# Quality Assurance Project Plan

# Screening for Pharmaceuticals in Wastewater Treatment Plant Effluents, Groundwater, and Surface Water in the Sequim-Dungeness Area

by
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*This plan was prepared by a licensed hydrogeologist.*
*A signed and stamped copy of the plan is available upon request.*

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February 2004

303(d) listings addressed in this study: None

Waterbody Number: WA-18-1100 (Bell Creek); WA-18-1300 (Cassalery Creek)

Ecology EIM Number: AJOH0043

| | |
|---|---|
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# Abstract

A plan is described for conducting a screening survey for pharmaceuticals and estrogen compounds in the Sequim-Dungeness area of northwest Washington state. Twenty-three prescription drugs, estrone, and beta-estradiol will be analyzed in wastewater treatment plant effluents, surface water, and groundwater. This is the first study of its type in Washington. The Sequim-Dungeness area was selected for several reasons including it being a retirement community where drug use is likely higher than average and because treatment plant effluents and reclaimed water are land applied.

# Background and Problem Statement

Clallam County and the Washington State Department of Ecology (Ecology) Southwest Regional Office have requested that a screening analysis be conducted for pharmaceuticals in wastewater treatment plant (WWTP) effluents from the city of Sequim and the Sunland development in the Dungeness River valley, as well as groundwater and surface water that may be impacted by these discharges. The objective is to investigate the potential for and status of pharmaceutical contamination of area waters from application of treated wastewater via re-use programs (Sequim) and conventional land application (Sunland). A limited effort was also requested to analyze pharmaceuticals in aquifers known to be affected by septic systems.

Sequim is a tertiary, high performing, reclaimed water plant that presently treats five to six million gallons per day (mgd). The influent is oxidized, coagulated, filtered, and disinfected. Final effluent meets Class A standards.

The treatment plant produces about 0.6 mgd of reclaimed water which goes to the city's Re-use Demonstration Site, constructed in 1999-2000 immediately north of Carrie-Blake Park (see Figure 1). It is one of the first facilities of its kind in the Pacific Northwest. Beneficial uses include garden and wetland creation, and cooling, aeration, and flow stabilization of Bell Creek. For the past year, the effluent has been used to augment creek flow by 0.1 cfs (0.07 mgd). Unused water is currently discharged to an outfall in Sequim Bay. (David Dougherty, Ecology, Personal Communication; Pacific Groundwater Group, 2000).

Sunland is a quasi-tertiary plant that has not been approved for reclaimed water. It is a land treatment facility that applies at, or above, agronomic rates. The spray field is adjacent to the plant and has been in use since 1979. Cassalery Creek flows along the north boundary of the facility. There is normally no overland discharge to the creek, but effluent may enter the creek via groundwater. Sunland plans an upgrade to achieve Class A reclaimed water status and intends to use it on their golf course. This upgrade is probably years away. (David Dougherty, Ecology, Personal Communication).

Bell and Cassalery Creeks are typically fed by groundwater discharge and irrigation tailwater. Irrigation diversions are from the Dungeness River, and occur year-round, but are highest during the growing season from mid-April to mid-September. The lowest flows are in September and October. The highest flows occur during winter rains and in the spring. (Pacific Groundwater Group, 2002).

The number and density of on-site sewage systems have increased in non-sewered portions of the Sequim-Dungeness area corresponding with the population increase in recent years. Blakemore et al. (1999) estimated that 7,000 on-site systems existed here in 1996. The relatively shallow depth to groundwater and lack of a low permeability layer in some areas makes the surficial aquifer vulnerable to contamination from above.

