Clallam County

Grant No. G1000003

GRANT TITLE: Northwest Straits Project: Clallam County Marine Resources Committee Administration and Action Projects.

TASK NO: 3.2 Groundwater Contamination Monitoring

(___) ANNUAL REPORT (January 1 – December 31)
(___) WORK PLAN
(___) PROGRESS REPORT No. 1 ☐ No. 2 ☐ No. 3 ☐
(___) FINAL PROGRESS REPORT
(___) PROJECT REPORT
(___) SUMMARY REPORT
(___) TECHNICAL REPORT
(XX) PROTOCOL
(XX) QUALITY ASSURANCE/QUALITY CONTROL

PERIOD COVERED: January 1, 2010 to June 18, 2010

DATE SUBMITTED: June 17, 2010

This report was funded in part through a cooperative agreement with the National Oceanic and Atmospheric Administration.

The views expressed herein are those of the author(s) and do not necessarily reflect the views of NOAA or any of its subagencies.

Quality Assurance Project Plan
for
Monitoring Stormwater Contaminants in the Shallow Aquifer Near Sequim, Clallam County, WA

CZM310 Grant Agreement No. G10-00003 Task 3.2
for Clallam County Marine Resources Committee

January 2010 (updated July 2010)

Prepared by
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Prepared for
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Coastal Zone Management

Approval Signatures

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Background

As planned with representatives of the Clallam County Marine Resources Committee (MRC), this project will investigate groundwater quality generally as well as specifically with regard to stormwater contaminants in a portion of the Dungeness watershed. The water quality of shallow marine waters in the watershed, particularly Dungeness Bay, is degraded by bacterial contamination causing closure of many areas to the harvest of shellfish. Nutrient contamination has also been documented and is suspected to contribute to macroalgae blooms (CCD, 2009 and Shaffer, 2002), which exacerbate water quality and habitat issues for fish and wildlife.

Groundwater is known to discharge from the aquifer system to lower-watershed streams as well as to marine water (Thomas 1999). The Sequim-Dungeness aquifers are known to be susceptible to contamination from land activities due to coarse soils and underlying geology. Nitrates have been found at levels elevated above natural conditions and rising, sometimes to levels exceeding the drinking water standard, since the first broad survey conducted by USGS in 1980 (Thomas 1999; Drost 1983 and 1986).

The MRC wanted this project to build on a 2005 study by Clallam County Health & Human Services Environmental Health (CCEH) establishing baseline groundwater quality with regard to stormwater-type contaminants for County residents with drinking water wells downgradient of commercial/light industrial development in City of Sequim's western city limits (Soule 2005). In this study, six wells were tested in May 2005 for nutrients (nitrates, TKN), metals (total), pesticides scan + PCBs, other organics (hydrocarbon ID, semi-volatile scan), pathogens (total coliform and Pseudomonas aeruginosa), and TDS; detectable results included very-low to moderately-high levels of nitrate, low to moderate TDS, and trace levels of chromium and zinc. Other parameters were not detected.

The study area for the 2005 groundwater-stormwater baseline study became the "focus area" for Phase I of the MRC project in 2009, which investigated relative vulnerability of study wells in the focus area and beyond using nitrate as an indicator (Soule 2009a, b). While no samples exceeded the drinking water standard for nitrates, five of 16 wells had nitrates above the trigger level (half the standard, or 5 mg/L nitrate as Nitrogen). 80% of sampled wells have nitrate levels indicating evidence of impact from human activities (>1 mg/L).[1] Recommendations from Phase I are incorporated into this Phase II monitoring plan as much as is feasible.

In addition to these objectives, the project also responds to goals of a concurrent stormwater assessment project managed by Clallam County Dept. of Community Development under an EPA grant, intended to result in stormwater management regulations. Recommendations received by state specialists cooperating on the EPA project were incorporated in the Phase I monitoring plan and final report (Pitz 2009a, b). In particular, Pitz recommended enlarging the area of interest beyond the focus area to include a larger region downgradient from historically urban zones, and to begin the groundwater quality assessment by "screening" study wells in the shallow aquifer to determine their relative vulnerability to contamination.

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[1] USGS (Drost 1983) reports statistics for 129 wells (90% from the shallow aquifer) sampled for nitrates in the Sequim-Dungeness area in June 1980. Results range from undetected to 2.50 mg/L, with a median of 0.37 mg/L (nitrate + nitrite as N). Similarly, USGS (Thomas 1999) reports (pg. 92), "For this study area, natural concentrations of nitrate… were estimated be lower than 1.0 mg/L.

Other studies directly relevant to this project include:

- Sinclair (2003), which documented nitrates in eight wells east of the Dungeness River seasonally over two years: results range from <0.01 (not detected) to 4.58mg/L nitrate as N, with a significant annual high in the late spring season.
- Simonds and Sinclair (2002), which established gaining and losing reaches of the Dungeness River.
- Streamkeepers of Clallam County stormwater and sediment sampling results (personal communication, January 2010), indicating low levels of organics, metals, and nutrients.
- Woodruff, et al (2009), which showed that ammonia in surface water samples was elevated in spring-fed creeks compared to the Dungeness River, and lacked seasonal differences. The authors speculate that the constancy of the speciation of nitrogen compounds year-round indicate a constant source, such as septic system effluent.
- Thomas et al (1999), the seminal hydrogeologic assessment for the Sequim-Dungeness region, including nitrate sampling of 65 wells in July-August 1996.

Note there are several studies of local groundwater quality indicated; however, the ambient groundwater quality in much of the Dungeness watershed has not been studied for more than a decade. Sampling under this project will fill the need for an update in the northeastern portion of the watershed, at least for the shallow aquifer.

