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Groundwater Quality Monitoring in the Shallow Aquifer near Sequim, Clallam County, WA

Phase II

FINAL DRAFT

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Summary

Concern about impacts to groundwater and water quality in general from stormwater runoff prompted the Clallam County Marine Resources Committee (MRC) to fund a two-phase study to determine the vulnerability of the shallow aquifer to stormwater contamination. For Phase I (2009), Clallam County Environmental Health (CCEH) staff in the Health & Human Services Department coordinated a field effort with the goal of determining generalized groundwater flow patterns around the City of Sequim, and the vulnerability of shallow wells to impacts from surface activities. Results from this effort were reported in *"Groundwater Quality Monitoring in the Shallow Aquifer near Sequim, Clallam County, WA: Phase II,"* June 2009.

For Phase II (2010), the purpose was to investigate groundwater quality in the shallow aquifer draining to streams and marine waters of the Dungeness watershed. Dual objectives included 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. (Soule 2010)

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Ambient groundwater quality was estimated through analysis of nitrate, ammonia, and chloride in up to 25 shallow domestic wells, along with pH, dissolved oxygen, and conductance. Data analysis of field nitrate measurements indicates that a third of all wells sampled have nitrates above 5 mg/L, which indicates advanced degradation from land activities and the possibility that other contaminants may be present – depending on the source(s) of nitrates – and which suggests that yearly testing is warranted. Up to 70% had a nitrate concentration above background (1 mg/L).[2] The drinking water standard for nitrate as N is 10 mg/L.

The wells with the highest nitrate concentrations are near developed areas in and around the city limits; wells with the lowest concentrations are in Dungeness, where the soils are dominated by clay and dissolved oxygen is low (<3 mg/L).

Four of seven wells had undetectable or at-detection levels of ammonia, and the highest concentration found was 0.515 mg/L. Table 5 contains complete results. For the five wells that were tested for ammonia in the Dungeness/Three Crabs Rd. community, all had undetectable nitrate (<0.4 mg/L). One of these had an ammonia concentration higher than the corresponding nitrate, making ammonia the predominant form of nitrogen. This well is located adjacent to Golden Sands canals which have relatively high ammonia according to Woodruff et. al., 2009.

Chloride results were 38 mg/L and lower, far from the drinking water standard of 250 mg/L. The highest concentrations of chloride, relatively speaking, were found in wells adjacent to salt water; the lowest were found in wells closest to the Dungeness River.

Potential stormwater contaminants including petroleum hydrocarbons, pesticides, PCBs, and metals were not detected in wells selected for their known vulnerability to impact from land uses (i.e., based on elevated nitrate concentrations). On the other hand, high nitrate concentrations were confirmed, and for some wells this implicates stormwater runoff or leakage from sewered residential and commercial areas as the probable source.

Recommendations include continued land use management efforts to oversee septic system maintenance, regulate septic system densities, and treat stormwater runoff to protect groundwater quality. Additional recommendations include continued education to prevent nonpoint source pollution and research into nitrogen loading, especially in the Dungeness / Three Crabs area.

[2] A note about field nitrate measurements: results for six split duplicates analyzed in a laboratory indicate that the field method may under-report actual nitrate concentration by up to about 25%. A linear correlation between field and lab replicates was applied to the complete data set, as summarized in the Results and Discussion section. Corrected results are reported here, and should be viewed as estimates.

Background and Objectives

As planned with representatives of the Clallam County Marine Resources Committee (MRC) in 2009-2010, the objectives of this two-phase project were to investigate groundwater quality in the shallow aquifer draining to streams and marine waters of the Dungeness watershed, with focus on the potential for stormwater contamination. The water quality of shallow marine waters in the watershed, particularly Dungeness Bay, is degraded by bacterial contamination causing closure of some areas to the commercial and/or recreational 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 project builds on a 2005 study by CCEH establishing baseline groundwater quality for County residents with drinking water wells downgradient of commercial/light industrial development in City of Sequim's western city limits (Soule 2005). In that study, six wells were tested in May 2005 for nutrients (nitrates, TKN), metals scan (total rather than dissolved), pesticides scan + PCBs, other organics (hydrocarbon identification, semi-volatile organics scan), pathogens (total coliform and Pseudomonas aeruginosa), and Total Dissolved Solids (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.

In 2009, Phase I of this project investigated relative vulnerability of study wells in the 2005 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 of 5 mg/L nitrate as Nitrogen. 80% of sampled wells had nitrate levels indicating evidence of impact from human activities (>1 mg/L).[3] Recommendations from Phase I were incorporated into the monitoring plan for Phase II as much possible, including provision for collection of ample replicates to evaluate field-lab discrepancies.

The MRC study also responds to goals of a concurrent stormwater assessment project managed by Clallam County Dept. of Community Development under a grant from the EPA, intended to result in stormwater management regulations. Recommendations received by state specialists cooperating on the EPA project have been incorporated during the planning and final reporting phases (Pitz 2009-2011). In particular, Charles Pitz guided project design for the two phases, beginning with a screening-level groundwater quality assessment for wells in the shallow

[3] 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."

aquifer near historically "urban" zones to determine their relative vulnerability to contamination. Phase II broadened the area surveyed for vulnerability while targeting sampling for stormwater contaminants on wells found in Phase I to be vulnerable. In addition, the correlation between field and lab replicates was initially documented by Pitz.

Finally, while many surface water quality and groundwater resource investigations have been conducted in the Dungeness watershed in recent years, the ambient groundwater quality overall has not been assessed 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 inorganic nitrogen concentrations found in groundwater-fed creeks[4] (Woodruff et. al. 2009) have generated interest in testing for ammonia in addition to nitrate in areas of fine-grained soils, shallow water table, and known sources of nitrogen (e.g., higher densities of septic systems).

[4] Woodruff et. al. (2009) reported 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.

Brief 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 involved 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.

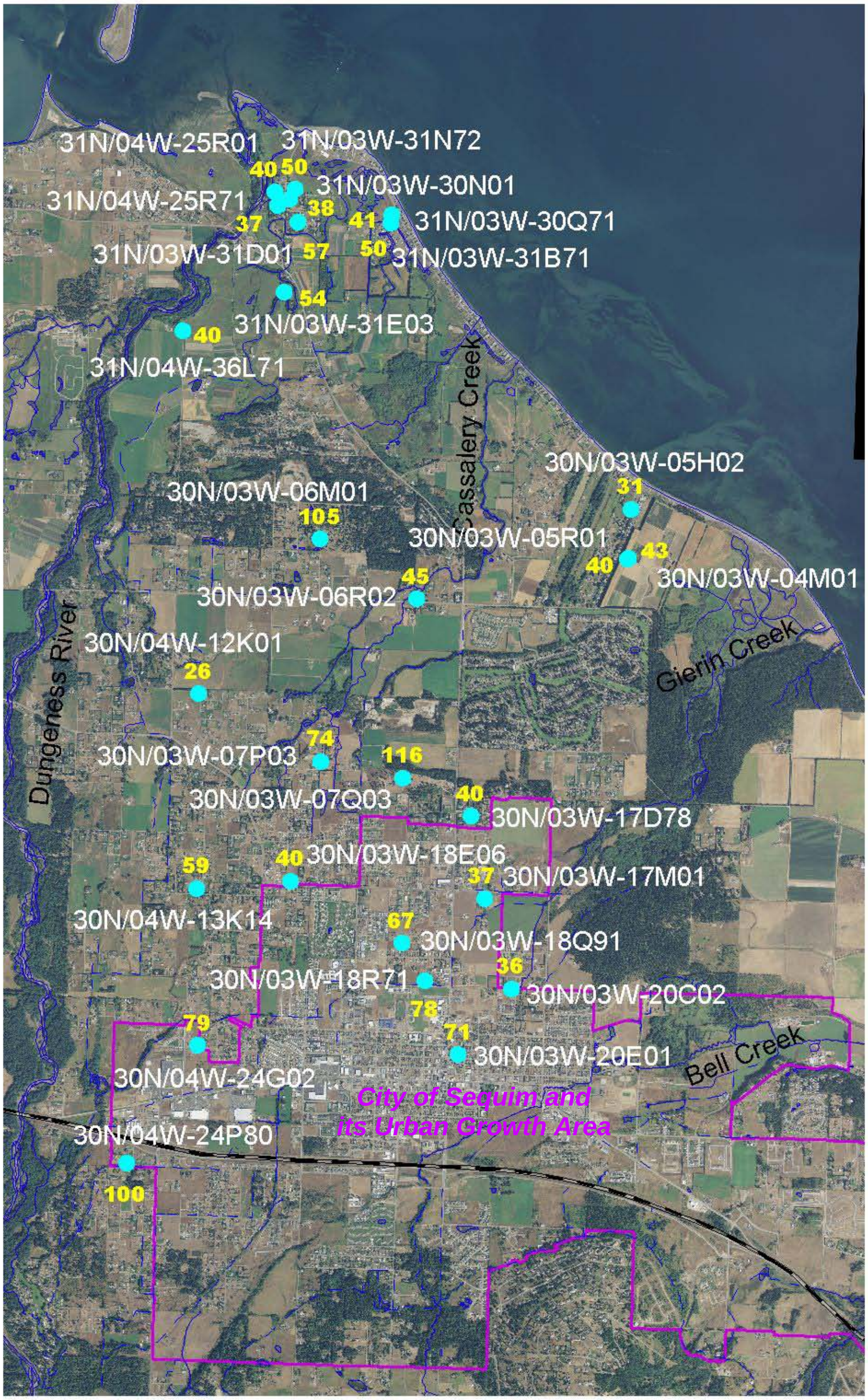
The budget did not allow for construction of project-specific monitoring wells, so CCEH selected several study wells used for Phase I and additional wells used for domestic water supply and completed in the shallow aquifer; preference was given to wells involved in previous groundwater quality studies. A side benefit of using shallow-aquifer domestic supply wells is that associated public-health risk was also assessed, and results mailed to participating well owners. 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) for their water supply.

Figure 1 features the study area and study wells.

Samples were collected and analyzed for nitrates in all cases, and bacteria, chlorides, ammonia, and selected stormwater contaminants in subsets of the study well group. The project followed the Quality Assurance Project Plan (QAPP) approved by Ecology (Soule 2010), involving procedures accepted by state and federal agencies for well and analyte selection, sampling and handling methods, laboratory analysis, data entry and management, and statistical analysis for quality assurance.

CCEH mailed all field measurements and lab results to each participating well owner. In addition to producing this report, CCEH presented project conclusions and recommendations to the Clallam County Marine Resources Committee in May 2011 and to the Sequim-Dungeness Clean Water Work Group in June 2011; the report is posted on www.clallam.net. Project and site information was submitted to Ecology's EIM in June; water quality and water level data will be submitted later this year.

Figure 1. Study area and study wells, showing well depth (in feet) and ID. All study wells are completed in the shallow aquifer.



Methods

A Quality Assurance Project Plan (QAPP) for Phase II was prepared by CCEH staff (Soule 2010) and approved by Ecology prior to commencement of well selection and field work. The QAPP formalized data quality objectives, specific sampling design, field protocols, laboratory methods, quality control approach, and how data and project reporting would be accomplished.

