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Quality Assurance Project Plan

Analyzing Pharmaceuticals and Personal Care Products in Effluent and Groundwater at Three Reclaimed Water Facilities

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Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

The plan for this study is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/1103103.html.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID AJOH0064.

Ecology's Activity Tracker Code for this study is 11-070.

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February 2011

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Signatures are not available on the Internet version.
WQP: Water Quality Program.
EAP: Environmental Assessment Program.
EIM: Environmental Information Management database.

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Abstract

Pharmaceuticals and personal care products (PPCPs) will be analyzed in effluents and groundwater at three reclaimed water treatment facilities in Washington State – Yelm, Quincy, and LOTT Martin Way – in the spring and fall of 2011. The objectives are to: (1) expand Ecology's understanding of PPCPs in reclaimed water, (2) assess impacts to groundwater at recharge sites, and (3) identify potential PPCP indicator compounds for future monitoring. The completed project will provide data on two reclaimed water samples, two upgradient groundwater samples, and four downgradient groundwater samples for each facility. The samples will be analyzed for 119 PPCPs and 27 synthetic or naturally-occurring steroids and hormones using isotopic dilution methods. Detection limits will be in the low parts per trillion.

Background

Pharmaceuticals and personal care products (PPCPs) include a wide array of prescription and over-the-counter drugs for humans and animals, as well as products such as shampoos, soaps, fragrances, and lotions. Their detection at low levels in surface water, groundwater, soils, and drinking water has led to concerns that they may have adverse impacts on humans or animals (EPA, 2010). The continual introduction of PPCPs into the environment causes a pseudo-persistence that might not otherwise exist (Halling-Sorenson et al., 1998).

Humans typically excrete 50% to 90% of the active ingredients in ingested pharmaceuticals, either unmetabolized or as metabolites (McGovern and McDonald, 2003). A King County, WA study found that about 30% of residents dispose of drugs in the sink or toilet (Grasso, 2009). These chemicals enter on-site sewage systems, municipal wastewater treatment plants (WWTPs), and reclaimed water treatment facilities (RWTFs).

Reclaimed water is treated wastewater that can be used for irrigation and other non-potable uses to extend water supplies. Tertiary-treated reclaimed water benefits from a set of treatment processes that provides a higher level of treatment and reliability than conventional secondary treatment WWTPs. The water released from a RWTF is designed to meet the quality standards for its intended use.

Advanced treatment processes used to reclaim water – such as reverse osmosis, multiple barriers or ozonation – are effective at reducing PPCP concentrations (Olivieri, 2008; Drury et al., 2006). PPCP levels in reclaimed water discharges are much lower than in conventional WWTP effluents (Lubliner et al., 2010; Cooperative Research Centre, 2007; Kinney et al., 2006).

Washington State currently has 321 municipal WWTPs and 24 RWTFs (Jones, 2008). Only a few WWTPs provide reclaimed water treatments because of the expense. In Washington, reclaimed water is distributed to public and private entities for commercial and industrial uses, applied to land for irrigation at agronomic rates, and used to recharge groundwater via surface percolation at permitted locations.

The Washington State Department of Ecology (Ecology) recently completed a literature review and field study on PPCPs and other chemical contaminants in municipal wastewater and their removal by different treatment technologies (Lubliner et al., 2010). Five facilities providing conventional secondary treatment, advanced nutrient removal, reclaimed water, and/or filtration were sampled once each in August 2008. Raw influent, effluent, and biosolids were analyzed. Of these five, the reclaimed water plants were Lacey-Olympia-Tumwater-Thurston County (LOTT) Budd Inlet, LOTT Martin Way, and Hayden WWTP in Idaho. Table 1 shows the PPCPs detected in reclaimed water. Steroids and hormones are a subset of PPCPs.

Table 1. PPCPs, Steroids, and Hormones Detected in Effluents from Three Washington Reclaimed Water Treatment Facilities in 2008.

Modified from Lubliner et al., 2010; N=3; ng/L = parts per trillion.