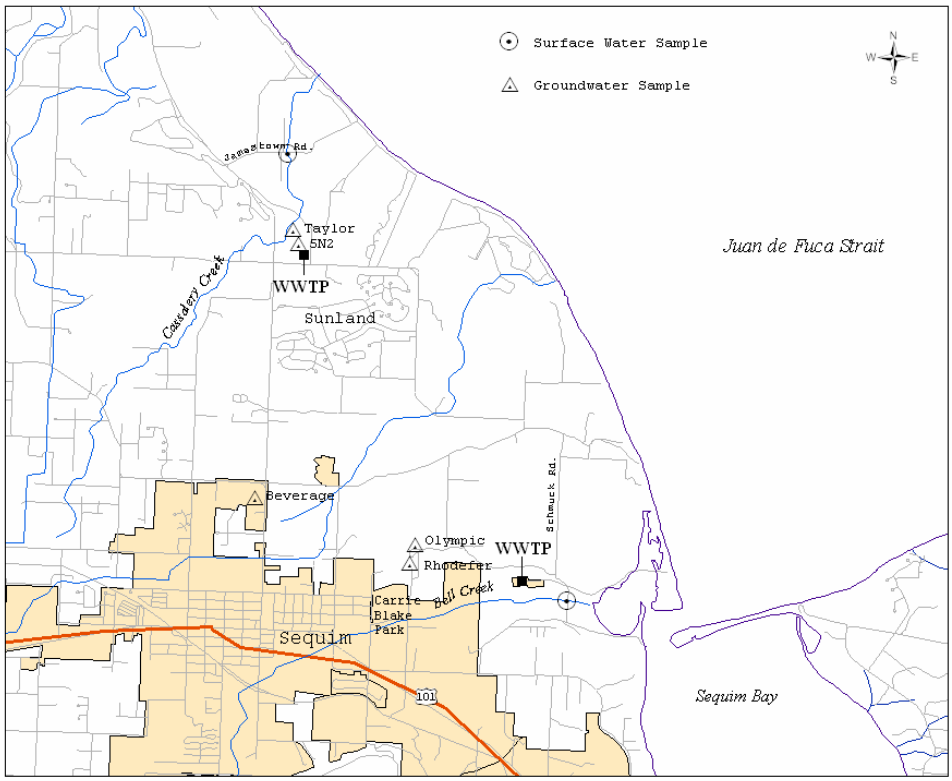


Figure 1. Study Area

Nitrate is an indicator of groundwater contamination from various sources, including on-site sewage. A statistically significant increase in nitrate since 1980, though slight, was reported in this area by Thomas et al. (1999). The largest area of high nitrate concentrations is east of the Dungeness River and north of Bell Creek, where values were up to 4.3 mg/L. The median nitrate concentration in groundwater in residential areas (1.3 mg/L) was also higher than in agricultural (0.55 mg/L) or natural grassland or forest areas (0.12 mg/L). Nitrate values were also highest in residential areas that have a high density of on-site systems compared to medium density systems, and lowest in low density areas.

Identifying emerging risks posed by previously unrecognized pollutants is one of the top five goals of the U.S. Environmental Protection Agency (EPA) Strategic Plan. Pharmaceuticals and certain personal care products (PPCPs) are a large and growing class of bioactive chemicals that, until recently, have received little attention. EPA has now devoted a website to this issue (http://www.epa.gov/nerlesd1/chemistry/pharma/ - Pharmaceuticals and Personal Care Products as Environmental Pollutants).

While some PPCPs are resistant to degradation, most have shorter environmental half-lives than conventional pollutants. Chronic discharge in sewage effluent, however, conveys a "pseudopersistence" to these compounds (Daughton, 2002). PPCPs generally occur in surface and groundwater at ng/L to ug/L concentrations, far below therapeutic thresholds, and many have been detected in surface and groundwater. The growing concern with these compounds stems from the fact that their potential for adverse human or ecological effects is almost entirely unknown.

The Sequim-Dungeness area is a rural region with a mild and relatively dry climate (15-20" or less annual rainfall). Approximately 4,445 of the county's 66,900 residents live in the city (1999). At the 1990 Census, 17,386 lived in the unincorporated area surrounding Sequim.

Sequim is a popular retirement center. Forty-four percent of the people are over the age of 59 (1990). Pharmaceutical use is, therefore, likely higher than average for Washington communities. These facts, coupled with land applied reclaimed water and waste water discharge into or adjacent to surface waters, and a vulnerable aquifer make Sequim-Dungeness a good candidate for a first effort to assess the potential for pharmaceutical contamination in state waters.

