



**Groundwater Quality in the
Agnew and Carlsborg area, Clallam County,
December 2000 - September 2002**

April 2003

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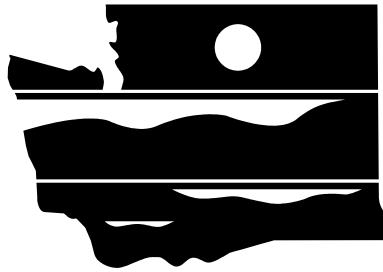
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E C O L O G Y

Groundwater Quality in the Agnew and Carlsborg area, Clallam County, December 2000 - September 2002

by
Kirk Sinclair

Environmental Assessment Program
Olympia, Washington 98504-7710

April 2003

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Table of Contents

	<u>Page</u>
List of Figures and Tables.....	ii
Conversion Factors and Vertical Datum.....	iii
Abstract.....	v
Acknowledgements.....	vi
Introduction.....	1
Study Purpose and Scope.....	1
Study Area Description.....	3
Previous Investigations.....	3
Well Numbering and Location System.....	3
Hydrogeologic Setting.....	5
Data Collection and Analysis Methods.....	9
Evaluation of Water Quality Trends.....	10
Study Findings.....	11
Groundwater Levels.....	11
Water Quality.....	11
Temperature, Specific Conductivity, pH, and Dissolved Oxygen.....	11
Nitrogen Compounds.....	17
Bacteria.....	17
Chloride.....	19
Total Iron and Manganese.....	19
Discussion.....	21
1. Water Quality Results and Drinking Water MCL Criteria.....	21
2. Evaluation of Nitrate+nitrite-N Trends (1980-2002).....	21
3. Data Seasonality.....	22
4. Inter-Laboratory Comparison of Split Sample Results.....	22
Summary and Conclusions.....	25
Recommendations.....	27
References.....	29

Appendices

- A. Data Tables
- B. Quality Assurance Review

List of Figures and Tables

	<u>Page</u>
Figures	
Figure 1. Map showing study area, mean annual precipitation, and geologic cross-section trace.	2
Figure 2. Well numbering and location system	4
Figure 3. Map of surficial geology, well locations, and potentiometric contours for the water-table aquifer in March 1996.	6
Figure 4. Hydrogeologic section A-A' showing principal aquifers and confining units within the study area.....	7
Figure 5. Water level, nitrate+nitrite-N, and chloride measurements for study area wells, 1978 to 2002.....	12
Figure 6. Map showing concentrations of nitrate+nitrite-N for study area wells, December 2000 to September 2002	18
Tables	
Table 1. Target analytes, test methods, and method detection limits	9
Table 2. Maximum contaminant level and groundwater quality criteria.....	16
Table 3. Summary of field measurements and laboratory analytical results for groundwater samples collected from December 2000 through September 2002	16
Table 4. Summary of nitrate+nitrite-N concentrations by sampling month	22

Conversion Factors and Vertical Datum

Multiply	By	To obtain
inch (in)	25.4	millimeter
foot (ft)	0.3048	meter
foot per mile (ft/mi)	0.1894	meter per kilometer
square ft (ft ²)	0.0929	square meter
acre	0.4047 4,047	hectare square meter
acre-foot (acre-ft)	1,233	cubic meter
cubic foot (ft ³)	0.02832	cubic meter
cubic foot per second per mile (ft ³ /sec/mi)	0.0176	cubic meter per second per kilometer
cubic foot per second per square mile (ft ³ /sec/mi ²)	0.01093	cubic meter per second per square kilometer
cubic foot (ft ³)	28.32	liter
mile (mi)	1.609	kilometer
square mile (mi ²)	2.59	square kilometer
gallon (gal)	3.785	liter
million gallons per day (Mgal/d)	0.04381	cubic meter per second

Temperature

To convert degrees Celsius (°C) to degrees Fahrenheit (°F), use the following equation:
 $^{\circ}\text{F} = (9/5 \times ^{\circ}\text{C}) + 32$.

To convert degrees Fahrenheit (°F) to degrees Celsius (°C), use the following equation:
 $^{\circ}\text{C} = 5/9(^{\circ}\text{F} - 32)$.

Sea Level

In this report, sea level refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929).

Altitude

In this report, altitude is measured in feet above mean sea level.

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Abstract

Eight wells in the Agnew and Carlsborg area of Clallam County were monitored quarterly from December 2000 through September 2002 for traditional field parameters and a small suite of laboratory-analyzed constituents to determine if groundwater quality has changed appreciably since area wells were first systematically sampled in 1980.

Based on this evaluation, nitrate+nitrite-N concentrations ranged from <0.01 to 4.58 mg/L. Concentrations of total persulfate nitrogen were similar, ranging from <0.01 to 4.31 mg/L. Fecal coliform bacteria were not detected in any samples; however, total coliform bacteria were detected in approximately 16 percent of total samples at concentrations ranging from 1 to 45 CFU/100 ml. Chloride concentrations ranged from 2.97 to 14.3 mg/L, while total iron and manganese concentrations ranged from <10 to 2540 µg/L and <1.0 to 795 µg/L, respectively.

Trend analysis of the nitrate data for each well suggests that, of the eight wells evaluated, three showed a statistically significant increase in nitrate concentration, four showed no trend, and one showed a decreasing trend.

Comparative evaluation of split samples processed at the Clallam County Environmental Laboratory and Ecology's Manchester Environmental Laboratory indicated good agreement in fecal coliform analyses and generally poor agreement in paired nitrate-N analyses.

Acknowledgements

This study could not have been undertaken without the contributions of others. In particular, I would like to thank the landowners who provided access to their property and wells; this study would not have been possible without their assistance and cooperation. Ann Soule provided counsel during initial project scoping meetings. Darrel Anderson, Nigel Blakley, Barb Carey, Howard Christenson, Dean Butz, Craig Graber, and Morgan Roose all helped at various times with field work. Melanie Kimsey, Barb Carey, and Ann Soule reviewed the draft report, while Joan Letourneau edited and formatted the report. Finally, thank you to the staff at Manchester Environmental Laboratory who provided courier and analytical laboratory services throughout this project.

Introduction

The Sequim-Dungeness peninsula in northeastern Clallam County has experienced rapid population growth in recent years, owing in part to Sequim's favorable reputation as a retirement community. Between 1976 and 1996 the peninsula's human population nearly tripled, and area land use progressively shifted from irrigated agriculture toward rural residential and urban development (Thomas et al., 1999). Much of this development centered around the city of Sequim and the outlying communities of Agnew, Carlsborg, and Jamestown (Figure 1). Sequim and the community of Sunland are the only regions of the peninsula served by sanitary sewers. All other development relies on individual or community septic systems to manage domestic wastewater.

Rapid population growth and the peninsula's reliance on groundwater to meet potable water needs prompted local officials to commission several regional and smaller scale water quality investigations over the past two decades (Drost, 1983; Soule, 1991; Sequim, 1994; Thomas et al., 1999; and Clallam County, 2000). Data from these investigations suggest that groundwater nitrate-N concentrations increased between 1980 and 1996 in some areas of the peninsula. This investigation was undertaken to provide current information on groundwater quality and trends within the high-growth areas surrounding Agnew and Carlsborg.

Study Purpose and Scope

This report summarizes a two-year sampling effort to evaluate groundwater quality conditions in the Agnew-Carlsborg area of Clallam County. The major objectives of this study were to:

1. Establish an ambient groundwater monitoring network for the Agnew-Carlsborg area that would complement and supplement ongoing monitoring by Clallam County Environmental Health.
2. Determine if nitrate-N concentrations vary seasonally and whether they have increased, decreased, or remained the same since area wells were first broadly sampled in 1980.
3. Conduct joint sampling with Clallam County Environmental Health staff to ensure that Ecology and Clallam County sampling methods and analytical results are consistent.

The preliminary work for this project began in June 2000 when historic groundwater data were compiled, an initial project scoping meeting was held, and work on the study quality assurance project plan began. Field water-quality sampling commenced in December 2000 and ran through September 2002. Eight wells were monitored quarterly during this period for traditional field parameters: temperature, specific conductivity, pH, dissolved oxygen, and groundwater level. During each site visit, water samples were collected for subsequent laboratory analysis of total persulfate nitrogen, nitrate+nitrite-N, total and fecal coliform bacteria, chloride, total iron, and total manganese. Split samples for nitrate+nitrite-N and fecal coliform bacteria were collected from a subset of the study wells on three occasions (June, September, and December 2001) for comparative analysis at Ecology's Manchester Environmental Laboratory and laboratory facilities maintained by Clallam County.

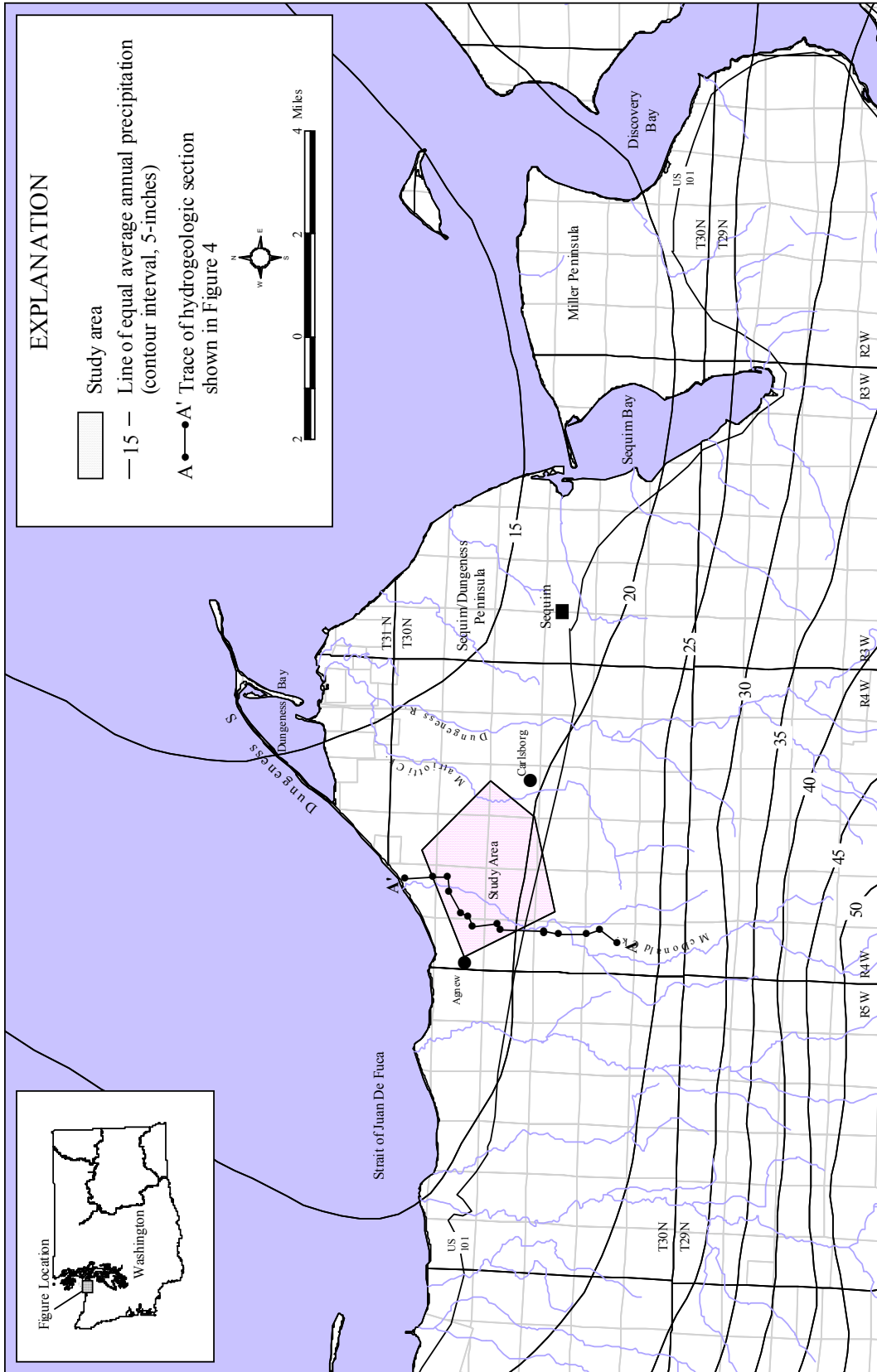


Figure 1. Map showing the study area, mean annual precipitation, and geologic cross-section trace. Precipitation isohyets after Miller et al., 1973; hydrogeologic cross-section (shown in Figure 4) after Thomas et al., 1999.

Study Area Description

As defined here, the communities of Agnew and Carlsborg encompass approximately six square miles or roughly 10 percent of the Sequim-Dungeness peninsula landmass (Figure 1). The Agnew-Carlsborg area lies near the northwestern extent of the Dungeness peninsula and is comprised of gently sloping to flat terrain to the north, with a few small interspersed hills to the south. The area is bisected by McDonald Creek on the west and Matriotti Creek on the east and lies at elevations ranging from roughly 100 feet near the Strait of Juan de Fuca to greater than 400 feet near the southern boundary of the study area.