Chemical Class	Compound	Reclaimed Water Concentrations (ng/L)
PPCPs by EPA Method 1694	Azithromycin	10-380
	Cimetidine	nd-310
	Carbamazepine	917-1,600
	Cotinine	nd-40
	Diphenhydramine	nd-343
	Erythromycin	nd-168
	Fluoxetine	42-58
	Gemfibrozil	nd-1,230
	Ibuprofen	30-158
	Metformin	542-1,760
	Naproxen	nd-251
	Ranitidine	nd-740
	Sulfamethoxazole	2-104
	Triclocarban	nd-77
	Triclosan	3-103
	Trimethoprim	nd-294
Steroids/ hormones by EPA Method 1698	Campesterol	nd-4
	Cholestanol	nd-50
	Coprostanol	7-148
	Ergosterol	nd-120
	Estrone	nd-39

nd: not detected.

The Ecology Water Quality Program (WQP) requested that follow-up sampling be conducted for PPCPs at selected reclaimed water facilities. The objectives of this project were to: (1) expand Ecology's understanding of PPCPs in reclaimed water, (2) assess impacts to groundwater at recharge sites, and (3) identify potential PPCP indicator compounds for future monitoring. This Quality Assurance (QA) Project Plan describes how the study will be conducted.

Project Description

Reclaimed water and groundwater will be collected at three Washington RWTFs during the spring and fall of 2011. The Yelm, Quincy, and LOTT Martin Way facilities have been selected for sampling (Figure 1). One upgradient well and two downgradient wells will be sampled at each plant, using established monitoring wells. The completed project will provide data on two reclaimed water samples, two upgradient groundwater samples, and four downgradient groundwater samples at each facility.

Figure 1. Approximate Location of Reclaimed Water Treatment Facilities to be Sampled for PPCPs, Steroids, and Hormones.

The samples will be analyzed for 119 PPCPs and 27 synthetic or naturally occurring steroids and hormones, using isotope dilution methods. Detection limits will be in the low parts per trillion.

The study will be conducted by Ecology's Environmental Assessment Program (EA Program). The samples will be analyzed by AXYS Analytical Services in Sidney, B.C. through a contract with the Ecology Manchester Environmental Laboratory (MEL). A final project report is scheduled for June 2012. This QA Project Plan follows the Ecology guidance in Lombard and Kirchmer (2004).

Organization and Schedule

The following people will be involved in this project. All are Ecology employees, except for the AXYS laboratory contact.

Table 2. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Jim McCauley Program Development Services Section, Water Quality Program Phone: 360) 407-7468	Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Art Johnson Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6766	Project Manager	Primary author of the QAPP. Lead for effluent sampling. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Pam Marti Groundwater/Forest & Fish Unit Statewide Coordination Section Phone: (360) 407-6768	Principal Investigator	Assists in preparing the QAPP. Lead for groundwater sampling. Analyzes and interprets data. Co-author of draft and final report.
Tanya Roberts Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-7392	Field Assistant, Data Engineer	Helps collect samples and records field information. Enters data into EIM.
Dale Norton Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Martha Maggi Groundwater/Forest & Fish Unit Statewide Coordination Section Phone: (360) 407-6453	Unit Supervisor for Principal Investigator	Provides internal review of the QAPP and approves the final QAPP.
Will Kendra Statewide Coordination Section Phone: 360-407-6698	Section Manager for Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for Principal Investigator and Study Area (W. Washington)	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Gary Arnold Eastern Operations Section Phone: (509) 454-4244	Section Manager for Study Area (E. Washington)	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
Devin Mitchell AXYS Analytical Services Ltd. (250) 655-5812	Project Manager	Laboratory contact
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

EIM: Environmental Information Management database.

Table 3. Proposed Schedule for Completing Field and Laboratory Work, Data Entry into EIM, and Reports.

Field and laboratory work	Due date	Lead staff
Field work completed	October 2011	Art Johnson / Pam Marti
Laboratory analyses completed	December 2011	
Environmental Information System (EIM) database		
EIM user study ID	AJOH0064	
Product	Due date	Lead staff
EIM data loaded	January 2012	Tanya Roberts
EIM quality assurance	February 2012	Dale Norton
EIM complete	March 2012	Tanya Roberts
Final report		
Authors	Art Johnson / Pam Marti	
Schedule		
Draft due to supervisor	April 2012	
Draft due to client/peer reviewer	May 2012	
Final (all reviews done) due to publications coordinator	June 2012	
Final report due on web	July 2012	

Sampling Design

Facility Selection

The three selected RWTFs – Yelm, Quincy, and LOTT Martin Way – all have groundwater recharge basins as a major component of their operations. Each facility has been operating for approximately five years or more and has an established groundwater monitoring program within the infiltration area, as required by the Reclaimed Water Permit. Existing monitoring wells will be used for this project. Appendix A has background information on each facility.