In addition, ammonia in groundwater has not been tested since 1996 (Thomas et. al. 1999), and results reported by Woodruff et. al. (2009) have generated interest in testing for ammonia in targeted study wells (near higher densities of septic systems in fine soils and/or groundwater-fed creeks sampled by Woodruff et. al.).

Project Description

As described in the previous section, the MRC chose to conduct this project for the purpose of investigating groundwater quality in the shallow aquifer draining to streams and marine waters of the Dungeness watershed. The specific approach involves determining (a) the ambient quality of shallow groundwater for a broad region (determined by the MRC as east of the Dungeness River downgradient from City of Sequim), as well as (b) the concentrations of specific stormwater contaminants for wells found in Phase I to be vulnerable to land activities. Figure 1 features the study area with regional groundwater flow directions indicated for the shallow aquifer; shellfish harvest closure areas are also shown.

The project budget does not allow for construction of monitoring wells, so CCEH will sample selected study wells (including several wells used for Phase I) used for domestic water supply and completed in the shallow aquifer. One benefit of this approach is to achieve a screening of the public-health risk associated with these shallow-aquifer wells used for drinking water. Thousands of residents in this portion of unincorporated Clallam County rely on private and small group wells tapping the shallow aquifer (as well as deeper aquifers).

Samples will be analyzed for nitrates and chlorides in all cases, and selected stormwater contaminants in the subset of wells found in Phase I to be vulnerable to land activities. A report describing the findings will be prepared for use by the MRC, Clallam County, and City of Sequim by January 2011.

This project will follow procedures accepted by state and federal agencies for well and analyte selection, sampling and handling methods, laboratory analysis, and statistical analysis (when needed). The general sequence of events follows:

1. Write monitoring plan and QAPP for review and approval by Ecology
2. Select and prioritize 25-40 study wells, depending on project budget for field time and lab analyses
3. Confirm contaminants for potential analysis and order bottles & filters from lab
4. Site visits and sampling
5. Laboratory analyses
6. Establish a database of study well, sampling information, and lab results
7. Perform data assessment and determine if additional sampling is needed
8. Interpret laboratory results and write report

Organization and Schedule

Clallam County MRC grant staff: *Prepares grant reports, manages overall project logistics.*

- Grant manager/project coordinator: Cathy Lear
- MRC staff: David Freed
- Financial manager: Debi Cook

Clallam County Environmental Health staff: *Prepares QAPP, designs sampling plan, conducts sampling, conducts and/or contracts for lab analyses, interprets results, and writes summary report.*

- Groundwater monitoring (MRC grant Task 3.2) project lead: Ann Soule
- CCEH Laboratory manager: Belinda Pero
- CCEH Manager: Andy Brastad

WA Department of Ecology: *Oversees project and budget for grant administration and provides technical assistance, reviews summary report.*

- Project Manager: Sasha Horst
- Technical Assistance (EAP): Charles Pitz
- Financial and Billing Officer: Sasha Horst
- Ecology Quality Assurance Officer: Bill Kammin

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Schedule

January-June 2010	QAPP review and approval
March-July 2010	Study wells identified; field work scheduled
August-November 2010	Field measurements and sampling
August-November 2010	Laboratory analyses
December 2010 – January 2011	Data QA review completed
January-February 2011	Project report drafted and sent out for review
February-March 2011*	Final task report completed and submitted to Ecology
March 2011	Data submitted to Ecology EIM database

*final due March 2011

Groundwater Monitoring Budget

Expenses	Admin	QAPP	Field prep	Field (est. 12 days)	Data entry/ analysis	Report	**OBJECT TOTALS**
Clallam Co. Sal & Ben	240.00	1,400.00	1,600.00	3,120.00	1,280.00	1,200.00	**8,840.00**
Indirect	60.00	350.00	400.00	780.00	320.00	300.00	**2,210.00**
Professional Services/Lab							
metals scan (5@$75)				375.00			**375.00**
hydrocarbon ID (5@$90)				450.00			**450.00**
pesticide-PCB scan (5@$170)				550.00			**550.00**
ammonia (optional) (8@$15)				120.00			**120.00**
Supplies							
Chemetrics reagents*; methanol				130.00			**130.00**
EH lab analysis bacti (30@$20)				600.00			**600.00**
EH lab analysis nitrate (25@$25)				625.00			**625.00**
Travel				100.00			**100.00**
TASK TOTAL	**300.00**	**1,750.00**	**2,000.00**	**6,850.00**	**1,600.00**	**1,500.00**	**14,000.00**

Quality Objectives

The purpose of collecting data for this project is for baseline information on ambient groundwater quality. Trace or undetectable levels are expected for most parameters, though state drinking water quality standards for coliform or nitrates could be expected to be exceeded on occasion. Field parameters are listed in Table 1 with the expected performance for the methods used. Project data quality objectives are established in Table 2, and Table 3 addresses measurement quality objectives for laboratory analyses. The data will not be used for regulatory purposes, so a higher level of precision was not chosen. Note that Table 4 in the next section indicates the state standard for each parameter.