Phase II included 27 wells total: five were selected based on relative vulnerability established in Phase I; two were used for water level measurement only, and not sampled. All are in current use for residential or commercial purposes except one, which was decommissioned a few weeks after measurement. Figure 1 shows study well locations and depths. Additional well characteristics and static water level measurements are included in Appendix A.

Chemical analyses were selected based on recommendations (Pitz 2009) that general vulnerability to contamination be assessed in "Phase I" before spending the resources necessary to sample and analyze for specific stormwater contaminants in "Phase II". Specifically, nitrate was chosen as a good screening parameter for both Phase I and II because it is conservative and mobile in groundwater relative to contaminants typical of stormwater such as hydrocarbons and metals, which are adsorbed by most soils for some length of time. In addition, field measurement of nitrate such as with a Chemetrics photometer reduces expense and provides immediate results. The QAPP details the selection process for all constituents; Table 1 lists potential water quality analyses and associated details.

Table 1. Constituents of interest

Constituents of interest	**Analytical method**	**Detection limit**	**State standard***	**Price per sample****	**Phase**
<u>nutrients</u>: Nitrate as N (NO_3 as N) Lab Nitrate as N (NO_3 as N) Field Ammonia (optional)	 SM 4500-NO3-D EPA 353.3 EPA 350.1	 0.5 mg/L 0.4 and 1.13 mg/L 0.005 mg/L	 10 mg/L 10 mg/L Not defined	 $25*** $1.25	 I and II I and II II
<u>other inorganics:</u> Chloride Field (optional)	 SM 4500-Cl- E	 2.5 mg/L	 250 mg/L	 $1	 II
<u>metals (total)</u>: chromium (Cr) copper (Cu) lead (Pb) nickel (Ni) zinc (Zn)	 EPA 200.7 ICP scan includes all metals listed, plus others	 0.001 mg/L 0.001 mg/L 0.001 mg/L 0.005 mg/L 0.001 mg/L	 0.1 mg/L 1.0 mg/L 0.05 mg/L 0.1 mg/L 5.0 mg/L	 $60 for scan	 II
<u>pesticides</u>: Pesticides & PCBs scan	 EPA 608 GC/EC	 Various (ug/L)	 Various	 $100	 II
<u>other organics</u>: Hydrocarbon identification	 NW-TPH-HCID	 Gas range: 30 ug/L Diesel: 100 ug/L Oil: 200 ug/L	 800 ug/L if benzene present	 $50	 II
<u>pathogens</u>: Total coliform and E. Coli	 SM9221B, 9222B	 Not detected (MPN or MF)	 1 colony/ 100 mL	 $20***	 I and II

*Ecology, 1996, Appendix A
**AmTest, Inc., 2004 – except for Chemetrics field nitrate and chloride kits with low per-sample cost
*** in 2009, Twiss Laboratory in Poulsbo; in 2010, Clallam County Environmental Health Laboratory

County staff and assistants visited all study sites during fall of 2010. Protocols established in the QAPP were followed for each task. Soule and volunteer assistants first attempted to access each well to measure static water level (20 wells were measured; results are in Appendix A). Next, a County hose was attached to the nearest spigot to purge the well, and staff collected grab samples in a bucket at 3-5 minute intervals. Dissolved oxygen, conductivity, pH and water temperature were measured from the bucket samples using hand-held probes. After field parameters stabilized, samples were collected for various laboratory analyses as per the QAPP.

Seven field replicates[5] were collected and submitted to the Clallam County Environmental Health Laboratory for nitrate analysis; three of these were split duplicates for laboratory precision. Five blanks were also submitted for lab nitrate analysis. Ammonia samples were collected for laboratory analysis from seven sites, six of which were in proximity to surface water detections of ammonia as described above. The project was budgeted for five analyses of potential stormwater contaminants. However, the QAPP dictated that 10% of samples had to be split duplicates, which meant only four different wells could be sampled for each parameter. Ammonia, TPH, pesticide/PCB, and metals samples were transported to AM Test Labs in Redmond, WA, for analysis.

Nitrate was measured in the field using a Chemetrics V-2000 photometer.[6] Chemetrics measurements for nitrate were made for eight "split duplicates," i.e., on the same grab sample. Three blanks were also tested in the field with the nitrate kit.

Chloride analysis was optional, of interest especially in wells close to the marine shoreline. Chloride was measured for 18 wells, also using the Chemetrics photometer; five split duplicates and four blanks were also measured. Because chloride is not a primary drinking water contaminant, precise results were not critical and laboratory verification of field kit results for quality assurance was not conducted. <u>Chloride results should be considered estimates</u>.

Other field activities included tagging the well with Ecology unique ID #s as needed, sketching and photographing the site.

It was intended that County building permit and state agency public water system data would be compiled and reported as well; however, resources ran out before that was accomplished.

Data entry of well log information and field notes to the County groundwater database was performed by Soule, who then mapped well locations in the County's GIS. Two-foot Lidar contours were used to establish wellhead elevations. Laboratory and field water quality results were entered by a volunteer with QC by Soule.

The author wishes to also acknowledge and express thanks to field assistants Dick, Rhonda, and Joe Dapcevich and data entry assistant Betsy Robins (all Clallam County Beachwatchers).

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[5] Because field measurements were done on the final grab sample collected over a 10-20 minute time frame, collection of a true "split duplicate" concurrent with the final grab sample was not always achieved. Three out of seven field replicates were true split duplicates.

[6] Chemetrics "Nitrate3" ampoules were used when the anticipated concentration of nitrate was above 2 mg/L. For samples expected to be under 3 mg/L, "Nitrate2" ampoules were used, with a range of 0.40 – 3.00 mg/L.

Results and Discussion

Appendix B contains complete results for all water quality parameters tested. A discussion of groundwater flow and each groundwater quality constituent follows.

Groundwater Flow

Static water level data are fundamental to any investigation of groundwater hydrology. The direction of groundwater flow may be estimated to be perpendicular to water level elevation contours, developed from point water level elevations for multiple wells tapping the same aquifer. Accurate measurements of the elevation of the ground surface at several wellheads, height of the measuring point used for each well, and depth to water when it is in equilibrium are all needed to determine flow direction accurately, in addition to details of the geologic layers each well passes through.

Figure 2 shows the water level elevations for the southern half of the study area for fall 2010 and the inferred direction of groundwater flow. This generally agrees with earlier estimations of groundwater flow direction for the area east of the Dungeness River near Sequim found in Thomas 1999. The north-east regional flow direction also corroborates findings of Simonds and Sinclair (2002) that the shallow aquifer receives infiltrated water from the Dungeness River for most of the River's lower sections, adding an eastward component to generally north-flowing groundwater.

While study wells in the central portion of the study area were also measured, water level contours can not be estimated without more closely-spaced data points, and unless it is known that the wells are under similarly-confined conditions. In any case, Thomas 1999 illustrates that the gradient flattens within a few miles of the coast (see Figure 3).

Wells in the Dungeness community measured in this study have water levels between 2 and 7 feet below ground surface. These results indicate that either the water table is very shallow, the wells are under pressure at depth from confining layers between the ground and the well intake, or both. In fact, the water table is very shallow in this low-elevation area where wetlands and springs are prevalent and the vertical component of groundwater flow is upward. In addition, well logs show multiple clay layers adding up to 30' or more within the upper 50' – creating semi-confined conditions for groundwater tapped by these wells. Finally, tidal pressure likely adds to the dynamic nature of groundwater flow in upper portions of the system. Because of these complications, groundwater flow direction for a specific depth is not mapped for the Dungeness area even though the shallow zones are expected to be flowing generally northward, discharging into surface water.

Nitrogen

Nitrate

As described under "Methods" above, nitrate is a good parameter for tracking general trends in groundwater quality. Groundwater in the Dungeness watershed is naturally low in nitrates (<1 mg/L as N), but when nitrates are present, the annual high may be around June (Sinclair 2003).

Figure 2. Water level elevations in study wells and inferred groundwater flow direction (perpendicular to shallow aquifer elevation contours).