Monitoring Wells

Three wells will be sampled at each facility, one upgradient well and two downgradient wells. Wells will be selected based on previous monitoring results and in consultation with each facility operator.

The following criteria will be considered when selecting the wells:

- The wells are properly constructed and capable of producing samples representative of the groundwater.
- The wells are screened in the upper-most saturated zone.
- The upgradient well represents groundwater unaffected by the reclaimed water.
- The downgradient wells are as close to the infiltration areas as possible.
- A driller's report (well log) is available for the wells.

Timing and Number of Samples

Groundwater

Groundwater samples will be collected in spring (April/May) and fall (September/October) to correspond to seasonal water table high and low levels. A total of six samples will be collected from each facility. Two upgradient groundwater samples from one monitoring well will be collected to provide water quality data on the aquifer before reclaimed water is discharged downgradient, one each for spring and fall. Four downgradient groundwater samples will be collected from two monitoring wells, two per season. The sample schedule will be coordinated with each facility to coincide with their existing monitoring schedules.

Effluents

As previously noted, some PPCP data have already been collected on reclaimed water from Washington RWTFs through the Lubliner et al. (2010) study. For this reason and due to budget constraints, RWTF effluent samples will be limited to one from each facility during spring and fall, for a project total of six samples in all.

Quality Control Samples

Field quality control (QC) samples for this project will consist of duplicate effluent and groundwater samples and field blanks. These samples are described in more detail under Quality Control Procedures.

Chemical Analyses

RWTF effluents and groundwater will be analyzed for PPCPs, steroids, and hormones. Lubliner et al. (2010) showed that fewer steroids and hormones were detected in reclaimed water relative to other PPCPs. Therefore, to reduce laboratory costs, steroids and hormones will be analyzed for spring 2011 only.

PPCPs will be analyzed by high performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS) following EPA Method 1694. Steroids and hormones will be analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) following EPA Method 1698. The samples will be analyzed by AXYS Analytical Services in Sidney, B.C. through a contract with the Ecology Manchester Environmental Laboratory (MEL). The same methods and laboratory were used in the Lubliner study. AXYS played a major role in developing these methods for EPA.

Methods 1694 and 1698 provide low detection limits for a large number of compounds: 119 PPCPs, 10 steroids, and 17 hormones (Appendix B). For the present effort, an expanded list of PPCPs is being analyzed (119 vs. 72 compounds in the Lubliner study). Detection limits will be in the low parts per trillion, 10 ng/L or less for most PPCPs and hormones (Appendix B). Steroids have higher detection limits, 25 – 1,000 ng/L, but are also typically encountered in higher concentrations.

One objective of this project is to identify surrogate compounds that could be used as indicators of PPCPs in groundwater at RWTF recharge sites or in other environments. A useful indicator is one that is widely used, relatively persistent, and readily analyzed. Several of the PPCPs and steroids being analyzed in the present study have been suggested as indicator compounds: caffeine, carbamazepine, diphenhydramine, coprostanol, and cholesterol (Zdwadzkas, 2006, Glassmeyer et al., 2005). Results on effluent and groundwater samples will be compared to identify PPCPs that co-occur and have the aforementioned characteristics of an indicator.

Total suspended solids (TSS), turbidity, and chloride will also be analyzed in effluent. These are among the water quality parameters each facility is required to monitor as part of their National Pollution Discharge Elimination System (NPDES) permit. The TSS and turbidity data will be used as a general indicator of effluent quality. The groundwater samples will be analyzed for chloride.

Summary

Table 4 summarizes the sampling design for this study.

Table 4. Sampling Design (number of samples)

Season/Facility	Effluent Samples	Groundwater Samples		QC Samples		Sample Subtotals
		Upgradient	Downgradient	Field Duplicates	Field Blanks	
Spring 2011 - PPCPs, steroids, and hormones analyzed						
Yelm	1	1	2			4
Quincy	1	1	2			4
LOTT Martin Way	1	1	2	1	2	7
					Total samples =	15
Fall 2011 - PPCPs analyzed						
Yelm	1	1	2	1		5
Quincy	1	1	2			4
LOTT Martin Way	1	1	2			4
					Total samples =	13

Sampling Procedures

Sample containers, preservation, and holding times for the effluent and groundwater samples are shown in Table 5.