The Agnew-Carlsborg area has a temperate-marine climate with warm dry summers and cool wet winters. The average annual precipitation is approximately 19 inches and varies from roughly 17 inches in the northern study area to approximately 21 inches in the south (Figure 1). Most of the annual precipitation falls as rain from November through February, with relatively little precipitation during the summer growing season. Local land use is dominated by grassland, irrigated agriculture, dairy farms, forest land, and rural residential development. Irrigated agriculture is heavily reliant on a long established series of irrigation ditches that are used seasonally to divert water from the Dungeness River (typically May 1 - September 30). The study area lies within three irrigation districts (Agnew, Dungeness, and Cline) and obtains a portion of its irrigation water from each company.

Previous Investigations

Groundwater quality conditions in the Agnew-Carlsborg area have been evaluated, on at least two occasions, as part of larger regional or state-wide investigations (Drost, 1986; and Turney, 1986). Drost (1983), Soule (1991), Sequim-Dungeness Groundwater Committee (1994), Thomas et al. (1999), and Clallam County (2000) sampled 138, 36, 340, 74, and 28 wells, respectively, during localized intensive studies of the Sequim-Dungeness area. The latter five intensive studies, of the Sequim-Dungeness area, provide both a baseline and subsequent points of comparison for evaluating the results of this investigation.

Well Numbering and Location System

The locations of all wells referenced in this report are described using the township, range, section, and quarter-quarter section convention. Range designations include a “W” and township designations include an “N” to indicate the well lies west and north of the Willamette meridian and baseline, respectively. Quarter-quarter sections are represented by a single capital letter. If more than one well is inventoried within a quarter-quarter section, a sequence number is added after the quarter-quarter designation to assure uniqueness. For example, the first inventoried well located in the northeast quarter of the southwest quarter of Section 7, Township 30N, Range 04W, is recorded as 30N/04W-07L01, the second well as 07L02, and so on (Figure 2).

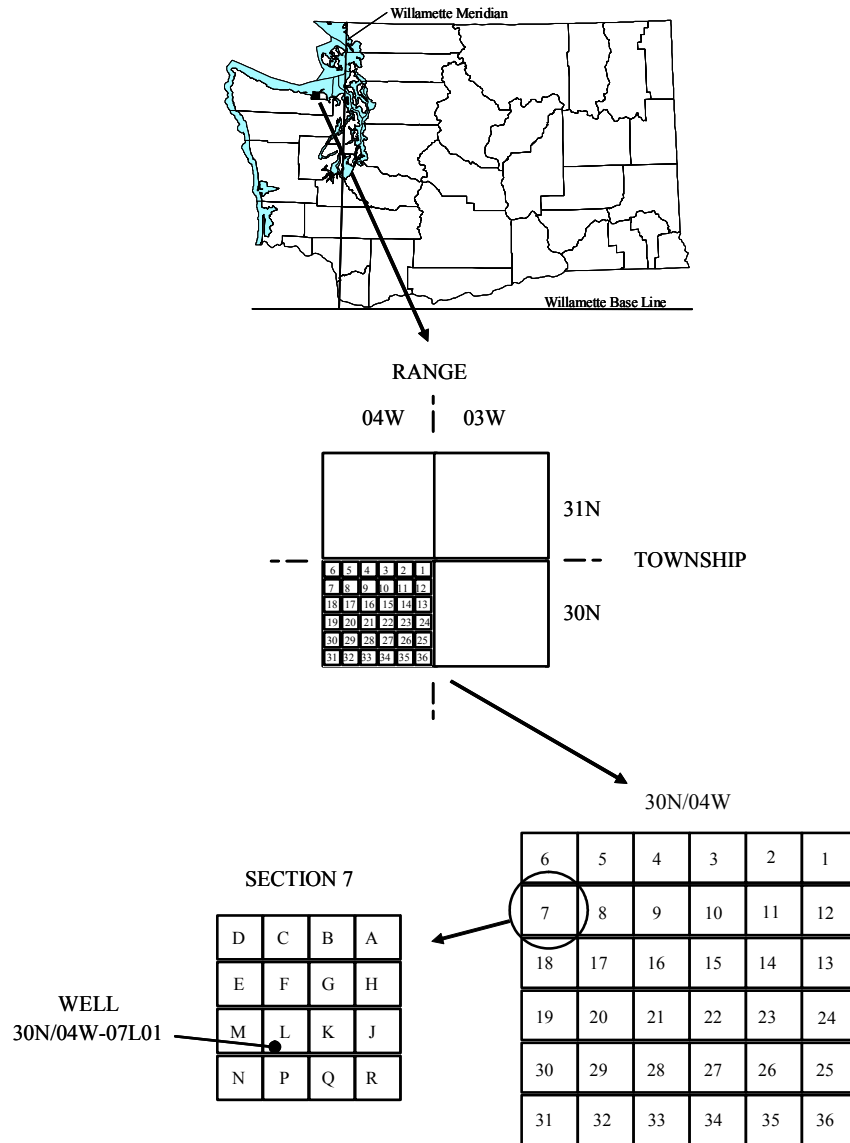


Figure 2 - Well numbering and location system.

This site location and numbering convention has been used for many years by Ecology, the U.S. Geological Survey (USGS), and others, and sometimes results in numbering conflicts between reports or agencies. Several wells previously inventoried by the USGS are referenced in this report. An attempt was made to preserve established location numbers to facilitate comparisons between this and prior publications. Readers wishing to cross reference this and prior reports should verify well identity via the construction details and descriptions provided in Table A-1 (see Appendix A).

All wells monitored during this study were assigned Department of Ecology unique well identification numbers consisting of three letters followed by three numbers (i.e., AAB827). The identification number is contained on an aluminum tag that was securely attached to the well casing or another permanent fixture of the water system.

Hydrogeologic Setting

The communities of Agnew and Carlsborg, like the greater Sequim-Dungeness peninsula, are underlain by a thick sequence of unconsolidated sediments and Tertiary age bedrock. Area bedrock consists of consolidated marine sediments (sandstone, siltstone, conglomerate, and mudstone) and submarine volcanic rocks (largely basalt flows and breccias) (Jones, 1996). Bedrock is mantled throughout the study area by unconsolidated Quaternary age glacial and interglacial sediments. These sediments were laid down over the past several hundred thousand years during repeated glacial incursions into the area and during intervening ice-free periods. The unconsolidated deposits are less than 100 feet thick near the southern study area boundary and increase to a known thickness of at least 600 feet in the northern study area (Figure 3).

Prior investigators grouped or subdivided the study area geologic deposits into seven hydrogeologic units based on their water development potential (Drost, 1983; Jones, 1996; and Thomas et al. 1999) (Figure 4). Starting at land surface, these units are defined as: the shallow (water table) aquifer (unit 1), the upper confining bed (unit 2), the middle aquifer (unit 3), the lower confining bed (unit 4), the lower aquifer (unit 5), undifferentiated unconsolidated deposits (unit 6), and bedrock (unit 7). The aquifers are composed largely of coarse-grained sand and gravel but may contain extensive lenses of finer-grained silt or clay. The confining beds consist mostly of fine-grained silt and clay but also may contain lenses of sand and gravel.

This study focused on the shallow aquifer (unit 1) which was laid down approximately 10,000 to 15,000 years ago during the Vashon Stade of the Frasier glaciation, the last major ice advance into the region. In many areas Vashon age deposits have been extensively reworked by modern alluvial processes.

Recharge to the shallow aquifer derives from several distinct sources including local precipitation, leakage from unlined irrigation ditches, percolation of unconsumed irrigation water, and leakage from streams. Thomas et al. (1999) used a daily water budget modeling approach developed by Bauer and Mastin (1997) to estimate groundwater recharge for the greater Sequim-Dungeness peninsula. For the Agnew-Carlsborg area, this evaluation showed that recharge from precipitation averages approximately 3.5 inches and ranges from 8 inches in the southern study area to approximately 1.8 inches in the northern study area. Percolation of unconsumed irrigation water and seepage losses from unlined irrigation ditches provides additional recharge to some regions of the study area. During the 1995-97 assessment period, Thomas et al. (1999) concluded that these sources contributed an additional 4.5 inches of recharge, on average, to the study area and provided as much as 28.9 inches of additional recharge to localized areas.

Water within the shallow aquifer generally moves from upland recharge areas in the southern study area toward natural points of discharge along area streams and the Strait of Juan de Fuca (Figure 3). Vertical flow between aquifer units is generally downward in the southern study area and transitions to upward flow near the Strait of Juan de Fuca.

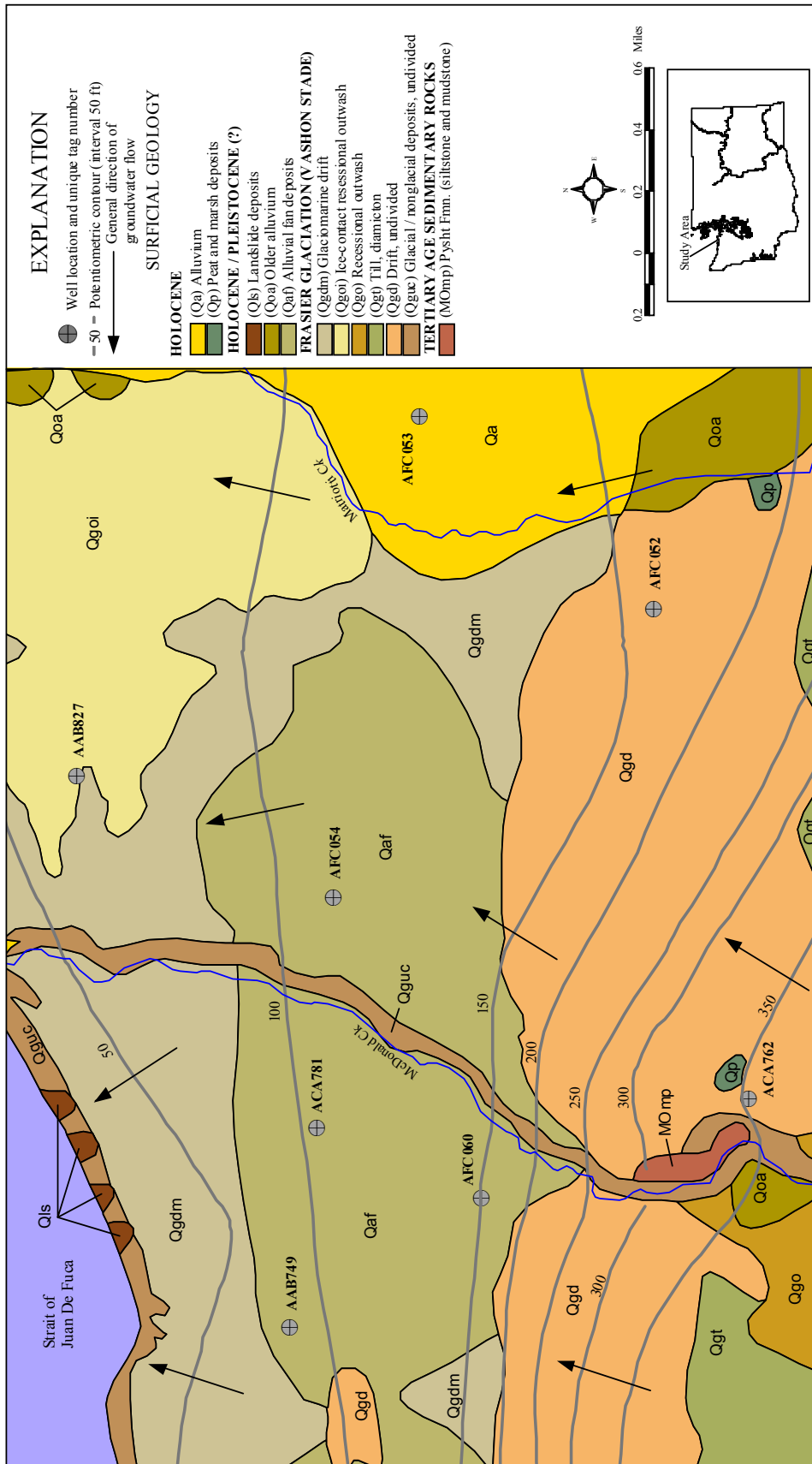


Figure 3. Map of surficial geology, well locations, and potentiometric contours for the water-table aquifer in March 1996, for the Agnew-Carlsborg area. Surficial geology after Schasse and Wegmann, 2000; potentiometric contours after Thomas et al., 1999.