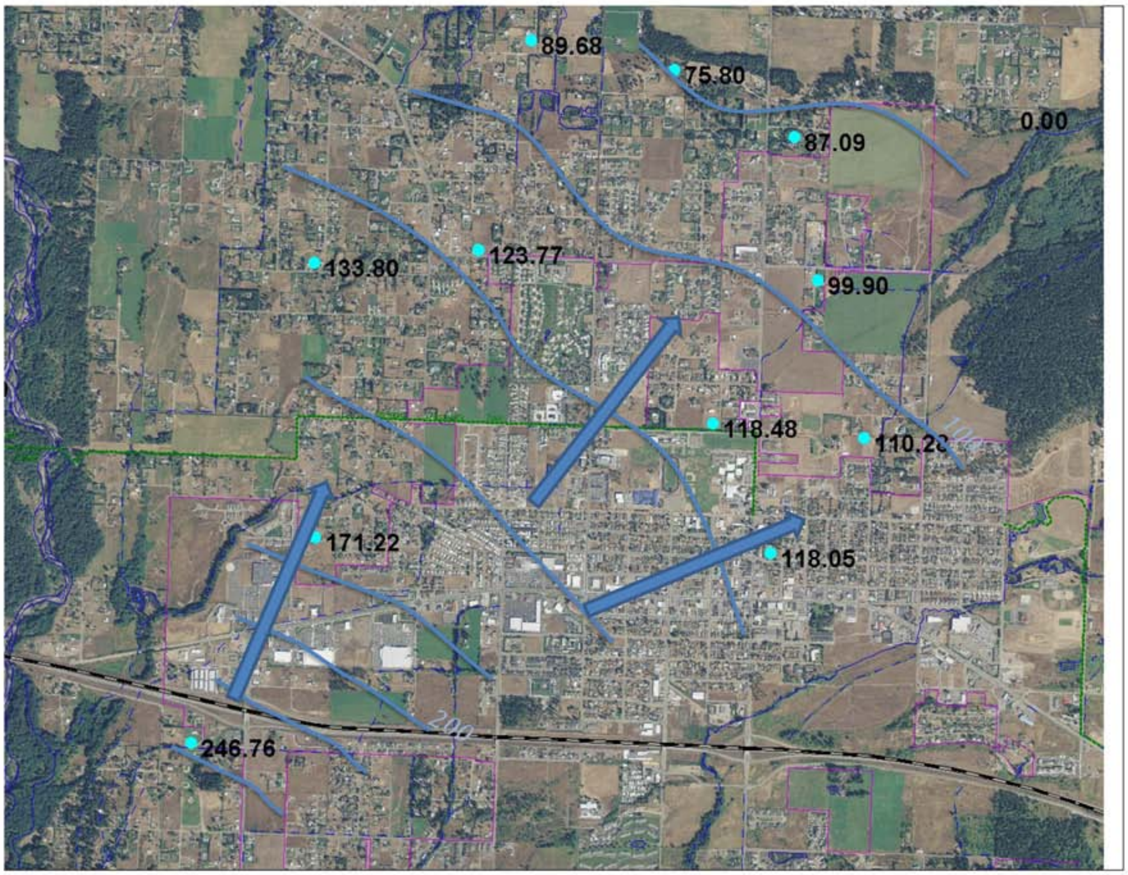
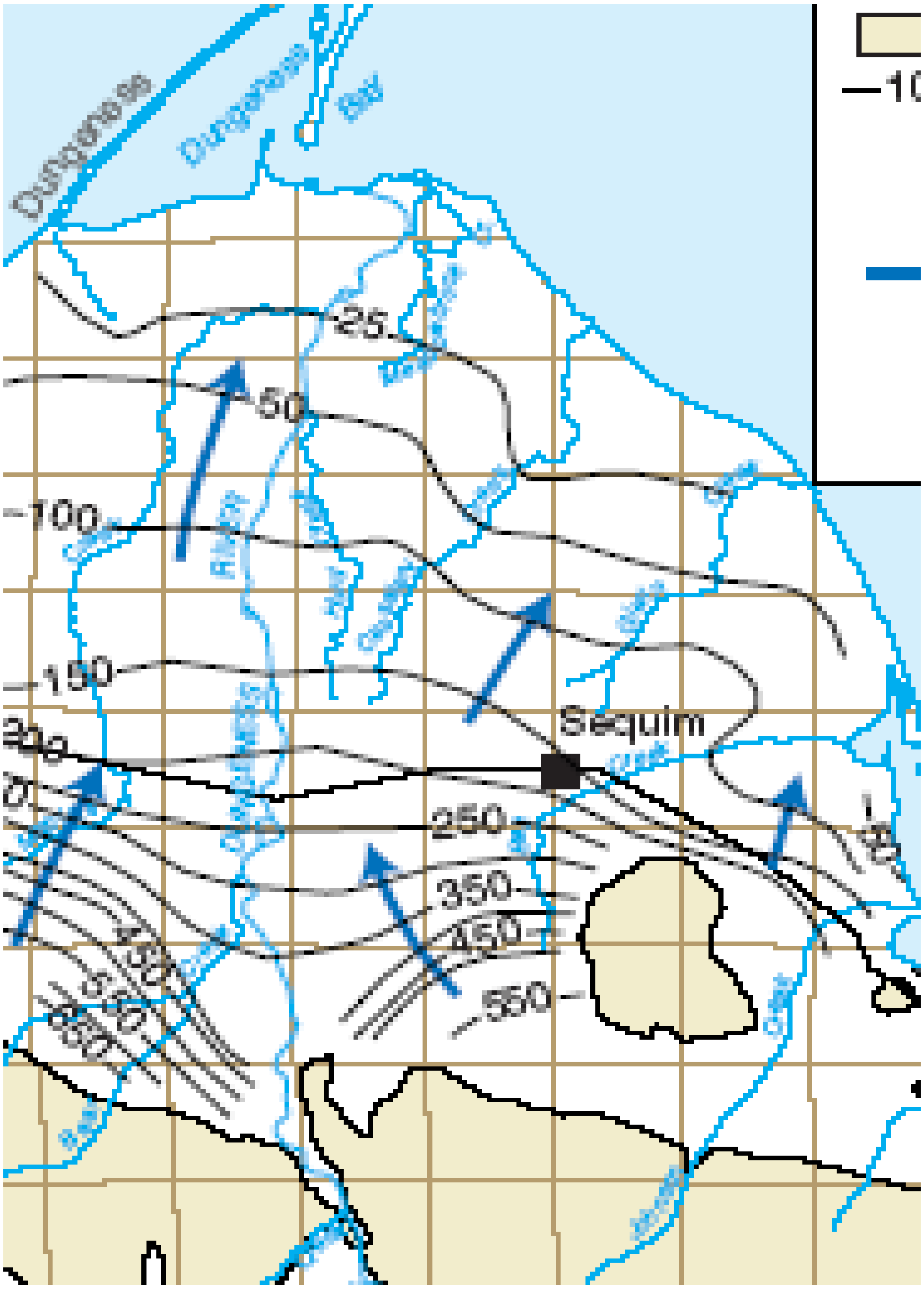


Figure 3. Regional groundwater flow; numbers indicate contours for the shallow aquifer. (from Thomas et. al. 1999)



When evaluating nitrate results for this project it is important to note that results for replicates analyzed by an accredited laboratory a day after field measurement were all higher than field results. This implies that the field nitrate measurement method under-reports actual nitrate concentration. Potential reasons for this are discussed in the next section on data quality. These data discrepancies are summarized in Table 2.

Table 2. Results of field and lab nitrate analyses conducted for replicate samples from seven wells sampled in Phase II.

Chemetrics field result (mg/L)	**EH Lab result for replicate**	**Difference**	**% of lab result**
7.53	10.6	**-3.07**	**71%**
6.28	8.63	**-2.35**	**73%**
6.29	8.36	**-2.07**	**75%**
2.77	4.5	**-1.73**	**62%**
1.05	2.13	**-1.08**	**49%**
0.85 (<1.13) (below field kit range)	2.1	-1.25	40%
0.28 (<1.13) (below field kit range)	0.67	-0.39	42%

Fortunately, a strong linear correlation was found when analyzing the relationship between these two data sets (Pitz 2011); the regression line and equation are shown in Figure 4. This correlation was applied to all "original" field measurements to obtain "corrected" nitrate concentrations listed in Table 3. Summary statistics for both sets of nitrate results are shown in Table 4. Please see the Data Quality Assessment section below for further discussion.

Figure 4. Linear relationship between seven original field measurements and associated lab results for replicate samples.

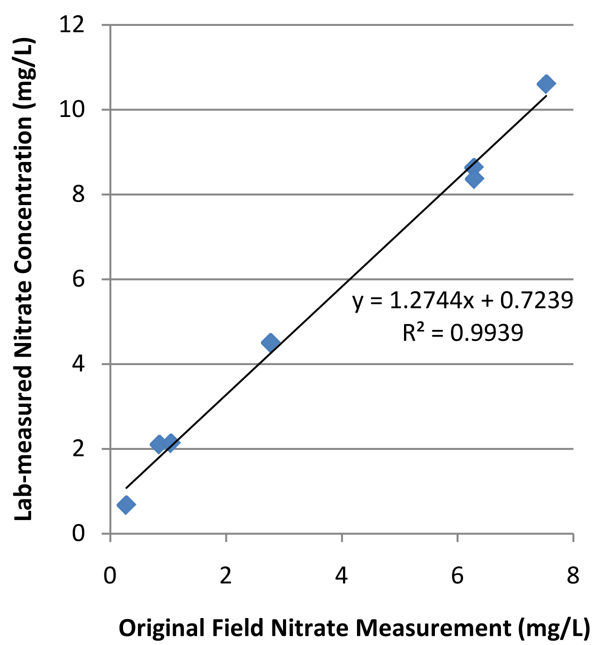


Table 3. Original, field-measured nitrate and "corrected" nitrate concentrations (based on linear regression shown in Figure 4).

Study Well ID	***Original Field Result (mg/L)***	***Below Method Detection Limit***	***Corrected Field Result Estimate (mg/L)***
31N/03W-31N72	0.06	x	0.8
31N/04W-25R71	0.06	x	0.8
31N/03W-31B71	0.07	x	0.81
31N/03W-30Q71	0.08	x	0.83
31N/03W-31D01	0.1	x	0.85
31N/03W-30N01	0.11	x	0.86
31N/04W-25R01	0.15	x	0.92
31N/03W-31E03	0.25	x	1.04
30N/04W-13K14	0.28	x	1.08
30N/03W-06R02	0.7		1.62
30N/03W-06M01	0.85	x	1.81
30N/03W-05H02	0.96		1.95
30N/04W-12K01	0.97	x	1.96
30N/03W-07Q03	1.03	x	2.04
30N/03W-04M01	1.05		2.06
30N/04W-24P80	1.13		2.16
30N/04W-24G02	2.77		4.25
30N/03W-18Q91	3.7		5.44
30N/03W-20C02	3.89		5.68
30N/03W-18E06	4.26		6.15
30N/03W-18R71	4.35		6.27
30N/03W-07P03	5.08		7.2
30N/03W-20E01	6.28		8.73
30N/03W-17D78	6.29		8.74
30N/03W-17M01	7.53		10.3

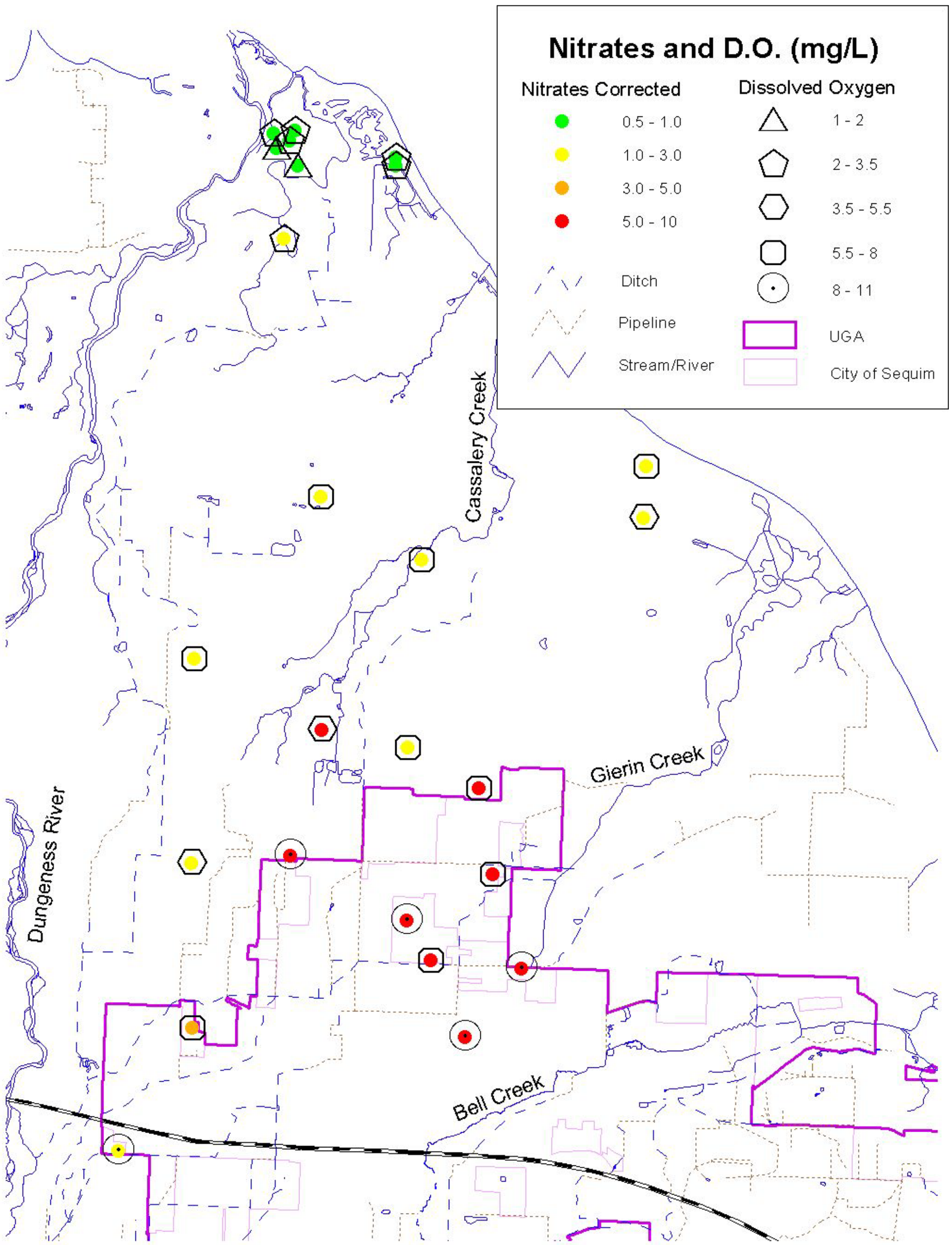
Table 4. Summary statistics for both original field nitrate results and "corrected" results after regression equation is applied. (n=25)

Field Results	***>1 mg/L***	***>5 mg/L***	***Minimum***	***Median***	***Maximum***
Original	about 50%	16%	Not detected (<0.4)	0.97	7.53
Corrected	about 70%	32%	(same)	1.96	10.3

In looking at the corrected field results, up to 70% of the 25 wells tested had a nitrate concentration above background (1 mg/L), indicating groundwater quality degradation from land activities. Potentially a third of all wells have nitrate above 5 mg/L, which indicates advanced degradation and the possibility that other contaminants may be present – depending on the source(s) of nitrates. The drinking water standard for nitrate as N is 10 mg/L.