Table 5. Sample Containers, Preservation, and Holding Times.

Analysis	Sample Size	Container	Field Preservation	Holding Time
PPCPs	1 L	HDPE	Cool to ≤ 4°C	48 hours (refrigerated) 7 days (frozen) 40 days (extraction)
Steroids/Hormones	1 L	HDPE	Cool to ≤ 4°C	48 hours (refrigerated) 7 days (frozen) 40 days (extraction)
Total Suspended Solids	1 L	Poly bottle	Cool to ≤ 4°C	7 days
Turbidity	500 mL	Poly bottle	Cool to ≤ 4°C	48 hours
Chloride	500 mL	Poly bottle	Cool to <4°C	28 days

Groundwater

Groundwater levels will be measured at each of the wells prior to sampling. Water level measurements will be made using a calibrated electric well probe in accordance with standard operating procedure (SOP) EAP052 (Marti, 2009).

Wells will be purged prior to sampling. A peristaltic or submersible pump will be used to collect samples from monitoring wells which do not have a dedicated pump. Wells will be purged at a rate of ≤1-liter/minute. The wells will be purged through a continuous flow cell where temperature, pH, conductivity, and dissolved oxygen will be monitored and recorded at regular intervals. Purging will continue until field parameter readings stabilize (Table 6).

Table 6. Well Purging Criteria.

Purge Parameter	Stabilization Criteria
pH	±0.1 standard unit
Temperature	±0.1 °C
Conductivity	±10 umhos/cm for values <1000 umhos/cm
	±20 umhos/cm for values >1000 umhos/cm
Dissolved Oxygen	±0.2 mg/L for values > 2 mg/L
Or	
All parameters	< ±10% change over 3 consecutive readings at 3 minute intervals

Samples will be collected from each well at the completion of purging. The flow cell will be disconnected and the samples collected directly from the pump's discharge tubing into appropriate sample containers (Table 5). Sample bottles for PPCPs and steroids/hormones will be provided by AXYS. Chloride bottles will be obtained from MEL. Nitrile gloves will be worn by field personnel collecting and manipulating the samples. Care will be taken not to contaminate the samples with extraneous material.

Filled sample bottles will be labeled with a unique sample number obtained from MEL, placed in plastic bags, then stored on ice-filled coolers pending their arrival at the laboratory (see below).

Field activities will be recorded in a bound notebook of waterproof paper. A hand-held GPS will be used to record sampling locations.

Effluents

To maximize comparability between datasets, sampling procedures for RWTF effluent will follow Lubliner et al. (2010). Individual grabs will be taken by hand in the morning, mid-day, and afternoon, and composited by equal volume into appropriate sample containers (Table 5). Sample bottles for PPCPs and steroids/hormones will be provided by AXYS. TSS, turbidity, and chloride bottles will be obtained from MEL. Nitrile gloves will be worn by field personnel collecting and manipulating the samples. Care will be taken not to contaminate the samples with extraneous material.

The samples will be kept in plastic bags on ice in coolers during the compositing period. Each sample will be assigned a unique sample number obtained from MEL.

The PPCP and steroids/hormones samples will be shipped in coolers with blue ice to AXYS by FedEx to arrive the morning of the next business day. The TSS, turbidity, and chloride samples will be transported on ice to Ecology headquarters and taken by courier to MEL the following day. Chain-of-custody procedures will be followed.

Field activities will be recorded in a bound notebook of waterproof paper. A hand-held GPS will be used to record sampling locations.

Laboratory Procedures

Table 7. Laboratory Procedures.

Analysis	Number of Samples	Expected Range of Results	Reporting Limit	Analytical Method	Laboratory
PPCPs	28	see Table 1	Appendix B-1	HPLC/MS/MS (EPA Method 1694)	AXYS
Steroids/Hormones	15	see Table 1	Appendix B-2	HRGC/HRMS (EPA Method 1698)	AXYS
Total Suspended Solids	8	1 - 10 mg/L	1 mg/L	Standard Methods 2540D	MEL
Turbidity	8	1-5 NTU	1 NTU	Standard Methods 2130D	MEL
Chloride	26	1-70 mg/L	0.1 mg/L	EPA Method 300.0	MEL

The analytical methods are briefly described below.

