review, Identification of Areas of Interest, Report Review	(360)676-2214
Andrew Craig	QA Project Plan Review, Identification of Areas of Interest, Report Review	(360)676-2217
Richard Grout	Bellingham Field Office Manager	(360)738-6255
Darrel Anderson	QA Project Plan and Report Review	(360)407-6453
Will Kendra	QA Project Plan and Report Review	(360)407-6698
Cliff Kirchmer	QA Review	(360)407-6455
Pam Covey	Sample Tracking	(360)407-8827
Dean Momohara	Analysis Supervisor	(360)871-8808
Stuart Magoon	Laboratory Director	(360)871-8801

Project participants and their responsibilities are listed below.

Schedule

Milestone	Date
QA Project Plan Approved	December 2002
Well Selection	January/February 2003
Sampling	2003: March, May, July, September, November 2004: January, March, May, September, November 2005: January, March
Draft Technical Report	August 2005
Final Technical Report	October 2005
EIM Data Entry	January 2006

Data Quality Objectives and Decision Criteria

The primary purpose of this project is to determine representative nitrate concentrations of groundwater in the vicinity of sampled wells. To minimize bias (systematic error) standard sample collection procedures will be used that minimize potential changes to sample chemistry during sampling. Samples will be preserved, handled, and stored using accepted procedures for maintaining sample integrity prior to analysis.

Based on previous studies, overall laboratory and sampling precision (random error) for nitrate+nitrite-N analysis should be within 15% relative percent difference (RPD) (Erickson, 1998). The precision and bias routinely obtained by the analytical method for nitrate+nitrite-N is adequate for this project.

The measurement quality objectives (maximum acceptable values) for this project are listed in Table 1.

Parameter	Accuracy ((Precision x2)+ Bias)	Precision (%RSD)	Bias (%)	Required Reporting Limit
Nitrate+Nitrite-N	19%	7	5	0.01 mg/L

Table 1.	Measurement	Quality	Objectives
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Electrical conductivity, temperature, pH, and dissolved oxygen will be determined at regular intervals during well purging prior to sampling. Stability of these results over sequential readings is used to indicate adequate purging. Data quality objectives are not applicable for this use.

The parameters, test methods, and the expected range of results for the project are listed in Table 2.

 Table 2. Field and Laboratory Parameters, Test Methods, Sample Preparation Methods, and Expected Concentration Ranges

		Test Method Standard Methods	Sample Preparation	Expected Range of
Parameter	Matrix	(APHA,1998)	Method	Results
Field Tests				
pН	Water	Orion Meter (4500-H ⁺)	None	5.5-7.5 SU
Temperature	Water	Orion Meter	None	7 to 15 °C
Electrical Conductivity	Water	Beckman Meter (2510) Membrane Electrode	None	100-1000 µmhos/cm
Dissolved Oxygen	Water	(4500-O G.)	None	0.1-10 mg/L
Laboratory Tests				
Nitrate+Nitrite-N	Water	4500 NO3 ⁻ I	None	0.01-70 mg/L

Study Design

The monitoring network consisting of about 30 to 35 wells will be established in the study area. The primary focus of the monitoring network will be the areas of elevated nitrate identified in Erickson (1998) and shown in Figure 2. Wells will be located in areas where land application practices have improved or will likely improve based on input from staff in the Bellingham Field Office. The initial list of candidate wells will be derived from wells that were sampled during previous studies. Factors that will be considered when selecting wells for the network include the following:

- Well location relative to areas known to have changed manure or wastewater application practices as identified by the Bellingham Field Office staff
- Well owner permission to sample for the long term
- Previous sampling history and elevated nitrate concentrations
- Well construction and sealing is adequate
- Well log is available or the well depth is known
- Well draws water only from the Sumas-Blaine Surficial Aquifer
- Sampling and water-level accessibility
- Water is untreated prior to the sampling point

In addition, if multiple wells are available in an area, the preferred well characteristics will be:

- The well is completed in the upper portion of the aquifer
- New well construction

Owners of candidate wells will be contacted by telephone and by onsite visits to discuss their willingness to participate in the project. If no existing water-supply wells exist in critical areas, monitoring wells will be installed provided drilling resources are available.