## Chemicals of Potential Interest

In a 1999 National Research Council report *Identifying Future Drinking Water Contaminants*, Giger reviewed research on the environmental occurrence of pharmaceuticals and antibiotics. Most of the studies Giger looked at had been done in Europe. Lipid regulators, analgesics/anti-inflammatories, and antiepileptics were detected most frequently in groundwater and surface water. Among the pharmaceuticals reported to occur in the highest concentrations were clofibric acid (metabolite of the lipid regulator clofibrate), ibuprofen, and carbamazepin (an antiepileptic). Maximum concentrations were 7,300 ng/L in groundwater (clofibric acid) and 1,000 ng/L in surface water (carbamazepin). Antibiotics were detected less frequently. Erythromycin and fluoroquinolone antibiotics appeared to be the most significant contaminants in wastewater and surface waters. Tetracyclines and penicillins were generally undetectable.

Daughton and Ternes (1999) did a more comprehensive synthesis of the literature on the environmental occurrence, distribution, and effects of PPCPs. They provide a chemical by chemical listing giving information on structure, use/origin, environmental occurrence, and toxicity. Chemicals prominently identified as being of potential environmental concern were lipid regulators, analgesics/anti-inflammatories, antiepileptics, antidepressants (e.g., fluoxetine), antineoplastics (e.g., ifosfamide), fragrances (musks), x-ray media (e.g., diatrizoate), oral

contraceptives (ethynyl estradiol), impotence drugs (viagra), and sunscreen agents (methylbenzylidene camphor).

The first and only nationwide reconnaissance on the occurrence of PPCPs in surface waters was conducted by the U.S. Geological Survey (USGS) in 1999-2000 (Kolpin et al., 2002). Five newly developed analytical methods were used to analyze approximately 60 PPCPs and 35 other organic compounds from 139 streams in 30 states. More than half of the PPCPs analyzed were antibiotics and relatively few of the chemicals identified in the above-mentioned review articles were looked for. Chemicals detected in more than 20 percent of the samples included acetaminophen, estriol (reproductive hormone), triclosan (antimicrobial), caffeine, nicotine, and several antibiotics.

Table 1 lists the PPCPs that will be analyzed for the Sequim-Dungeness project and shows the basis for their selection. An initial target list was developed from recommendations in the Daughton and Ternes review. Other chemicals were then added that had been detected in the USGS national study or were currently under consideration for groundwater monitoring in the state of California. The final list includes several additional analytes that are routine target compounds for EPA-sponsored PPCP research being conducted by the State University of New York at Stony Brook (SUNYSB), the contractor selected for the present study.

SUNYSB will use two methods to analyze the Table 1 compounds. The first is an HPLC-MS method that targets 23 human prescription and nonprescription drugs and their select metabolites. The second is an HPLC-MS method for estrone and beta-estradiol, components or transformation products of drugs used in hormone replacement therapy. The birth control additive ethynyl estradiol will not be reported as it is typically lost in the clean-up step for this method. It occurs in sewage effluents in lower concentrations than estrone or beta-estradiol and their levels will provide a relative indication of how much ethynyl estradiol could be present.

Table 2 lists other compounds that were considered for analysis in this project, but ultimately dropped due to lack of an adequate method, high cost, instrument problems at SUNYSB, or their being phased out of use (e.g., clofibrate).

Table 1. PPCPs to be Analyzed for the Sequim-Dungeness Study

| Chemical | Use/Origin | Basis for Selection | Rank Among Top 200 U.S. Prescriptions 2002* | Rank Among Top 25 Washington State Prescriptions 2003** |
|---|---|---|---|---|
| Fenofibric acid | Lipid regulator (metabolite) | 1,4 | 129 | |
| Carbamazepine | Antiepileptic | 1,3,4 | | |
| Norfluoxetine | Antidepressant (metabolite) | 1,2,4 | 31 | 5 |
| Codeine | Analgesic | 2,4 | 1 | 3 |
| Hydrocodone | Codeine metabolite | 2,4 | 1 | 3 |
| Antipyrine | Anesthetic | 4 | | |
| Caffeine | Simulant | 2,3,4 | | |
| Paraxanthine | Caffeine metabolite | 4 | | |
| Cotinine | Nicotine metabolite | 2,4 | | |
| Nicotine | Stimulant | 4 | | |
| Cimetidine | Ulcer drug | 2,4 | | |
| Raniditine | Ulcer drug | 2,4 | 39 | 11 |
| Diltiazem | Cardiac drug | 2,4 | 92 | |
| Nifidapine | Antianginal | 4 | 194 | |
| Salbutamol | Bronchial dilator | 2,4 | 12 | 9 |
| Sulfamethoxazole | Antibacterial | 2,4 | | |
| Trimethoprim | Antibacterial | 2,4 | | |
| Warfarin | Anticoagulant | 2,4 | 57 | 23 |
| Estrone | Hormone component | 2,3,4 | | |
| beta-Estradiol | Hormone component | 1,2,3,4 | | |
| Erythromycin | Antibiotic | 2,4 | | |
| Acetaminophen | Anti-inflammatory | 2,3,4 | 32 | 14 |
| Ketoprofen | Anti-inflammatory | 4 | | |
| Metformin | Antihyperglycemic | 2,4 | 38 | 15 |
| Diphenyhdramine | Antihistamine | 4 | | |