EPA Method 1694: *Pharmaceuticals and Personal Care Products in Water Soil, Sediment and Biosolids by HPLC/MS/MS.* Method 1694 determines PPCPs in environmental samples by high performance liquid chromatography combined with tandem mass spectrometry using isotope dilution and internal standard quantitation techniques. (www.epa.gov/waterscience/methods/method/files/1694.pdf)

EPA Method 1698: *Steroids and Hormones in Water, Soil, Sediment, and Biosolids by HRGC/HRMS.* Method 1698 determines steroids and hormones in environmental samples by isotope dilution and internal standard high resolution gas chromatography combined with high resolution mass spectrometry. (www.epa.gov/waterscience/methods/method/files/1698.pdf)

Standard Methods 2540D*: Total Suspended Solids Dried at 103-105^{o}C.* A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter dried to a constant weight.

Standard Methods 2130B. *Turbidity: Nephelometric Method.* The intensity of light scattered by a sample under defined conditions is compared with the intensity of light scattered by a standard reference suspension.

EPA Method 300.0. *Chloride.* The water sample is injected into a stream of carbonate-bicarbonate eluant and separated on the basis of relative affinities for a low capacity, strongly basic chromatographic column. A conductivity detector determines the separated anions.

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that uncertainties are minimized and results are comparable to the data reported in Lubliner et al. (2010) and other studies on PPCPs, steroids, and hormones at reclaimed water treatment facilities. These objectives will be achieved through careful attention to the sampling, measurement, and QC procedures described in this plan.

Measurement Quality Objectives

Measurement quality objectives (MQOs) for the PPCP and steroids/hormones analyses will be: (1) the QC acceptance criteria specified in EPA Methods 1694 and 1698 and (2) the detection and reporting limits that AXYS anticipates achieving with these methods.

QC acceptance criteria vary with analyte and are listed in Table 12 of Method 1694 and Table 5 of Method 1698 (www.epa.gov/waterscience/methods/method/files/1694.pdf , www.epa.gov/waterscience/methods/method/files/1698.pdf). Acceptance criteria have been established for calibration verification, initial precision and recovery, ongoing precision and recovery, and labeled compound recovery.

AXYS detection and reporting limits for each target analyte in Methods 1694 and 1698 are listed in Appendix B of this QA Project Plan. It is recognized that unanticipated interferences could cause these limits to be raised for certain analytes in some project samples.

Data outside MQOs will be evaluated for appropriate corrective action by AXYS and MEL.

Quality Control Procedures

Field

Selected samples will be collected in duplicate to assess variability in the data. One pair of duplicate effluent samples will be analyzed in the spring and one pair of duplicate groundwater samples will be analyzed in the fall.

The potential for contamination arising from sampling procedures, sample containers, preservation, or transport will be assessed with field blanks. AXYS will provide a bottle blank for the PPCP and steroids/hormones analyses. A pump blank will be prepared for the groundwater samples by pumping blank water, obtained from AXYS, through the groundwater sampling system into sample containers. The field blanks will be analyzed for the initial sample collection in the spring to establish that contamination is not a data quality issue.

Laboratory

Table 8 summarizes the type and frequency of laboratory QC samples that AXYS and MEL will analyze. The project team will provide duplicate samples.

Table 8. Laboratory Quality Control Samples.

Analysis	Procedural Blanks	OPR Standards	Laboratory Control Samples	Labeled Compounds	Duplicate Samples
PPCPs	1/batch	1/batch	NA	all samples	1/batch
Steroids/Hormones	1/batch	1/batch	NA	all samples	1/batch
TSS	1/batch	NA	1/batch	NA	1/batch
Turbidity	1/batch	NA	1/batch	NA	1/batch
Chloride	1/batch	NA	1/batch	NA	1/batch

OPR: ongoing precision and recovery.
NA: not applicable.

Laboratory Cost Estimate

Table 9. Cost Estimate for Laboratory Analyses.

PPCPs		Steroids/Hormones		Ancillary Parameters		Total Cost**
Number of Samples	Cost per Sample*	Number of Samples	Cost per Sample*	Number of Samples	Cost per Sample†	
Spring 2011(FY11)						
15	$ 1,937	15	$ 1,218	13	$ 36	$44,491
Fall 2011 (FY12)						
13	$ 1,937	not analyzed		13	$ 36	$23,565

*Includes MEL 25% surcharge for contracting and data review (PPCPs=$1,500+$15 EDD+$35 data package; steroids/hormones=$925+$15 EDD+$35 data package).
†TSS ($11.42), turbidity ($11.42), chloride ($13.50); includes a 50% discount for MEL.
**One duplicate sample per batch analyzed at no charge; groundwater not analyzed for TSS or turbidity.

