PCB Monitoring at Walla Walla and College Place Wastewater Treatment Plants, 2006-07

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PCB Monitoring at Walla Walla and College Place Wastewater Treatment Plants, 2006-07

by
Brandi Lubliner

Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

303(d) Listings Addressed in this Study:

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

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Abstract

This 2006-07 Department of Ecology study presents monitoring results for polychlorinated biphenyls (PCBs) in the influent, effluent, and sewer service networks of the Walla Walla and College Place Wastewater Treatment Plants (WWTPs).

The purpose of the study was to (1) establish whether effluent discharges currently exceed U.S. Environmental Protection Agency (EPA) human health water quality criteria, and (2) assess the extent to which the contamination is internal or external to each facility.

The study was done as a result of PCB wasteload allocations established through a 2005 Total Maximum Daily Load (water cleanup plan) for the Walla Walla River watershed.

The findings of this 2006-07 study indicate that the effluent concentrations are almost meeting the EPA human health criterion for PCBs.

The study assists the Cities of Walla Walla and College Place in identifying PCB sources within their service areas. The cities should continue to identify and clean up likely nonpoint (diffuse) sources of PCBs. This will reduce the influent concentrations of PCBS to the WWTPs as recommended in the Total Maximum Daily Load implementation schedule.

Acknowledgements

The author of this report would like to thank the following people for their contributions to this study:

- Waste Water Treatment Plant Operators: Bill Slovensky, William Breshears, and Bill Putnam.
- City of Walla Walla: Frank Nicholson.
- Washington State Department of Ecology Staff: Dan Dugger and Kristin Kinney for field sampling assistance.
- Karin Feddersen for detailed laboratory work and many consultations.
- Art Johnson for report contributions.
- Joan LeTourneau and Cindy Cook for formatting and editing the final report.

Introduction

In 1996, the Walla Walla River was listed by Washington State under Section 303(d) of the federal Clean Water Act for non-attainment of the Environmental Protection Agency human health criteria for 4,4'-DDE, 4,4'-DDD, dieldrin, chlordane, hexachlorobenzene, heptachlor epoxide, and PCB-1260 in edible fish tissue. The listings are based on sampling done by the Washington State Department of Ecology (Ecology) in 1993 (Davis et al., 1995). Chlorinated pesticides, their breakdown products, and polychlorinated biphenyls (PCBs) are no longer used in the United States, having been banned in the 1970s and 1980s for ecological concerns. These chemicals are now classed as probable human carcinogens by EPA.

In 2002-2003, Ecology initiated a Total Maximum Daily Load (TMDL) evaluation of chlorinated pesticides and PCBs in the Walla Walla River and its tributaries (Johnson et al., 2004). Wasteload and load allocations were assigned for PCBs in Garrison Creek and Mill Creek because of the PCB levels detected in the College Place and Walla Walla Wastewater Treatment Plant (WWTP) effluents (Table 1).

Table 1. 2002-2003 PCB Concentrations in Effluents from Walla Walla and College Place WWTPs (ng/L; parts per trillion).

WWTP	Date	Total PCBs (ng/L)
Walla Walla	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	5/28-29/02	2.5
	9/10-11/02	0.92
	12/2-3/02	1.3
	2/24-25/03	0.53

From Johnson et al., 2004.

The TMDL submittal report suggested that nonpoint (diffuse) sources coming into the WWTPs may be contributing to elevated PCB levels found in the WWTP effluent. Future remedial actions directed at nonpoint sources may help to alleviate the PCB problem in the discharges from the WWTPs (Gray et al., 2005).

The WWTP wasteload allocations were calculated as the product of the human health water quality criterion (0.17 ng/L) and the National Pollutant Discharge Elimination System permit limit for the average monthly effluent flow (Johnson et al., 2004) (Table 2). The remaining loading capacities of Mill Creek and Garrison Creek were allocated to nonpoint sources. The Walla Walla WWTP effluent discharges to Mill Creek, and the College Place WWTP discharges seasonally to Garrison Creek (Figure 1).

Table 2. TMDL Assigned Total PCB Wasteload and Load Allocations for Mill Creek and Garrison Creek (gm/day) (Johnson et al., 2004).