Figure 5 shows the geographical distribution of "corrected" nitrate concentrations. The wells with the highest concentrations are near developed areas in and around the city limits—much of which is sewered; wells with lowest concentrations are in Dungeness, where the soils are dominated by clay and dissolved oxygen is low (<3 mg/L).

Figure 5. Nitrate ("corrected" field measurement) and dissolved oxygen results. Nitrification requires sources of both nitrogen and oxygen. Elevated nitrates are very unlikely to be found when D.O. is below 2 mg/L.



Ammonia
Samples from seven wells were tested in a laboratory for ammonia concentration in order to make a preliminary comparison of the relative concentrations of inorganic nitrogen species. Oxygenated groundwater facilitates nitrification of ammonia and nitrite to nitrate, making it unlikely to find ammonia in groundwater with >2-3 mg/L dissolved oxygen (D.O.). Most of the ammonia sampling sites were chosen because they are close to surface water detections of ammonia, and have relatively low dissolved oxygen. See Figure 6.

Four of seven wells had undetectable or at-detection levels of ammonia; the highest concentration found was 0.515 mg/L. Table 5 contains complete results. For the five wells that were tested for ammonia in the Dungeness/Three Crabs Rd. community, all had undetectable nitrate (<0.4 mg/L). One of these had an ammonia concentration higher than the corresponding nitrate, making ammonia the predominant form of nitrogen. This well is located adjacent to Golden Sands canals which have relatively high ammonia (reported in Woodruff et. al. 2009).

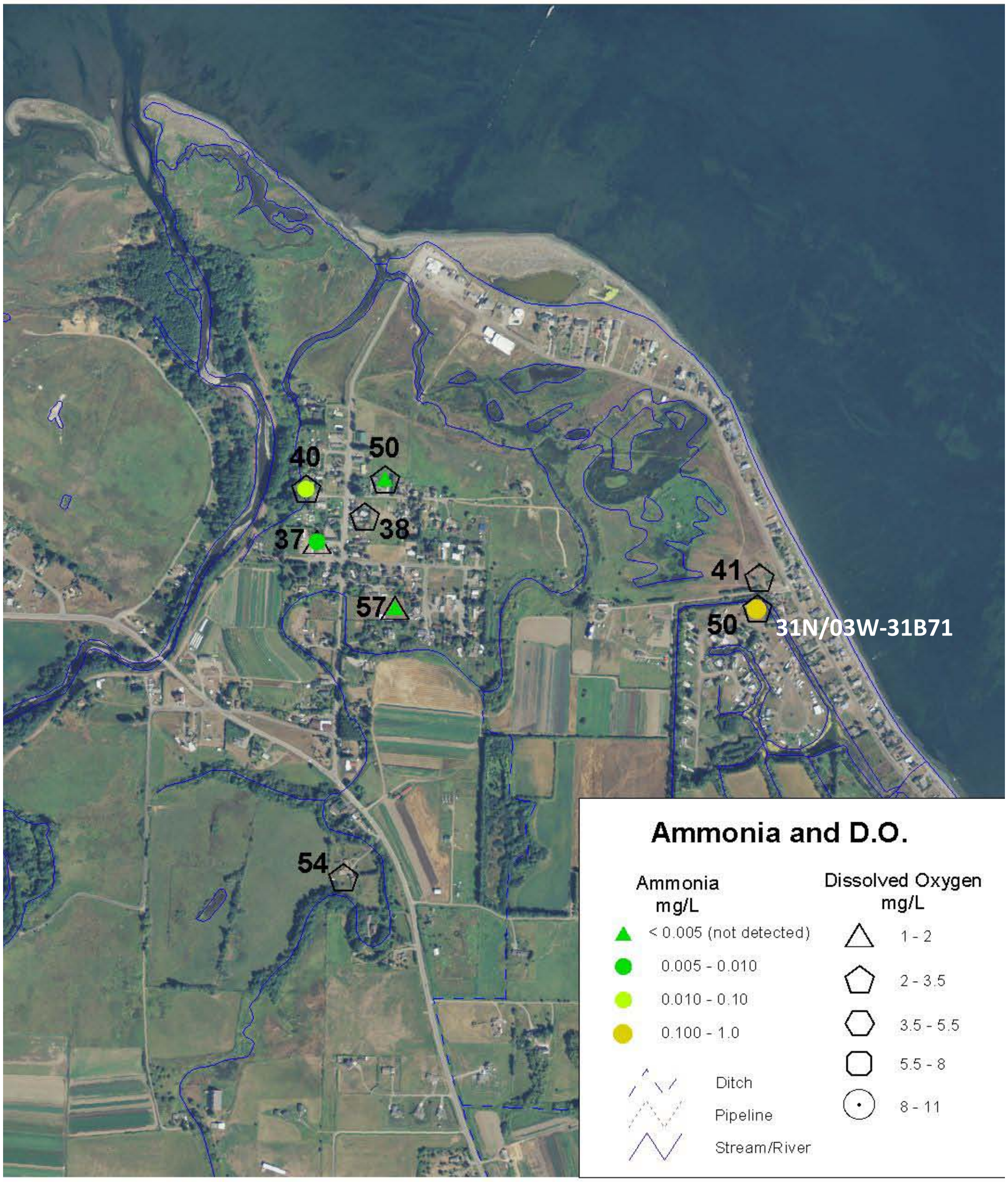
Table 5. All ammonia results in order of decreasing concentration,
and showing corresponding nitrate and dissolved oxygen concentration.

Well ID	Well Depth	Area	Ammonia-Nitrogen (mg/L)	Nitrate-Nitrogen (mg/L)	Dissolved Oxygen (mg/L)
31N/03W-31B71	50	Three Crabs Rd	0.515	<0.4	2.32
31N/04W-25R01	40	Dungeness	0.042	<0.4	2.43
30N/03W-04M01	43	Jamestown Beach	0.027	1.05	4.23
31N/04W-25R71	37	Dungeness	0.005	<0.4	1.45
31N/03W-31D01	57	Dungeness	<.005	<0.4	1.39
31N/03W-31N72	50	Dungeness	<.005	<0.4	3.37
30N/03W-17M01	37	North of Sequim	<.005	7.86	7.44

Nitrogen sources discussion
Many activities potentially contaminate groundwater, especially where soils are very permeable and/or the water table is shallow. Nitrate contamination in groundwater can be caused by over-fertilizing, accumulations of animal waste, septic systems, and potentially by a leak in sewage conveyance pipes.[7] Nitrate concentrations within aquifers change from season to season and time to time depending on the concentration, amount, and timing of contamination entering the aquifer, as well as the aquifer media (clay, sand, etc.), oxygen concentration (see above for more detail), and potential for dilution and/or denitrification. Historic land uses may cause “legacy” contamination as nitrogen compounds deep in the soil continue to leach out over time, after the land use has changed. Urban stormwater does not typically contain substantial loadings of nitrogen compounds unless the runoff contains fertilizer such as from intensively managed lawns or gardens, or dissolved pet waste. More information and an illustration of nitrates found in urban areas around Sequim may be found under the Stormwater Contaminants heading, below.

[7] Acid deposition from the atmosphere may also be a source of nitrogen compounds, but is expected to be minor relative to other anthropogenic sources in this region.

Figure 6. Ammonia results for the Dungeness area, including dissolved oxygen (D.O.) and well depth. Ammonia is more likely to be found than nitrate when a source of nitrogen is present but D.O. is not.



In Phase I, CCEH compiled and analyzed two external sets of recent nitrate data to extend the investigation further. First, a plot of nitrate values associated with building permits since 2006 showed a few occurrences of nitrates in the 3-5 mg/L range to the southwest and north of the city limits. There was one value >5 mg/L, in an area where only the lowest levels were found in this MRC study.

Second, a cursory review of nitrate results between 2006 and 2010 for community water systems testing at the County lab showed several occurrences of 3-5 mg/L nitrates to the southwest and north of the city limits, but nothing >3 mg/L in the northwestern-most area. There were also at least 6 occurrences of nitrates >5 mg/L to the north of the city. Well depths were not available with these data sets, but the majority of wells drilled in the study area are completed in the shallow aquifer according to Ecology's well log database and USGS 1999.

These analyses illustrate a common finding in local studies of nitrates in groundwater: nitrate concentrations may vary from low to high across small distances. Geologic and hydrologic variation in the subsurface, distinct well construction and sealing, and diverse, erratic sources of nitrogen released to the environment all contribute to inconsistent distribution of nitrates found from sampling domestic wells.

For example, the groundwater flow directions shown in Figures 2 and 3 support the theory that infiltration of relatively uncontaminated Dungeness River water[8] could be diluting nitrates to some extent, over some distance. Irrigation ditches that aren't lined or piped usually also leak water, but high nitrate wells are found both near and distant to these. Factors to consider when testing these correlations include ditch water quality for the study period at these sites, and volume of ditch leakage, at minimum.

Dissolved Oxygen

Groundwater dissolved oxygen is of interest partly because it plays a role in the occurrence of nitrogen compounds. The nitrification process involves oxidation of organic nitrogen and ammonia to nitrite and nitrate. Groundwater with a high level of D.O. such as might be found in shallow, fast-moving, and/or more permeable zones would facilitate the nitrification process when nitrogen is present. Likewise, low D.O. levels would inhibit nitrification. (However, note that other factors including presence of certain bacteria also influence nitrification.)