Data Verification

AXYS will provide a case narrative and complete data package (Tier 4 deliverables) for each sample batch. The PPCP and steroids/hormones data will be provided in Excel spreadsheet format.

MEL will conduct a review of the AXYS data packages and verify that (1) methods and protocols specified in the QA Project Plan and MEL contract were followed; (2) that all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and (3) that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, procedural blanks, calibration, labeled compound and internal standard recoveries, ion abundance ratios, ongoing precision and recovery, duplicates, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their review.

MEL will provide results for the TSS, turbidity, and chloride analyses following standard procedures. A case narrative will meet the requirements for a data verification report.

The project lead will examine the data reviews, case narratives, and data packages. To determine if project MQOs have been met, results for laboratory control samples, sample duplicates, calibration verification, initial precision and recovery, ongoing precision and recovery and labeled compound recoveries will be compared to QC limits. The method and transfer blank results will be examined to verify there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for "non-detects" and to determine if any values exceed the lowest concentration of interest. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

Data Management Procedures

All project data will be loaded into Ecology's Environmental Information Management database (EIM). Data entered into EIM follow a formal data verification review procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer from the project team.

Data Analysis

Once the data have been verified, the project lead will determine if they can be used to make the calculations, determinations, and decisions for which the project was conducted. If the results are satisfactory, data analysis will proceed.

Summary statistics will be calculated for each chemical and outliers identified. The data will be plotted to compare and contrast PPCP, steroid, and hormone profiles among RWTFs, in effluent vs. groundwater, and between spring and fall. The results will be compared to the RWTF data reported in Lubliner et al. (2010) and similar studies. Compounds that appear to be potentially useful as indicators of PPCPs in groundwater will be indentified.

Audits and Reports

Audits

Ecology's Laboratory Accreditation Program establishes whether a laboratory has the capability to provide accurate, defensible data. Accreditation involves an evaluation of the laboratory's quality system, staff, facilities and equipment, test methods, records, and reports.

Ecology has not accredited any laboratories for Methods 1694 or 1698 because they are relatively new (published December 2007). Ecology's Quality Assurance Officer has waived the requirement of accreditation for this project. AXYS is accredited by Ecology for other mass spectrometry methods.

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request.

Reports

The following reports will be prepared for this project:

1. A draft technical report for review by the client and other interested parties; the tentative date for the draft is May 2012. The report will include a summary of data collection activities, explanation of any major deviations from the QA Project Plan, data analysis details, summary statistics, graphics, maps, conclusions, and recommendations. Responsible staff: Art Johnson and Pam Marti.
2. The final technical report for this project is scheduled for June 2012. Responsible staff: Art Johnson and Pam Marti.

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Appendices

Appendix A. Background Information on the Reclaimed Water Treatment Facilities to be Sampled for PPCPs, Steroids, and Hormones during 2011.

Facility	Location	Permit No.	Year Permit Authorized	Process of Treatment	Average Monthly Flow (MGD)	Receiving Water
LOTT, Martin Way Reclaimed Water Plant	Olympia, WA	ST6206	2006	Enhanced biological nitrogen removal (EBNR) with membrane filtration. (Membrane biological reactors (MBRs). Sodium hypochlorite disinfects the treated water before distribution.	2.0	Constructed wetland ponds and groundwater recharges basins.
City of Yelm Reclaimed Water Plant	Yelm, WA	WA0040762	2005	Sequencing batch reactor (SBR) technology for secondary treatment (biological oxidation) and nitrogen removal. Advanced treatment follows with chemical coagulation, upflow sand filters, and chlorine disinfection.	1.0 (capacity)	Constructed surface and submerged wetlands that polish the reclaimed water before it recharges the groundwater.
City of Quincy Reclaimed Water Plant	Quincy, WA	ST5278	2006	Two activated sludge lagoons using sequencing batch reactor technology (SBR) to remove nitrogen and attain secondary treatment standards. The SBR discharges to an equalization basin that reduces peak flows to a lower more uniform flow. The reduced flow rate allows smaller sizing of advanced treatment units that produce Class A reclaimed water. These units include chemical coagulation, continuous backwash upflow sand filters, and disinfection with ultraviolet (UV) light.	1.5	Recharge groundwater through six infiltration basins.