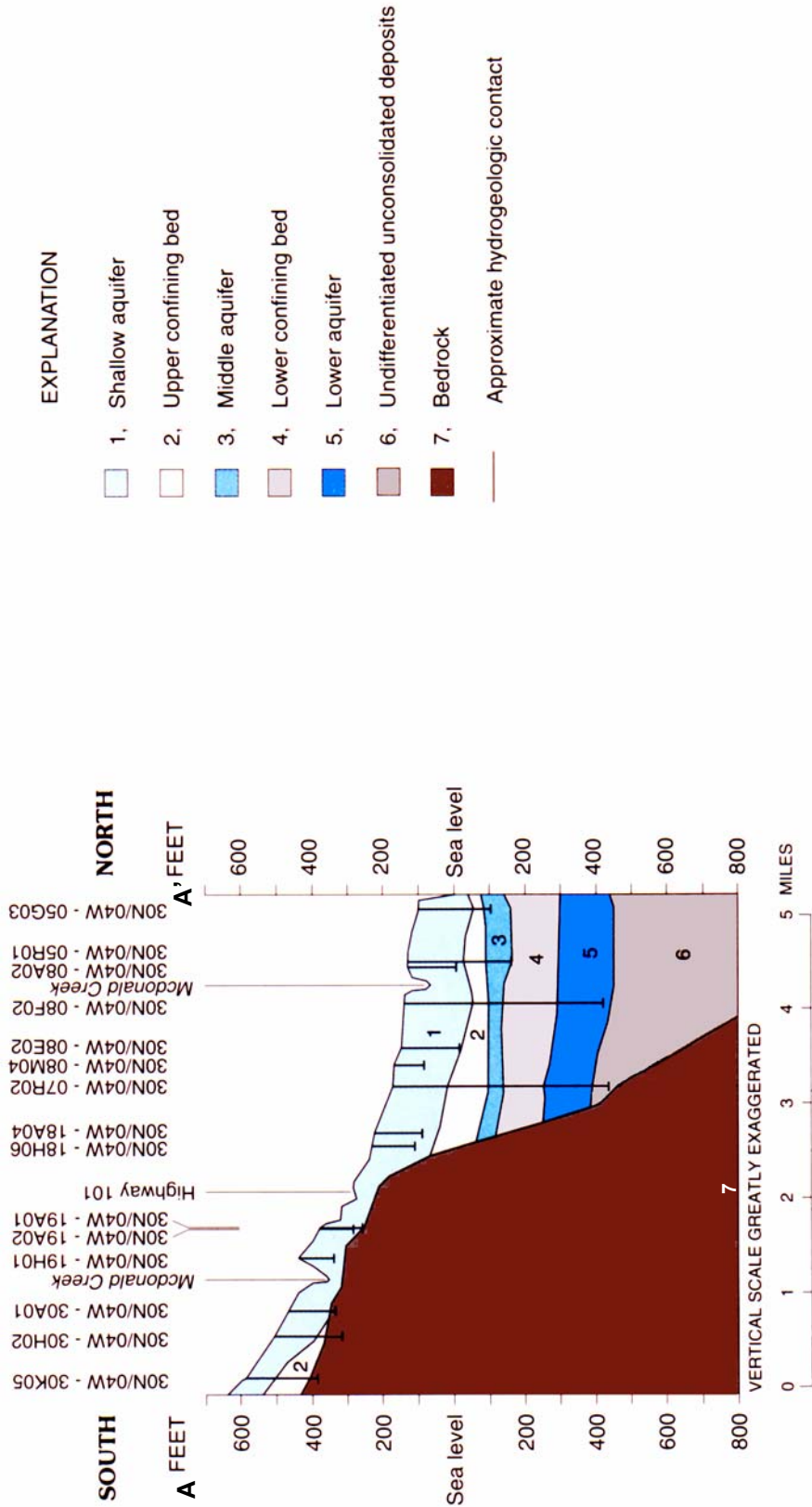


Figure 4. Hydrogeologic section A-A' showing principal aquifers and confining units within the study area. (modified from Thomas et al., 1999)

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Data Collection and Analysis Methods

Field sampling for this study began in December 2000 and continued through September 2002. Sampling techniques followed the procedures specified in the quality assurance project plan (Sinclair, 2000). Eight wells were sampled quarterly during this period for common field parameters (groundwater level, temperature, specific conductivity, pH, and dissolved oxygen) and a small suite of laboratory analyzed constituents (total persulfate nitrogen, nitrate+nitrite-N, total and fecal coliform bacteria, chloride, total iron, and total manganese) (Table 1). These parameters were selected for evaluation because they provide an indication of overall water quality and are typically present in a number of contaminant sources. Shallow wells (those completed in unit 1) were targeted for sampling, since they are the most likely to be impacted by increased septic discharges, changing agricultural practices, or other land use activities (Appendix A: Tables A1 and A2).

Table 1. Target analytes, test methods, and method detection limits.

Parameter	Test Method	Detection Limit
<i>Field Measurements</i>		
Temperature	WTW multiline P4 meter with Sentix 41-3 probe	0.1°C
Specific conductivity	WTW multiline P4 meter with Tetracon 325 probe	1 µs/cm
pH	WTW multiline P4 meter with Sentix 41-3 probe	0.1 SU
Dissolved oxygen	WTW multiline P4 meter with Cellox 325 probe	0.1 mg/L
<i>Laboratory Parameters</i>		
Total persulfate nitrogen	SM4500NB	0.10 mg/L
Nitrate+nitrite-N	SM4500NO3I	0.01 mg/l
Coliform, total (MF)	SM16-909B	1 CFU/100mL
Coliform, fecal (MF)	SM16-909C	1 CFU/100mL
Chloride	EPA 300.0	0.1 mg/L
Iron (total)	EPA 200.7	10 ug/L
Manganese (total)	EPA 200.7	1 ug/L

MF: Membrane filter method

SU: Standard units

CFU: Colony forming units

A commercial flow cell was used to ensure that purging and sampling techniques remained consistent throughout the project. Sampled wells were purged at approximately five gallons per minute, the maximum rate for the flow cell. Field parameter values were recorded at three-minute intervals during purging which continued until all field parameters had stabilized. For this project, stabilization was defined as less than a 5 percent difference between the measured parameter values for two successive 3-minute recording intervals. Samples were collected in pre-cleaned bottles supplied by the Manchester Environmental Laboratory and stored on ice

pending their arrival at the laboratory. Field meters were calibrated at the start of each sampling day in accordance with the manufacturer's instructions.

Groundwater levels were measured during each site visit prior to initiating well purging. Water levels were measured with a calibrated electric well probe (E-tape) in accordance with standard USGS methodology (Stallman, 1983). Duplicate water-level measurements were made at each site to evaluate measurement precision and to ensure that the well-water level was not recovering from recent pumping. Individual water-level measurements were made to the nearest 0.01 foot and were then rounded to the nearest 0.1 foot for reporting purposes.

Evaluation of Water Quality Trends

Trends in groundwater nitrate concentrations were evaluated via hypothesis testing; a null hypothesis (H_0) of no trend was tested against the alternative hypothesis (H_A) of an increasing trend in nitrate concentration over the period 1980 to 2002. In similar fashion, a null hypothesis was formulated and tested to assess declining trends in nitrate concentration over this period. In both cases, the evaluation was performed using a significance level (or "p-value") of 0.05. The significance level is a measure of the strength of evidence for accepting or rejecting the null hypothesis. A p-value of 0.05 means that there is a 5 percent chance that the null hypothesis is correct.

The nonparametric Mann-Kendall test was used for hypothesis testing, since the sample data need not conform to a particular statistical distribution and missing data are allowed (Gilbert, 1987). The Mann-Kendall statistic (S) is calculated as follows:

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(x_j - x_k)$$

where $\text{sgn}(x_j - x_k)$ is an indicator function with values of -1, 0, or 1 as shown below

$$\begin{aligned} \text{sgn}(x_j - x_k) &= 1 && \text{if } x_j - x_k > 0 \\ \text{sgn}(x_j - x_k) &= 0 && \text{if } x_j - x_k = 0 \\ \text{sgn}(x_j - x_k) &= -1 && \text{if } x_j - x_k < 0 \end{aligned}$$

Positive S values which meet the method acceptance criteria indicate that the null hypothesis (no trend) should be rejected in favor of the alternative hypothesis (a statistically significant upward trend in nitrate concentration) (Gilbert, 1987). Similarly, negative S values indicate that the null hypothesis (no trend) should be rejected in favor of the alternative hypothesis (a statistically significant downward trend in nitrate concentration).

Study Findings

Groundwater Levels

Quarterly groundwater level measurements were made in six of the eight wells sampled during this investigation, with a total of seven to eight measurements per well (Appendix A: Table A-3). Based on these measurements, area groundwater levels were generally highest in March and lowest during September to December (Figure 5 and Table A-3). Annual groundwater level fluctuations ranged from 1.6 to 4.8 feet and averaged approximately 2.7 feet for the six wells monitored. As one might expect, those wells lying in areas of greatest annual groundwater recharge generally exhibited the largest annual variation in groundwater levels.

Two wells, AAB827 and AAB749, have partial water level histories dating back to the late 1970's. Evaluation of the entire data histories for these wells suggests that both have experienced a slight (1-2 foot) decline in water levels (Figure 5).

Water Quality

Temperature, Specific Conductivity, pH, and Dissolved Oxygen

Groundwater temperature was measured during this study to help define an appropriate purge volume prior to collecting samples for laboratory analysis. Measured groundwater temperatures ranged from a low of 8.5°C to a high of 12.9°C and averaged 10.7°C (Appendix A: Table A3). Groundwater temperatures generally mirrored seasonal air temperatures and were warmest in June (average 10.8°C) and September (average 11.7°C) and coolest in December (average 10.2°C) and March (average 10.1°C). There is no formal groundwater-quality standard for temperature (Tables 2 and 3).

Specific conductivity is a measure of water's ability to conduct an electrical current and is related to the concentration and charge of dissolved ions in water. Specific conductivity is regulated as a secondary (aesthetic) contaminant in drinking water at concentrations greater than 700 $\mu\text{S}/\text{cm}$. During this study, measured specific conductivity values ranged from 113 to 418 and averaged 279 $\mu\text{S}/\text{cm}$ @ 25°C.

pH plays many important roles in the chemical and biological systems of natural waters and can control the solubility of metal compounds and the rate or magnitude of chemical reactions. pH is regulated as a secondary (aesthetic) contaminant in drinking water at values less than pH 6.5 or greater than pH 8.5, since values outside this range may corrode plumbing fixtures or reduce the effectiveness of water treatment such as chlorination (U.S. EPA, 1986). The pH values measured during this study ranged from 5.80 to 7.75 and averaged 6.98. One well (ACA762) had unusually low pH values relative to other wells and violated water quality standards for pH during all but one sampling event. This is likely a natural condition, since the well is completed at a shallow depth and is bordered by significant peat and marsh deposits.

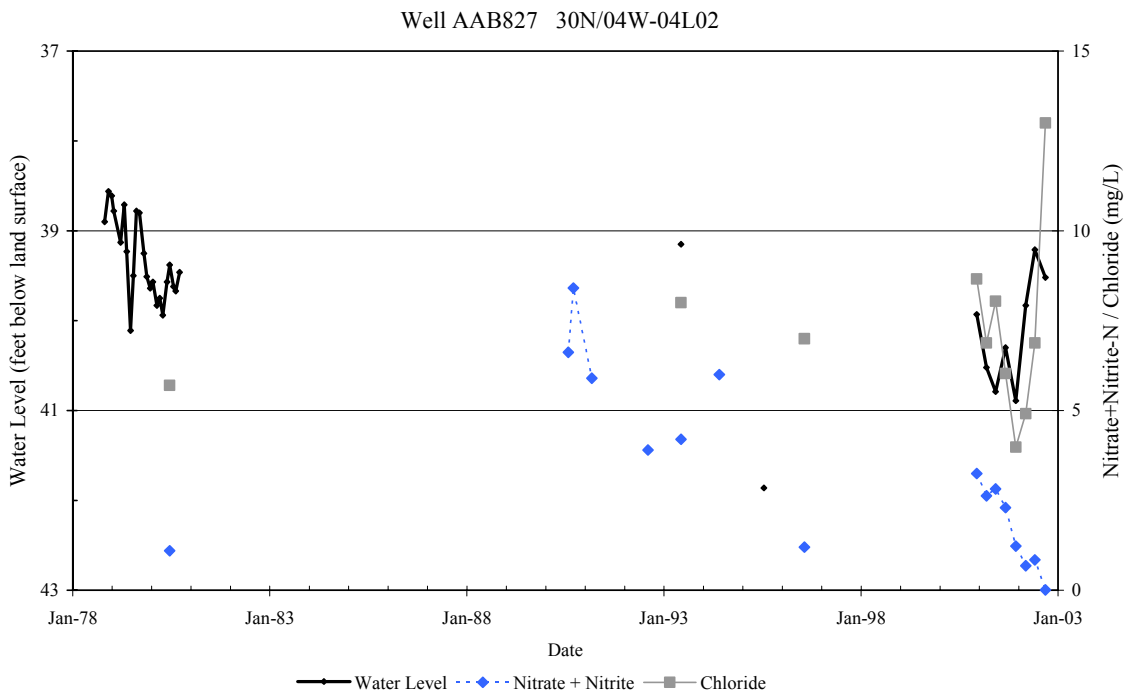
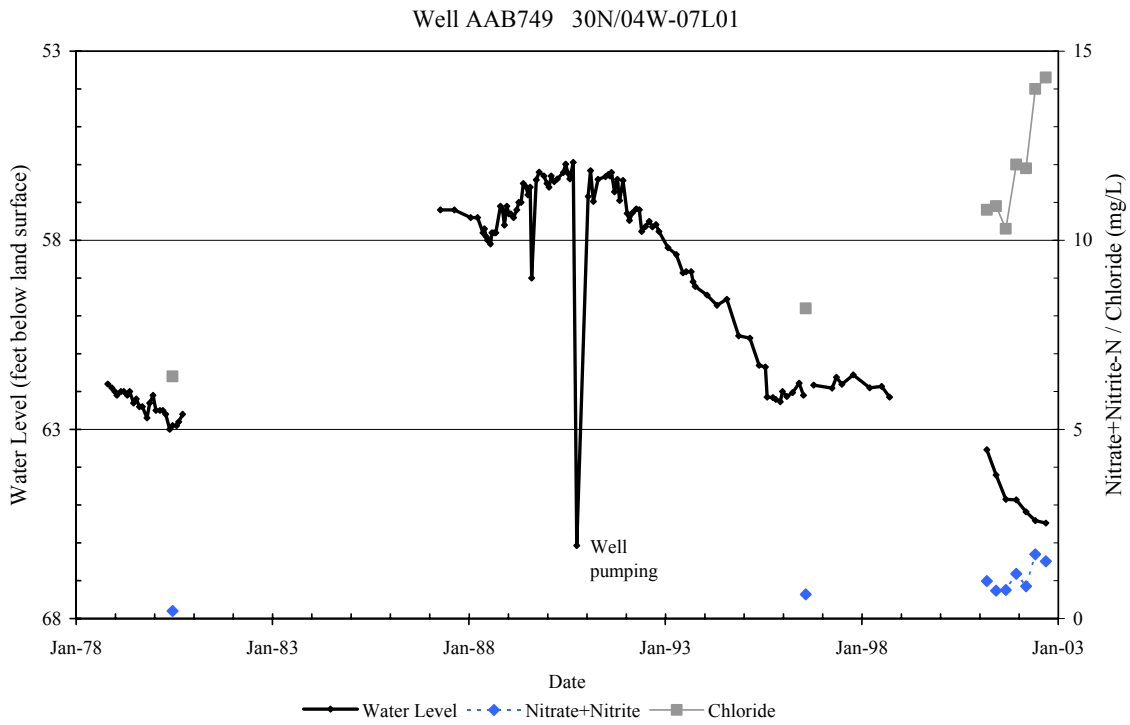