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

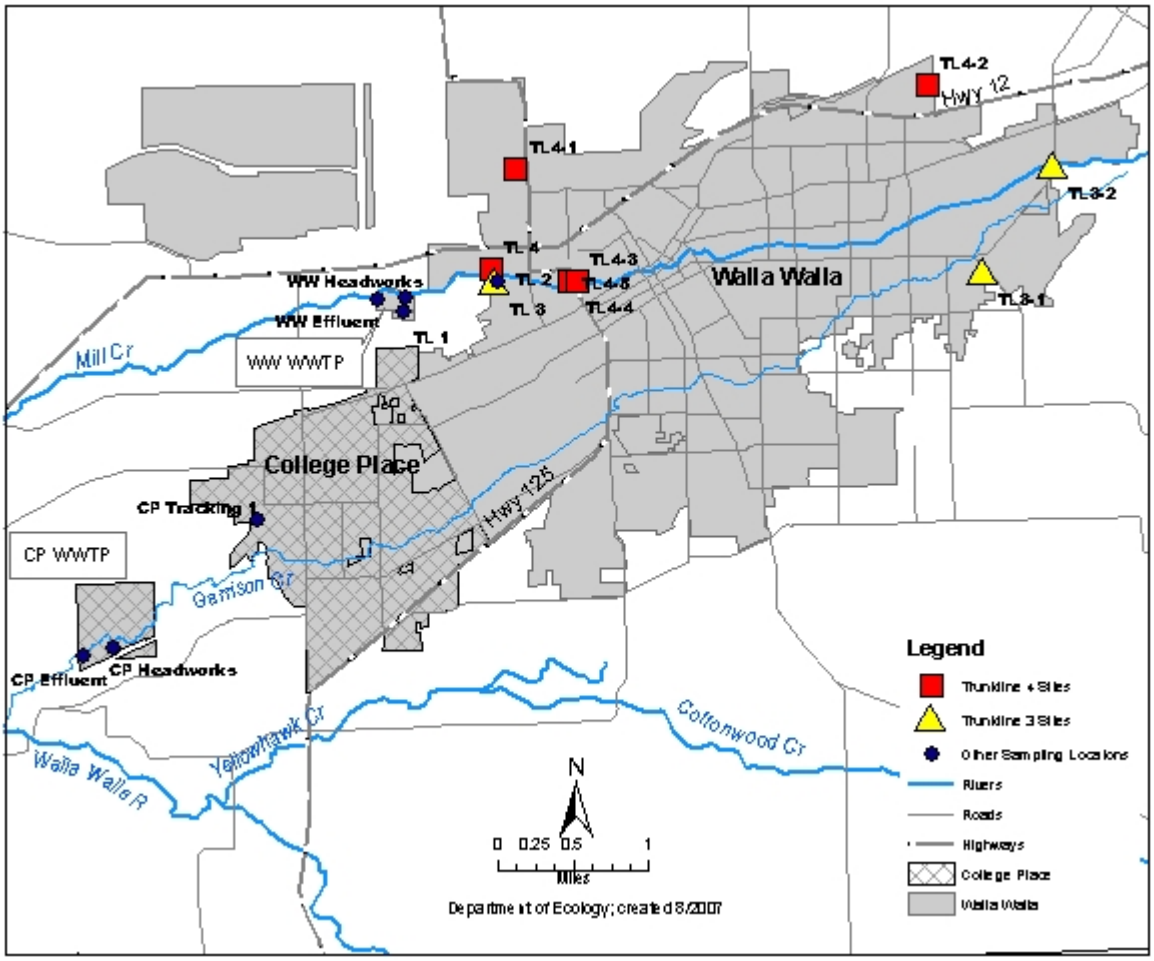

Figure 1. Map of WWTPs and Sewer Service Network Sampling Locations.

The cities of Walla Walla and College Place requested additional PCB monitoring be done to verify the levels observed during the TMDL study and to assess the source of contamination. In response, Ecology's Environmental Assessment Program monitored PCBs in influent and effluent from the Walla Walla and College Place WWTPs during 2006 - 2007. The goal of the study was to better characterize PCB loading and to assist the cities in identifying PCB sources within their service areas.

Flow data were obtained from WWTP records. The latitude and longitude of the sampling sites was recorded from a portable GPS unit.

Methods

In accordance with the Quality Assurance Project Plan (QAPP) for this project (Johnson, 2006), composite samples were collected on three occasions at each WWTP, once each during December 2006, February 2007, and April 2007. On all three occasions, the samples were collected from the influent and effluent from both WWTPs, as well as from the four incoming sewer service trunklines to the Walla Walla WWTP.

Wastewater samples from the sewer service network in Walla Walla and College Place, were analyzed for total suspended solids (TSS), conductivity, and PCB congeners[1]. The complete set of 209 PCB congeners includes the 12 most toxic PCBs (also known as dioxin-like PCBs), designated by the World Health Organization.

The samples were analyzed for PCBs by EPA Method 1668A, an isotopic dilution method using labeled congeners, which individually quantifies each PCB congener. This method was chosen as it may allow for enhanced source tracking of PCB sources throughout the sewer service network. Low detection limits for individual PCB congeners were achieved using a high-resolution gas chromatography/mass spectrometry (HRGC/MS) analysis. Total PCBs is reported as the sum of detected congeners, with no concentration given to non-detects.

The final number of samples taken in the study, laboratory methods used, range of results, and reporting limits can be found in Table 3.

Table 3. Laboratory Methods and Reporting Limits for Monitored Parameters.

