



Quality Assurance Project Plan

PCB Monitoring at Walla Walla WWTPs

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October 2006

303(d) Listings Addressed in this Study

Mill Creek (WA-32-1060) – PCBs
Garrison Creek (WA-32-2000) – PCBs

Project Tracker Code: 07-065

Approvals

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Abstract

A Quality Assurance Project Plan is provided for monitoring polychlorinated biphenyls (PCBs) in influent and effluent from the Walla Walla and College Place wastewater treatment plants. The purpose of this effort is to establish whether these discharges currently exceed human health water quality criteria and to assess the extent to which the contamination is internal or external to each facility. This work is being done as a result of PCB wasteload allocations recently established through a Total Maximum Daily Load for the Walla Walla River.

Background

A recent Total Maximum Daily Load (TMDL) for the Walla Walla River (Gray et al., 2006) established wasteload allocations for polychlorinated biphenyls (PCBs) in final effluents from the Walla Walla and College Place Wastewater Treatment Plants (WWTPs). The Walla Walla plant [9.6 million gallons per day (mgd)] discharges to Mill Creek and the College Place plant (1.6 mgd) discharges to Garrison Creek, both are tributary to the Walla Walla River (Figure 1).

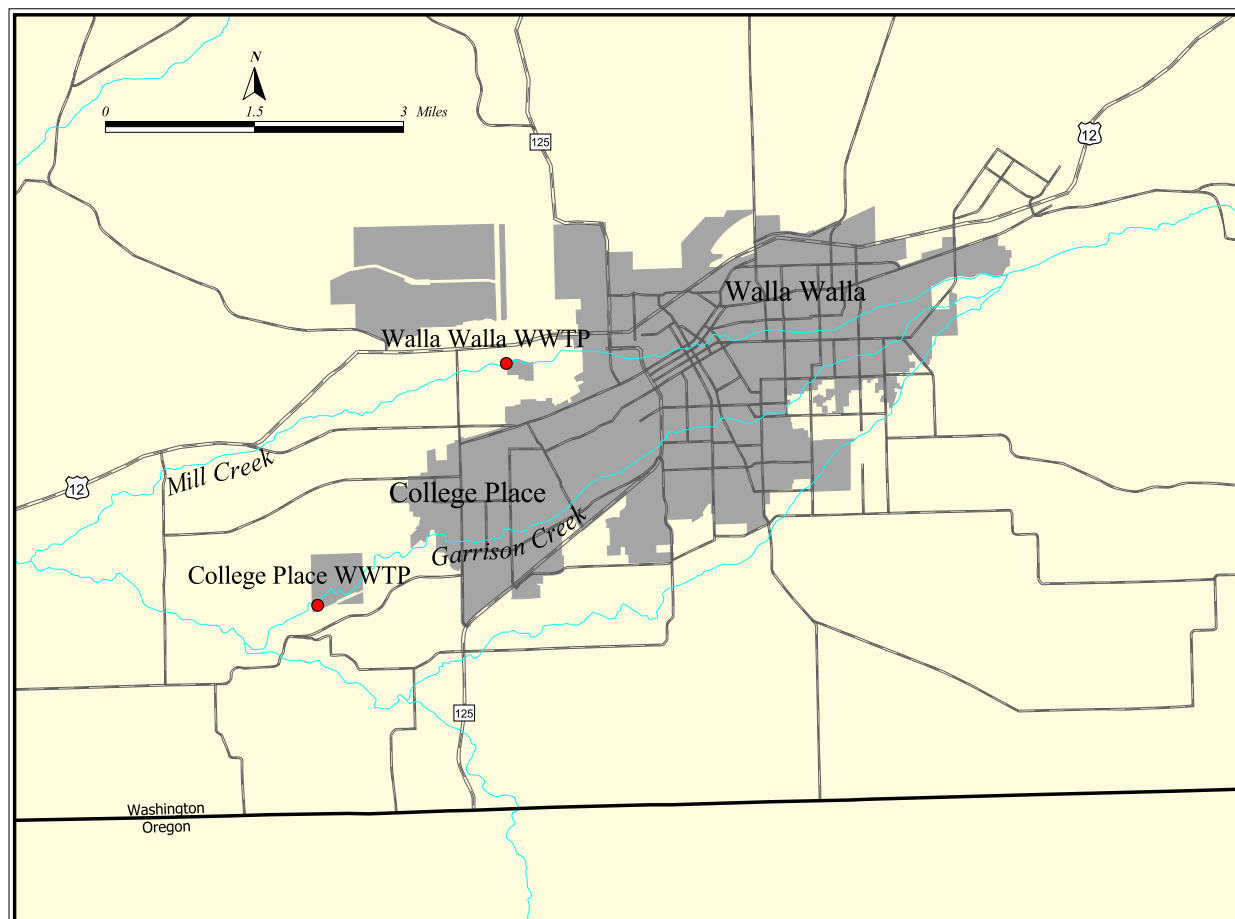


Figure 1. Location of Walla Walla and College Place WWTPs.

Polychlorinated biphenyls monitoring by the Department of Ecology (Ecology) during the technical study for the TMDL (Johnson et al., 2004) showed total PCB concentrations in final effluents from these facilities ranged from 0.65–0.88 ng/L and 0.53–2.5 ng/L (parts per trillion), respectively (Table 1). Because these concentrations exceeded the Washington State human health criterion of 0.17 ng/L total PCBs, wasteloads were allocated as required by the Clean Water Act. The allocation was calculated as the product of the human health criterion and average monthly plant flow, times a conversion factor (Table 2).