In this study the range of D.O. was 1.4 – 9.2 mg/L (12 – 83%); all wells with nitrates above 3 mg/L had D.O. above about 4 mg/L. Note that D.O. levels can't be used to predict high nitrates since there may not be a source of nitrogen. As expected, there were no wells with low D.O. and nitrates above background.

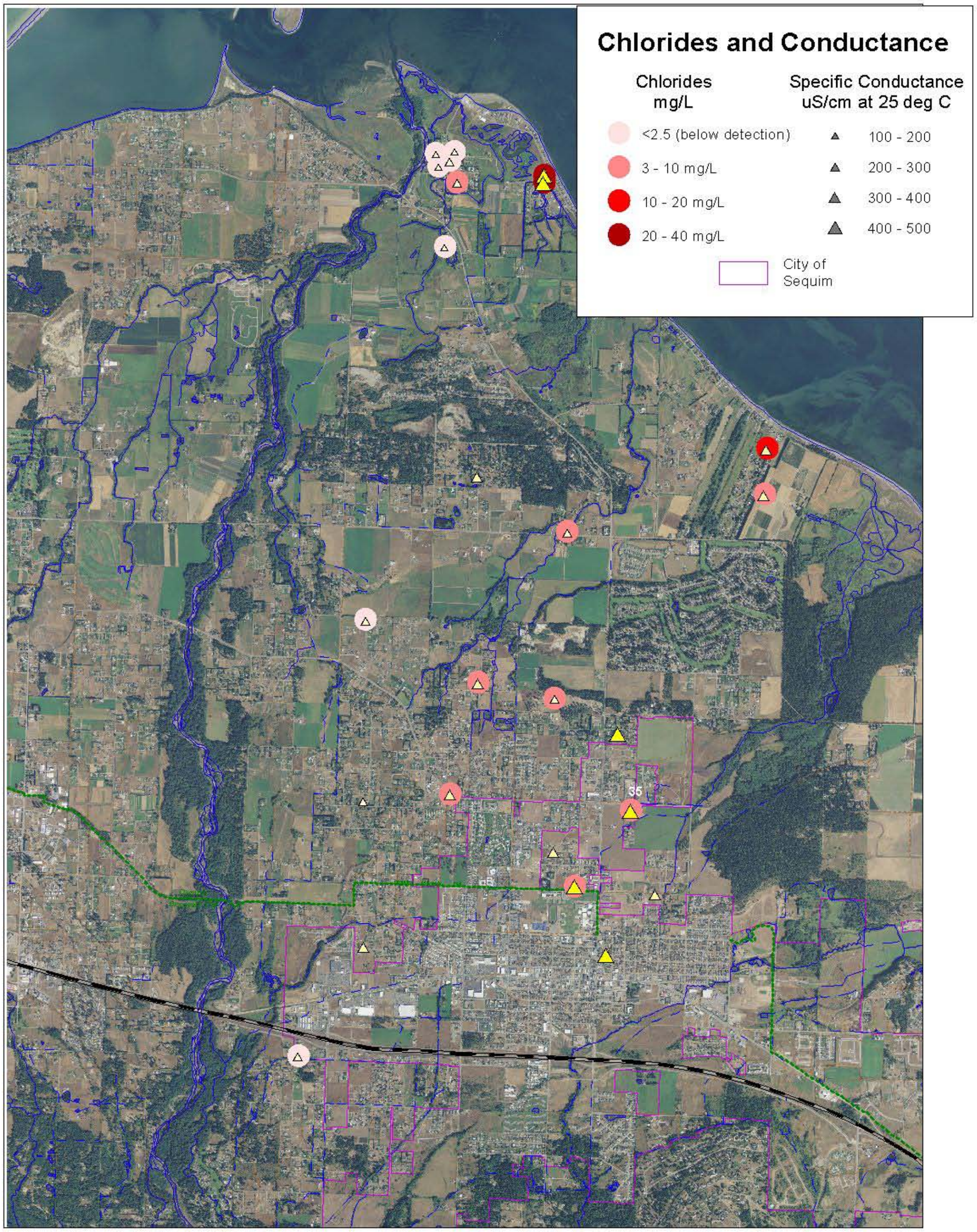
Chloride

Field measurement of chloride in 18 wells showed low concentrations consistent with previous studies (Drost 1986, Thomas et. al. 1999), as seen in Figure 7. Relative to all measurements

[8] Total Nitrogen in Dungeness River samples from river miles 3.2 and 11 ranged less than 0.3 mg/L in recent sampling (2006-08) (unpublished data, Jamestown S'Klallam Tribe 2009)

made in this study, the highest concentrations were found adjacent to the marine shoreline (where some mixing is expected) and the lowest were nearest to the Dungeness River. As discussed under nitrogen, above, the River is low in chloride relative to groundwater, which means River leakage would effectively dilute groundwater chloride concentrations.

Figure 7. Chloride results, with conductance as well.

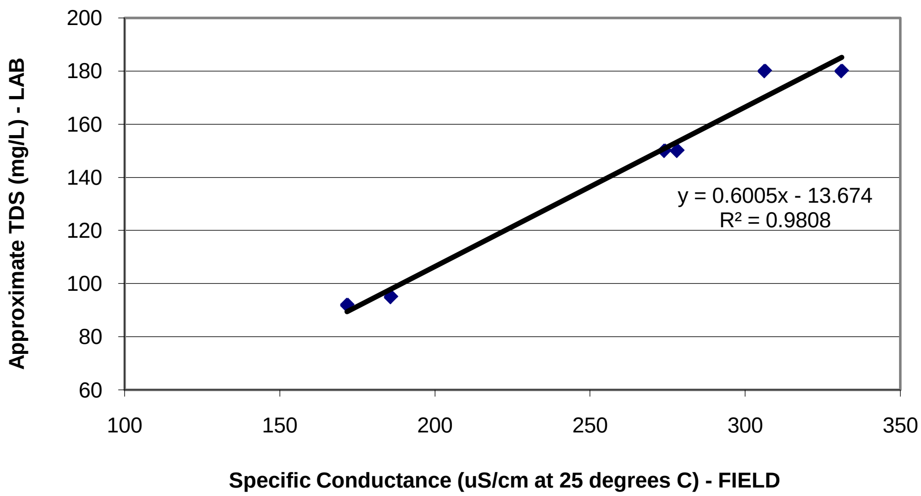


Specific Conductance

Specific conductance is highly dependent on the amount of dissolved solids in water. A relationship between field-measured specific conductance (in microsiemens per cm standardized to 25^{o}C) and lab-measured total dissolved solids (TDS, in mg/L) was established in a 2005 study of groundwater quality in the south-western part of the study area, and is presented in Figure 7 below. Like nitrates, high concentrations of dissolved solids in water are a concern for human as well as ecosystem health. Excessive concentrations of dissolved solids can render water unfit for drinking or supporting aquatic life.

Chloride contributes to combined dissolved solids in water, so high conductance may sometimes indicate high chloride (note Figure 7). The state groundwater quality criterion for TDS is 500 mg/L, and for chloride (a secondary standard) is 250 mg/L (Chapter 173-200 WAC).

Figure 8. Correlation Diagram: TDS and Specific Conductance
(from Soule 2005)



Although TDS was not directly measured in this study, the correlation shown above was used to estimate TDS from specific conductance for each study well in Table 6. From this equation, TDS might be a concern if specific conductance were in the range of 800-900 uS/cm @ 25^{o}C, or higher.

A weak correlation between specific conductance and chloride suggests that conductance would probably need to be substantially higher than 500 uS/cm @ 25^{o}C before chloride concentration might be a concern. Note, however, that an *increasing trend* in chloride could indicate advancing seawater intrusion, a problem which is sometimes irreversible.

Table 6, Specific conductance, chloride, and
estimated (calculated) TDS for Phase II study wells

Location_ID	Date	Specific Conductance (uS/cm@25C) (measured in field)	TDS (calculated)	Chloride (mg/L) (lab analysis)
31N/04W-25R71	10/7/2010	173.4	90	<2.5
31N/03W-31E03	11/4/2010	183.8	97	<2.5
31N/04W-25R01	12/8/2010	186.4	98	<2.5
31N/03W-31N72	10/13/2010	196.7	104	<2.5
31N/03W-30N01	10/11/2010	200.7	107	<2.5
30N/04W-12K01	10/28/2010	209.4	112	<2.5
31N/03W-31D01	10/26/2010	212.2	114	4.96
30N/04W-13K14	12/2/2010	231.3	125	
30N/03W-06R02	10/13/2010	240.7	131	2.64
30N/03W-07Q03	12/3/2010	261	143	4.5
30N/04W-24P80	11/4/2010	287.2	159	<2.5
30N/03W-18Q91	11/4/2010	329.9	184	
30N/04W-24G02	11/18/2010	334.6	187	
30N/03W-18E06	10/28/2010	335.6	188	5.89
30N/03W-07P03	10/14/2010	341.3	191	7.68
30N/03W-04M01	12/2/2010	346.2	194	6.85
30N/03W-20C02	11/18/2010	349.5	196	
30N/03W-05H02	10/14/2010	371.9	210	11.04
30N/03W-06M01	12/2/2010	377.4	213	
31N/03W-30Q71	10/11/2010	409.2	232	38.04
31N/03W-31B71	10/7/2010	411.1	233	32.38
30N/03W-17D78	11/16/2010	423	240	
30N/03W-17M01	11/16/2010	436.3	248	7.83
30N/03W-18R71	12/3/2010	440	251	8.9
30N/03W-20E01	11/18/2010	501	287	
	Average	***312***	***173***	***7***
	Median	***335***	***187***	***5***
	Range	***173 - 501***	***90 - 287***	***<2.5 - 38***
	MCL	***n/a***	***500***	***250***

Other Field Parameters

In this study, temperature and pH data were collected primarily for determining the adequacy of well purging prior to sampling. It is worth noting that all well water is within the normal pH range and not acidic; the well with the highest pH is the same well with elevated ammonia. All field parameters are included in Table 7.

Table 7. Summary statistics for field parameters
for 25 wells tested.

Parameter	Min	Median	Max
Temperature (^{o}C)	8.3	10.9	12.7
pH (standard units)	6.8	7.7	8.5
Specific conductance (microsiemens/cm at 25^{o} C)	173	335	501
Dissolved oxygen (mg/L)	1.4	5.9	9.2

Pathogens

Eighteen study wells were tested for total coliform bacteria presence/absence and, if present, checked for E. coli. All tested negative except one which was confirmed positive for coliform but negative for E. coli. The homeowner treated the well with chlorine and on the second re-test it sampled negative for coliform.

Stormwater Contaminants

Sites at which stormwater contaminants were sampled are shown in Figure 9. Complete lab results are included in Appendix B. In summary, there is no evidence that shallow-aquifer drinking water wells vulnerable to land activities are experiencing contamination from metals or organics; however, advanced nitrate contamination is evident.