1 = Recommended by Daughton and Ternes (1999)
2 = Detected in USGS national study (Koplin et al., 2002)
3 = Under consideration for ground water monitoring in California (DHS 2003-draft)
4 = Routine target compound for Stony Brook University, NY
*http://www.rxlist.com/top200a.htm
**Group Health Cooperative (R. Johnson, May 29, 2003 email)

Table 2. Chemicals of Potential Interest That Could not be Analyzed at This Time

| Chemical | Use/Origin |
|---|---|
| Gemfibrozil | Lipid regulator |
| Phenytoin | Antiepileptic |
| Primidone | Antiepileptic |
| 17a-Ethynyl estradiol | Oral contraceptive |
| Fluoroquinolone carboxylic acids | Antibiotics |
| Ibuprofen | Anti-inflammatory |
| Triclosan | Antiseptic |
| Clofibric acid | Lipid regulator (metabolite) |
| Fluvoxamine | Antidepressant |
| Paroxetine | Antidepressant |
| Ifosfamide | Antineoplastic |
| Cyclophosphamide | Antineoplastic |
| Diatrizoate (Na) | X-ray media |
| Iopamidol | X-ray media |
| Iopromide | X-ray media |
| Nitromusks | Fragrance |
| Aminomusks | Fragrance |
| Sulfonamides | Antibotic |
| Acetylsalicylic acid | Anti-inflammatory |
| Sildenafil citrate | Impotence drug |
| Methylbenzylidene camphor | Sunscreen agent |

# Project Description

The goal of this project is to identify PPCPs that persist in WWTP effluents and septic systems in the Sequim-Dungeness area and are entering groundwater or surface water.

The project will be conducted by the Ecology Environmental Assessment Program (EA Program), with PPCP analyses being done by SUNYSB. The Ecology Manchester Environmental Laboratory (Manchester) will do the conventional water quality analyses and validate the data received from SUNYSB.

Project objectives are as follows:

- Screen for pharmaceuticals and estrogens in Sequim and Sunland WWTP effluents, groundwater from wells potentially affected by these effluents, and water from Bell and Cassalery Creeks downstream of the water-reuse/land application sites.

- Conduct a similar screening of groundwater from a well in an area known to be affected by private septic systems.

- Prepare a report of findings that identifies compounds that persist in effluents and/or septic systems and are present in groundwater and/or surface water.

# Project Organization

| | |
|---|---|
| EAP Project Lead | Art Johnson (360-407-6766) |
| EAP Hydrogeologist | Barbara Carey (360-407-6769) |
| SWRO Client | Cynthia Nelson (360-407-0276) |
| Clallam County Client | Ann Soule (360-417-2424) |
| EAP Toxics Studies Unit Supervisor | Dale Norton (360-407-6765) |
| Manchester Environmental Laboratory Director | Stuart Magoon (360-871-8813) |
| State University of New York at Stony Brook | Bruce Brownawell (631-632-8658) |
| Ecology Quality Assurance Officer | Cliff Kirchmer (360-407-6455) |
| EIM Data Entry | To Be Determined |

# Schedule

| | |
|---|---|
| October 31, 2003 | Draft QAPP Completed |
| November 17-18, 2003 | Samples Collected and Submitted to SUNYSB and Manchester |
| February 2004 | Laboratory Analyses and QA Review Completed; Data Reported to Project Lead |
| May 2004 | Draft Project Report Completed and Sent Out for Comments |
| July 2004 | Final Project Report Completed |
| August 2004 | Data Entered into Ecology EIM Database |

# Measurement Quality Objectives

The techniques being used to analyze PPCPs for this project are part of an ongoing research effort. Therefore, strict measurement performance criteria have not been established. SUNYSB gauges the acceptability of their results as follows:

In the pharmaceuticals' analysis, acceptable levels for all blanks are below instrument detection limits. 13C caffeine is used as an internal standard. All samples of similar type should have a 13C caffeine response within 10 percent of each other. Spiked blanks are analyzed with each sample set. Compounds that have <50 percent recovery are reported as "estimated."