Table 1. PCB Concentrations in Final Effluents from Walla Walla WWTPs
(ng/L; parts per trillion)

	Date	Total PCBs
Walla Walla WWTP	5/28-30/02	0.88
	9/10-11/02	0.65
	12/2-3/02	0.75
	2/24-25/03	0.87
College Place WWTP	5/28-29/02	2.5
	9/10-11/02	0.92
	12/2-3/02	1.3
	2/24-25/03	0.53

Table 2. Wasteload and Load Allocations for PCBs in Garrison Creek and Mill Creek

	Mill Creek	Garrison Creek
Wasteload Allocation for WWTP (gm/day)	0.0062	0.0011
Load Allocation for Nonpoint (gm/day)	0.023	0.0017
Loading Capacity (gm/day)	0.029	0.0028

The cities of Walla Walla and College Place are concerned that these wasteload allocations are overly strict and would be prohibitively expensive to achieve. They have requested that additional PCB monitoring be done to verify the levels observed during the technical study and assess the source of contamination.

Project Description

The Ecology Environmental Assessment (EA) Program will monitor PCBs in influent and effluent from the Walla Walla and College Place WWTPs. Three pairs of composite samples will be collected from each facility during December 2006 through April 2007. The samples will be analyzed for PCB congeners* using low-level methods.

As a first step toward identifying PCB sources within the Walla Walla WWTP service area, an effort will be made to assess the relative importance of the four influent trunk lines that enter the plant. Composite samples will be collected from each trunk line in parallel with the influent and effluent sampling. These samples will also be analyzed for PCB congeners.

* In the United States, PCBs were primarily manufactured and sold under the trade name Aroclor. PCBs are typically analyzed as equivalent concentrations of commercial Aroclor mixtures (e.g., PCB-1254) or as individual compounds, referred to as PCB congeners. A congener analysis affords much lower detection limits than an Aroclor analysis.