Figure 5. Water level, nitrate+nitrite-N, and chloride measurements for study area wells, 1978 to 2002.

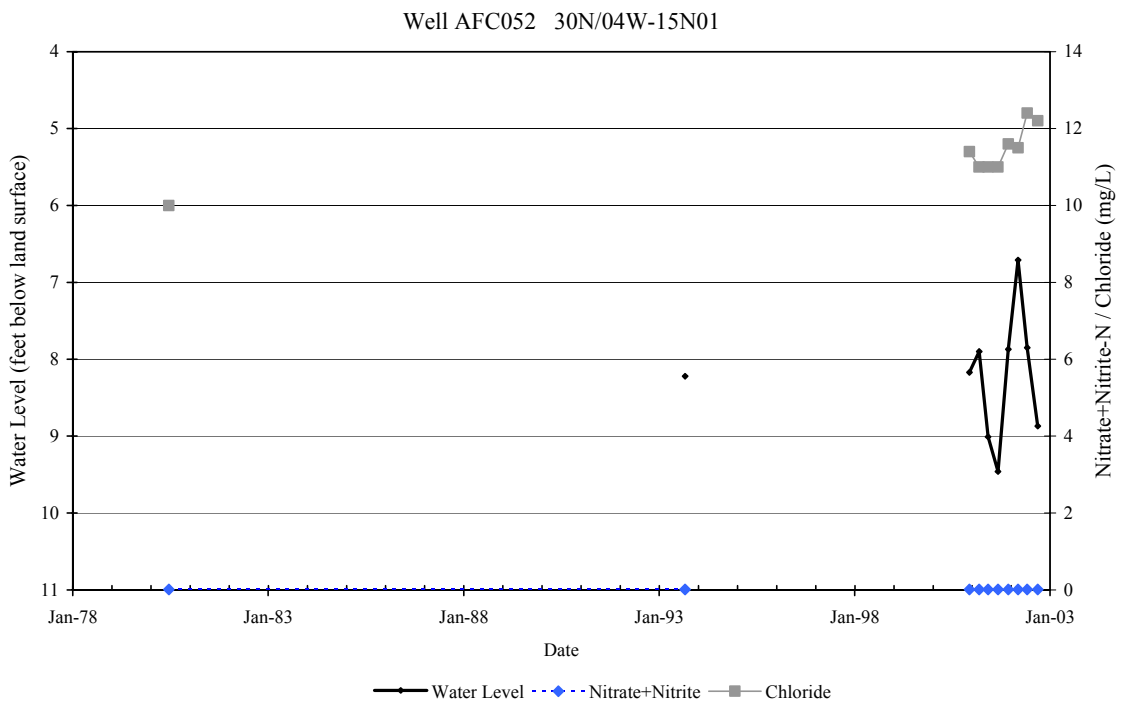
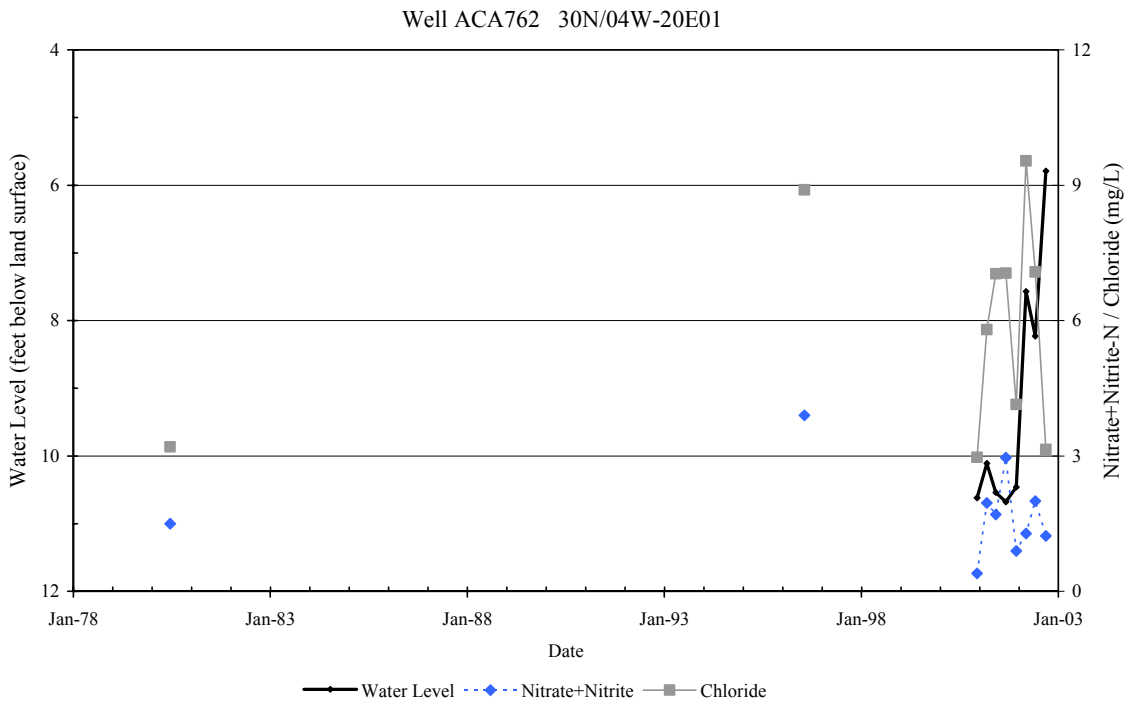


Figure 5 (continued). Water level, nitrate+nitrite-N, and chloride measurements for study area wells, 1978 to 2002.

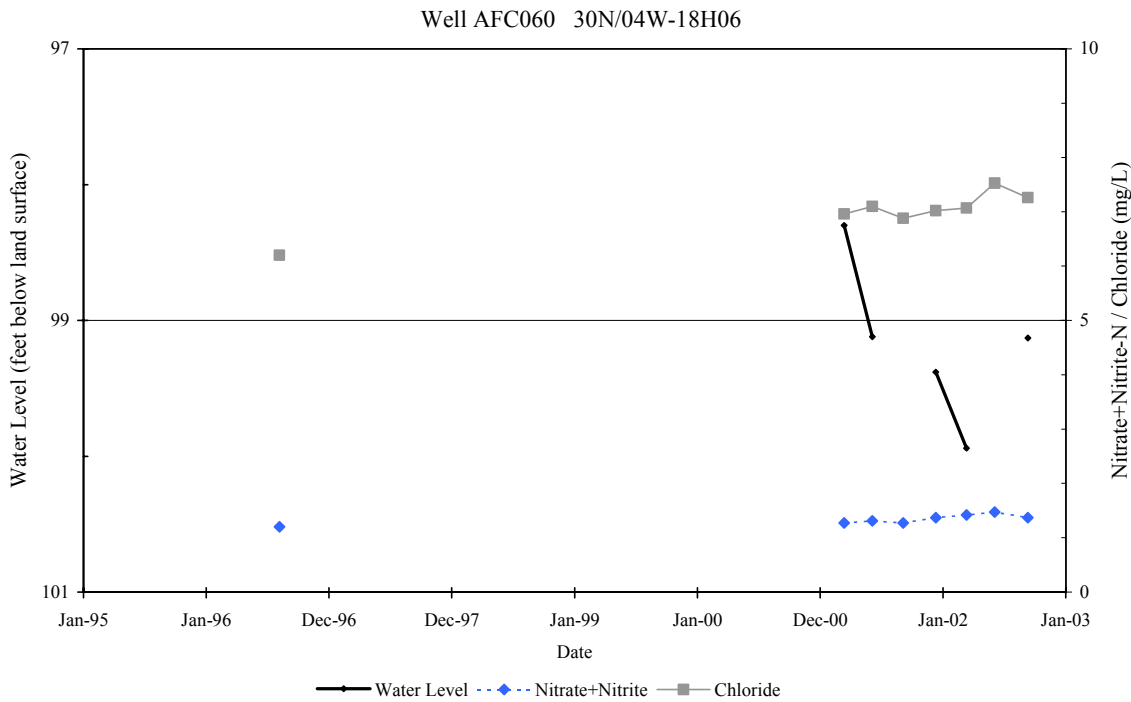
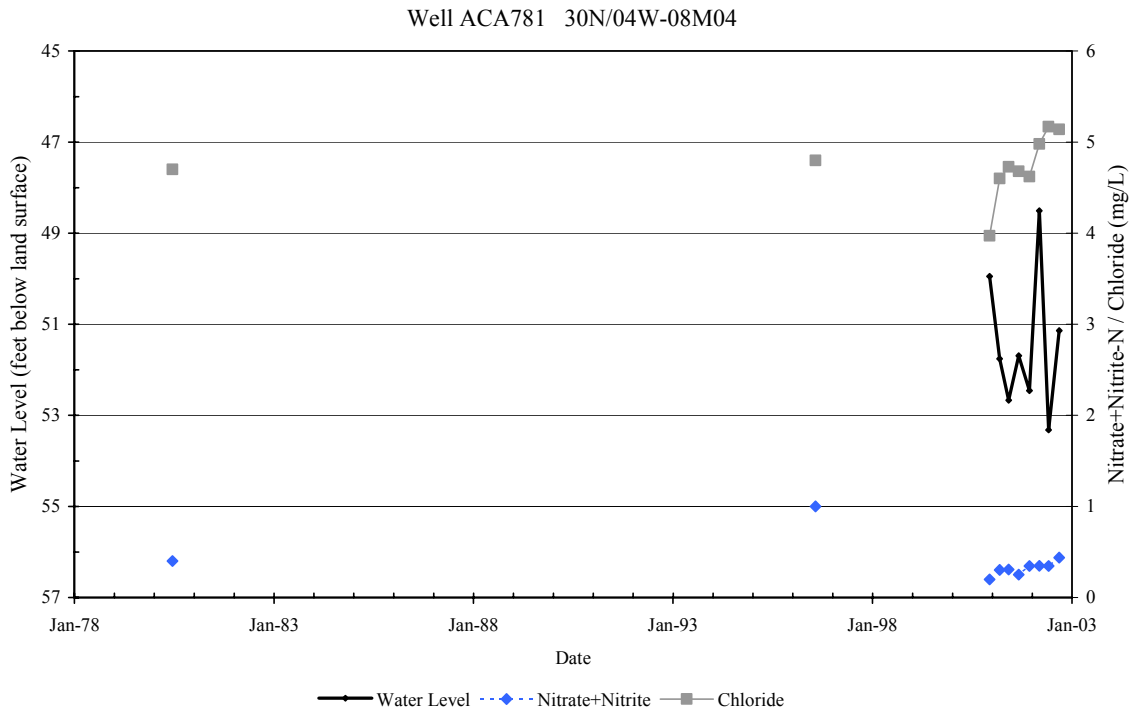


Figure 5 (continued). Water level, nitrate+nitrite-N, and chloride measurements for study area wells, 1978 to 2002.