In the estrogen analysis, acceptable levels for all blanks are below instrument detection limits. Deuterated standards of the target analytes are used as recovery standards and deuterated equilin is added prior to the analysis as an internal standard. Data with recoveries greater than 70 percent are accepted. If there is reason to expect lower recoveries based on differential suppression of ionization between surrogate and internal standards caused by the sample matrix, lower recoveries can be accepted because the isotope standards have gone through the whole procedure.

Quality control requirements for these analyses are in the method descriptions which will be attached as Appendix A when received from the contract laboratory.

Detection limits in the pharmaceuticals analysis are typically 0.1 – 2 ng/L for surface water and one-to-two orders of magnitude higher in sewage effluent. For tertiary effluents, as in the present study, detection limits will likely be similar to or an order of magnitude higher than in surface water. Detection limits of 0.02 – 0.06 ng/L are typically achieved in the estrogen analysis.

No specific data quality objectives are being set for conventional parameters, beyond meeting Manchester's normal acceptance criteria.

# Sampling Design

This study will collect and analyze limited numbers of samples, as is appropriate for a screening survey. The samples will be collected on November 17-18, 2003.

A time frame of mid-October was initially selected for the field work as being worst-case for surface water, with the irrigation season ended and the creeks being at low flow. However, the services of the contract laboratory could not be secured in time. November samples will be more representative of general water quality conditions in these creeks as opposed to extreme low flow.

All samples will be analyzed for the Table 1 chemicals. Ancillary parameters will include temperature, pH, conductivity, nitrate+nitrite-N, and total suspended solids. Stream flow will be measured at the time the surface water samples are taken.

## Wastewater Treatment Plant Effluents

One sample each of final effluents from the Sequim and Sunland WWTPs will be analyzed. The samples will be composites of an early morning grab (~0800) and an early afternoon grab (~1500). Effluent flow in WWTPs is highest in the morning, but can be more concentrated in the afternoon. A replicate sample will be collected at one of the plants (see Field Quality Control).

## Groundwater

A total of five wells will be sampled: two near the Sunland land application site, two near the city of Sequim Reuse Demonstration Site and one in an area of high nitrate concentrations (Figure 1, Table 3). These wells were selected in consultation with Anne Soule, hydrogeologist with Clallam County. The criteria for selecting wells included the following:

- The well is downgradient of the site of interest.
- A driller's report (well log) is available for the well (if possible).
- The well is screened in as shallow an aquifer as possible—above any clay layer (if possible).
- The well is capable of producing samples representative of the groundwater.
- The well does not have a water treatment device (such as a water softener or iron treatment system) or a large storage tank that cannot be bypassed during well purging and sampling.
- The current well owner must grant access to the well.

Table 3. Wells to be Sampled

| Well ID | Location | Type of Well | Depth (ft) | Well Log? |
|---|---|---|---|---|
| 5N2 | Sunland land application site | monitoring | 44 | yes |
| Taylor Ranch | 444 Taylor Ranch Rd. | private | 49 | yes |
| Olympic Meadows Farm | 154 Bell Meadow Lane | private | 60? | no |
| Rhodefer Road | N. end N. Rhodefer Rd. | community | ? | ? |
| Beverage Street | 885 N. Beverage St. | private | 67 | yes |

A peristaltic or submersible pump will be used to collect samples from monitoring wells which do not have a pump. Domestic wells will be sampled using the existing pump. One sample will be collected from each well after purging.

## Surface Water

One water sample each will be collected from Bell Creek and Cassalery Creek. Bell will be sampled at Schmuck Road, just before it flows into Sequim Bay (Figure 1). This site is approximately 1 mile below Carrie Blake Park. Cassalery will be sampled at Jamestown Road, approximately ½ mile below the Sunland WWTP. A replicate sample will be collected at one of the creeks (see Field Quality Control). All samples will be simple grabs. Results will reflect a range of possible PPCP sources within each watershed, including but not limited to WWTP effluent.