Organization and Schedule

Organization

Name	Organization	Phone No.	Role
Brandi Lubliner	EAP-WES-TSU	360-407-7140	Project Lead
Art Johnson	EAP-WES-TSU	360-407-6766	QAPP Prep.
Steve Golding	EAP-WES-TSU	360-407-6701	Field Assistance
Donovan Gray	ERO-TMDL/WU	509-329-3458	Client
Dale Norton	EAP-WES-TSU	360-407-6765	Unit Supervisor
Dean Momohara	Manchester Laboratory	360-871-8808	Unit Supervisor
Karin Feddersen	Manchester Laboratory	360-871-8829	Contract Lab Services
Stuart Magoon	Manchester Laboratory	360-871-8801	Lab Director
Bill Kammin	EAP	360-407-6964	QA Officer
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Schedule

Field Work and Laboratory Analysis	
Sample Collection	December 2006, February 2007, April 2007
Lab Analyses Completed	June 2007
Final Report	
Report Author	Brandi Lubliner
Schedule	
Report Supervisor Draft Due	September 2007
Report Client/Peer Draft Due	October 2007
Report External Draft Due	November 2007
Report Final Due (Original)	December 2007
Environmental Information System (EIM) Data Set	
EIM Data Engineer	Carolyn Lee
EIM User Study ID	DTY C2224
EIM Study Name	PCB Monitoring at Walla Walla WWTPs
EIM Completion Due	December 2007

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that uncertainties are minimized and results are comparable to data from previous monitoring. These objectives will be achieved through careful attention to the sampling, measurement, and quality control (QC) procedures described in this plan.

Measurement Quality Objectives

The Ecology Manchester Laboratory and their contractors are expected to meet all QC requirements of the analytical methods being used for this project. Measurement quality objectives (MQOs) are shown in Table 3.

Table 3. Measurement Quality Objectives for Monitoring PCBs at Walla Walla WWTPs

Analysis	Check Stds./ Lab Control Samples (% recov.)	Duplicate Samples (RPD)	Labeled Congeners (% recov.)	Lowest Concentrations of Interest
PCB congeners	50 - 150	≤ 50	25 - 150	10 pg/L
TSS	80-120	<20	NA	1 mg/L
Conductivity	80-120	<20	NA	1 umhos/cm

NA = not applicable

Check standards and laboratory control samples (LCS) contain known amounts of analyte and indicate bias due to sample preparation and calibration. Results on duplicate (split) samples provide estimates of analytical precision.

The PCB congener analysis for this study is being done by an isotopic dilution method using labeled congeners. The 12 PCBs designated as toxic by the World Health Organization (also known as dioxin-like PCBs) and the earliest and latest eluted congener at each level of chlorination are determined by isotope dilution quantitation. The remaining congeners are determined by an internal standard quantitation technique.

The lowest concentrations of interest shown in Table 3 are those practically attainable within budget constraints of this project. It is anticipated that the concentrations encountered at the WWTPs will exceed these levels.

Sampling Design

The City of Walla Walla is authorized to discharge treated and disinfected effluent to Mill Creek from December 1 through April 30 of each year, subject to the effluent limits and conditions of its National Pollution Discharge Elimination System (NPDES) permit. The city is required by a 1927 court order to deliver up to 7.9 mgd of treated and disinfected wastewater to the Gose and Blallock Irrigation Districts from May 1 through November 30. The NPDES permit allows diversion of the effluent to the irrigation districts from April 15 through December 15. The irrigation districts can choose to use the effluent or divert it to Mill Creek.

College Place effluent is used for irrigation during the summer period (May - October). In November through April, the effluent is discharged directly to Garrison Creek.

Composite influent and effluent samples will be collected on three occasions at each facility during the periods the WWTPs discharge directly to receiving waters; once each during December 2006, February 2007, and April 2007. The composites will be taken over a two-day period. Effluent data obtained by the EA Program for other WWTPs has shown only minor variations in PCB concentrations over two-days (Golding, 2002). Each composite will consist of four grab samples: two in the morning and two in the afternoon. The grabs will be hand collected to avoid contamination that could occur with an auto-sampler. A similar set of samples will be collected for the four Walla Walla WWTP trunk lines. The specific location of the influent, effluent, and trunk line samples will be determined in consultation with the treatment plant operators and the Ecology Eastern Regional Office (ERO). To the extent practical, the influent and effluent grabs will be timed according to how long it takes wastewater to move through each facility.