Parameter	Number of Samples	Analytical Method	Range of Results	Reporting Limit	Analytical Laboratory
PCB Congeners	40	EPA Method 1668A	0.1 - 50 ng/L	0.013 ng/L	Pacific Rim Laboratories, Inc.
Total Suspended Solids	14	EPA Method 160.3 or SM 2540	1 - 240 mg/L	1 mg/L	Manchester Environmental Laboratory
Conductivity	14	EPA Method 120.1 or SM 2510B	290 - 670 µmhos/cm	1 µmhos/cm	Manchester Environmental Laboratory

At each sample site, composites were taken over a two-day period. Effluent data obtained by the Environmental Assessment Program for other WWTPs show only minor variations in PCB concentrations over two days (Golding, 2002). Influent and effluent samples were analyzed for PCB congeners, TSS, and conductivity. TSS and conductivity were included as routine wastewater parameters. The trunkline and other source tracking sites were analyzed for PCBs only.

[1] 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.

Each composite sample consisted of four grabs: two in the morning and two in the afternoon. The grabs were taken by hand using either clean[2] glass jars or clean[2] teflon-lined pole samplers. Each grab filled the sample container in 1/4 increments. Field personnel wore powder-free nitrile gloves at all times during sample collection, and field personnel followed standard health and safety procedures. The composites were maintained on ice and in the dark during collection and transport to Manchester Environmental Laboratory. The PCB congener samples were sent by Fed-Ex to Pacific Rim Laboratories, Inc., a contractor selected by Manchester Environmental Laboratory (MEL). Chain of custody was maintained.

Mid-study, Ecology's Water Quality Program provided additional funding for more samples to be collected in the source-tracking effort. Therefore, seven additional sites throughout the sewer service network were added to the final sampling run in April 2007. Figure 1 shows the location of the study sites. All field sites were selected in consultation with the WWTP operators, city engineers, and Ecology.

[2] Priority pollutant cleaning according to EPA Quality Assurance/Quality Control specifications (EPA, 1990) outlined in the Quality Assurance Project Plan for this project, (Johnson, 2006).

Data Quality

Manchester Environmental Laboratory (MEL) and Pacific Rim Laboratories, Inc. met all quality control (QC) requirements of the analytical methods outlined in the quality assurance project plan for this project (Johnson, 2006). All quality objectives were met, and data are considered usable for making calculations, determinations, and decisions for which the project was conducted. Case summaries of all data reports are provided in Appendix A. Complete data are available from the author on request.

Data Verification Review

MEL and the project lead extensively reviewed the contract laboratory methods, protocols, and results. This verification process includes checking that:

1. Holding times, instrument calibration, procedural blanks, laboratory control sample analyses, and appropriateness of data qualifiers assigned were acceptable and appropriate.
2. All calibrations, checks on quality control, and intermediate calculations were performed for all samples.
3. Data are consistent, correct, and complete, with no errors or omissions.
4. Targets for reporting limits have been met, and non-detects were not counted in the total PCB values.

Laboratory Quality Control (QC)

Data from this study were reviewed for qualitative and quantitative precision and bias following EPA method 1668A for PCBs, standard methods (SM) 2510B for conductivity, and SM2540D for TSS.

Calibration

All samples arrived at MEL within the appropriate timeframe for analysis and at the proper temperature, and were subsequently stored at 4°C. Conductivity and TSS calibrations and checks were performed in accordance with the appropriate method and were within acceptable limits.

The PCB calibration standards were within 20% relative standard deviations for target analytes and 35% for all the labeled internal standard compounds. Calibration recovery standards were within QC limits of 70 – 130% for target analytes, and 50-150% for the labeled reference compounds.

Internal Standard Recoveries

Internal standard compounds (referred to as ‘surrogates’), used to indicate bias due to sample preparation and calibration, were found to be within the method specified QC limits of 25-150% for all labeled compounds, with several exceptions. Congener results in the samples have been

qualified with “J” for detected analytes and “UJ” for non-detects showing a possible low bias. A high bias in detected congeners has been qualified with a “J”. Congener values qualified with “UJ” are not included in the corresponding homolog.

On-going Precision and Recovery

One liter of laboratory water was spiked with 1 ng each of 72 PCB congeners and carried through the extraction and clean-up procedure. Recoveries of all PCBs were within the acceptable range of 50-150%. These samples for conductivity and TSS were recovered within adequate ranges, indicating there were no interferences from the field samples to bias the results.

Method Blanks

Laboratory water known as the *method blank* is carried through the extraction and clean-up procedure. No analytically significant levels of analyte were detected in the blanks for conductivity and TSS.

Low levels of certain target compounds for PCBs were detected in method blanks and also in the samples. If the concentrations of a congener in a sample were less than ten times that of the corresponding method blank, a “UJ” qualifier was assigned to describe the result as not detected. A “J” is used to qualify the results of the totals for the corresponding homolog, indicating it is an estimated value. The values for these congeners are not included in the totals reported for either the corresponding homologue or the total PCBs. In cases where the sample concentration for a congener was greater than ten times that of the blank, the blank result is considered insignificant relative to the native concentrations detected in the sample.

Field Blanks

Two field blanks for PCBs only were analyzed to detect contamination arising from sample containers or sample handling. Field blanks were prepared by transferring a portion of organic-free water supplied by MEL from one bottle to another in the field, which mimicked the grab sampling procedure. One field blank was poured at each of the WWTPs. The field blank values were lower than the laboratory method blank values which indicate there was no container or sample handling contamination. Table 4 shows the values of the laboratory method blanks and the field transfer blanks.