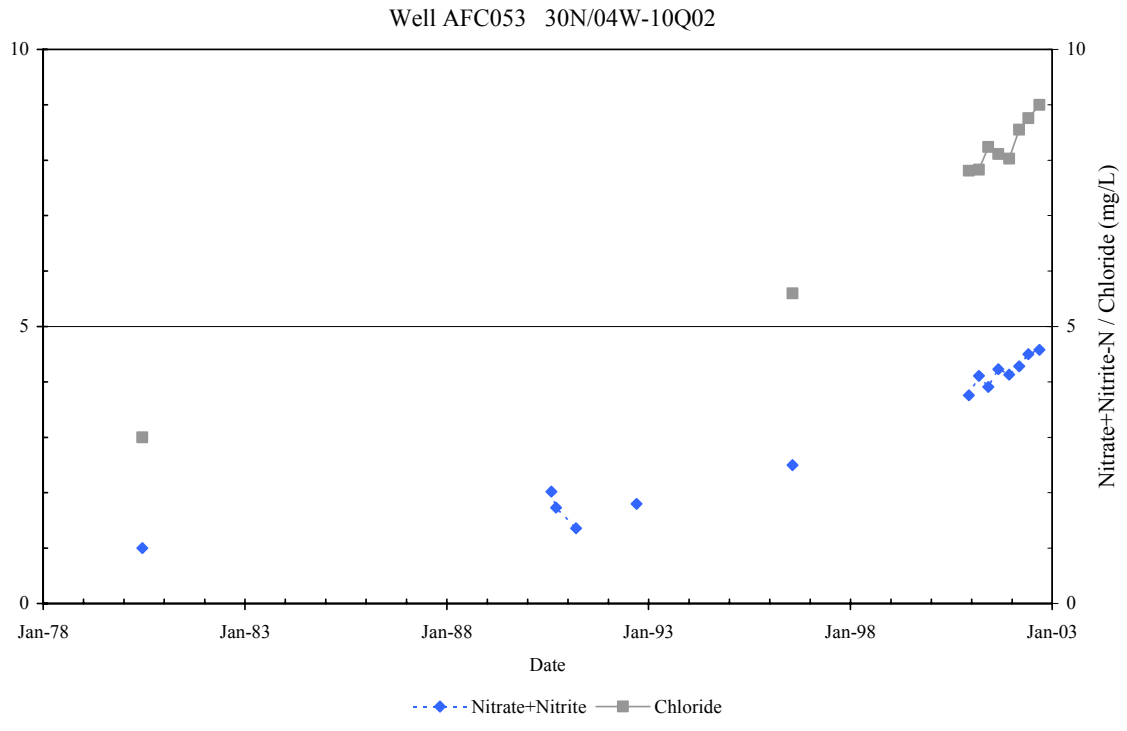
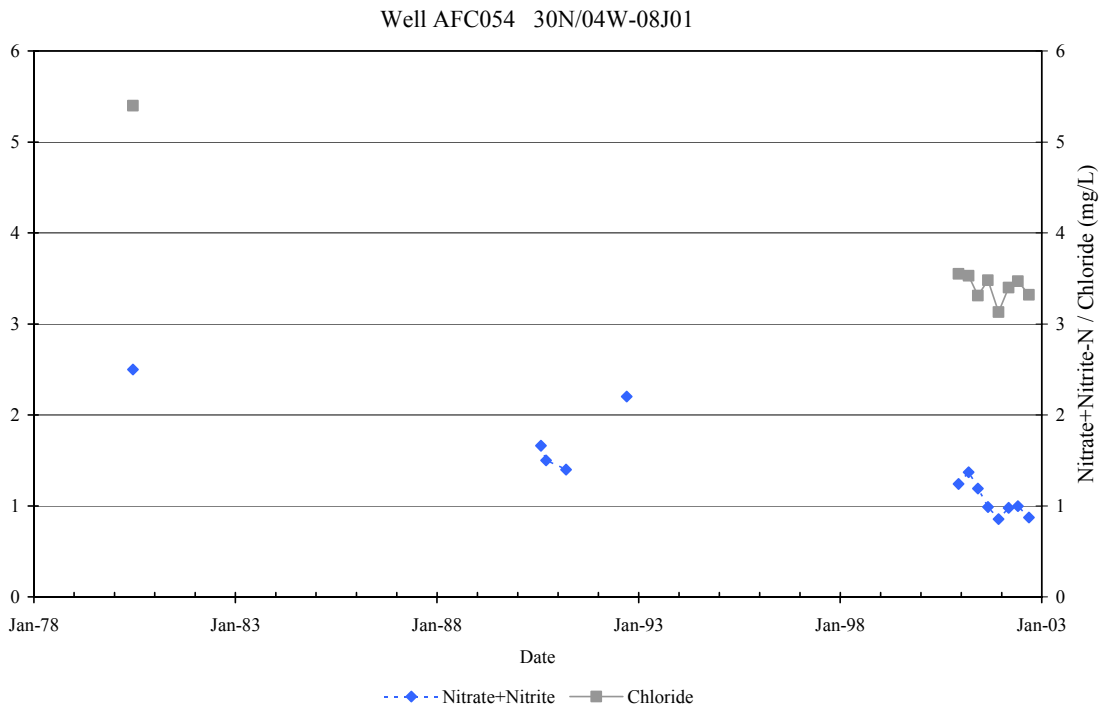


Figure 5 (continued). Water level, nitrate+nitrite-N, and chloride measurements for study area wells, 1978 to 2002.

Table 2. Maximum contaminant level and groundwater quality criteria.

Parameter	Primary MCL ¹	Secondary MCL ¹	Groundwater Quality Criteria ²
<i>Field Measurements</i>			
pH	None	None	6.5 - 8.5 standard units
Specific Conductivity	None	700 umhos/cm	None
Temperature	None	None	None
Dissolved Oxygen	None	None	None
<i>Laboratory Parameters</i>			
Total persulfate nitrogen	None	None	None
Nitrate+nitrite-N	10 mg/L	None	10 mg/L
Coliform, total (MF)	1 CFU/100 mL	None	1 CFU/100mL
Coliform, fecal (MF)	None	None	None
Chloride	None	250 mg/L	250 mg/L
Iron (total)	None	0.3 mg/L	0.3 mg/L
Manganese (total)	None	0.05 mg/L	0.05 mg/L

¹ - Maximum Contaminant Level: Primary MCL values are based on human health criteria; secondary MCL values are based on aesthetic considerations such as taste, smell, or color (Chapter 248-54 WAC).

² - Chapter 173-200 WAC (Water quality standards for ground waters of the State of Washington).

Table 3. Summary of field measurements and laboratory analytical results for groundwater samples collected from December 2000 through September 2002.

Parameter	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum
Temperature (C°)	62	8.5	10.025	10.9	11.4	12.9
pH (standard units)	62	5.8	6.73	6.975	7.235	7.75
Dissolved oxygen (mg/L)	61	0.04	1.04	3.37	6.15	11.7
Specific conductivity (µs/cm@ 25 C°)	62	113	206	276.5	370	418
Fecal coliform (#/100mL)	62	<1	<1	<1	<1	<1
Total coliform (#/100 mL)	62	<1	<1	<1	<1	45
Nitrate+nitrite-N (mg/L)	62	0.01	0.346	1.185	1.7	4.58
Total persulfate nitrogen (mg/L)	62	0.02	0.368	1.24	1.83	4.31
Chloride (mg/L)	62	2.97	4.64	7.075	10.1	14.3
Total iron (µg/L)	62	19	40	123.5	320	2540
Total manganese (µg/L)	62	1.1	<2	<10	55.5	795

mg/L - milligram per liter

µs - microsiemens per centimeter

#/100mL - number of colonies per hundred milliliter

< - less than

µg/L - microgram per liter

The concentration of dissolved oxygen in groundwater can significantly affect many geochemical or biological processes such as the solubility of iron and the oxidation or reduction of nutrients. Concentrations of dissolved oxygen ranged from 0.04 to 11.7 mg/L and averaged 3.8 mg/L. Two wells (AAB749 and AFC052) generally had concentrations lower than 1 mg/L (mean values of 0.79 and 0.85 mg/L respectively) which suggests that reducing conditions prevailed at these locations during the study period. The remaining wells had mean dissolved oxygen concentrations ranging from 2.36 to 7.15 mg/L indicating oxidizing conditions at these locations. There is no groundwater-quality standard for dissolved oxygen.

Nitrogen Compounds

Nitrogen compounds such as ammonium (NH₄⁺) and nitrate (NO₃⁻) are important nutrients for plant and bacterial growth. Nitrate is generally the dominant form of nitrogen in groundwater since ammonium and nitrite (NO₂⁻) are typically converted to nitrate through bacterial processes. For the purposes of this evaluation, nitrate-N and nitrate+nitrite-N were treated as equivalent analyses to enable direct comparisons of historic (nitrate-N) and current (nitrate+nitrite-N) data. High nutrient concentrations in groundwater may indicate contamination by animal waste or sewage, nitrogen-rich fertilizers, or industrial discharges. Nitrate-N is regulated as a primary contaminant in drinking water at concentrations greater than 10 mg/L where it can inhibit the oxygen-carrying capacity of blood and cause methemoglobinemia (blue-baby syndrome) in infants.

The nitrate+nitrite-N values measured during this study ranged from 0.01 to 4.58 mg/L and averaged 1.42 mg/L for the study wells as a whole (Figures 5 and 6). Two wells (ACA781 and AFC052) had consistently low nitrate+nitrite-N concentrations and averaged less than 0.40 mg/L while one well (AFC053) averaged 4.19 mg/L. The remaining study wells had average nitrate+nitrite-N concentrations ranging from 1.06 to 1.72 mg/L. None of the sampled wells exceeded the drinking water standard for nitrate-N during this evaluation (Tables 2 and 3).

Values for total persulfate nitrogen closely followed those of nitrate+nitrite-N, ranging from 0.02 to 4.31 mg/L and averaging 1.46 mg/L. The generally good correspondence between nitrate+nitrite-N and total persulfate nitrogen suggests that concentrations of ammonia and organic nitrogen are quite low.

Bacteria

Two classes of bacteria, total coliform and fecal coliform, were evaluated during this study. Total coliform bacteria represent a broad class of microorganisms that occur in untreated surface water, soil, or decaying vegetation. They are also found in the intestines of warm- and cold-blooded animals where they aid in food digestion. Fecal coliform is a subgroup of total coliform that is found only in the intestines and fecal matter of warm-blooded animals.

Collectively, coliform bacteria generally pose no direct health risk to humans. However, their presence in groundwater may indicate that a well or aquifer has been contaminated by human or animal fecal matter, surface water, or other coliform-rich waste products. Fecal coliform

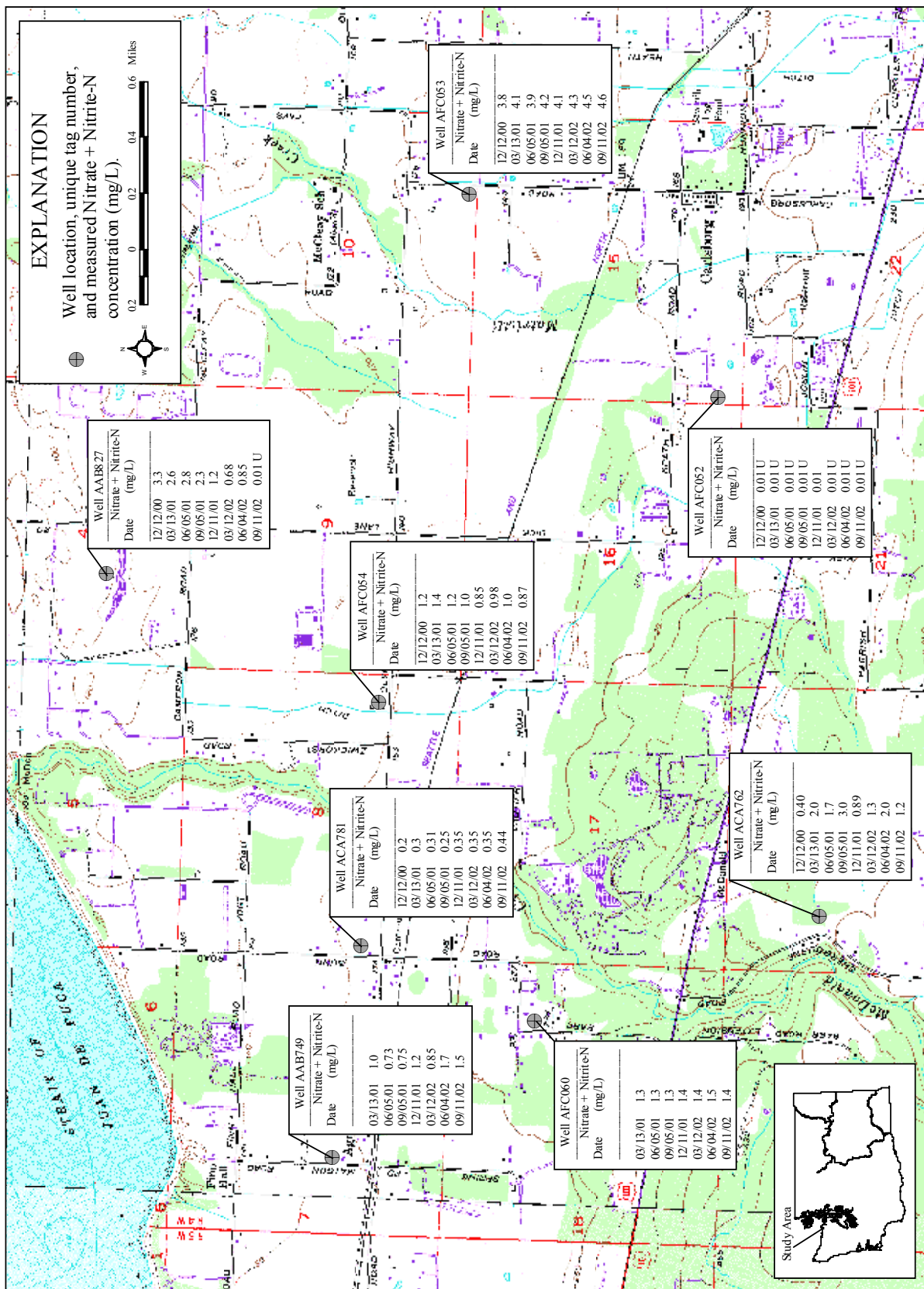


Figure 6. Map showing concentrations of nitrate+nitrite-N for study area wells, December 2000 to September 2002.