The composites will be analyzed for PCBs, Total Suspended Solids (TSS), and conductivity, except trunk line samples will not be analyzed for TSS or conductivity. Low detection limits will be achieved by using a high-resolution gas chromatography/mass spectrometry (HRGC/MS) analysis for individual PCB congeners. TSS and conductivity are being included as routine wastewater parameters.

Sampling Procedures

Each composite will consist of two separate grabs per day (morning and afternoon) for two days. The grabs will be taken by hand using glass jars cleaned to EPA QA/QC specifications. Each grab will be used to fill a similarly cleaned one-gallon glass jar in 1/4 increments. The composites will be maintained on ice and in the dark during collection. The composites will be split into appropriate containers for PCB congeners, TSS, and conductivity. Sample containers, preservation, and holding times are shown in Table 4.

Table 4. Sample Containers, Preservation, and Holding Times for Wastewater Samples

Parameter	Container*	Preservation	Holding Time
PCBs	1 L amber glass; Teflon lid	Cool to 4°C	1 year [†]
TSS	1 L poly bottle	Cool to 4°C	7 days
Conductivity	500 mL poly bottle	Cool to 4°C	28 days

*Sample containers obtained from the analyzing laboratory

[†]After adjusting to pH 2-3 at laboratory

Field personnel will wear nitrile gloves at all times during sample collection and will follow standard health and safety procedures. Flow data will be obtained from WWTP records and the City of Walla Walla (trunk lines). The latitude and longitude of the sampling sites will be recorded from a GPS.

The PCB congener samples will be sent by Fed-Ex to arrive the following morning at a contract laboratory selected by the Ecology MEL. The TSS and conductivity samples will be returned to Ecology Headquarters (HQ) and held in a secure cooler for later transport to Manchester. Chain of custody will be maintained.

Measurement Procedures

Table 5 shows the numbers of samples to be analyzed, expected range of results, required reporting limits, and sample preparation and analysis methods. Methods were chosen that give reporting limits equal to or less than the lowest concentrations of interest. Reporting limits vary with congener. Other methods may be used by MEL or their contractors after consulting with the project lead.

Table 5. Laboratory Procedures for Monitoring PCBs at Walla Walla WWTPs

Analysis	Matrix	Field Samples*	Number of Expected Range of Results	Reporting Limit	Sample Prep Method
PCB congeners	Influent/Effluent	28	0.1 - 100 ng/L total PCBs	10 pg/L	NA
TSS	"	14	5 - 200 mg/L	1 mg/L	NA
Conductivity	"	14	400-800 umhos/cm	1 umos/cm	NA

*including field duplicates and field blanks (PCBs only)
 NA = not applicable

The City of Walla Walla has requested that the data from each sample collection be provided in time to decide if they want to obtain splits from the next round of samples. MEL will, therefore, need to arrange for laboratory analysis and data review to be completed within a two-month period.

Quality Control Procedures

The field and laboratory quality control (QC) samples to be analyzed for this project are shown in Table 6.

Table 6. QC Samples for PCB Monitoring at Walla Walla WWTPs

Parameter	Field		Laboratory			
	Blanks	Duplicate Samples	Check Std./LCS	Method Blanks	OPR Stds./Labelled Cmpds.	Lab Duplicate
PCBs (infl./effl.)	2/project	2/project	1/batch	1/batch	all samples	none
TSS	NA	2/project	1/batch	1/batch	NA	1/batch
Conduct	NA	2/project	1/batch	1/batch	NA	1/batch

Field QC Samples

QC samples for influent and effluent will consist of two transfer blanks and two duplicate (split) samples. The transfer blanks and duplicates will be submitted blind to the laboratory.

The transfer blank is intended to detect contamination arising from sample containers or sample handling. The blank will be prepared using a sample bottle filled with organic-free water by the analyzing laboratory. The bottle will be opened in the field and a portion of its contents transferred to a new bottle each time a corresponding grab is taken at that site, in essence mimicking the grab sampling procedure.