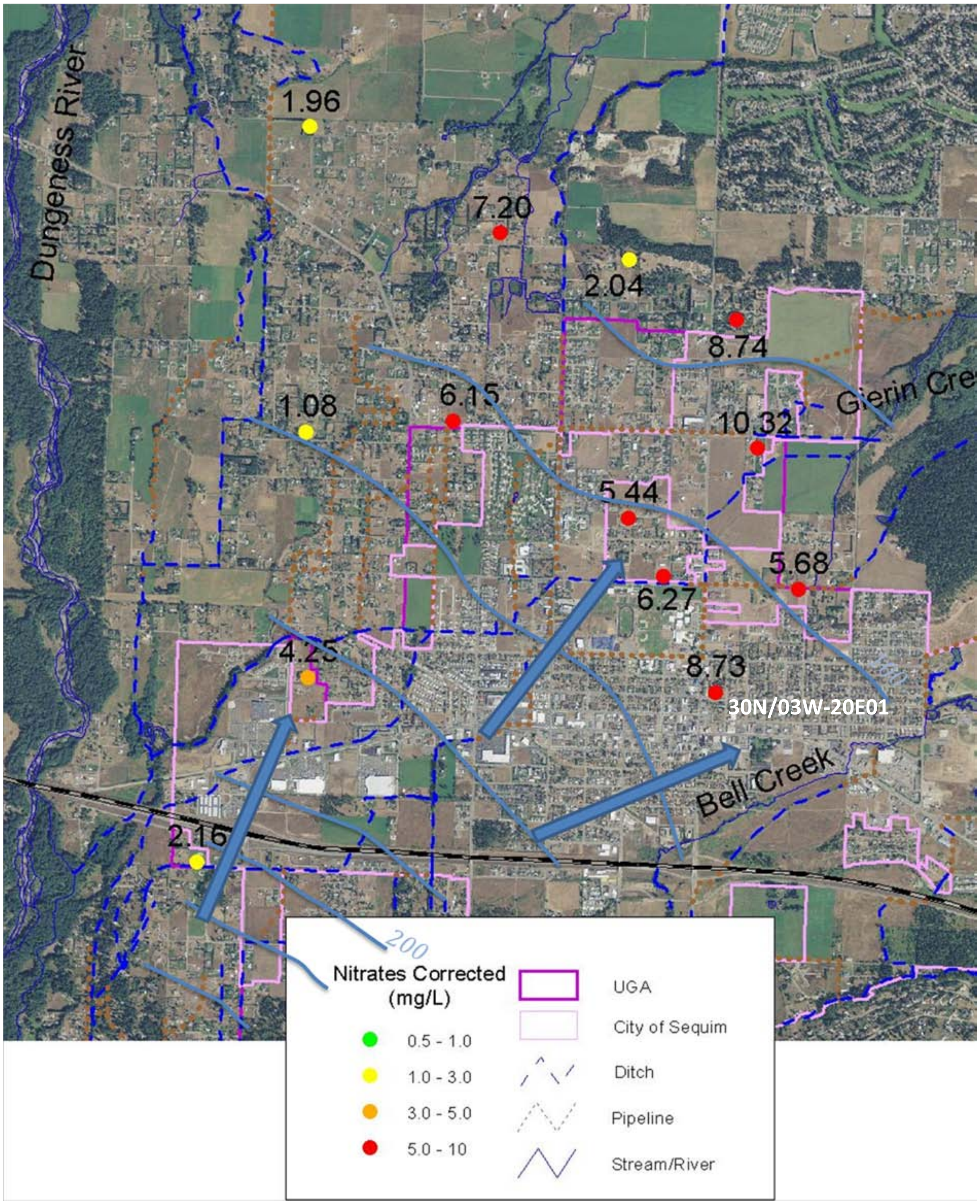
Metals
A total metals-minerals scan was conducted for four study wells (and one split duplicate), with 12-15 of 33 parameters detected at no more than trace levels. For parameters with groundwater quality criteria established, results were one to three orders of magnitude below the criteria. There were detections for several parameters for which no criteria have been established; in these cases there is no basis for interpreting health or environmental risk and detections are assumed to be typical and/or natural and of negligible concern.

Pesticides & PCBs
A scan for organics including pesticides and PCBs was conducted for four study wells (and one split duplicate). There were no detections of 26 parameters in any of the wells.

Hydrocarbons
A scan for petroleum hydrocarbons was conducted on four study wells (and one split duplicate). There were no detections in the oil and diesel range; however, all four had trace detections in the gasoline range – a very surprising result since it is improbable that contamination would be present in all four wells, whether from the same or separate sources. CCEH discussed results with the analyzing lab and learned that most uses of this method of analysis include sampling for benzene to better "fingerprint" the presence of actual gasoline hydrocarbons (as opposed to other small-chain carbon molecules such as methyl or vinyl chloride). One plausible explanation for detections on all four study wells is that plastic (PVC) water pipe is degrading, interfering with the test for stormwater contaminants. (AM Test 2011)

Nitrates
Four of the five wells used to assess vulnerability to stormwater contamination had nitrate levels indicating advanced degradation; the fifth indicates moderate degradation (based on corrected nitrate estimates from Table 3). In the case of well 30N/03W-20E01, close to downtown Sequim, the upgradient neighborhood is all sewered and septic systems are at a distance, in moderate-low densities (see Figure 9). This suggests another source of nitrogen may be responsible for high nitrates in this well (8.73 mg/L), such as fertilizer leaking into the ground with stormwater recharge and/or leaking sewage conveyance pipes. Other study wells with nitrates >5 mg/L have upgradient recharge areas that are partly or fully served by onsite septic systems.

Figure 9. Southern-central study area showing land uses (areas within city limits are sewered; 2009 aerial photo), estimated nitrate concentrations, water table contours and estimated groundwater flow direction (arrows).



Data Quality Assessment

Data Validation

Precision

Field nitrate split duplicate pairs:	**21%**	***Does NOT meet DQO (barely)***
Lab nitrate split duplicate pairs:	4%	Does meet DQO
Field-lab nitrate replicate pairs:	**26%**	***Does NOT meet DQO***
Field chloride split duplicate pairs:	1.5%	Does meet DQO
Lab ammonia split duplicate pairs:	**25%**	***Does NOT meet DQO***
Lab bacteria split duplicate pair:	0%	Does meet DQO
Lab metals/minerals split dupe pairs:	2-2.7%	Does meet DQO

Analytical Bias

Blanks	meets DQO for all parameters
Matrix spikes	
Nitrate – lab	***not known (no spikes conducted)***
Ammonia	meets DQO
Metals	meets DQO
Pesticides-PCBs	meets DQO
Check standards	
Nitrate – lab	meets DQO
Nitrate – field	meets DQO
Chloride – field	***not known (no check standard available)***
Ammonia	meets DQO
Metals	meets DQO
Pesticides-PCBs	meets DQO

Completeness

Goal of 80% usable data for everything except bacteria, which was 90%. This objective was met for all parameters **provided** that field nitrate results are replaced with corrected estimates.

Appendix B contains quality assurance calculations for all parameters reported.

Discussion about Nitrates

CCEH staff used the Chemetrics photometer in the County EH Laboratory to measure nitrate check standards both for Phase I and Phase II. For Phase I, the relative difference was 2-14% in three cases where the known nitrate concentration ranged from 1-10 mg/L. The RPD was 23% when nitrate was around 0.5 mg/L, and 100% when nitrate was <0.5 mg/L (typical when close to/below the method detection limit). In Phase II, the RPD was 0.2% and 4.6% for two measurements of a 10.0 mg/L check standard, and 13%, 23%, and 11% for three measurements of 4.96 mg/L check standards. As expected, closer agreement was achieved for higher levels.

These results are within the Data Quality Objective for nitrate, which indicates good agreement between the Chemetrics kit and lab standards when analyzed in the lab at room temperature.

Conversely, there is evidence from both Phase I and II replicate analyses that the Chemetrics photometer may under-report nitrate concentration in the field. In Phase I, two field measurements made using the Chemetrics photometer were 25% and 39% lower than associated laboratory results on replicate samples analyzed at Twiss Analytical in Poulsbo (using ion electrode method SM4500-NO3-F). In Phase II, seven replicates were collected total and analyzed for nitrate at the CCEH Lab (using ion electrode method SM4500-NO3-D); five of these had concentrations well above the detection limit for both methods. Field measurements were from 49-79% of associated laboratory analyses conducted one day later; the RPD for the five pairs ranged from 23-68% (well above the DQO).

This high level of variability is surprising given the relatively good agreement between methods indicated by check standards in the lab, described above. The difference may be due to changing conditions, potentially including:

- the additional time between collection of the grab sample (from which field measurements were made) and the lab sample (suggesting that nitrate concentration increases as purge time increases); and/or
- the time lag before lab analysis (suggesting changes in chemistry during storage).

Another possibility is that the temperature of the sample during analysis could influence the method and thus the measured result – for either or both methods. (Chemetrics 2011; Pitz 2011)

<u>The implications of field nitrate variability on this study are not large because the objective to screen current ambient water quality for the study area is fulfilled based on corrected estimates of nitrate concentration</u>. The conclusions from using corrected estimates are not significantly different than using original measurements, except that the aerial extent of elevated nitrates increased. Of course, it is very important for well owners to be aware that their drinking water may have higher nitrates than originally reported – especially when they're above 3-4 mg/L. CCEH routinely informs participants of test results, study reports, and related information.

<u>Discussion about Ammonia</u>

Precision objectives were not met for ammonia analyses because the laboratory was erroneously tracking an objective of 28%. <u>Implications are minimal since project objectives for inorganic nitrogen involved preliminary screening only</u>, and additional factors (e.g., sampling was conducted in a high-flow setting exposed to atmospheric conditions) also warrant caution in the use of ammonia results for management decisions without further research. (AmTest 2011)

<u>Discussion about Chloride</u>

<u>Chloride results should be considered estimates of actual concentration</u>, because no duplicates for quality assurance were collected and check standards were not available within the project time frame or budget.

Conclusions and Recommendations

Several conclusions may be made from the Phase II study of groundwater quality in and around Sequim, as follows:

- New information from monitoring ambient groundwater quality in the study area includes:
    - Advanced degradation evidenced by nitrate concentrations >5 mg/L were found in areas of higher-density residential and commercial land uses.
    - Impacts from land activities evidenced by nitrate concentrations >1 mg/L were found in most areas, except where clay soils are most prevalent and available dissolved oxygen appears to be minimal.
    - Ammonia was found above background in one well adjacent to surface water with known high ammonia levels; otherwise, ammonia was not detected or found at trace levels in six other wells tested.
    - Estimated chloride concentrations were generally very low with the exception of the two wells very close (about 100 yards) to the marine shoreline. On the other hand, even these concentrations were a fraction of the drinking water standard.
    - Groundwater chlorides (and possibly nitrates) may be diluted by recharge (leakage) from the Dungeness River.
    - Dissolved oxygen ranges from low to moderate; whenever nitrates are elevated above background, the D.O. is at least 2 mg/L.
    - Specific conductance and estimated Total Dissolved Solids is low to moderate.
    - pH is well within normal range except for one well with pH 8.45 (the same well that had elevated ammonia).
    - Nitrate measurements made in the field using the Chemetrics V-2000 photometer likely under-estimate true nitrate concentration.