Table 1
Field Measurements Summary and Performance Objectives

PARAMETER	ANALYTICAL METHOD	ACCURACY (deviation from true value)	RANGE OF INSTRUMENT	REPORTING LIMIT
Static water level	Electrical tape	+/- .03 feet	0 – 300 feet	0.01 feet
pH	EPA 150.1 Electrometric	+/-0.2 pH units	0 – 14 pH units	0.01 pH unit
Temperature	N/A Thermometer	+-0.2 deg C	-5 – +75 deg C	0.1 deg C
Dissolved Oxygen	EPA 360.1 Membrane Electrode	+/-2% air saturation	0 – 200% air saturation; 0 – 20 mg/L	0.1 mg/L
Conductivity	EPA 120.1 Specific Conductance, uS at 25 deg C	+/-10 uS/cm +/- 5%	0 – 4999 uS/cm	1 uS/cm

Table 2
Project Data Quality Objectives

PARAMETER	PRECISION[2]	BIAS	REPORTING LIMIT	COMPLETE-NESS
	%RSD	%	Concentration Units	Minimum % usable data
Nitrogen (Nitrate as N)[3]-lab	15	5	0.5 mg/L	80%
Nitrogen (Nitrate as N)-field	15	10	0.4 and 1.1 mg/L[4]	80%
Ammonia—lab	15	5	0.01 mg/L	80%
Chloride—field	15	10	2.5 mg/L	80%
Metals ICP (scan)	30[5]	5	Varies by metal	80%
Pesticides (scan)	25[5]	5	Various	80%
Hydrocarbon ID	25	5	Various	80%
Total coliform[6]	NA	NA	Colony Count	90%
E. coli	NA	NA	Presence/absence	90%

[1]Accuracy: the difference between the analytical result and a reference of known value (due to systematic and random error in the laboratory).

[2]Precision: the random variability among repetitive measurements of the same sample (random

error).
[3]The expected range of results for nitrate as N is <0.50 to 20 mg/L. Most samples will probably fall within the range <0.50 to 2.0 mg/L.
[4]Depending on range of kit: “Nitrate 2” ranges 0.40-3.00 mg/L; “Nitrate 3” ranges 1.13-11.3 mg/L as N
[5]For performance characteristics for specific analytes, see Attachments A and B
[6]The expected range of results for total coliform is 0 to confluent growth. The presence of any total coliform and/or E. coli will be cause for immediate action by CCEH, starting with re-sampling, and notifying the well owner of recommended corrective actions.

Table 3
Measurement Quality Objectives for Laboratory* Analyses

Parameter	Check Standard (LCS)	Duplicate Samples	Matrix Spikes	Matrix Spike-Duplicates	Surrogate Standards	Lowest Concentrations of Interest
	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Units of Concentration
Nitrogen (Nitrate as N) (lab)	90-110%	20%	80-120%	20%	NA	0.01 mg/L
Nitrogen (Nitrate as N) (field)	85-115%	20%	NA	NA	NA	0.40 mg/L
Chloride (field)	85-115%	20%	NA	NA	NA	2.5 mg/L
Ammonia	90-110%	20%	80-120%	20%	NA	0.01 mg/L
Metals ICP scan**	85-115%	NA	70-130%	20%	NA	varies
Pesticide-PCB scan***	85-115%	NA	20-180%	50%	NA	NA
Hydrocarbon ID	NA	NA	NA	NA	NA	NA

*CCEH Laboratory for Nitrate as Nitrogen (lab) (360-417-2334), all others AmTest Laboratories, Kirkland, WA (425-885-1664)
**see Attachment A for list of metals and QC values (AmTest, July 2010)
***see Attachment B for list of pesticides and QC values (AmTest, July 2010)

Sampling Process Design (Experimental Design)

The approach involves determining (a) the general quality and concentration of nitrates in shallow groundwater for the broad region (defined as east of the Dungeness River downgradient from City of Sequim and discharging to marine water—see Figure 1), and (b) the concentrations of specific stormwater contaminants for wells found in Phase I to be vulnerable to land activities.

CCEH will visit and sample selected study wells (including several wells used for Phase I) used for domestic water supply and completed in the shallow aquifer. (The project budget does not allow for construction of any monitoring wells.) Samples will be analyzed for nitrates and chlorides in all cases, and selected stormwater contaminants in the subset described above.

Details of the study approach include the following:

1. Write monitoring plan and QAPP for review and approval by Ecology

2. Select 25-40 study wells
Wells completed in the shallow aquifer will be considered with emphasis on the region downgradient of urban areas in and around Sequim and east of the Dungeness River. Study wells from Phase I with levels of nitrates elevated above 5 mg/L will be selected for stormwater contaminant "extended" sampling (minimum of 4 wells); these are illustrated in Figure 2. Another 25 new study wells (minimum) will be selected for "screening" for ambient nitrate (and optionally chloride and ammonia as well), and measurement of field parameters (temperature, pH, conductivity, and dissolved oxygen or D.O.). At least two screening wells will be selected from areas south (upgradient) of urban zones. Priorities for well selection include:

a. Must have a willing well owner (and tenant if applicable),
b. Must have a well report (log),
c. May have records from previous investigations,
d. Must have an accessible wellhead for measurement of water level,
e. Must not be located adjacent to an unlined irrigation ditch or pond,
f. Should tap shallowest zones of the water table aquifer, and
g. Must be able to produce raw (untreated) and fresh (not from a storage tank) samples.

3. Select contaminants for potential analysis
Stormwater contaminants from commercial/retail/ road environments may include nutrients, salts, pathogens, Total Organic Carbon (TOC), pesticides/herbicides, other organics, and heavy metals. Which of these stormwater runoff constituents might be contaminating groundwater in this study area depends on several factors, including the following:

- Whether the contaminant exists in the runoff: Recent results of stormwater sampling under the EPA project mentioned above show evidence of certain metals, some nutrients and organics, but little or no pesticide compounds.
  - a pesticide/herbicide scan will likely still be conducted on some samples since stormwater sampling did not conclusively eliminate the potential for these contaminants to be present in stormwater; only wells located near potential sources of these products will be tested
- The treatment applied to runoff: Ranges from no treatment (direct infiltration drywell or drainline) to sophisticated detention basins and filters at many places in the urban and surrounding areas.
- The mobility and persistence of the constituent: Varies from highly mobile and conservative (e.g., nitrates in groundwater) to easily adsorbed (metals and organics).
- The characteristics of the soils and underlying strata: The surficial geology underlying most of Sequim is glacial in origin, primarily outwash gravels and sands. Soils vary but are predominantly coarse-grained and thus poor filters.