Table 4 shows the numbers and types of samples to be analyzed for this project and an estimate of the laboratory costs.

Table 4. Number of Samples to be Analyzed and Estimate of Laboratory Costs

| Analysis | WWTP Effluent | Ground-water | Surface Water | Field Blank | Total Samples | Cost per Sample | Cost Subtotals |
|---|---|---|---|---|---|---|---|
| Pharmaceuticals | 3 | 5 | 3 | 1 | 12 | 400 | 4800 |
| Estrogens | 3 | 5 | 3 | 1 | 12 | 400 | 4800 |
| Nitrate+Nitrite-N* | 0 | 5 | 2 | 0 | 7 | 13 | 91 |
| TSS | 2 | 0 | 2 | 0 | 4 | 10 | 40 |
| | | | | | | Analytical Cost | $9,731 |
| | | | | | | Manchester Surcharge** | $1,200 |
| | | | | | | Total = | $10,931 |

*Cost includes 50% discount for Manchester Laboratory

**Review of SUNYSB data

# Field Procedures

Sample containers, preservation, and holding times for this project are shown in Table 5. Sample containers for PPCPs will be obtained from SUNYSB, with preservative added. TSS and nitrate-nitrite bottles will be obtained from Manchester, with preservative added.

Table 5. Field Procedures

| Parameter | Min. Sample Size | Container | Preservation | Holding Time |
|---|---|---|---|---|
| Pharmaceuticals | 1 L | 1L amber glass, teflon lid | Cool to 4°C | filter within 2 days* |
| Estrogens | 1 L | 1L amber glass, teflon lid | 10mL formalin, 4°C | * |
| Nitrate+Nitrite-N | 125 mL | 125 mL poly bottle | $H_2SO_4$ to pH<2, 4°C | 28 days |
| TSS | 1 L | 1 L poly bottle | Cool to 4°C | 7 days |

*Holding time for extraction/analysis not established; samples will be extracted within 7 days and analyzed within 14 days

The PPCP samples will be shipped by FedEx to arrive at SUNYSB the morning after collection. Samples for conventional parameters will be returned to the EA Program Operations Center for next day pick up by the Manchester courier. All samples will be accompanied by a chain-of-custody record and the coolers sealed with chain-of-custody tags or tape.

## Effluents

Effluent composites from the Sequim and Sunland WWTPs will be collected by filling the sample containers with equal amounts of water from morning and afternoon grabs. One-liter amber glass jars obtained from SUNYSB will be used to take the grabs. The samples will be kept on ice and in the dark during the compositing period. Field personnel will wear nitrile gloves while doing the sampling.

pH and conductivity will be measured when the grabs are taken. pH will be determined with an Orion Model 25A meter and conductivity with a Beckman Model RB-5 conductivity bridge. Temperature will be recorded from a meter or precision thermometer. A Magellan 320 GPS will be used to determine the latitude and longitude of the effluent sampling sites.

## Surface Water

Water samples from Bell and Cassalery Creeks will be collected from center channel directly into the appropriate sample containers. The samples will be put on ice immediately on collection. pH, conductivity, and temperature will be measured as described above for WWTP effluents. Stream flow will be gauged with a Swoffer Model 2100 or Marsh-McBirney 201 meter and top-setting rod. A Magellan 320 GPS will be used to determine the latitude and longitude of the sampling sites.

## Groundwater

Wells selected for sampling will be field located on USGS 1:24,000 quad maps for subsequent analysis and plotting via Arcview GIS software. Groundwater levels will be measured at each of the study wells prior to sampling, if possible. Water level measurements will be made using a calibrated electric well probe or steel tape in accordance with standard USGS methods (Stallman, 1983).

Wells will be purged prior to sampling. A peristaltic or submersible pump will be used for the monitoring well which does not have a pump. Domestic wells will be purged using the existing pump in the well and a garden hose rinsed thoroughly with tap water. The hose will be connected as close to the well head as possible. The purge rate will be measured using a calibrated 5-gallon bucket and stop watch and recorded. Purge water will discharge to an enclosed flow cell where temperature, pH, conductivity, and dissolved oxygen will be monitored and recorded every three minutes.