MGD: million gallons per day

Appendix B. Chemicals to be Analyzed

Table B-1. PPCPs Analyzed by EPA Method 1694.
(Provided by AXYS Analytical Services Ltd. 12/7/2010.)

Matrix	Water/Effluent	
Units/Sample Size	ng/L based on 1 L sample	
Analyte	MDL	RL based on Low Cal.
List 1 - Acid Extraction in Positive Ionization		
Acetaminophen	33.2	60
Ampicillin [1]	NA	1.5
Azithromycin	3.2	1.5
Caffeine	28.5	15
Carbadox	4.5	1.5
Carbamazepine	5.3 [2]	1.5
Cefotaxime	14.6	6
Ciprofloxacin	6.5	6
Clarithromycin	1.4	1.5
Clinafloxacin	4.5	6
Cloxacillin	6.3	3
Dehydronifedipine	1.3	0.6
Digoxigenin	8.5	6
Digoxin	50.4 [2]	15
Diltiazem	1.0	0.3
1,7-Dimethylxanthine	218	150
Diphenhydramine	1.1	0.6
Enrofloxacin	10.2 [2]	3
Erythromycin-H20	0.4	0.3
Flumequine	3.2	1.5
Fluoxetine	4.4	1.5
Lincomycin	2.0	3
Lomefloxacin	4.4	3
Miconazole	2.0	1.5
Norfloxacin	19.3	15
Norgestimate	5.5	3.0
Ofloxacin	21.7	1.5
Ormetoprim	0.8	0.6
Oxacillin	5.8	3.0
Oxolinic acid	1.3	0.6

Matrix	Water/Effluent	
Units/Sample Size	ng/L based on 1 L sample	
Analyte	MDL	RL based on Low Cal.
Penicillin G	1.7	3.0
Penicillin V	3.6	3.0
Roxithromycin	0.2	0.3
Sarafloxacin	87.6 [3]	15.0
Sulfachloropyridazine	1.4	1.5
Sulfadiazine	1.0	1.5
Sulfadimethoxine	0.6	0.3
Sulfamerazine	0.3	0.6
Sulfamethazine	1.0	0.6
Sulfamethizole	0.8	0.6
Sulfamethoxazole	0.5	0.6
Sulfanilamide	8.9 [5]	15.0
Sulfathiazole	1.5	1.5
Thiabendazole	0.2 [4]	1.5
Trimethoprim	2.3	1.5
Tylosin	NA	6.0
Virginiamycin	3.6 [5]	3.0
List 2 – Tetracyclines in Positive Ionization		
Anhydrochlortetracycline	12.2	15.0
Anhydrotetracycline	10.7	15.0
Chlortetracycline	15.5	6.0
Demeclocycline	12.7	15.0
Doxycycline	4.0	6.0
4-Epianhydrochlortetracycline	7.6 [4]	15.0
4-Epianhydrotetracycline	5.5	60.0
4-Epichlortetracycline	31.6	15.0
4-Epioxytetracycline	6.9	6.0
4-Epitetracycline	4.8	6.0
Isochlortetracycline	5.2	6.0
Minocycline	17.9 [4]	60.0
Oxytetracycline	4.7	6.0
Tetracycline	7.1	6.0
List 3 - Acid Extraction in Negative Ionization		
Bisphenol A	3502	2500.0
Furosemide	27	40.0

Matrix	Water/Effluent	
Units/Sample Size	ng/L based on 1 L sample	
Analyte	MDL	RL based on Low Cal.
Gemfibrozil	1.6	1.5
Glipizide	5.7	6.0
Glyburide	5.2	3.0
Hydrochlorothiazide	51	20.0
2-hydroxy-ibuprofen	171	80.0
Ibuprofen	17	15.0
Naproxen	10	3.0
Triclocarban	2.2	3.0
Triclosan	65	60.0
Warfarin	2.2	1.5
List 4 - Basic Extraction in Positive Ionization		
Albuterol	0.72	0.3
Amphetamine	2.1	1.5
Atenolol	1.0	0.6
Atorvastatin	0.76	1.5
Cimetidine	0.67	0.6
Clonidine	3.2	1.5
Codeine	3.9	3.0
Cotinine	1.4	1.5
Enalapril	0.26	0.3
Hydrocodone	1.4	1.5
Metformin	47	30.0
Oxycodone	0.63	0.6
Ranitidine	1.0	0.6
Triamterene	0.33	0.3
List 5 - Acid Extraction in Positive Ionization		
Alprazolam	0.52	0.3
Amitriptyline	0.71	0.3
Amlodipine	1.44	1.5
Benzoylecgonine	0.33	0.3
Benztropine	0.35	0.3
Betamethasone	8.80 [3]	1.5
Cocaine	0.17	0.2
DEET	0.20	0.2
Desmethyldiltiazem	0.60 [3]	0.2