bacteria were not detected in any of the water samples collected during this study. Total coliform bacteria were detected in 10 of 62 samples at values ranging from 1 to 45 CFU/100 ml. Five wells exceeded federal drinking water standards for total coliform (≥ 1 CFU/100 mL) while three wells exceeded the standard during two or more samplings (Table 2 and Appendix A: Table-A3).

Chloride

Chloride is considered a secondary (aesthetic) contaminant in drinking water at concentrations greater than 250 mg/L (Table 2). None of the wells sampled during this study exceeded the drinking water standard for chloride. Chloride concentrations were generally low, ranging from 2.97 to 14.3 mg/L and averaging 7.5 mg/L.

Total Iron and Manganese

Iron plays many important biochemical roles in plant and animal life cycles and serves as an oxygen transporter in blood. In oxygenated groundwater, iron is typically present only in trace amounts. It may be more prevalent under reducing conditions and can reach concentrations of 1-10 mg/L as Fe^{2+} . Iron is regulated as a secondary (aesthetic) contaminant in drinking water at concentrations greater than 0.30 mg/L (or 300 $\mu\text{g/L}$), where it can encrust plumbing fixtures or stain laundry. The total iron concentrations measured during this study ranged from 19 to 2,540 $\mu\text{g/L}$ and averaged 237.7 $\mu\text{g/L}$. Six of the eight wells sampled exceeded the drinking water standard for iron at least once during the investigation. Two wells, ACA781 and AFC052, exceeded the standard during five or more sampling events.

Manganese, like iron, is a vital micro-nutrient and is required in small amounts to maintain plant and animal health. Manganese is regulated as a secondary (aesthetic) contaminant in drinking water at concentrations greater than 0.05 mg/L (or 50 $\mu\text{g/L}$) due to its objectionable taste and propensity to stain laundry and plumbing fixtures. Total manganese concentrations during this study ranged from 1.1 to 795 $\mu\text{g/L}$ and averaged 73.6 $\mu\text{g/L}$. Two wells, AFC052 and AFC054, exceeded the drinking water standard for total manganese during all sampling events, while one well, AAB827, exceeded the standard during one sample event.

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Discussion

This study was undertaken to establish an ambient groundwater monitoring network for the greater Agnew-Carlsborg area of Clallam County. In addition, the study was designed to answer four questions:

1. Do current water quality conditions violate applicable drinking water standards for any of the evaluated constituents?
2. How do current trends in nitrate concentration compare with those defined by Thomas et al. (1999)?
3. Do area nitrate values vary seasonally?
4. How do the Ecology and Clallam County split sample results compare?

Discussion and conclusions related to each of these questions are presented in the following sections.

1. Water Quality Results and Drinking Water MCL Criteria

Most residents of the Agnew-Carlsborg area obtain their household water from individual wells or small public water systems located near their homes, and they use on-site septic systems to treat and dispose of household sewage and gray water. A primary objective of this investigation was to broadly determine whether on-site waste-water disposal and other land-use practices have adversely impacted groundwater quality, since area wells were last systematically sampled in 1996. One means of evaluating potential impacts from land-use practices is to compare water quality results against federal and state maximum contaminant level (MCL) criteria for drinking water (Table 2). Based on the study findings, groundwater within the greater Agnew-Carlsborg area generally meets state and federal drinking water standards for the constituents evaluated.

Primary MCL criteria for nitrate-N were met in all cases. Total coliform bacteria were detected in approximately 16 percent of samples and were found on one or more occasions in five of the eight wells sampled during this study. While coliform bacteria generally pose no direct health risk to humans, their presence in well water indicates possible contamination by sewage or other fecal matter. Numerous wells exceeded secondary (aesthetic) drinking water quality criteria for pH, total iron, and total manganese during one or more sampling events.

2. Evaluation of Nitrate+nitrite-N Trends (1980-2002)

Thomas et al. (1999) evaluated trends in nitrate concentration for the greater Sequim-Dungeness peninsula using data from three peninsula-wide sampling events conducted in 1980 (129 wells), 1992 (316 wells), and 1996 (65 wells). Roughly 70 to 90 percent of the wells sampled during these evaluations were completed in the shallow aquifer (unit 1). Thomas et al. (1999) concluded that there was a statistically significant increase in nitrate concentrations in the greater Sequim-Dungeness area between 1980 and 1992, and between 1980 and 1996, but not between

1992 and 1996. The median nitrate concentrations observed during these events were 0.37 mg/L (1980), 0.55 mg/L (1992), and 0.46 mg/L (1996).

Because the sample population (number of wells) for this study was significantly smaller than previous investigations and covered only a localized area of the larger Sequim-Dungeness peninsula, direct comparisons against Thomas's trend data were not possible. Instead, this study used the non-parametric Mann-Kendall test to identify trends in the nitrate data for each of the study wells. Based on this evaluation, three wells, AAB749, AFC060, and AFC053, showed statistically significant increases in nitrate-N concentration between 1980 and 2002. Of the remaining wells, four, ACA762, ACA781, AAB827, and AFC052, showed no significant trend, and one, AFC054, showed a statistically significant decline in nitrate-N concentration.

Chloride concentrations generally followed the same trends in individual wells as nitrate-N. Three wells, AAB749, AFC053, and AFC060, showed increasing chloride concentrations between 1980 and 2002; one well, AFC054, showed a decrease; and three wells, AAB827, ACA762, and ACA781, showed no apparent trend. One well, AFC052, showed increasing chloride concentrations while nitrate-N values showed no trend.

3. Data Seasonality

Detecting long-term trends in environmental data is often complicated by inconsistent sampling procedures (over time or among sampling staff) or seasonal differences between sampling events. The influence of these factors can be minimized by establishing and adhering to a consistent sampling methodology carried out on a fixed schedule. Table 4 summarizes the nitrate+nitrite-N concentrations measured during the quarterly sampling conducted for this investigation. Based on the months sampled, the highest mean nitrate+nitrite-N concentrations were observed in June while the lowest values were observed in December.

Table 4. Summary of nitrate+nitrite-N concentrations (in mg/L) by sampling month.

	December	March	June	September
Min	0.01 U	0.01U	0.01 U	0.01 U
Max	4.13	4.28	4.5	4.58
Mean	1.35	1.41	1.49	1.42
Median	1.04	1.13	1.25	1.11
N*	14	16	16	16

* Total number of samples. Non-detect values were used to calculate the above statistics by assuming the sample concentration equaled one half the method detection limit.

4. Inter-Laboratory Comparison of Split Sample Results

The final objective of this study was to conduct a comparative evaluation of the analytical results obtained at the Clallam County Environmental Laboratory (CCEL) and Ecology's Manchester Environmental Laboratory (MEL) for nitrate+nitrite-N and fecal coliform bacteria. For the

evaluation CCEL used a nitrate electrode screening technique to quantify nitrate-N concentrations while MEL used an automated cadmium reduction technique to quantify nitrate+nitrite-N. These methods were considered equivalent for the purposes of this comparative evaluation since nitrite is seldom found in groundwater above trace amounts (Matthess, 1982).

Eleven sample splits were collected for comparative analysis at CCEL and MEL. Nitrate-N concentrations in five samples were below 1 mg/L and could not be directly compared since they fell below the effective detection limit for the nitrate electrode. Evaluation of the remaining six samples revealed relatively large differences between the analytical results for the two laboratories (Table A5). In five of six cases, CCEL determinations for nitrate-N significantly exceeded the values determined by MEL, suggesting a consistent pattern of under reporting nitrate+nitrite-N concentrations at MEL or conversely a pattern of over reporting nitrate-N concentrations at CCEL. In all but one case the difference between the CCEL and MEL determinations exceeded the project quality assurance criteria for percent relative standard deviation and relative percent difference (5% and 10% respectively) (Tables A5 and B-1).

Laboratory quality assurance/quality control data were reviewed for the samples processed at MEL and were found to be within acceptable limits. This suggests the problem may lie with the analytical methods and laboratory techniques employed by CCEL for estimating nitrate-N concentrations.

The split-sample results for fecal coliform bacteria produced comparable results, with both laboratories indicating non-detects in all cases.

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Summary and Conclusions

Eight wells in the Agnew and Carlsborg area of Clallam County were sampled quarterly from December 2000 through September 2002 to assess the distribution and concentration of nitrate+nitrite-N, total persulfate nitrogen, total iron, total manganese, total and fecal coliform bacteria, and chloride in area groundwater. Sixteen percent of samples failed to meet the primary maximum contaminant level (MCL) criteria for total coliform bacteria. In addition, numerous samples exceeded secondary (aesthetic) MCL criteria for pH, total iron, and total manganese. Three wells showed statistically significant increases in nitrate-N concentration between 1980 and 2002, four showed no increase, and one showed a statistically significant decrease. Area nitrate values were generally highest in June (average 1.49 mg/L) and lowest in December (average 1.35 mg/L).

Comparative evaluation of split samples processed at the Clallam County Environmental Laboratory (CCEL) and Ecology's Manchester Environmental Laboratory (MEL) indicated good agreement in fecal coliform analyses and generally poor agreement in paired nitrate-N analyses. CCEL determinations for nitrate-N consistently exceeded values obtained by MEL and exceeded the project quality assurance criteria for percent relative standard deviation and relative percent difference by wide margins. Laboratory quality assurance/quality control (QA/QC) data were reviewed for those samples processed at MEL and were found to be within acceptable limits. This suggests the problem may lie with the analytical methods and laboratory techniques employed by CCEL for estimating nitrate-N concentrations.

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Recommendations

The results of this study provide a useful benchmark of water quality conditions within the greater Agnew and Carlsborg areas. Periodic monitoring of the network established during this study should continue on a twice yearly basis, in June and December, to allow county staff to track the effects of land-use changes on water quality over time.

The large discrepancies in analytical results for nitrate-N samples processed at the Clallam County Environmental Laboratory (CCEL) and Ecology's Manchester Environmental Laboratory (MEL) suggest a problem in laboratory analytical procedures at one or both facilities. Review of laboratory QA/QC data for those samples processed at MEL met applicable acceptable criteria. This suggests the problem may lay at CCEL. The cause of the noted discrepancies would best be evaluated through a formal audit of CCEL's, and perhaps MEL's, analytical procedure for determining nitrate-N concentrations in water.