Precision of Duplicate Samples

Two field duplicate samples were taken for PCBs, and one field duplicate was taken for TSS and conductivity. Field duplicates are samples taken side-by-side in the field.

Duplicates provide estimates of field and laboratory variability. Variability can be expressed as the relative percent difference (RPD) between a sample and its duplicate, Equation 1.

$$\textbf{RPD} = \left(\frac{\text{difference of 2 results}}{\text{mean}} \right) \times 100 \qquad \textbf{Equation 1}$$

Table 4 shows total PCB values for the blanks and field duplicate samples.

Table 4. Laboratory and Field Quality Control Data for Total PCBs (ng/L).

Date Sampled	Method Blanks	Field Blanks	WW_Trunkline_4 and Duplicate	CP_Effluent and Duplicate	WW_TL3-1 and Duplicate	Statistics
Dec 12-13, 2006	0.096	-	42.00	0.243	-	Sample
	-	-	49.50	0.266	-	Sample dup
	-	-	45.75	0.250	-	Mean
	-	-	16%	9%	-	RPD
	-	-	5.30	0.02	-	Standard deviation
Feb 13-14, 2007	0.048	0.03	-	-	-	Sample 1
	-	0.05	-	-	-	Sample 2
	-	0.04	-	-	-	Mean
	-	NA	-	-	-	RPD
	-	0.01	-	-	-	Standard Deviation
Apr 10-11, 2007	0.147	-	11.63	-	9.68	Sample
	0.111	-	11.08	-	9.18	Sample dup
	0.10*	-	11.36	-	9.43	Mean
	-	-	5%	-	5%	RPD
	0.040*	-	0.39	-	0.35	Standard deviation

Trunkline = Main feeder pipeline.
*Mean and standard deviation for all four method blank measurements.
Dup = duplicate.
RPD = relative percent difference.

Two sample bottles collected virtually at the same time are expected to be within 20% RPD for PCBs. A larger RPD would indicate a problem with the field collection, transportation, or potentially laboratory bias. The RPD for the two duplicated samples ranges from 5-16%, which is acceptable. The RPD for TSS and conductivity on the single College Place WWTP effluent sample was below 1% for both parameters. The RPD between field blank samples was not calculated because these samples were collected at two different WWTPs and are not intended to be duplicates.

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Results and Discussion

Influent and Effluent Concentrations

Influent and effluent samples taken during three time periods from the Walla Walla and College Place WWTPs were analyzed for PCBs, TSS, and conductivity. The results are summarized in Table 5.

Table 5. Influent and Effluent Results from Walla Walla and College Place WWTPs.

WWTP	Total PCBs (ng/L)		TSS (mg/L)		Conductivity (µmhos/cm)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Walla Walla						
Dec 12-13, 2006	44.10	0.40	180	1	363	292
Feb 13-14, 2007	11.10	0.48	158	1	417	336
Apr 10-11, 2007	8.86	0.25	129	1	370	293
Mean	*21.35*	*0.38*	*156*	*1*	*383*	*307*
College Place						
Dec 12-13, 2006	12.90	0.254*	240	1*	640	486*
Feb 13-14, 2007	22.60	0.336	218	1	628	482
Apr 10-11, 2007	10.74	0.35	181	1	673	462
Mean	*15.41*	*0.30*	*213*	*1*	*647*	*472*

* December effluent results are the mean of the sample and duplicate.

The mean effluent concentrations from Walla Walla and College Place WWTPs for total PCBs were 0.38 and 0.30 ng/L, respectively. The mean effluent TSS (1 mg/L) and conductivity (307-472 µmhos/cm) are within reasonable ranges for typical WWTP effluents. TSS adheres to the NPDES permit limits for both WWTPs.

All PCB influent concentrations are considerably higher than the effluent concentrations at the time these samples were collected. The WWTPs were reducing PCB concentrations by two orders of magnitude, most likely through the sediment removal processes, although this has not been verified.

Table 1 shows the 2002-03 PCBs effluent concentrations from the TMDL technical study (Johnson et al., 2004). In Table 6, the mean effluent concentrations of the two studies are compared to each other and to the mean values.

Table 6. Comparison of Mean Total PCB Concentrations (ng/L) for WWTP Effluents.

Sample	TMDL Study May 2002 to Feb 2003	This Study Dec 2006 to April 2007	One Standard Deviation
Walla Walla	0.79 ng/L	0.38 ng/L	0.12
College Place	1.31 ng/L	0.30 ng/L	0.05

The WWTPs effluents are now lower by a factor of 2 and 4.4 for Walla Walla and College Place, respectively. The 2005 TMDL report did explain that the College Place WWTP was experiencing a TSS upset when the TMDL samples were being collected. This may have led to the higher concentrations of PCBs detected as part of that study (Johnson et al., 2004).

Comparison to Human Health Criteria

A comparison between the effluent concentrations and the human health criteria is presented in Figure 2, data shown in Table 6.