Samples will be collected only after flow cell measurements stabilize and after a minimum of 20 minutes. The flow cell will be disconnected for sample collection. Samples will be collected directly into the appropriate containers.

# Chemical Analysis

Table 6 shows the laboratory procedures to be used in the project.

Table 6. Laboratory Procedures

| Analysis | No. of Samples | Expected Range of Results | Sample Prep Method | Analytical Method |
|---|---|---|---|---|
| Pharmaceuticals | 12 | <0.1 - 1,000 ng/L | Filter | HPLC-MS |
| Estrogens | 12 | <0.02 - 1,000 ng/L | - - | HPLC-MS |
| Nitrate+Nitrite-N | 7 | 0.1 - 5 mg/L | NA | EPA 353.2 |
| TSS | 4 | 1- 50 mg/L | NA | EPA 2540D |

NA = not applicable

The pharmaceuticals method is outlined in Kolpin et al. (2002). The compounds are extracted from 1 liter water samples using SPE cartridges. The adsorbed compounds are eluted with methanol. The extract is reduced to near dryness under nitrogen gas and then brought to a final volume of 1 mL in acetonitrile. Compounds are separated and measured by HPLC-MS in positive ion mode.

The estrogen method is described in Ferguson et al. (2001). Samples are extracted from water by solid-phase extraction and the resulting extract is purified by passing it over a selective immuno-affinity extraction column. The only significant change from Ferguson et al. is that time-of-flight MS is used instead of single quadrupole MS, providing additional sensitivity and confirmation based on accurate mass.

Complete descriptions of these two methods will be attached as Appendix A when received from the contract laboratory.

# Quality Control

Table 7 shows the quality control (QC) samples to be analyzed for this project.

Table 7. Quality Control Procedures

| Parameter | Field QC | | Laboratory QC | | | |
|---|---|---|---|---|---|---|
| | Replicate Samples | Bottle Blank | Method Blanks | Spiked Blanks | Labeled Compounds | Surrogates |
| Pharmaceuticals | 2 | 1 | 2/batch | 2 batch | each sample | each sample |
| Estrogens | 2 | 1 | 2/batch | 2 batch | each sample | none |
| Nitrate+Nitrite-N | 0 | 0 | 1/batch | 1/batch | NA | NA |
| TSS | 0 | 0 | 1/batch | 1/batch | NA | NA |

NA = not applicable

## Field Quality Control

Three field QC samples each for pharmaceuticals and estrogens analysis will be prepared for this project--two replicate samples and one blank. Results from analyzing the replicates will provide an estimate of the total variability in the data (field + laboratory). A bottle blank will be used to detect contamination arising from sample containers or sample handling.

The Sunland effluent and Bell Creek samples will be collected in replicate, representing two types of matrices. Sunland was selected over Sequim because of the lower level of treatment it provides; and therefore, likely higher detection frequency of PPCPs. Bell Creek was selected over Cassalery Creek in light of its receiving Sequim effluent.

The bottle blanks will consist of 1-liter amber glass sample bottles filled with organic-free water by SUNSYB. The bottle blanks will be carried into the field and treated as samples.

## Laboratory Quality Control

Laboratory Quality Control samples will include method blanks, spiked blanks, labeled compounds, and surrogates. The use of these samples is described in the methods descriptions which will be attached as Appendix A when received from the contract laboratory.

# Data Review, Verification, and Validation

SUNSYB will verify the data and submit a data package with the deliverables described in Appendix A. Manchester will conduct a review of the contract laboratory's data and case narratives. Manchester will validate that methods and protocols specified in SUNYSB's analytical procedures were followed; that all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of instrument calibration, blanks, recovery data, precision data, and appropriateness of data qualifiers assigned. Manchester will prepare a written report on the results of their data review.

# Data Quality Assessment

Once the data have been verified and validated, the project lead will make a determination if the data can be used to make the determinations for which the project was conducted. The project lead will review the contract laboratory's data package and Manchester's data validation report. The project lead will check these data and reports for completeness and reasonableness. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

Accepted data will be analyzed and interpreted for the project report. This will include an evaluation of the significance of chemicals detected in field blanks, calculating RPDs for replicate samples, contrasting effluent quality between the two WWTPS, identifying any apparent links between chemicals detected in effluents and the receiving environment, and comparing to results of similar studies on other waterbodies. An attempt will be made to assess the likelihood of ecological and human health risk posed by detected chemicals, to the extent possible.