Table 4 lists testing parameters of interest in the two groups of Phase II study wells: first, the "nitrate screening" group, which broadens the area screened in Phase I in the down-gradient direction, closer to marine and stream shorelines; and second, the "extended sampling" group, for intentionally targeted wells identified in Phase I as vulnerable (to investigate presence of stormwater contaminants). Also included in Table 4 are corresponding state standards and costs of analysis.

Table 4
Constituents of Interest

Constituents of interest & study well group ("extended" or "screen")	State standard*	Price per analysis**
<u>nutrients</u>: "extended" & "screen" Nitrogen (Nitrate as N) Lab Nitrogen (Nitrate as N) Field Ammonia (optional)	 10 mg/L 10 mg/L Not defined	 $25*** $1.25**** $15
<u>other inorganics</u>: "extended" & "screen" Chloride (Cl) Field	 250 mg/L	 $1****
<u>metals (total)</u>: "extended" only chromium (Cr) copper (Cu) lead (Pb) nickel (Ni) zinc (Zn)	 0.1 mg/L 1.0 mg/L 0.05 mg/L 0.1 mg/L 5.0 mg/L	 $75 (ICP scan)
<u>pesticides</u>: "extended" only Pesticides & PCBs scan	 Various	 $170
<u>other organics</u>: "extended" only Hydrocarbon identification	 None	 $90
<u>pathogens</u>: "extended" only; "screen" wells optional Total coliform and E. Coli	 1 colony/100mL	 $30***

*WA Dept. of Ecology, 1996, Appendix A
**AmTest, Inc., price sheet (2010)
***when included in 2010, will be by Clallam County Environmental Health Laboratory
****supply cost only (Chemetrics photometer ampoules, one-time-use in field); does not include photometer or field time required to perform analysis

4. Site visits and sampling
Visit at least 25 wells for nitrate screening and at least 4 study wells for extended sampling. Confirm access to wellhead for water level measurement and ability to collect raw samples from the well during first visit. Tasks should also include well tagging, location on an orthophoto, and digital photos whenever possible. If the study area were more localized it would be best to visit each site initially to measure water levels and confirm expected localized groundwater flow direction. In this study, assumption of the regional groundwater flow direction from previous reports is appropriate, so a single visit to each study well and single samples (with the exception of QC samples) are adequate to accomplish project objectives. *See next section for details on measurement and sampling methods.*

5. Laboratory analyses as needed, conducted by labs listed with Table 4

6. Establish a database of study well, sampling information, and lab results

Wellhead location will be established in the County's GIS, along with elevation to the nearest 0.5 ft. determined using 2-ft.-interval LIDAR coverages. CCEH maintains an Access database of information on wells used for water quality and water resource investigations. Database tables were designed to facilitate submittal of project data to Ecology's EIM system.

7. Perform data assessment and determine if additional site visits or sampling are needed

8. Interpret laboratory results and write report
The report will include a summary of field methods, figures showing study wells and interpreted groundwater flow direction; tables of well characteristics, measurements, and raw lab results; comparison of results to water quality standards, including accuracy limitations of field nitrate methods;, and discussion of results and recommendations for further study. A draft report will be circulated for comment to project partners including Ecology prior to final publication. Participating well owners will be sent results for their well plus a copy of the final report.

Sampling Procedures

General procedures at all study well sites:

- Take thorough field notes for all steps using standard site visit forms, including sketch of well location showing road approach.
- Indicate well location on an orthophoto or GPS or other electronic device.
- Photograph well from at least two perspectives.
- Tag well if not yet tagged, using state unique ID tags, and complete associated forms for submittal to Ecology.
- Attempt static water level measurement.
- Purge well in order to produce raw groundwater.
- Measure field parameters (temperature, pH, conductivity, and D.O.) following manufacturer's instructions for maintenance, calibration, and operation.
- Collect and measure groundwater samples for nitrate and chloride concentration using Chemetrics photometer following manufacturer's instructions for maintenance, calibration (using reference solutions), and operation.
- For field QC for nitrates, for 20% of all field nitrate measurements, collect a split sample for a 2^{nd} field measurement as well as for lab analysis. Split samples for lab analysis will be submitted primarily from sites with a field nitrate measurement >2 mg/L and *all* sites with field nitrate measurement >5 mg/L.
- For field QC for chlorides, for 20% of all field chloride measurements, collect a split sample for a 2^{nd} field measurement.
- Samples for lab analysis of ammonia will only be collected from sites where the purge measurement of D.O. was <2 mg/L. (optional constituent for testing)
- Store and transport all samples to laboratories for analysis according to standard procedures.

Procedures at selected "extended" sampling sites will include the above steps, plus:

- Collect groundwater samples for laboratory analysis following procedural guidance found in Koterba, 1995, and laboratory sample collection procedures (see Attachment A, AmTest Sample Collection Procedures) including requirements for containers, preservation, and holding times (AmTest Laboratories, Inc. and Clallam County Environmental Health Lab).

Specific Water Level and Sampling Procedures

1. Water level measurements will be made prior to pumping the well for water quality sampling. The pump will be turned off or otherwise regulated so that it does not come on while measuring devices are in the well. The tape will be disinfected using dilute (20:1) chlorine bleach solution immediately before it enters each well, each time a new measurement is started. After the initial measurement is recorded, subsequent measurements will be made at 30 second intervals until readings agree within +/- 0.03 ft. If a static water level measurement is not obtainable, the water level record will be noted that the well status is not static. (Water level measurements will be made using a calibrated electric well probe by Waterline Environmental, Ltd., or a steel tape using standard USGS and Ecology methods (WA Dept. of Ecology EAP, 2009).)