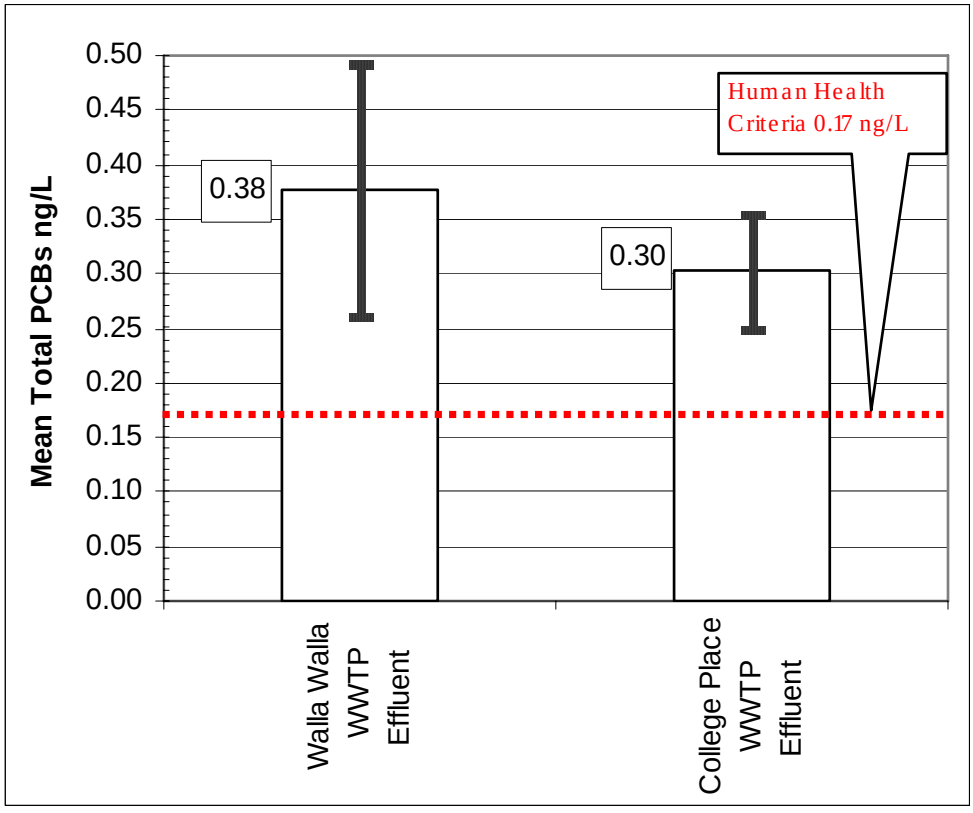

Figure 2. WWTP Effluents and the EPA Human Health Criteria for PCBs.

The error bars in Figure 2 represent one standard deviation from the mean. The PCB concentrations found in the WWTP effluents are relatively small and appear to have decreased since the TMDL study. The mean effluent concentrations for total PCBs at Walla Walla and College Place WWTPs exceeded the human health criterion of 0.17 ng/L total PCBs by factors of 2.2 and 1.8, respectively.

A rigorous statistical analysis of these data was not performed because it is evident that there are small differences in these small numbers. For example, just one standard deviation in the effluent data yields an exceedance of the criterion by only 0.08 ng/L. This number, although technically above the criterion, is not meaningfully significant. Given that there has already been an improvement in effluent concentrations between the TMDL and this study, it seems reasonable to conclude that the WWTPs are capable of meeting the human health criterion.

Source Tracking PCBs in the Sewer Service Network

In addition to sampling the influent and effluent at the WWTPs, this study assessed the relative importance of influent lines that enter the Walla Walla plant. One influent line to the College Place WWTP was also sampled. The results for total PCBs in the influent trunklines and other sewer service area sites sampled are provided in Table 7.

Table 7. Total PCB Concentrations for Sewage Samples Taken During the 2006-07 Study.

Location_ID	Dec 12-13, 2006	Feb 13-14, 2007	Apr 10-11, 2007	Overall Average
Walla Walla WWTP				
WW Headworks	44.10	11.10	8.86	21.35
WW Effluent	0.40	0.48	0.25	0.38
WW Trunkline 1	6.39	8.17	7.05	7.20
WW Trunkline 2	5.96	9.04	8.80	7.93
WW Trunkline 3	14.80	16.10	4.88	11.93
WW Trunkline 4	45.75*	9.92	11.35*	22.34
WW TL4-1	-	7.57	11.29	9.43
WW TL4-2	-	-	3.75	-
WW TL4-3	-	-	7.55	-
WW TL4-4	-	-	19.19	-
WW TL4-5	-	-	19.42	-
WW TL3-1	-	-	9.43*	-
WW TL3-2	-	-	16.69	-
College Place WWTP				
CP Headworks	12.90	22.60	10.74	15.41
CP Effluent	0.25*	0.34	0.35	0.31
CP TL1-1	-	-	15.47	-

*Mean of duplicate samples.