# Reports

On or before May 2004, the project lead and project hydrogelogist will prepare a draft report on results of the screening study and provide it to Clallam County, SWRO, and others for review and comment. The report will include:

- Maps of the study area showing sampling sites.
- Descriptions of field and laboratory methods.
- Copies of well logs.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical data.
- Observations on significant findings and conclusions.
- Recommendations on need for and design of follow-up studies.

A final project report is planned for July 2004 and will address all review comments. The data will be entered into EIM.

# References


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# Appendix A

# Analytical Methods

**(to be attached when received from the contract laboratory)**

# Appendix B

# Washington State Department of Ecology
# Data Deliverables

EPA SW-846, Volume 1B, Chapter 1, September, 1994, contains the forms I through X and examples of qualifiers to be used. Equivalent forms may be substituted.
The appropriate form(s) for data summaries are given in brackets following the corresponding sections.

Deliverables shall include all data necessary to enable Ecology personnel to perform an independent assessment of the results. As applicable, the deliverables shall include, but not be limited to:

1. *Chain of Custody Record*
   Include the SIGNED white or yellow copy of the "Request for Laboratory Services" with DATE OF RECEIPT CLEARLY MARKED.

2. *A Case Narrative*
   Discussion of any abnormalities or difficulties encountered during analysis, such as matrix interferences, spike recoveries, precision data, method blank contamination, holding time violations, sample condition upon receipt, and any other considerations affecting the data that the data user and/or reviewer needs to know about. Define any qualifiers used.

3. *Data Summary Information*
   A summary of the sample results and method blank results. Dates prepared and analyzed shall be included, along with the analytical results which are to be appropriately rounded to two significant figures. Report Practical Quantitation Limits (PQL's) of non-detected compounds based on the lowest initial calibration standard analyzed and according to the appropriate method - *unless otherwise stated in the request*. Adjust PQL's for sample weight/volume, dilutions, % solids, etc., rounding PQL's up to two significant figures.
   [Form I or an acceptable equivalent.]

4. *Quality Control and Quality Assurance Summary Data*
   Surrogate recoveries, target analyte recoveries, precision data, including duplicate results, spike results, laboratory control sample results, check standards, spiking levels, Quality Control (QC) limits, and method blank summaries (if more than one method blank is performed; this is used to indicate which method blank corresponds to which samples). All surrogate recoveries and target analyte concentrations shall be calculated from the instrument and column appropriate for the method of analysis. If recoveries are excessively outside QC limits and considered non-correctable, the contact person at Ecology is to be notified immediately.
   [Forms I through IV, or their acceptable equivalents.]

5. *Instrument Tuning Information (Where Applicable)*
   Raw data and summaries from the appropriate GC/MS tuning compound (e.g., bromofluorobenzene or decafluorotriphenylphosphine) for date(s) of initial calibration, (continuing calibration,) and sample analyses.
   [Form V or an acceptable equivalent.]

6. *Instrument Response Printouts*
   The charts, graphs, spectrograms, (including mass spectrograms of TLC and TIC compounds), chromatograms, reconstructed ion chromatograms or other instrument A/D printouts. Peaks shall be normalized to the highest peak of interest when possible (not the solvent peak); at a minimum, peaks used for identification must be distinguishable to the naked eye, and any manual integration must be apparent.

7. *Calibration or Standardization Information*
   All data pertaining to standards used for identification and quantitation, including raw data from both initial and continuing calibration standards. Indicate which standard(s) was (were) used in the calculations of the analytes. Surrogates are to be added to all calibration standards.
   [Forms VI through IX, or their acceptable equivalents.]

8. *Preparation/Digestion/Extraction Information*
   Dates of preparations, initial sample amount used for analysis, any aliquots or dilutions taken, final volumes or weights, percent solids calculation worksheet, name(s) of the analyst(s) performing the work. Also include amount of surrogate and spiking compounds added to the sample during preparation (in <u>weight per volume</u> *OR* <u>total weight</u>).

9. *Deliverables to be Received by Date Specified in SOW*