2. A white, plastic garden hose (property of EHS) will be attached to a faucet as close to the well head as possible. If no outlet exists in the system before the point water enters a pressure tank, then the first available faucet will be used. (Wells will not be used for the study if it isn't possible to collect a sample prior to chemical treatment or aeration of the well water.) The hose will be placed to transmit well water from the faucet to a point at least 20 feet downslope from the well head.

3. Wells with casings of six inches will be pumped for at least ten minutes. Bucket samples should be collected carefully to avoid excessive oxygenation, with a purge rate no faster than 8 gpm. If the discharge point follows the pressure storage tank in the system (only if necessary), or if the pump is slow, purging will take longer. Purging rate will be measured using a bucket and stopwatch, and recorded on the sampling record. The goal is to purge the well until most field parameters stabilize before samples are collected.

4. At 3-5 minute intervals, pH, conductivity, dissolved oxygen, and water temperature measurements will be made according to probe manufacturer's instructions on grab samples collected in a plastic bucket from the hose stream, carefully to avoid excessive oxygenation. Before and after each measurement, all equipment probes will be rinsed with distilled water and blotted with lint-free wipes. (pH will be measured using a YSI Model 60 pH Meter; conductivity, dissolved oxygen, and water temperature will be measured using a YSI-85 Multimeter.)

5. After temperature stabilizes to within 0.2 degree Celcius, conductivity stabilizes to +/-5%, and pH stabilizes to +/-0.2 pH units over ten minutes, then sampling procedures may commence. Keep in mind that purging with a hose and bucket in hot weather may affect the bucket samples' representation of ambient conditions in the aquifer.

<u>6. Sample collection, storage, handling, and transfer procedures and holding times provided by the laboratory will be followed for each analyte</u>.

Sample containers and associated preservatives will be supplied by the laboratory, as described in Table 6, below. Container labels will be filled out for each sample on site, with site code, date, time, preservative if any, analysis requested, and sampler initials. Field replicates will be coded using a unique reference (so they're "blind") not associated with the site. Samples will be obtained directly from the spigot when the pump is running to minimize the contribution from storage tanks. Metals samples will be filtered using equipment supplied by the laboratory. Samples will be stored in a refrigerator and/or cooled with blue ice to 4^{o}C to ensure storage requirements are met until receipt by the laboratory conducting the analyses. CCEH is responsible for maintaining chain of custody of samples throughout all steps, using forms supplied by the laboratory.

Table 6
Sample Containers, Preservation and Holding Times

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
Nitrogen (Nitrate as N)	Water	100 mL	polyethlene	None	48 hrs
Ammonia	Water	100 mL	polyethlene	H_2SO_4	28 days
Metals ICP scan	Water	750 mL	polyethlene	Nitric acid rinsed	28 days
Pesticide-PCB scan	Water	2 L	Brown glass	None	7 days
Hydrocarbon ID	Water	1 L	Brown glass	None	7 days
Total Coliform	Water	100 mL	polyethlene	10-35 mg $Na_2S_2O_3$	30 hrs

Lab Measurement Procedures

The matrix for all samples collected for this project will be water (groundwater from wells). Table 7 lists measurement methods to be used for field and lab analyses.

Table 7
Measurement Methods (Field and Laboratory)

Analyte	**Expected Range of Results**	**Reporting limit**	**Analytical Method**	**Lab**
nutrients: Nitrogen (Nitrate as N) Nitrogen (Nitrate as N) **(Field)** Ammonia (optional)	ND – 15 mg/L	0.5 mg/L 0.4 mg/L 0.005 mg/L	SM 4500-NO3-D EPA 353.3 EPA 350.1	CCEH Chemetrics AmTest
other inorganics: Chloride **(Field)**	2.5 – 40	2.5 mg/L	SM 4500-Cl- E	Chemetrics
metals (total): chromium (Cr) copper (Cu) lead (Pb) nickel (Ni) zinc (Zn)	ND – 2 mg/L	0.001 mg/L 0.001 mg/L 0.01 mg/L 0.005 mg/L 0.001 mg/L	EPA 200.7 (ICP scan includes all metals listed, plus others)	AmTest

pesticides: Pesticides & PCBs scan	ND – 500 ug/L	Various (ug/L)	EPA 608 (GC/EC)	AmTest
other organics: Hydrocarbon identification	ND – 500 ug/L	Various (ug/L)	NWTPH-HCID	AmTest
pathogens: Total coliform & E. Coli	absent – confluent	MPN or MF	SM 9221B, 9222B	CCEH

NOTES:
AmTest is an accredited laboratory in Kirkland, WA. Owner/manager is Kathy Fugiel, 425-885-1664.
CCEH = Clallam County Environmental Health Laboratory. Accredited with the state. Conducts and records QC protocols regularly for nitrate procedures. Lab Manager is Belinda Pero, 360-417-2334.
Chemetrics = a commercial, portable photometer with one-time-use ampoules for evaluating samples in the field. Zeroing of the instrument is performed using a manufacturer-supplied blank prior to each sample. Analysis against standard reference solutions will be conducted prior to commencement of field work. All field measurements will be conducted by CCEH personnel.