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Appendices

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Appendix A

Data Tables

Table A1 - Physical description of monitored wells

Table A2 - Drillers lithologic descriptions for monitored wells

Table A3 - Water quality results for monitored wells

Table A4 - Quality assurance review of field and laboratory duplicate samples and laboratory method blanks

Table A5 - Quality assurance review of Ecology and Clallam County sample splits

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Table A1 - Physical Description of Monitored Wells Within the Agnew and Carlsborg Area

Well Tag Number	Local Number	Site Latitude	Site Longitude	Water Use	Land surface altitude (feet)	Completed well depth (feet)	Casing diameter (inches)	Completion type and open interval (feet)	Well yield (gpm)	Draw-down (feet)	Drawdown test method and duration (hours)	Hydro-geologic unit
AAB827	30N/04W-04L02	480714	1231209	D	121	56	6	S(6 in) 54-56	10	NA	NA	1
AAB749	30N/04W-07L01	480627	1231449	D	156	92	6	O	30	NA	NA	1
AFC054	30N/04W-08J01	480621	1231242	D	158	56	6	S 51-56	17	13	NA	1
ACA781	30N/04W-08M04	480623	1231350	D	170	84	6	S(5 in) 78-84	18	49	B1.5	1
AFC053	30N/04W-10Q02	480607	1231020	D	138	82	6	S(5 in) 76-81	65	12	B2	1
AFC052	30N/04W-15N01	480518	1231114	D	175	28	6	S(5 in) 26-28	12	NA	NA	1
AFC060	30N/04W-18H06	480549	1231409	D	230	121	6	S(5 in) 116-121	20	NA	1	1
ACA762	30N/04W-20E01	480455	1231337	D	380	38	6	P 16-22,23-28	20	5	2.5	1

Water Use: D-domestic supply

Completion type and open interval: P-perforations; S-screen; O-open end

Drawdown test method and duration: B-bailer test; NA-test period duration unknown

Hydrogeologic unit: After Thomas et al, 1999

Latitude, Longitude: degrees, minutes, and seconds (NAD27)

Table A2 - Drillers Lithologic Logs for Monitored Wells in the Agnew and Carlsborg Area

Well tag number	Local number	Driller's description of materials encountered during well construction	Thickness (feet)	Depth of bottom (feet)	Driller's name	Year Drilled
AAB827	30N/04W-04L02	Brown clay, sand	16	16	Van Ausdle	1974
		Brown clay, sand and gravel	14	30		
		Tan clay, gravel	10	40		
		Brown clay, sand	12	52		
		Brown clay, sand, and gravel	5	57		
		Brown clay, sand	10	67		
		Blue sand	5	72		
AAB749	30N/04W-07L01	Brown clay, sandy	26	26	Van Ausdle	1974
		Brown clay and coarse sand	14	40		
		Sand	28	68		
		Blue clay	5	73		
		Sand	12	85		
		Brown clay and fine sand	5	90		
		Gravel	2	92		
AFC054	30N/04W-08J01	Open hole (previous hand dug well)	15	15	Stoican	1960
		Silt	29	44		
		Brown clay, sandy	9	53		
		Sand and gravel	3	56		
ACA781	30N/04W-08M04	Topsoil	6	6	Louies	1978
		Gravel	29	35		
		Hardpan	37	72		
		Sand and pea-gravel, water	12	84		
AFC053	30N/04W-10Q02	Brown topsoil and stones	1	1	Stoican	1976
		Brown gravel and rocks	14	15		
		Brown to gray cemented gravel	22	37		
		Brown tight gravel and sand	3	40		
		Brown very fine sand	5	45		
		Brown coarse sand, water	5	50		
		Brown medium to coarse sand	31	81		
Black crumbly clay and sand	1	82				
AFC052	30N/04W-15N01	Topsoil	1	1	Van Ausdle	1974
		Brown clay	14	15		
		Brown sand	9	24		
		Sand and gravel	4	28		
		Sand	6	34		
AFC060	30N/04W-18H06	Topsoil	2	2	Louie's	1992
		Brown clay	6	8		
		Brown sand and gravel, clay binder	24	32		
		Brown sand	33	65		
		Gray clay	40	105		
Brown sand, water	16	121				
ACA762	30N/04W-20E01	Topsoil	2	2	Stoican	1977
		Brown cemented gravel, water	22	24		
		Brown sand and gravel, water	3	27		
		Brown clay	4	31		
		Gray shale	49	80		

Table A3 - Laboratory Water Quality Results for Monitored Wells in the Agnew-Carlsborg Area

Well Tag	Sample Date	Field measurements					Laboratory analyses						
		Depth to groundwater (ft below land surface)	Ground-water Temperature (deg C)	pH (standard units)	Specific Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Fecal Coliform (CFU/100mL)	Total Coliform (CFU/100mL)	Total Nitrate+ Nitrite-N (mg/L)	Total Persulfate Nitrogen (mg/L)	Chloride (mg/L)	Total Iron (ug/L)	Total Manganese (ug/L)
AAB749	3/13/01	63.5	10	7.22	309	0.18	1 U	2	0.99	0.97	10.8	234	11.8
AAB749	6/5/01	64.2	10.4	7.24	302	0.04	1 U	5	0.73	0.80	10.9	398	9
AAB749	9/5/01	64.9	11.5	6.34	300	0.24	1 U	12	0.75	0.78	10.3	267	10.7
AAB749	12/11/01	64.9	9.9	7.21	309	0.68	1 U	1 UJ	1.2	1.2	12	180	8.8
AAB749	3/12/02	65.2	9.9	7.21	319	0.99	1 U	1 UJ	0.85	0.87	11.9	264	12.6
AAB749	6/4/02	65.4	10.6	7.08	316	1.1	1 U	1 UJ	1.7	1.6	14	120	10 U
AAB749	9/11/02	65.5	11.1	7.19	330*	2.3	1 U	1 U	1.5	1.5	14.3	908	17
AAB827	12/12/00	39.9 R	10.5	6.73	309	1	1 U	6 J	3.3	4	8.7	320	3.6
AAB827	3/13/01	40.5 R	10.9	6.77	302	0.81	1 U	1 U	2.6	2.6	6.9	288	3
AAB827	6/5/01	40.8 R	11.5	6.73	309	0.37	1 U	1 U	2.8	3	8.0	21	2 U
AAB827	9/5/01	40.3	11.5	6	309	1.5	1 U	1 U	2.3	2.5	6.0	127	1.8
AAB827	12/11/01	40.9	11.4	6.75	267	3.4	1 U	45	1.2	1.3	4.0	88	1 U
AAB827	3/12/02	39.8	12.1	6.67	287	1.7	1 U	1 UJ	0.7	0.74	4.9	36	1.6
AAB827	6/4/02	39.2	11.5	6.52	277	1.9	1 U	10 J	0.85	0.87	6.9	56	10 U
AAB827	9/11/02	39.5	12.4	7.47	367*	1.5	1 U	1 UJ	0.01 U	0.07	13	2540	369
ACA762	12/12/00	10.6	9.8	6.32	113	1.8	1 U	1 U	0.40	0.44	3.0	140	2.1
ACA762	3/13/01	10.1	8.5	6.67	138	9.6	1 U	1 U	2	2	5.8	160	2 U
ACA762	6/5/01	10.5	9.3	6.39	149	6.3	1 U	1 U	1.7	1.9	7.0	97	2 U
ACA762	9/5/01	10.7	11.9	5.8	166	5.2	1 U	1 U	3	3.7	7.1	75	1.1
ACA762	12/11/01	10.5	11.4	6.33	134	2.5	1 U	1 UJ	0.89	1	4.1	274	3.1
ACA762	3/12/02	7.6	9	6.4	128	11.7	1 UJ	1 UJ	1.3	1.5	9.5	241	2.7
ACA762	6/4/02	8.2	9.2	6.36	153	11.6	1 U	1 U	2	2	7.1	75	10 U
ACA762	9/11/02	5.8	12.7	6.49	131*	8.5	1 U	1 U	1.2	1.3	3.1	529	10 U
ACA781	12/12/00	50	9.2	6.79	188	6.2	1 U	1 U	0.20	0.19	4.0	67 J	1.4
ACA781	3/13/01	51.8	9.6	6.91	179	4.6	1 U	1 U	0.30	0.30	4.6	472	4.5
ACA781	6/5/01	52.7	11.6	6.84	193	4.6	1 U	1 U	0.31	0.33	4.7	70	2 U
ACA781	9/5/01	51.7	12	6.17	186	4.9	1 U	1 U	0.25	0.26	4.7	675	4.4
ACA781	12/11/01	52.5	10.1	6.9	189	6.6	1 U	1 UJ	0.35	0.37	4.6	356	1.8
ACA781	3/12/02	48.5	9.9	6.84	197	7.4	1 U	1 U	0.35	0.38	5.0	580	4.1
ACA781	6/4/02	53.3	11.3	6.76	201	6.5	1 U	1 U	0.35	0.34	5.2	120	10 U
ACA781	9/11/02	51.1	11.6	6.86	195*	7.4	1 U	1 U	0.44	0.40	5.1	460	10 U
AFC052	12/12/00	8.2	10.2	7.65	410	0.04	1 U	1 U	0.01 U	0.02	11.4	320	344
AFC052	3/13/01	7.9	9.7	7.66	409	0.84	1 U	25	0.01 U	0.06	11	345	381
AFC052	6/5/01	9.0 R	11.5	7.66	402	0.37	1 U	1	0.01 U	0.05	11	241	386

Table A3 - Laboratory Water Quality Results for Monitored Wells in the Agnew-Carlsborg Area

Well Tag	Sample Number	Field measurements					Laboratory analyses						
		Depth to groundwater (ft below land surface)	Ground-water Temperature (deg C)	pH (standard units)	Specific Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Fecal Coliform (CFU/100mL)	Total Coliform (CFU/100mL)	Total Nitrate+ Nitrite-N (mg/L)	Total Persulfate Nitrogen (mg/L)	Chloride (mg/L)	Total Iron (ug/L)	Total Manganese (ug/L)
AFC052	9/5/01	9.5	12.8	7.02	399	0.49	1 U	1 U	0.01 U	0.07	11	377	360
AFC052	12/11/01	7.9	9.2	7.69	410	0.96	1 U	1 UJ	0.01	0.07	11.6	487	365
AFC052	3/12/02	6.7	9.8	7.68	405	-	1 U	1 UJ	0.01 U	0.08 J	11.5	508	419
AFC052	6/4/02	7.9	10.9	7.57	404	1.2	1 U	1 U	0.01 U	0.08	12.4	290	428
AFC052	9/11/02	8.9	11	7.62	418*	2	1 U	1 U	0.01 U	0.08	12.2	390	795
AFC053	12/12/00	NA	9.6	7.7	371	5.6	1 U	3	3.76	3.9	7.8	20 U	1 U
AFC053	3/13/01	NA	9.6	7.74	375	9.7	1 U	1 U	4.11	3.9	7.8	20 U	2 U
AFC053	6/5/01	NA	10.8	7.75	374	5.1	1 U	1 U	3.91	4.1	8.2	20 U	2 U
AFC053	9/5/01	NA	11.2	7.14	372	5.7	1 U	1 U	4.23	4	8.1	10 U	1 U
AFC053	12/11/01	NA	10.3	7.74	383	7.3	1 U	1 UJ	4.13	4.3	8.0	20 U	1 U
AFC053	3/12/02	NA	10.1	7.71	388	7.3	1 U	1 U	4.28	4.3	8.6	20 U	1 U
AFC053	6/4/02	NA	10.9	7.64	390	7.3	1 U	1 U	4.50	4.1	8.8	50 U	10 U
AFC053	9/11/02	NA	11	7.71	404*	7.2	1 U	1 UJ	4.58	4.3	9	50 U	10 U
AFC054	12/12/00	NA	10.1	6.96	233	2.1	1 U	1 U	1.2	1.3	3.6	20 U	53.8
AFC054	3/13/01	NA	10.1	7.01	229	0.21	1 U	1 U	1.4	1.3	3.5	20 U	60.2
AFC054	6/5/01	NA	10.9	6.97	227	0.13	1 U	1 U	1.2	1.3	3.3	20 U	56.6
AFC054	9/5/01	NA	11.4	6.14	221	0.41	1 U	1 U	0.99	1	3.5	39	56.1
AFC054	12/11/01	NA	10.8	6.98	227	2.1	1 U	1 UJ	0.85	0.89	3.1	42	60.3
AFC054	3/12/02	NA	10.9	6.92	232	1.4	1 U	1 U	0.98	0.99	3.4	29	68.3
AFC054	6/4/02	NA	11.2	6.91	228	2.2	1 U	1 U	1	0.95	3.5	150	60
AFC054	9/11/02	NA	11	6.98	229*	3.5	1 U	1 U	0.87	0.79	3.3	71	123
AFC060	3/13/01	98.3	10.2	7.09	268	3.9	1 U	1 U	1.3	1.2	7.0	129	2 U
AFC060	6/5/01	99.1	11	6.98	270	4.2	1 U	1 U	1.3	1.4	7.1	65	2 U
AFC060	9/5/01	P	12.9	6.39	266	4.3	1 U	4	1.3	1.3	6.9	722	12.8
AFC060	12/11/01	99.4	10.6	7	274	5.9	1 U	1 UJ	1.4	1.4	7.0	19	1 U
AFC060	3/12/02	99.9	10.7	6.98	275	5.5	1 U	1 U	1.4	1.4	7.1	20	1 U
AFC060	6/4/02	P	10.9	6.92	276	5.5	1 U	1 U	1.5	1.4	7.5	50 U	10 U
AFC060	9/11/02	99.1	11.7	7.01	282*	6.2	1 U	1 U	1.4	1.3	7.3	94	10 U

J -analyte positively identified, the numeric result is an estimate; U -analyte not detected at or above the reported value; UJ -analyte not detected at or above the estimated value.

P -the well was pumping, water level not measured; R -well recently pumped, water level slowly recovering; NA -well access restriction, water level not measured; * -laboratory measurement.