Duplicates will provide estimates of analytical variability. The duplicates will be prepared by filling two sample bottles from the same set of grabs. One influent and one effluent sample will be duplicated.

Laboratory QC Samples

The QC procedures routinely followed by MEL or required of its contractors will be satisfactory for purposes of this project.

Laboratory Cost Estimate

The laboratory cost associated with this project is estimated to be \$24,700 (Table 7). The cost estimate includes MEL's 25% surcharge for contract laboratory analyses and the 50% discount for samples analyzed at MEL.

Table 7. Laboratory Cost Estimate for PCB Monitoring at Walla Walla WWTPs

Location	Frequency	Sites	Field Blanks	Field Duplicate	PCB Congeners	TSS / Conduct.*	Totals
Walla Walla WWTP	3	6	1	1	875	18	17626
College Place WWTP	3	2	1	1	875	18	7126
						Total	\$24,752

*TSS and conductivity not analyzed for trunk lines

Data Management Procedures

Field data and observations will be recorded in a bound notebook of waterproof paper.

The data package from MEL will include a case narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated QC results. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met. This should include results for all check standards/LCS, method blanks, ORP standards/labeled compounds, and lab duplicates included in the sample batch.

All project data will be entered into Excel spreadsheets. All entries will be independently verified for accuracy by another individual on the project team.

All project data will be entered into Ecology's Environmental Information Management System (EIM). Data entered into EIM follow a formal Data Validation Review Procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

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

The PCB congener analyses will be contracted out to a laboratory accredited by Ecology for Method 1668A. The Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports and established that the laboratory has the capability to provide accurate, defensible data. Results of on-site assessments and proficiency testing studies are available from Ecology on request.

The following reports will be prepared for this project:

- 1) The data from each round of sampling will be provided to the City of Walla Walla and City of College Place, without interpretation, as soon as practical after review by MEL and the project lead.
- 2) A draft technical report will be prepared for review by Eastern Regional Office (ERO), stakeholders, and other interested parties on or before November 2007. The responsible staff member is Brandi Lubliner.
- 3) A final technical report is anticipated in December 2007. The responsible staff member is Brandi Lubliner.
- 4) The project data will be entered into Ecology's EIM System on or before December 2007. The responsible staff member is Carolyn Lee.

Data Verification and Validation

The contract laboratory will conduct a review of all laboratory data and case narratives. The contractor will verify that methods and protocols specified in this QAPP 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 holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. A case summary will meet the requirements for a data verification report.

To determine if project MQOs have been met, results for check standards/LCS, duplicate samples, and labeled compounds will be compared to QC limits. The field and method blanks' 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.

MEL and the project lead will review the laboratory data packages, verify the report, and validate the data. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

As noted previously, MEL is being requested to validate the data for each sample set and provide it to the project lead within two months from the time of sample collection.

Data Quality (Usability) Assessment

Once the data have been verified and validated, 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.

Data analysis will include, but not necessarily be limited to, compiling summary statistics and constructing plots to examine the distribution of the PCB concentrations detected in the samples and to compare PCB levels in the influent versus effluent. The PCB concentration/human health criterion ratio will be calculated for each effluent sample and displayed in dot density plots to illustrate the extent to which criteria are or are not exceeded. The PCB concentrations measured in the Walla Walla trunk lines will be compared among the four influent streams to rank them as sources.

References

Golding, S. 2002. Spokane Area Point Source PCB Survey, May 2001. Washington State Department of Ecology, Olympia, WA. Publication No. 02-03-009. www.ecy.wa.gov/biblio/0203009.html.

Gray, D., K. Baldwin, and A. Johnson. 2006. Walla Walla River Chlorinated Pesticide and PCBs Total Maximum Daily Load (Water Cleanup Plan). Washington State Department of Ecology, Olympia, WA. Publication No. 05-10-1295. www.ecy.wa.gov/biblio/05101295.html.

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