Quality Control

Field QC

All field parameters will be measured using the instruments described above. Replicate measurements are made continuously at each well site. Ongoing maintenance and calibration involves the following, most often in the office/lab:

- pH – a minimum of a 2-point calibration is conducted on the instrument several times each year, which brackets the typical concentration of groundwater samples. A three-point calibration should be performed whenever possible.
- Conductivity – the calibration of the instrument is conducted several times each year, with a 0.01 M KCl standard solution.
- DO – recalibrate each time the instrument is turned on according to manufacturer's instructions. Inspect probe for bubbles or damage before each use.
- Photometric methods (nitrate, chloride) – calibration using standard reference solutions will be performed in the EH lab according to manufacturer's instructions.

All field QC samples will be labeled and treated as ordinary (but blind) samples and their results reported and assessed in terms of the project objectives along with other sample results. Two types of field QC samples will be collected by staff:

- Split duplicates
  Field duplicates are samples which are collected by splitting the sample flow into two bottles and are preserved, stored, and analyzed under identical conditions. An estimate of the precision or random error due to sampling can only be made if the results of the field

duplicates are significantly above method detection levels. Therefore, samples selected for duplication should be those expected to produce amply detectable results.

- Blind field blanks
  Throughout the project, a blind field blank of distilled water will be exposed to the same process the samples go through, and submitted with a unique sampling episode (at least 5 over the project period). These results will be used to provide an estimate of the overall accuracy of the analytical results.

Laboratory QC

All lab QC results will be reported along with sample results. In the event of poor lab QC performance, all lab QC samples and field samples for the batch will be reanalyzed. If sample volumes are too low for reanalysis or if no corrective action is taken, data will be discussed in a validation report in which the lab provides their judgment of the impact of any QC results which fail to meet the data quality goals, and qualify the results as to their usefulness.

It is expected that at least 25 wells will be sampled once each for the various parameters listed here. Given this approximate number of samples, a QC regimen is described in Table 8:

Table 8
QC Samples, Types and Frequency

Parameter	Field		Laboratory *(Field for Chemetrics)*			
	Blanks	Split-Duplicates*	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spikes
Static water level	NA	3	NA	NA	NA	NA
pH	NA	2	NA	NA	NA	NA
Temperature	NA	2	NA	NA	NA	NA
Dissolved Oxygen	NA	2	NA	NA	NA	NA
Conductivity	NA	2	NA	NA	NA	NA
Nitrogen (Nitrate as N)—lab	5	10%	2	1	2	1
Nitrogen (Nitrate as N)—*field*	*3*	*20%*	*2*	*3*	*20%*	*NA*
Ammonia (lab)	NA	10%	2	1	2	1
Chloride—*field*	*3*	*20%*	*NA*	*NA*	*20%*	*NA*
Metals ICP scan	NA	10%	1	1	1	1
Pesticide scan	NA	10%	1	1	1	1
Hydrocarbon ID	NA	10%	1	1	1	1
Total coliform	2	2	**	NA	NA	NA
E. coli	NA	NA	**	NA	NA	NA

*Minimum number/percent of split-duplicates to be collected
**CCEH lab performance tests are regularly conducted on 10 samples to check results against outside lab results (commercially-developed tests); reagents tested (each batch) for presence/absence and E. coli

Data Management Procedures

All field results, including water levels, well discharge rates, field parameter results, and well and location information will be recorded on Groundwater Sampling Records and Water Level Records that will be maintained throughout the length of the project, transcribed into the CCEH groundwater database, and eventually archived in project files. Staff-collected field parameters and laboratory results also will be entered into the database, and submitted to Ecology's EIM after data quality assessment is complete.

The laboratory will verify its results and submit a report with a case narrative, in both hard copy and spreadsheet format (for the data). The CCEH project lead will review the laboratory's results for completeness and reasonableness, and validate the data to determine if it met the MQOs for the project. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-sampling and/or re-analysis considered.

Audits and Reports

This project is short in duration in that it involves only one or two seasons of sampling, and only one sample suite for each study well. The budget is also very limited, making auditing an extraneous activity. At the end of each quarter, the CCEH project manager will update MRC project coordinators as to progress and difficulties encountered, if any.

CCEH's draft project report will be submitted to Ecology and MRC project coordinators for review. It will include a summary of field methods, figures showing study wells and interpreted groundwater flow direction, tables of well characteristics and raw lab results, comparison of results to water quality standards, and discussion of results and recommendations for further study. The QA assessment will be included as an appendix.

The final report will be mailed or emailed to all project participants in addition to the distribution list included above. The data sets resulting from the project will be submitted to Ecology's EIM after completion of verification and validation.

Data Verification

Once the data have been reviewed and verified, the CCEH project lead will validate the data to determine if the measurement quality objectives have been met for various sampling episodes.

1. Precision will be estimated by calculating the relative percent standard deviation (%RSD) between results for split-duplicate pairs. These values provide an indication of the degree of random variability introduced by sampling and analytical procedures. These values will be compared to the mean duplicate concentration (over the entire concentration range reported during the project) to assess the ability of the data to meet the project MQOs. (The %RSD for

duplicate pairs at, or near, the reporting limit are typically higher than the allowed error described by the MQOs but are small in absolute terms and will not disqualify data from use.)

- Field replicate and laboratory duplicate data will be used to estimate total and analytical precision through the equation for relative percent difference (RPD) and the equation for pooling estimates of standard deviation from pairs (s_p):

$$RPD = \left(\frac{|C_1 - C_2|}{C_1 + C_2}\right) \times 200$$

where C_1 = first split-duplicate result and C_2 = second split-duplicate result

$$s_p = \sqrt{\frac{\sum D^2}{2m}}$$

where D is the positive difference between each pair of results, and m is the number of pairs.

2. 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, and review of analytical results for blank samples.

3. Completeness will be assessed by dividing the number of valid analyses (those meeting MQOs) by the number of samples analyzed. If needed, replacement samples will be obtained and adjustments in subsequent sampling events will be made, if possible.