- New information resulting from monitoring for potential stormwater contaminants in wells found to be vulnerable to land activities follows. At the time of this study (Fall 2010), there were:
    - no detections of pesticides or PCBs;
    - non-elevated / trace-level metals (total, rather than dissolved);
    - indications of petroleum hydrocarbon (gasoline range) which were more likely resulting from PVC in plumbing than from aquifer contamination; and
    - elevated nitrates.

Conclusions from Phases I and II combined include:

- On a regional scale, the shallow aquifer may be fairly well protected from many stormwater contaminants.
- The shallow aquifer is susceptible to nitrate contamination in most areas, from stormwater and known potential sources such as septic systems and fertilizer.
- Factors affecting nitrate concentration at a given property include, at minimum:
    - Zone of the aquifer, and whether clay layers are present in the geologic profile
    - Proximity to and volume/concentration of the source of contamination

        - Whether the source is current and ongoing or historic
    - Integrity of the well seal around the upper casing (related to age/construction)
    - Rate and direction of groundwater flow (varies by season and pumping patterns)
    - Amount of dilution from uncontaminated irrigation ditches, ponds, and streams
    - Whether the sample is from the plumbing, well casing, or fresh from the aquifer

Recommendations include:

- Land management
    - Ensure stormwater runoff from urban, suburban, and agricultural communities is treated prior to entering the environment, including into the aquifer.
    - Ensure septic systems are designed and maintained to prevent incidental as well as accumulated contamination of surface water and aquifers.
    - Ensure septic system densities are regulated according to soil type, to avoid accumulating nitrate contamination.
    - Ensure that sewer facilities are maintained to prevent contamination through leakage into the environment.
    - Continue to enforce and review stormwater facility monitoring programs required by City of Sequim or Clallam County.
    - Future stormwater treatment facilities should monitor groundwater quality from downgradient monitoring wells (rather than facility effluent or lysimeters; see Appendix A from Soule 2009, Phase I).
- Education
    - Use of nitrogen fertilizer outdoors may impact groundwater quality, as seen in research from other areas that are sewered but built on coarse-grained soils.
    - Educate well owners about the importance of a solid well seal and maintaining a contaminant-free zone (100’ radius) around the wellhead.
- Research
    - Study nitrogen loading into the perched water table in Dungeness / Three Crabs.
    - Sample groundwater seeps in the nearshore for nutrients and other contaminants.
    - Continue ambient monitoring including field measurement of D.O. and specific conductance.
    - Continue to track trends in regional nitrate concentrations by taking advantage of publicly-available data, such as from County building permits and state-regulated public water systems.
    - Investigate possible correlations between groundwater nitrate and ammonia concentrations and proximity to surface water, well age and construction, soil type and underlying geology, current land uses such as septic system density, historic land uses such as dairy farms, and other factors.
    - Investigate nitrate variability over different purge times, storage times, and sample conditions (temperature, dissolved oxygen), and using different methods.

The net result of Phase I and II investigations of groundwater quality and stormwater impacts has greatly advanced the understanding and implications of these topics for the study area. The author wishes to thank the Clallam County Marine Resources Committee for its forward thinking in associating marine water quality with the health of the upland environment, and specifically with groundwater that ultimately discharges to fresh and marine surface waters.

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APPENDIX A. Study Well Construction and Water Level Information, MRC Groundwater Quality Project, Fall 2010

Well Location ID	Tag_Number	Ecology Database Log_ID	Elevation (feet above sea level)	Completion Date	Depth (feet)	Diameter (inches)	Completion	Open_Start (feet depth)	Open_Stop (feet depth)	MP Height (feet)	SWL ATC	SWL Fall 2010
30N/03W-04M01	BBB086	47553	24.2	4/21/1980	43	6	Perf/Slotted	26	35	0	6	
30N/03W-05H02	AAB821	43905	15.6	6/23/1976	31	6	Open End	31	31	0.9	5	6.5
30N/03W-05R01	AAB744	277214	24.3	6/8/1965	40	10	Perf/Slotted	20	38	0.5	6	8.8
30N/03W-06M01	ACA657	44864	123.3	3/7/1978	105	6	Open End	105	105	0.8	83	
30N/03W-06R02	BBB089	43897	63.6	7/6/1979	45	6	Open End	45	45	0	25	
30N/03W-07P03	ACA599	51133	110.0	5/9/1978	74	6	Open End	74	90	1.1	19	21.4
30N/03W-07Q03	ACA539	46526	134.0	7/18/1991	116	6	Screen	111	116	0.9	57	59.1
30N/03W-17D78	BBB073	44624	108.3	8/22/1990	40	6	Open End	40	40	1.3	15	22.5
30N/03W-17M01	ACA515	50051	123.8	12/21/1976	37	6	Open End	37	37	0.5	10	24.4
30N/03W-18E06	ACA514	no log found	150.0	no log found	40	6				0.6		26.8
30N/03W-18Q91	BBB076	275961	160.2	9/1/1993	68	6	Screen	63	66	0	31.5	
30N/03W-18R71	BBN274	not yet assigned	162.0	1/4/2010	78	6	Screen	73	78	1.7	44	45.2
30N/03W-20C02	BBB078	48356	140.0	5/8/1971	36	6	Open End	36	36	0.7	9.5	30.4
30N/03W-20E01	BBB085	52872	173.0	10/11/1977	71	6	Gravl Pack Scrn	66	71	0.8	26	55.8
30N/04W-12K01	ACA782	57859	108.2	11/9/1977	26	6	Open End	26	26	0.5	6	10.5
30N/04W-13K14	BBB087	59592	160.0	5/14/1990	59	6	Screen	56	59	0.9	23	27.1
30N/04W-24G02	ACA651	56953	237.0	12/5/1975	79	6	Open End	79	79	0.8	55	66.6
30N/04W-24P80	BBB084	56910	307.2	2/2/1992	100	6	Screen	95	100	1.5	47	61.9
31N/03W-30N01	BBB082	60085	14.0	3/13/1975	39	6	Open End	39	39	0	4	
31N/03W-30Q71	AFA398	249011	9.0	10/25/1999	40	6	Screen	36	40	0	4	
31N/03W-31B71	ACB283	60498	10.0	7/16/1998	50	6	Screen	44	50	1.2	4	4.2
31N/03W-31D01	BBB088	277535	16.0	4/23/1976	57	6	Perf/Slotted	55	57	0.6	7	6.9
31N/03W-31E03	BBB083	57181	22.0	6/24/1985	54	6	Screen	49	54	0.7	3.5	4.1
31N/03W-31N72	ABQ739	60472	10.5	8/12/1996	50	6	Open End	49	49		3.75	4.0
31N/04W-25R01		58315	wellhead not found	9/10/1975	40	6	Screen	36	40	0	5	
31N/04W-25R71	AGP270	59263	14.0	1/31/1986	37	6	Screen	32	37	0.7	5	5.7
31N/04W-36L71	AEJ955	60817	32.4	2/26/1999	40	6	Screen	35	40	1.8	1	2.8

MP = Measuring Point
SWL = Static Water Level
ATC = At Time of Construction

APPENDIX B. Water Quality Results, MRC Groundwater Quality Project, Fall 2010

AMBIENT MONITORING PARAMETERS											
		Temperature	pH	Specific Conductance	Dissolved Oxygen	Nitrogen as Nitrate-Nitrite		Nitrogen as Nitrate-Nitrite	Nitrogen as Nitrate	Nitrogen as Ammonia	Chloride
	Method:	YSI 85 in Field	YSI 60 in Field	YSI 85 in Field	YSI 85 in Field	Chemetrics (original measurement) EPA353.3	*Below Detection Limit?*	Chemetrics (corrected estimate)	Clallam Co Env Health Lab SM4500NO3D	AM Test EPA350.1	Chemetrics SM4500CL-E
Well ID	Date	degrees C		uS/cm@25C	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L
30N/03W-04M01	12/2/2010	8.3	7.07	346.2	4.23	1.05		2.06	2.13	0.027	6.85
30N/03W-05H02	10/14/2010	10.7	6.94	371.9	5.98	0.96		1.95			11.04
30N/03W-06M01	12/2/2010	10.1	7.39	377.4	5.89	0.85	*U*	1.81	2.1		
30N/03W-06R02	10/13/2010	10.4	6.8	240.7	7.6	0.7		1.62			2.64
30N/03W-07P03	10/14/2010	11.7	7.77	341.3	4.92	5.08		7.2			7.68
30N/03W-07Q03	12/3/2010	10.8	7.3	261	5.84	1.03	*U*	2.04			4.5
30N/03W-17D78	11/16/2010	11.6	7.58	423	7.98	6.29		8.74	8.36		
30N/03W-17M01	11/16/2010	11.5	7.53	436.3	7.44	7.53		10.32	10.6	<.005	7.83
30N/03W-18E06	10/28/2010	11.8	7.79	335.6	8.09	4.26		6.15			5.89
30N/03W-18Q91	11/4/2010	11.1	7.76	329.9	8.26	3.7		5.44			
30N/03W-18R71	12/3/2010	11.8	7.59	440	6.68	4.35		6.27			8.9
30N/03W-20C02	11/18/2010	11.9	7.75	349.5	8.63	3.89		5.68			
30N/03W-20E01	11/18/2010	12.7	7.62	501	8.7	6.28		8.73	8.63		
30N/04W-12K01	10/28/2010	10.9	6.84	209.4	7.51	0.97	*U*	1.96			<2.5
30N/04W-13K14	12/2/2010	9.9	7.88	231.3	5.07	0.28	*U*	1.08	0.67		
30N/04W-24G02	11/18/2010	11.1	7.71	334.6	7.43	2.77		4.25	4.5		
30N/04W-24P80	11/4/2010	10.9	7.88	287.2	9.2	1.13		2.16			<2.5
31N/03W-30N01	10/11/2010	11	7.76	200.7	2.53	0.11	*U*	0.86			<2.5
31N/03W-30Q71	10/11/2010	10.8	8.26	409.2	2.91	0.08	*U*	0.83			38.04
31N/03W-31B71	10/7/2010	10.7	8.45	411.1	2.32	0.07	*U*	0.81		0.515	32.38
31N/03W-31D01	10/26/2010	10.3	7.44	212.2	1.39	0.1	*U*	0.85		<.005	4.96
31N/03W-31E03	11/4/2010	9.8	7.21	183.8	2.65	0.25	*U*	1.04			<2.5
31N/03W-31N72	10/13/2010	11.1	7.98	196.7	3.37	0.06	*U*	0.8		<.005	<2.5
31N/04W-25R01	12/8/2010	9.7	7.68	186.4	2.43	0.15	*U*	0.92		0.042	<2.5
31N/04W-25R71	10/7/2010	10.7	7.79	173.4	1.45	0.06	*U*	0.8		0.005	<2.5