Well Sampling and Representativeness

The sampling network will be sampled bi-monthly (every other month) for two years. To minimize the effects of altering the water chemistry of groundwater samples, the following procedures will be used:

- Samples will be obtained from as close to the wellhead as possible
- Samples will be obtained prior to any water treatment
- Wells will not be sampled that, based on visual inspection, do not have adequate surface seals or may be contaminated by surface runoff
- Wells and water delivery systems will be purged a minimum of 15 minutes before sampling
- Samples will be obtained when the pump is running to minimize the contribution from storage tanks

Completeness

The goal for completeness is 95%. Because this study is intended to define the seasonal variability of nitrate concentrations at each well, it is important that all wells have a nearly complete sampling record. Samples will be packed carefully so that they arrive intact at the laboratory. In the event that a sample is damaged during transit or testing, wells will be resampled and a new sample will be submitted for testing. The laboratory should notify the project lead as soon as possible when a sample is damaged or deemed unsuitable for analysis.

Comparability

Results from this study should be comparable to results from previous Ecology and US Geological Survey studies in this area. The test method and sampling procedures by Ecology sampling teams will be the same as were used for previous Ecology nitrate studies and are comparable to US Geological Survey methods. Routine test methods used at Manchester Laboratory will be adequate for this study.

Duration of the Project

The monitoring network will be sampled bi-monthly for two years. The results will define the variability of the nitrate concentrations at each of the wells and will be used to define the long-term sample frequency. The methods, results, and findings will be described in a technical report which will be finalized in October 2005.

Field Procedures

Well Locations

Wells will be located on topographic maps (1:24000) and using Magellan Global Positioning System (GPS) instrumentation. GPS well locations will be recorded as latitude and longitude coordinates.

Sampling Methods

Water levels will be measured in each well, if accessible and the well owner gives permission, prior to sampling using a commercial electric probe. Measurements will be recorded to 0.01 feet and will be accurate to 0.03 feet. The well probe will be decontaminated with sequential rinses of 10% bleach solution and de-ionized water between wells.

Wells and water lines will be purged prior to sampling. Samples will be obtained from taps as close to the wellhead as possible. Samples should be obtained only when the pump is discharging to minimize the effects of obtaining water from storage tanks. To do this a "Y" fitting will be attached to the tap whenever possible. Samples will be obtained from one "Y" outlet while most of the discharge is directed through the other outlet. A hose will be attached to the primary "Y" discharge outlet to direct discharge to a suitable location. A hose-bib adapter will be attached to the second "Y" discharge outlet and will be used to direct flow to the sample bottle.

Electrical conductivity, pH, dissolved oxygen, and temperature will be measured at five-minute intervals during purging. Whenever possible field parameter measurements will be determined in a flow cell. Purging will continue until these parameters have stabilized. Stability criteria, based on previous field experience, are listed in Table 3.

		Change for
Parameter	Criteria	Typical Value
Electrical Conductivity	10 µmhos/cm	7%
pН	0.2 Std Units	3%
Temperature	0.2°C	2%
Dissolved Oxygen	0.3 mg/L	10%

Purging will be considered complete when two consecutive sets of parameter readings show changes less than the criteria listed above.

Samples will be placed in bottles obtained from Manchester Laboratory. Bottle materials, preservatives, and holding times for the nitrate+nitrite-N are listed below:

- Bottle: 125 mL, wide-mouth polyethylene
- \circ Preservative: Sulfuric acid to pH<2, Refrigerated at 4°C
- Holding Time: 28 days

All samples will be placed in coolers with ice. Two hundred and fifty (250) microliters of 1:1 sulfuric acid will be added to sample bottles at Manchester Laboratory before bottles are shipped. The pH of the acidified sample will be verified in the field. The sampling team will transport samples to the Ecology Headquarters Building. The Ecology laboratory courier will transport samples to the Ecology/EPA Manchester Laboratory in Manchester, Washington.

Laboratory Procedures

Nitrate+nitrite-N concentrations will be determined using the cadmium reduction flow injection method, Standard Methods (20th Edition) 4500 NO3⁻I (Manchester Laboratory, 2002). The laboratory costs include 50% discount for Manchester Lab.

Quality Control Procedures

Field Quality Control

All field meters will be calibrated in accordance with the manufacturers' instuctions at the start of each day and midway through the day. Duplicate results will be obtained at a minimum of 10% of the wells to determine overall precision of field parameters.