Results of the QC assessment will be prepared for inclusion in the final project report as an appendix.

Data Quality (Usability) Assessment

CCEH will assess whether the data for various analytes can be used to make the determinations for which the project was conducted.

- The purposes of the water quality data collection in this project are to provide baseline information about ambient nitrate concentrations in the shallow aquifer discharging to marine water, and to update the status of stormwater contaminants in vulnerable wells downgradient from urban areas. No specific agency decision will be forthcoming based on the results. If project MQOs have been met for various sampling episodes and graphical representations can be fairly interpreted, the data will be considered acceptable for use (except as qualified during the data review and validation process) and no additional data quality assessment will be needed.

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Dungeness Area, Clallam County, Washington. U.S. Geological Survey, Water-Resources Investigations Report 99-4048, 165 p.

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Figures and Attachments

Figure 1. Study area: Dungeness River lower watershed east side, showing groundwater flow directions for the shallow aquifer and closure areas for commercial shellfish harvest.

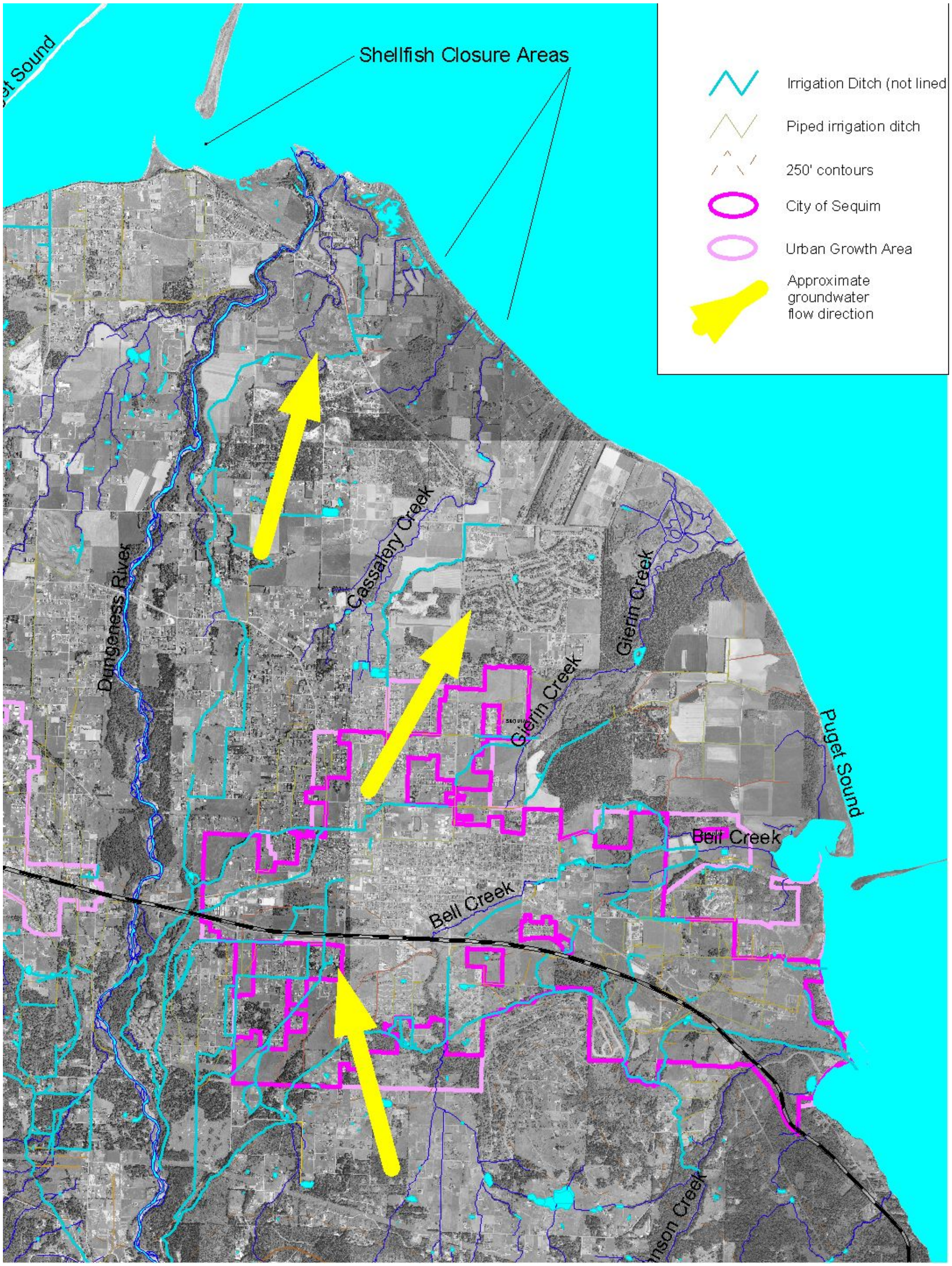
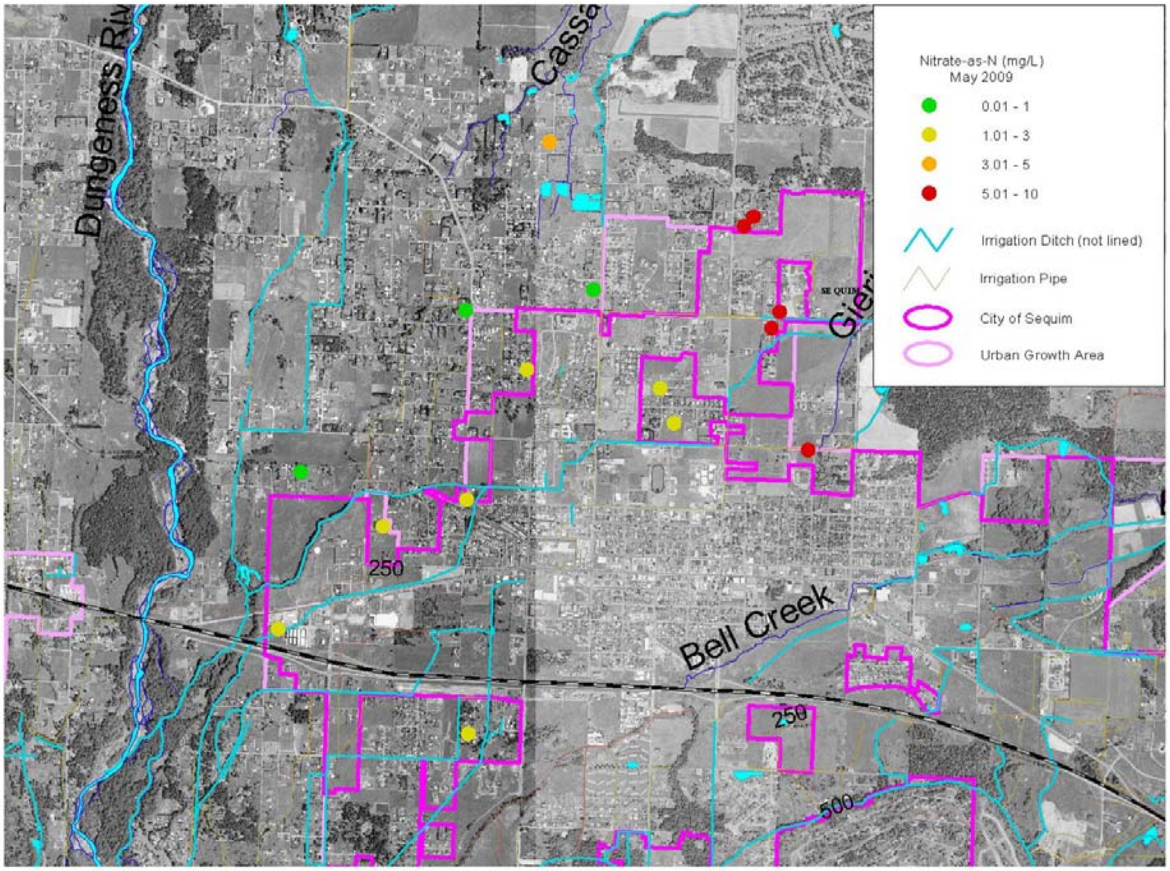