PCB concentrations measured in the Walla Walla trunklines are ranked in descending order of importance as sources of PCBs to the Walla Walla WWTP:

- Trunkline 4 – Tracking samples TL4-4 and TL4-5
- Trunkline 3 – Tracking sample TL3-2
- Trunkline 2
- Trunkline 1

Conclusions

The following conclusions are made as a result of this study:

- Both Walla Walla and College Place WWTPs were found to be reducing PCB concentrations by two orders of magnitude from influent to effluent samples.
- Effluent concentrations have improved since the 2005 TMDL study and are on track in meeting the EPA human health criterion. The observed exceedances of the criterion do not appear to be meaningfully significant.
- Improvements could be made in future studies of this nature. The detection limit (0.13 ng/L), the method blank "noise" level (0.14 ng/L, see Table 4), and the human health criterion are relatively close to one another.

Recommendation

The following recommendation is made as a result of this study:

- Two of the four Walla Walla influent trunklines (numbers 3 and 4) appear to have higher PCB concentrations than the other two trunklines. As a first priority, the city should work to identify PCB sources within the service area of trunklines 3 and 4.

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Appendix A. Case Summaries of All Data Reports

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Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

January 3, 2007

Subject: General Chemistry Walla Walla WWTP PCB - 50

Project No: 193206

Officer: Brandi Lubliner

By: Dean Momohara

Summary

The samples were analyzed by the following methods: Standard Methods (SM) 2540D for total suspended solids (TSS) and SM2510B for conductivity.

All analyses requested were evaluated by established regulatory quality assurance guidelines.

Sample Information

Samples were received by Manchester Environmental Laboratory on 12/14/06. All coolers were received within the proper temperature range of 0°C - 6°C. All samples were received in good condition. Five (5) samples were received and assigned laboratory identification numbers 504184, 504185 and 504187 – 504189.

Holding Times

All analyses were performed within established EPA holding times.

Calibration

Conductivity instrument calibrations and calibration checks were performed in accordance with the appropriate method. All initial and continuing calibration checks were within control limits. Oven temperatures were recorded before and after each analysis batch and were within acceptable limits.

Method Blanks

No analytically significant levels of analyte were detected in the method blanks associated with these samples.

Matrix Spikes

NA

Replicates

All associated duplicate relative percent differences of samples with concentrations greater than 5 times the reporting limit were within the acceptance range of 0% - 20%.

Laboratory Control Samples

All laboratory control sample recoveries were within the acceptance limits of 80% - 120%.

Other Quality Assurance Measures and Issues

U - The analyte was not detected at or above the reported result.

Bold - The analyte was present in the sample. (Visual Aid to locate detected compounds on report sheet.)

Please call Dean Momohara at (360) 871-8808 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory

7411 Beach Drive East, Port Orchard Washington 98366

January 5, 2007

Subject:	**Walla Walla WWTP – Part I**
Samples:	06- 504180 through 504185, 504187, 504188
Project ID:	1932-06
Laboratory:	Pacific Rim Laboratories, Inc.
Project Officer:	Brandi Lubliner
By:	Karin Feddersen KF

Data Review for PCB Congener and PCB Equivalent Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and bias following EPA method 1668A.

Samples were prepared and analyzed according to EPA method 1668A.
Results have been reported in picograms per Liter (pg/L).

Several groups of congeners coelute. The reported value is a sum total of all the coeluting congeners.

Holding Times

EPA method 1668A allows storage of samples for one year from the date of collection if stored in the dark at 0-4 °C. Extraction and analysis took place within this time frame. The samples were verified to be at the proper temperature upon receipt at the contract lab, and were subsequently stored at 4 °C.

Blanks

Low levels of certain target compounds were detected in the laboratory blanks. These congeners were also detected in the samples. If the concentration of a congener in a sample was less than ten times that of the corresponding method blank, a "UJ" qualifier was added to the result, or "J" for totals of each homolog. In cases where the sample concentration for a congener was greater than ten times that of the blank, the blank result is considered insignificant relative to the native concentration detected in the sample. No qualification is warranted in these situations.

Calibration

The calibration standards were within 20% relative standard deviations (RSD) for all target analytes and 35% for all the labeled reference compounds (Internal Standards).

All calibration verification standard recoveries were within QC limits of 70% to 130% for target analytes and 50% to 150% for the labeled reference compounds.

All the ion abundance ratios and relative retention times were within QC criteria.

Internal Standard Recoveries

Recoveries for these samples were all within the method specified QC limits of 25% to 150% for all labeled compounds.

Ion abundance ratios

Each congener reported as detected met the isotopic abundance ratio and retention time criteria for positive identification with several exceptions; results for which have been qualified "N" or "NJ". The values reported for these congeners are not included in the totals for the corresponding homolog.

On-going Precision and Recovery (OPR)

Target analyte recoveries were within quality control limits of 50 to 150%. Labeled compound recoveries were within quality control limits of 30 to 140%.