METALS & MINERALS	EPA 200.7	All sampled on 11/16-18/2011 and analyzed by AM Test			
Well ID:	30N/03W-17M01	30N/03W-20C02	30N/03W-20E01	30N/04W-24G02	
Parameter	Result (mg/L)	Result (mg/L)	Result (mg/L)	Result (mg/L)	Detection Limit
Aluminum	U	U	U	U	0.01
Antimony	U	U	U	U	0.01
Arsenic	U	U	U	U	0.01
Barium	0.01	0.0086	0.0124	0.0044	0.0005
Beryllium	U	U	U	U	0.0005
Boron	U	U	U	U	0.05
Cadmium	U	U	U	U	0.0005
Calcium	66	54	78	50	0.05
Chromium	U	U	U	U	0.001
Cobalt	U	U	U	U	0.001
Copper	0.003	0.002	0.004	0.005	0.001
Iron	U	0.013	0.055	0.045	0.005
Lead	U	U	U	U	0.01
Lithium	U	U	U	U	0.005
Magnesium	12	10	14	10	0.05
Manganese	0.0008	0.0009	0.0015	0.0016	0.0005
Mercury	U	U	U	U	0.01
Molybdenum	U	U	0.006	0.007	0.005
Nickel	U	U	U	U	0.005
Phosphorus	U	U	U	U	0.01
Potassium	1.1	0.69	0.97	0.82	0.1
Selenium	U	U	U	U	0.01
Silicon	8.7	7.8	8.5	7.6	0.05
Silver	U	U	U	U	0.01
Sodium	7.6	5.8	7.8	5.3	0.05
Strontium	0.339	0.2	0.27	0.26	0.0005
Sulfur	5.4	3.6	5.4	3.9	0.05
Thallium	U	U	U	U	0.01
Tin	0.01	0.012	0.008	0.012	0.005
Titanium	U	U	U	U	0.001
Vanadium	U	0.006	0.006	U	0.005
Yttrium	U	U	U	U	0.0005
Zinc	0.006	0.004	0.027	0.011	0.001

PESTICIDES & PCBs EPA 608 All sampled on 11/16/2011 and analyzed at AM Test					
Well ID:	30N/03W-17D78	30N/03W-20C02	30N/03W-20E01	30N/04W-24G02	
Parameter	Result (ug/L)	Result (ug/L)	Result (ug/L)	Result (ug/L)	Detection Limit
Aldrin	*All Below Method Detection Limit*				0.003
Alpha BHC					0.003
Beta-BHC					0.003
Chlordane					0.01
Delta-BHC					0.003
Dieldrin					0.003
Endosulfan I					0.003
Endosulfan II					0.003
Endosulfan Sulfate					0.003
Endrin					0.003
Endrin Aldehyde					0.003
Heptachlor					0.003
Heptachlor Epoxide					0.003
Lindane					0.003
Methoxychlor					0.003
PCB-1016					0.05
PCB-1221					0.05
PCB-1232					0.05
PCB-1242					0.05
PCB-1248					0.05
PCB-1254					0.05
PCB-1260					0.05
pp-DDD					0.003
pp-DDE					0.003
pp-DDT					0.003
Toxaphene					0.025

PETROLEUM HYDROCARBONS NW-TPH HCID All sampled on 11/16-18/2011 and analyzed at AM Test					
Well ID:	30N/03W-17M01	30N/03W-20C02	30N/03W-20E01	30N/04W-24G02	
Parameter	Result (ug/L)	Result (ug/L)	Result (ug/L)	Result (ug/L)	Detection Limit
Diesel	U	U	U	U	100
Gasoline	140	620	140	360	30
Oil	U	U	U	U	200

APPENDIX C. Data Quality Assessment, MRC Groundwater Quality Project, Fall 2010

A. Check Standards

	method	MQO	% Recovery min / max	analyte	NOTE
Nitrates--Lab tested					**Within MQO**
	SM 4500-NO3-D	90-110%	101-104%	Nitrate	
Nitrate-Nitrite--Field tested (Chemetrics)					**Within MQO**
	EPA 353.3	85-115%	99.8-105%	Nitrate-Nitrite	
Chloride--Field tested (Chemetrics)					*Check standard not tested*
	SM 4500-Cl-E	85-115%	*not known*	Chloride	*due to lack of standard avail.*
					Chloride results considered estimates only
Metals and Minerals					**Within MQO**
	EPA 200.7	85-115%	94.5	Vanadium	
			110	Silicon, Silver	
Pesticides-PCBs					**Within MQO**
	EPA 608	85-115%	87.5	Delta-BHC	
			105	Dieldrin, pp-DDD, pp-DDT, Endrin Aldehyde	
Ammonia Nitrogen					**Within MQO**
	EPA 350.1	90-110%	97.4-104%	Ammonia	

B. Split-Duplicates

Nitrate split-dupe lab samples -- LAB results (MQO = 20%)

Dupe pairs	non-neg Diff	x200	C1 + C2	RPD	NOTE		non-neg Diff squared			
10.6	0.1	20	21.10	**0.95**	**All are within MQO**		0.010	standard deviation from these pairs:		
10.5								**s(p) =**	sqrt [sum of (non-neg diff)squared / 2*number of pairs]	
8.36	0.51	102	17.23	**5.92**			0.260		0.274 / 6	0.0457
8.87									sqrt [0.457]	
8.63	0.06	12	17.32	**0.69**			0.004		0.214	
8.69						sum	0.274	**%RSD =**	100*[0.214 / mean]	**95.8**
	0.223	mean								**Within DQO**

Nitrate split-dupe from grab sample -- FIELD/CHEMETRICS results (MQO = 20%)

Dupe pairs	non-neg Diff	x200	C1 + C2	RPD	NOTE		non-neg Diff squared				
7.2	0.66	132	15.06	**8.76**	**All are within MQO**		0.436				
7.86											
6.62	0.66	132	12.58	**10.49**			0.436				
5.96											
3.93	0.09	18	7.77	**2.32**			0.008	standard deviation from these pairs:			
3.84								**s(p) =**	sqrt [sum of (non-neg diff)squared / 2*number of pairs]		
6.03	0.5	100	12.56	**7.96**			0.250		1.448 / 14	=	0.103
6.53									sqrt [0.103]		
4.99	0.17	34	10.15	**3.35**			0.029		0.32		
5.16											
4.06	0.4	80	8.52	**9.39**			0.160	**%RSD =**	100*[0.32 / mean]		**78.9**
4.46											**NOT within DQO**
3.88	0.36	72	7.40	**9.73**			0.130				
3.52						sum	1.448				
	0.406	mean									

Nitrate REPLICATES -- FIELD/CHEMETRICS result compared with LAB result (MQO = 20%)

	Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**	**NOTE**		non-neg Diff squared			
Lab	8.36	1.74	348	14.98	**23.23**	**NOT within the MQO**		3.028	standard deviation from these pairs:		
Field	6.62								**s(p) =**	sqrt [sum of (non-neg diff)squared / 2*number of pairs]	
Lab	10.6	2.74	548	18.46	**29.69**	**NOT within the MQO**		7.508		19.105 / 10	1.9105
Field	7.86									sqrt [1.9105]	
Lab	8.63	2.1	420	15.16	**27.70**	**NOT within the MQO**		4.410		**1.382**	
Field	6.53										
Lab	4.5	1.73	346	7.27	**47.59**	**NOT within the MQO**		2.993	**%RSD =**	100*[1.382 / mean]	**73.6**
Field	2.77										**NOT within DQO**
Lab	2.1	1.1	220	3.10	**70.97**	*Results close to detection limit*					
Field	1	(actually <1.13)				*should not be used to determine RPD*					
Lab	2.13	1.08	216	3.18	**67.92**	**NOT within the MQO**		1.166			
Field	1.05										
Lab	0.67	na				*Results close to detection limit*					
Field	<1.13					*should not be used to determine RPD*					
		1.878	mean				sum	19.105			

Chloride - FIELD/CHEMETRICS results (MQO = 20%)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**	**NOTE**	non-neg Diff squared				
7.83	0.9	180	14.76	**12.20**	**within MQO**		0.810	standard deviation from these pairs:		
6.93								**s(p) =**	sqrt [sum of (non-neg diff)squared / 2*number of pairs]	
11.04	0.08	16	22.00	**0.73**	**within MQO**		0.006		0.831 / 6	0.1385
10.96									sqrt [0.139]	
8.9	0.12	24	17.92	**1.34**	**within MQO**		0.014		**0.372**	
9.02						sum	0.831			
	0.367	mean						**%RSD =**	100*[0.372 / mean]	**101.5**
										Within DQO

Ammonia - LAB results (MQO = 20%)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**	**NOTE**
0.005	0.005	1	0.005	**200.00**	*Results close to detection limit*
0.000	*(not detected)*				*should not be used to determine RPD*

Ammonia split-dupe lab samples -- LAB results (MQO = 20%)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**	**NOTE**	non-neg Diff squared				
0.033	0.007	1.4	0.06	**23.73**	**NOT within MQO**		0.000049	standard deviation from these pairs:		
0.026								**s(p) =**	sqrt [sum of (non-neg diff)squared / 2*number of pairs]	
0.022	0.004	0.8	0.05	**16.67**	**within the MQO**		0.000016		0.000074 / 6	0.000012
0.026									sqrt [0.000012]	
0.027	0.003	0.6	0.06	**10.53**	**within the MQO**		0.000009		**0.003512**	
0.03						sum	0.000074			
	0.004667	mean						**%RSD =**	100*[0.003512 / mean]	**75.3**
<0.005	0	0	0.00	**na**	*Results close to detection limit*					**NOT within DQO**
<0.005					*should not be used to determine RPD*					

Metals & Minerals (no MQO established)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**	**Analyte**
3.6	0.1	20	7.30	**2.74**	Sulfur
3.7					
10	0.2	40	19.80	**2.02**	Magnesium
9.8					
54	1	200	107.00	**1.87**	Calcium
53					
0.2	0.004	0.8	0.40	**2.02**	Strontium
0.196					

Pesticides-PCBs (no MQO established)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**
(all non-detect)				

Hydrocarbon ID (no MQO established)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**

Total coliform bacteria (no MQO established)

Dupe pairs	non-neg Diff	x200	C1 + C2	**RPD**			
							%RSD = 100
0	0						**Within DQO**
0							

C. Matrix Spikes					**Matrix Spike Duplicates**					
	method	MQO	**% Recovery**	analyte	MQO	**RPD**	analyte	**NOTE**		
Nitrates--Lab-tested			min / max			max		*No matrix spike data*		
	SM 4500-NO3-D	80-120%	*N/A*	Nitrate	20%		Nitrate	*available from EH Lab*		
				Nitrate						
Metals and Minerals								**Within MQO**		
	EPA 200.7	70-130%	85.6	Beryllium	20%	6.1	Potassium			
			122	Potassium						
Pesticides-PCBs								**Within MQO**		
	EPA 608	20-180%	52	PCB-1260	50%	21	Delta-BHC			
			125	pp-DDT						
Ammonia Nitrogen								*Results close to detection limit*		
	EPA 350.1	80-120%	108-116%	Ammonia	20%	*N/A**	Ammonia	*should not be used for QA*		
					*typically spike duplicates are					
					not conducted unless analyte					
					is commonly not detected					
D. Blanks										
All blind field blanks resulted in nondetects for all parameters and all methods except one;										
the ammonia blank was "measured" right at the method detection limit.										