Matrix	Water/Effluent	
Units/Sample Size	ng/L based on 1 L sample	
Analyte	MDL	RL based on Low Cal.
Diazepam	0.28	0.3
Fluocinonide	25.7 [3]	6.0
Fluticasone propionate	3.26	2.0
Hydrocortisone	357 [3]	60.0
10-hydroxy-amitriptyline	0.15	0.2
Meprobamate	7.88	4.0
Methylprednisolone	57.3 [3]	4.0
Metoprolol	2.83	1.5
Norfluoxetine	1.07	1.5
Norverapamil	0.10	0.2
Paroxetine	2.85	4.0
Prednisolone	19.6	6.0
Prednisone	42.4	20.0
Promethazine	0.15	0.4
Propoxyphene	0.40	0.3
Propranolol	1.04	2.0
Sertraline	0.30	0.4
Simvastatin	NA	20.0
Theophylline	536 [3]	60.0
Trenbolone	6.39	4.0
Trenbolone acetate	0.31	0.3
Valsartan	9.66	4.0
Verapamil	0.15	0.2

MDL: Method detection limit.
RL: Reporting limit.
[1] Due to instability, accuracy of Ampicillin data is unknown.
[2] Determined MDL value is slightly above the spiking amount.
[3] Determined MDL value exceeds the spiking level and is an estimated value.
[4] MDL results is < 1/10 spiking level.
[5] Estimated.

Table B-2. Steroids and Hormones Analyzed by EPA Method 1698.
(Provided by AXYS Analytical Services 12/7/2010.)

Matrix	Water/Effluent
Units/Sample Size	ng/L based on 1 L sample
Analyte *Sterols*	LMCL based on Low Cal.
Campesterol	25
Cholestanol	25
Cholesterol	1000 [1]
Coprostanol	62.5
Desmosterol	62.5
Epicoprostanol	62.5
Ergosterol	62.5
ß-Sitosterol	1000 [1]
ß-Stigmastanol	62.5
Stigmasterol	25
Hormones	LMCL based on Low Cal.
17ß-Estradiol	7.5
17α-Estradiol	7.5
17α-Ethinyl Estradiol	7.5
ß-Estradiol-3-Benzoate	7.5
17α-Dihydroequilin	7.5
Androstenedione	18.75
cis-Androsterone	7.5
Desogestrel	7.5
Equilenin	7.5
Equilin	7.5
Estriol	7.5
Estrone	7.5
Mestranol	7.5
Norethindrone	7.5
Norgestrel	7.5
Progesterone	18.75
Testosterone	7.5

LMCL: Lower method calibration limit.
[1] Lab blank background levels
Samples will generally be reported below the LMCL levels above.

Appendix C. Glossary, Acronyms, and Abbreviations

Glossary

Chloride: One of the major inorganic constituents in water and wastewater.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

Acronyms and Abbreviations

Following acronyms and abbreviations are used in this report.

AXYS	AXYS Analytical Services
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GPS	Global positioning system
HPLC/MS/MS	High performance liquid chromatography/tandem mass
HRGC/HRMS	High resolution gas chromatography/high resolution mass spectrometry
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NPDES	(See Glossary above)
NTU	Nephelometric turbidity units
PPCP	Pharmaceuticals and personal care products
QA	Quality assurance

QC	Quality control
RPD	Relative percent difference
RWTF	Reclaimed Water Treatment Facility
SOP	Standard operating procedures
TSS	(See Glossary above)
WWTP	Wastewater Treatment Plant

Units of Measurement

°C	degrees centigrade
mg/L	milligrams per liter (parts per million)
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
s.u.	standard units
umhos/cm	micromhos per centimeter