Data Qualifier Codes

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R {REJ} - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

SAMPLE RECEIPT FORM / CHEMICAL ANALYSIS FORM

FILE #: PR61266

CLIENT: WA Dept. of Ecology
Manchester Laboratory
7411 Beach Drive East
Port Orchard WA 98366-8204
USA

Phone – 360-871-8829
Email: KFED461@ecy.wa.gov

RECEIVED BY: D. Hope **DATE/TIME:** December 15 KF ~~April 19~~, 2006 (1:00 p.m.)

CONDITION: okay, temperature 2 °C

# of Containers	Sample Type	Sample (Client Codes)	Lab Codes	Test Requested
2	water	50-4188	PR61266	PCB congeners
1	water	50-4187	PR61267	PCB congeners
1	water	50-4185	PR61268	PCB congeners
1	water	50-4184	PR61269	PCB congeners
1	water	50-4181	PR61270	PCB congeners
1	water	50-4182	PR61271	PCB congeners
1	water	50-4180	PR61272	PCB congeners
2	water	50-4183	PR61273	PCB congeners

STORAGE: Stored at 4 °C
ANALYTES: HRGC/HRMS analysis for 209 congener PCB

SPECIAL INSTRUCTIONS: PQL: 10 pg/L

METHODOLOGY
Reference Method: PCB: SOP LAB02, EPA Method 1668a

Data summarized in Data Report Attached

Report sent to: Karin Feddersen Date: December 29, 2006

Case Narrative – PCBs

Sample Preparation
Samples were analyzed in one batch commencing on December 15, 2006. The batch consisted of eight samples, two duplicate samples, a blank and a spike (LCS). Approximately 1 L of water was spiked with 2 ng each of 27 carbon-13 labelled PCB surrogates and extracted with 3 x 100 mL dichloromethane. The extract was collected in a 500 mL boiling flask and concentrated to 1 mL by rotary evaporator. The sample was reconstituted in 5 mL of hexane and placed in a vial to which 10 mL of concentrated H_2SO_4 is added. Clean-up standard is added at this time (5 ng, note the analyst was suppose to put in 2 ng but mistakenly put in 5 ng). It is vigorously shaken and left sit overnight to allow the layers to separate. The extract is then cleaned up in a mixed bed silica gel column (basic, neutral and acidic silica gel). If color persists on the column it is repeated. Final cleanup is with basic alumina. The eluate from the alumina column is concentrated by rotary evaporator to 2 mL and final reduction to 20 µL is by a gentle stream of nitrogen. Recovery standard (2 ng) is added and the final volume made up to 20 µL.

Instrument Calibration
All samples were analysed on a Micromass Ultima "M" series high resolution mass spectrometer coupled with an HP5890 Series II gas chromatograph. The column used was a 60 m DB5-MS, 0.25 µm, 0.25 mm i.d.

1. All LOC/Toxic CBs are calibrated as per EPA 1668a §10.4.

An initial five point calibration (CS-LO, CS-1 to CS-4) consisting of the first and last eluting congener in for each homolog plus the twelve toxic PCBs was run covering the range of 0.2 ng/mL to 400 ng/mL. Surrogate and recovery standards are kept at a constant 100 ng/mL. CS-5 (2000 ng/mL) was run but not used as the calibration worksheet only allows for 6 data sets (CS-LO, CS-1 to CS-4 and CS-209)

- CS-5 was run and data is submitted as a CalVer. With the exception of the MoCB, it meets all requirements of a CalVer, therefore it can be assumed that the instrument is linear to the CS-5 level (2000 ng/mL). It should be noted that no analyte exceeds CS-4 levels.
- Internal standards were quantified relative to the Recovery Standard in the same function as follows:
    - Function 1: no recovery standard in this function therefore use PCB-009L as per method.
    - Function 2: use PCB-009L as per method for PCB004L and PCB015L
    - Function 3: use PCB-052L as per method for PCB019L, PCB037L and PCB054L. Also use for PCB104L.
    - Function 4: use PCB-101L as per method for PCB123L, PCB118L. Also use for PCB081L, PCB077L and PCB155L.
    - Function 5: use PCB-138L as per method for PCB167L, PCB156L, PCB157L, PCB169L and PCB188L. Also use for PCB114L, PCB105L,

PCB126L and PCB202L. The calibration table was incorrectly set up for PCB188L, using PCB-194L rather than PCB-138L. Manual calculations were done using PCB-138L. A copy of the spreadsheet is given behind the RRF table.

- Function 6: use PCB-194L as per method for PCB189L, PCB205L, PCB206L, PCB208L and PCB209L

2. All other CBs are calibrated by internal standard as per EPA 1668a §10.5 with the following exceptions:

- All other CBs are calibrated against the average response for all internal standards in a given LOC. OpusQuan only allows for two Internal Standards to be averaged, whereas the method lists three for the TeCBs, six of the PeCBs and five for the HxCBs. Factors to convert from two IS to multiple IS were determined, firstly within the cali table, and then for the samples. The two factors were combined and then used to recalculate the data. All factors are listed on the OpusQuan sheets.
- Concentrations for natives and internal standards are as follows:
  - MoCB, DiCB and TriCB @ 25 ng/mL
  - TeCB, PeCB, HxCB and HpCB @ 50 ng/mL
  - OcCB, NoCB @ 75 ng/mL
  - All internal standards @ 100 ng/mL

Calibration Verification

The calibration was verified at the beginning and ending of every run or every 12 hours with a mid-point standard (CS-3, 50 ng/mL). All CalVer's were acceptable. A CS-LO was run at the end of the run and is also presented as a CalVer. It meets criteria.