A field duplicate sample will be collected for each ten well samples and submitted to the laboratory as a blind sample. A field duplicate is a second sample from the same well using identical sampling procedures. After the initial sample is collected, the pump will be shut off for about five minutes to allow the aquifer to equilibrate. For the duplicate sample the entire purging and sampling procedure will be repeated. Duplicate sample results will provide an estimate of overall sampling and analytical precision. One blind reference sample will be submitted with each sampling episode. This sample result will be used to provide an estimate of the overall accuracy of the analytical results.

Laboratory Quality Control

Routine laboratory quality control procedures will be adequate to estimate laboratory precision and accuracy for this project. Laboratory quality control samples consist of blanks, duplicates, matrix spikes, and check standards (laboratory control samples) (Manchester Laboratory, 2002).

Duplicates will be used to assess analytical precision. Matrix spikes will be used to indicate bias due to matrix interferences. Check standards will be used to estimate bias due to calibration. Laboratory blanks will be used to measure the response of the analytical system at a theoretical concentration of zero.

Data Reduction and Management Procedures

All field results – including water levels, well discharge rates, and field parameter results – will be recorded on well sampling sheets that will be maintained throughout the length of the project and eventually archived in project files. Field data will be entered in spreadsheets and may be entered in the Ecology Environmental Information Management database, if appropriate.

All laboratory data will be entered into the Laboratory Information Management System. Report sheets will be sent to the project lead in electronic and hard copy formats. Data will be entered in spreadsheets for evaluation and presentation in graphical formats.

Data Review and Validation

All laboratory data will undergo a quality assurance review by Manchester Laboratory staff to verify that quality control samples met acceptance criteria as specified in the standard operating procedure for that method. Appropriate qualifiers will be attached to results that did not meet requirements. An explanation for the data qualification will be described in a quality assurance memorandum attached with the data package.

After receiving the data package, the project lead will verify that the results have met the measurement quality objectives for bias, precision, and accuracy for that sampling episode. Precision will be estimated by calculating the RPD for field duplicate results. Analytical bias is assumed to be within acceptable limits if laboratory quality control limits are met for blanks, matrix spikes, and check standards. Sampling bias will be assured by verifying that the correct sampling and handling procedures were used. Overall accuracy will be estimated by comparing the measured result with the true value of the blind reference sample. Goals for completeness will then be evaluated and, if needed, replacement samples will be obtained and adjustments in subsequent sampling events will be made.

Data Quality Assessment

If data quality objectives have been met for all sampling episodes, the data will be considered acceptable for use except as qualified during the data review and validation process. The data will be used to identify a long-term sample frequency and to evaluate the trends of nitrate concentrations in the aquifer over the two-year monitoring period.

The results will be evaluated using the Seasonal Kendall statistical test or equivalent at the 95% confidence level to identify trends. The Seasonal Kendall test is appropriate for data with seasonal cycles and can be used even if there are missing, tied, or non-detect values (Gilbert, 1987). Also, the data do not need to be normally distributed for valid results. For the Seasonal Kendall test, the null hypothesis assumes that no trend is present. The null hypothesis is rejected for a downward trend if the test statistic is negative and the absolute value of the calculated

statistic is greater than the theoretical critical value. The null hypothesis is rejected for an upward trend if the test statistic is positive and the absolute value of the calculated test statistic is greater than the theoretical critical value.

Reporting

After the data are reviewed for each sampling episode, the results for each well will be sent to the respective well owner (and well user if different than the well owner). The results sent will include the date sampled, the nitrate+nitrite-N concentration for that sampling event, and field parameter results.

All nitrate+nitrite concentrations for this study will be reported in terms of nitrogen (N, atomic weight 14), that is, the amount of nitrogen present as nitrate+nitrite and designated as nitrate+nitrite-N. Alternatively, other studies may report nitrate+nitrite results in terms of NO₃ (atomic weight 62). A concentration of 10 mg/L as nitrate-nitrite-N corresponds to a concentration of 44.3 mg/L nitrate+nitrite-NO₃ (ratio of atomic weights 62/14).

After two years of monitoring, a draft report will be prepared that describes methods, results, a statistical analysis of the nitrate trends, and recommendations for sampling frequency for long-term monitoring and modifications to the monitoring program. After review and addressing reviewers' comments, a final report will be prepared. The draft report should be completed in August 2005 and finalized in October 2005.

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