Table A4 - Quality Assurance Review of Field and Laboratory Duplicate Samples and Laboratory Method Blanks

Sample Date		Field Replicate Samples							Laboratory Duplicate and Blank Samples						
		Total Nitrate+ Nitrite (as N) (mg/L)	Total Persulfate Nitrogen (mg/L)	Total Coliform (CFU/100mL)	Fecal Coliform (CFU/100mL)	Total Chloride (mg/L)	Total Iron (ug/L)	Total Manganese (ug/L)	Total Nitrate+ Nitrite (as N) (mg/L)	Total Persulfate Nitrogen (mg/L)	Total Coliform (CFU/100mL)	Fecal Coliform (CFU/100mL)	Total Chloride (mg/L)	Total Iron (ug/L)	Total Manganese (ug/L)
12/12/00	Sample	3.76	3.88	3	1 U	7.81	20 U	1 U	0.01 U	NT	1 U	1 U	2.97	NT	NT
	Rep/Duplicate	3.75	3.98	3	1 U	7.85	20 U	1 U	0.01	NT	1 U	1 U	2.93	NT	NT
	RPD	0.26	2.54	0.0	NA	0.51	NA	NA	NA	NA	NA	NA	1.36	NA	NA
	%RSD	0.13	1.27	0.0	NA	0.26	NA	NA	NA	NA	NA	NA	0.68	NA	NA
	Lab blank	--	--	--	--	--	--	--	--	--	--	--	--	20 U	1 U
03/13/01	Sample	0.978	0.972	1 UJ	1 U	10.4	217	11.7	0.978	1.99	1 U	1 U	5.8	NT	NT
	Rep/Duplicate	0.99	0.973	2	1 U	10.8	234	11.8	0.978	2.01	1 U	1 U	5.75	NT	NT
	RPD	1.22	0.11	NA	NA	3.77	7.53	0.85	0.00	1.00	NA	NA	0.87	NA	NA
	%RSD	0.61	0.05	NA	NA	1.89	3.77	0.43	0.00	0.50	NA	NA	0.43	NA	NA
	Lab blank	--	--	--	--	--	--	--	--	--	--	--	--	20 U	2 U
06/05/01	Sample	0.734	0.804	5	1 U	10.9	398	9	1.31	1.4	1 U	1 U	7.1	NT	NT
	Rep/Duplicate	0.75	0.836	4	1 U	10.9	421	10	1.32	1.39	1 U	1 U	7.32	NT	NT
	RPD	2.2	3.9	22.2	NA	0.0	5.6	10.5	0.8	0.7	NA	NA	3.1	NA	NA
	%RSD	1.1	2.0	11.1	NA	0.0	2.8	5.3	0.4	0.4	NA	NA	1.5	NA	NA
	Lab blank	--	--	--	--	--	--	--	--	--	--	--	--	20 U	2 U
09/05/01	Sample	0.753	0.778	12	1 U	10.3	267	10.7	0.01 U	3.71	7	1 U	6.88	NT	NT
	Rep/Duplicate	0.756	0.79	7	1 U	10.8	266	11.5	0.01 U	3.72	15	1 U	6.9	NT	NT
	RPD	0.4	1.5	52.6	NA	4.7	0.4	7.2	NA	0.3	72.7	NA	0.3	NA	NA
	%RSD	0.2	0.8	26.3	NA	2.4	0.2	3.6	NA	0.1	36.4	NA	0.2	NA	NA
	Lab blank	--	--	--	--	--	--	--	--	--	--	--	--	10 U	1 U
12/11/01	Sample	1.18	1.24	1 UJ	1 U	12	190	8.7	1.37	0.981	1 UJ	1 U	4.14	NT	NT
	Rep/Duplicate	1.18	1.24	1 UJ	1 U	12	180	8.8	1.38	0.986	1 UJ	1 U	4.01	NT	NT
	RPD	0.0	0.0	NA	NA	0.0	5.4	1.1	0.7	0.5	NA	NA	3.2	NA	NA
	%RSD	0.0	0.0	NA	NA	0.0	2.7	0.6	0.4	0.3	NA	NA	1.6	NA	NA
	Lab blank	--	--	--	--	--	--	--	--	--	--	--	--	20 U	1 U
03/12/02	Sample	0.818	0.841	1 UJ	1 U	12	275	12	1.28	0.892	1 UJ	1 U	11.5	NT	NT
	Rep/Duplicate	0.854	0.869	1 UJ	1 U	11.9	264	12.6	1.28	0.869	1 UJ	1 U	11.6	NT	NT
	RPD	4.3	3.3	NA	NA	0.8	4.1	4.9	0.0	2.6	NA	NA	0.9	NA	NA
	%RSD	2.2	1.6	NA	NA	0.4	2.0	2.4	0.0	1.3	NA	NA	0.4	NA	NA
	Lab blank	--	--	--	--	--	--	--	--	--	--	--	--	20 U	1 U
06/04/02	Sample	1.7	1.61	1 UJ	1 U	13.9	130	10 U	2	0.335	1 U	1 U	7.08	NT	NT
	Rep/Duplicate	1.7	1.61	1 UJ	1 U	14	120	10 U	2.04	0.344	1 U	1 U	6.99	NT	NT
	RPD	0.0	0.0	NA	NA	0.7	8.0	NA	2.0	2.7	NA	NA	1.3	NA	NA
	%RSD	0.0	0.0	NA	NA	0.4	4.0	NA	1.0	1.3	NA	NA	0.6	NA	NA
	Lab blank	--	--	--	--	--	--	--	0.01 U	0.025 U	--	--	0.10 U	50 U	10 U
09/11/02	Sample	1.51	1.48	1 U	1 U	14.3	908	17	1.23	NT	1 U	1 U	3.14	NT	NT
	Rep/Duplicate	1.53	1.49	1 U	1 U	14.3	726	16	1.25	NT	1 U	1 U	3.12	NT	NT
	RPD	1.3	0.7	NA	NA	0.0	22.3	6.1	1.6	NA	NA	NA	0.6	NA	NA
	%RSD	0.7	0.3	NA	NA	0.0	11.1	3.0	0.8	NA	NA	NA	0.3	NA	NA
	Lab blank	--	--	--	--	--	--	--	0.01 U	0.025 U	--	--	0.10 U	0.05 U	0.01 U

Relative percent difference (RPD): Calculated for a pair of results, x_1 and x_2 , as $100 \cdot (x_1 - x_2) / (\text{average}[x_1 \text{ and } x_2])$

Percent relative standard deviation (%RSD): Calculated for a pair of results, x_1 and x_2 , as $100 \cdot s / (\text{average}[x_1 \text{ and } x_2])$, where s is the standard deviation of the sample pair.

U - analyte not detected at or above the reported value; UJ - analyte not detected at or above the estimated value.

Bold values indicate an exceedence of the project precision criteria.

Table A5 - Quality Assurance Review of Ecology and Clallam County Sample Splits

Sample Date	Laboratory	Nitrate + nitrite (as N) mg/L					Fecal Coliform CFU/100mL				
		Well tag number					Well tag number				
		ACA762	AFC060	AAB749	ACA781	AFC054	ACA762	AFC060	AAB749	ACA781	AFC054
6/5/2001	Ecology	1.7	1.3	0.73	--	--	--	--	--	--	--
	County	1 U*	1.8	1.5	--	--	--	--	--	--	--
	RPD	109	35	66	--	--	--	--	--	--	--
	%RSD	55	17	33	--	--	--	--	--	--	--
9/5/2001	Ecology	3	1.3	0.75	0.25	--	1 U	1 U	1 U	1 U	--
	County	3	1.4	1 U*	1 U*	--	1 U	1 U	1 U	1 U	--
	RPD	0	11	40	66	--	NA	NA	NA	NA	--
	%RSD	0	6	20	33	--	NA	NA	NA	NA	--
12/11/2001	Ecology	0.89	1.4	--	0.35	0.85	1 U	1 U	--	1 U	1 U
	County	1.1	1.6	--	1 U*	1.1	1 U	1 U	--	1 U	1 U
	RPD	24	13	--	36	22	NA	NA	--	NA	NA
	%RSD	12	7	--	18	11	NA	NA	--	NA	NA

Relative percent difference (RPD): Calculated for a pair of results, x_1 and x_2 , as $100 \cdot (x_1 - x_2) / (\text{average}[x_1 \text{ and } x_2])$

Percent relative standard deviation (%RSD): Calculated for a pair of results, x_1 and x_2 , as $100 \cdot s / (\text{average}[x_1 \text{ and } x_2])$, where s is the standard deviation of the sample pair.

U -analyte not detected at or above the reported value; * - a value of 0.5 (one half the reported detection limit) was used to calculate summary statistics.

Bold values indicate an exceedence of the project precision criteria.

Appendix B

Quality Assurance Review

The data quality objectives for this study were defined prior to the onset of data collection and are described in the study Quality Assurance Project Plan (Sinclair, 2002 and Table B-1). Quality assurance covers a broad array of field sampling and laboratory analytical activities. Some field activities, such as measuring the water level in a well, are largely procedural in nature, and data quality can be assured by employing and adhering to standardized field methods (see below). Other activities, such as sample collection, require the analysis of quality control samples in order to evaluate data quality. The quality assurance procedures Ecology followed for each of these broad activity classes is described below.

Sample Handling and Chain of Custody

For this study Ecology followed the quality control procedures specified in Barcelona et al. (1985) during sample collection and transport. Samples were collected in pre-cleaned bottles supplied by Manchester Environmental Laboratory. Pre-acidified bottles were used to collect samples for nitrate+nitrite-N, and total persulfate nitrogen. To minimize the potential for sample contamination, the metals samples were not acidified prior to their arrival at the laboratory (usually less than 24 hours). Filled sample bottles were labeled and stored on ice pending arrival at the laboratory. Sample chain-of-custody procedures were followed throughout the project, and all samples arrived at the laboratory in good condition.

A few samples for total/fecal coliform were not processed within accepted holding times. The results for these samples carry a "J" qualifier to indicate that the samples were analyzed outside of the normal processing timeline (Tables A-3 and A-4). In addition, a number of the total/fecal coliform samples had high background counts which may yield reported values that are lower than the "true" value. These samples also carry the "J" qualifier.

Table B -1 Project Data Quality Objectives.

Parameter	Accuracy (2*precision + bias)	Precision (%RSD)	Bias	Lowest level of interest
pH (field)	20	5	10	NA
Specific Conductivity (field)	20	5	10	25 µS/cm @ 25 °C
Temperature (field)	NA	NA	NA	NA
Dissolve Oxygen (field)	20	5	10	0.5 mg/L
Total Persulfate Nitrogen	20	5	10	0.1 mg/L
Nitrate+Nitrite-N	20	5	10	0.1 mg/L
Coliform, total (MF)	70	30	10	1 CFU/100 mL
Coliform, fecal (MF)	70	30	10	1 CFU/100 mL
Chloride	20	5	10	1 mg/L
Iron (total)	20	5	10	5 ug/L
Manganese (total)	20	5	10	1 ug/L

RSD – relative standard deviation

MF – membrane filter

Evaluation of Field Replicate and Laboratory Duplicate Samples

In order to assess overall sampling and analytical precision, field replicate samples were collected and submitted "blind"¹ to the laboratory during each sampling event. Precision for each of the field replicate and laboratory duplicate analyses was quantified by evaluating the relative percent difference (RPD)² and percent relative standard deviation (%RSD)³ for each sample pair. The resulting values were then tabulated and compared to the project data quality objectives to assess overall data quality (Tables A4 and B1). The errors associated with field replicate and laboratory duplicate analyses were within the project acceptance criteria (5% and 10% for %RSD and RPD respectively) for all but a few sample pairs.

Duplicate analyses for total coliform exceeded the project minimum precision criteria on three occasions. Since the results were below the statistical minimum of 20 colonies per plate, these exceedences are not considered significant. Additional exceedences were noted for total iron (three occasions) and total manganese (two occasions). In most cases these exceedences were quite small and do not significantly affect data analysis and interpretation.

Laboratory Quality Assurance

The Manchester Environmental Laboratory follows a strict set of procedures to ensure the quality of the data they generate. Where appropriate, instrument calibration is performed before each analytical run and is checked against initial calibration verification standards and blanks. Calibration standards and blanks are analyzed at a frequency of approximately 10% during each run and then again at the end of each sample run. The laboratory also uses procedural blanks, spiked samples, and laboratory control sample (LCS) analyses as additional checks of data quality. Throughout this study, the constituent concentrations for blank samples fell below the analytical detection limit for target analytes. Spiked sample and LCS analyses also met the specified acceptance criteria throughout this project. Based on this evaluation, the data generated during this study are of high quality and can be used without qualification except as noted above and in Table A3.

¹ The term "blind" refers to "identical" samples that were submitted to the laboratory under different sample numbers.

² Calculated for a pair of results, x_1 and x_2 , as $100 \cdot (x_1 - x_2) / \text{average}[x_1 \text{ and } x_2]$

³ Calculated for a pair of results, x_1 and x_2 , as $100 \cdot s / (\text{average}[x_1 \text{ and } x_2])$, where s is the standard deviation of the sample pair.