Figure 2. Well set from 2009 Phase I sampling, showing potential wells for “extended” stormwater contaminant sampling (those with nitrate > 5 mg/L).



ATTACHMENT A. AmTest Laboratories ICP Metals QC Values

	Detection Limit	Matrix Spikes	Matrix spike Duplicate
	mg/l	**% Rec**	% RPD
ALUMINUM	**0.010**	70-130	6.8
ANTIMONY	**0.010**	70-130	11
ARSENIC	**0.010**	70-130	5.1
BARIUM	**0.0005**	70-130	19
BERYLLIUM	**0.0005**	70-130	5.3
BISMUTH	**0.050**	70-130	
BORON	**0.050**	70-130	
CADMIUM	**0.0005**	70-130	9.3
CALCIUM	**0.050**	70-130	16
CHROMIUM	**0.001**	70-130	9.8
COBALT	**0.001**	70-130	
COPPER	**0.001**	70-130	6.0
IRON	**0.005**	70-130	7.0
LEAD	**0.010**	70-130	6.6
LITHIUM	**0.005**	70-130	
MAGNESIUM	**0.05**	70-130	15
MANGANESE	**0.0005**	70-130	6.7
MERCURY	**0.01**	70-130	
MOLYBDENUM	**0.005**	70-130	5.9
NICKEL	**0.005**	70-130	6.4
PHOSPHORUS	**0.010**	70-130	
POTASSIUM	**0.10**	70-130	14
SELENIUM	**0.010**	70-130	6.8
SILICON	**0.05**	70-130	
SILVER	**0.010**	70-130	
SODIUM	**0.05**	70-130	9.8
STRONTIUM	**0.0005**	70-130	
SULFUR	**0.05**	70-130	
THALLIUM	**0.010**	70-130	6.1
TIN	**0.005**	70-130	
TITANIUM	**0.001**	70-130	
VANADIUM	**0.005**	70-130	
YTTRIUM	**0.0005**	70-130	
ZINC	**0.001**	70-130	6

ATTACHMENT B. AmTest Laboratories Pesticides & PCBs QC Values

Pesticides & PCB's	Matrix spike Recovery Limits % recovery	Matrix spike duplicate % RPD
Aldrin	43.7-118	32
Endrin Aldehyde	37.2-140.6	25
Heptachlor	72.6-108	27
Heptachlor Epoxide	50.122.1	20.4
Alpha-BHC	53-126	23.1
Beta-BHC	60.2-136.4	21.4
Delta-BHC	48.138.3	28.2
Dieldrin	47.9-117.9	14.3
Endrin	51-129.2	25.2
Endosulfan I	54.4-126	18.3
Endosulfan II	51.5-129	17.5
Endosulfan Sulfate	51-123	19.1
Toxaphene		
Chlordane		
Methoxychlor	70-181	54.1
PP-DDD	65.1-136.1	34.5
PP-DDT	66.3-136.2	47.5
PP-DDE	39.5-132.1	24.4
PCB-1016		
PCB-1221		
PCB-1232		
PCB-1242		
PCB-1248		
PCB-1254		
PCB-1260	49.07-122.3	46.1