Mass Resolution

The high resolution mass spectrometer was operated at a resolution of >10,000 This resolution was checked every 12 hours and documented in hardcopy

Results

Data could not be quantified in one pass with OpusQuan (quantification program) because of the limitation of analytes in a run table (72). Therefore five separate quantification programs were used as follows:

- P2091, MoCB and DiCB
- P2092, TrCB and TeCB
- P2093, PeCB
- P2094, HxCB
- P2095, HpCB, OcCB, NoCB and DeCB.

For the purpose of this data, Reporting Limits/Detection Limits were set at 10 pg/L (PQL) for all analytes except the dioxin-like PCBs where the limit was set at 2-3 pg/L. All data between 2-10 pg/L was "J" flagged.

Any data that failed to meet acceptable ion ratios has been flagged with an N.

Surrogate Recoveries
Recoveries were acceptable (25-150%) for the samples,

All clean-up standards met acceptable recoveries (30-135%) for samples. Note that PCB-178L was recalculated against IS PCB138L. The calibration table was incorrectly set up for PCB178L (Function 5), using PCB-194L (Function 6) rather than PCB-138L (Function 5). Manual calculations were done using PCB-138L. A copy of the spreadsheet is given behind the RRF table.

QC Samples

Blanks
One blank carried through the extraction and clean-up procedure. PC06653B showed trace amounts of a number of CBs. Analytes are "B" flagged if the data point is <10x the level found in the blank.

Spikes
One litre of lab water was spiked with 1 ng each of 72 PCB congeners and carried through the extraction and clean-up procedures. Recoveries of all toxic PCBs and window defining PCBs were within the acceptable range of 50-150%. All of the other PCBs were also within that range.

David Hope, CEO

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

February 22, 2007

Subject: General Chemistry Walla Walla WWTP

Project No: 113207

Officer: Brandi Lubliner

By: Dean Momohara

Summary

The samples were analyzed by the following methods: Standard Methods (SM) 2540D for total suspended solids (TSS) and SM2510B for conductivity.

All analyses requested were evaluated by established regulatory quality assurance guidelines.

Sample Information

Samples were received by Manchester Environmental Laboratory on 2/15/07. All coolers were received within the proper temperature range of 0°C - 6°C. All samples were received in good condition. Four (4) samples were received and assigned laboratory identification numbers 074184, 074185, 074187 and 074188.

Holding Times

All analyses were performed within established EPA holding times.

Calibration

Conductivity instrument calibrations and calibration checks were performed in accordance with the appropriate method. All initial and continuing calibration checks were within control limits. Oven temperatures were recorded before and after each analysis batch and were within acceptable limits.

Method Blanks

No analytically significant levels of analyte were detected in the method blanks associated with these samples.

Matrix Spikes

NA

Replicates

All associated duplicate relative percent differences of samples with concentrations greater than 5 times the reporting limit were within the acceptance range of 0% - 20%.

Laboratory Control Samples

All laboratory control sample recoveries were within the acceptance limits of 80% - 120%.

Other Quality Assurance Measures and Issues

U - The analyte was not detected at or above the reported result.

Bold - The analyte was present in the sample. (Visual Aid to locate detected compounds on report sheet.)

Please call Dean Momohara at (360) 871-8808 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory

7411 Beach Drive East, Port Orchard Washington 98366

March 29, 2007

Subject:	**Walla Walla WWTP – Part II**
Samples:	07- 074180 through 074190
Project ID:	1132-07
Laboratory:	Pacific Rim Laboratories, Inc.
Project Officer:	Brandi Lubliner
By:	Karin Feddersen

Data Review for PCB Congener and PCB Equivalent Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and bias following EPA method 1668A.

Samples were prepared and analyzed according to EPA method 1668A.
Results have been reported in picograms per Liter (pg/L).

Several groups of congeners coelute. The reported value is a sum total of all the coeluting congeners.

Holding Times

EPA method 1668A allows storage of samples for one year from the date of collection if stored in the dark at 0-4 °C. Extraction and analysis took place within this time frame. The samples were verified to be at the proper temperature upon receipt at the contract lab, and were subsequently stored at 4 °C.

Blanks

Low levels of certain target compounds were detected in the laboratory blanks. These congeners were also detected in the samples. If the concentration of a congener in a sample was less than ten times that of the corresponding method blank, a "UJ" qualifier was added to the result; and "J" for totals of each corresponding homolog. In cases where the sample concentration for a congener was greater than ten times that of the blank, the blank result is considered insignificant relative to the native concentration detected in the sample. No qualification is warranted in these situations.

Calibration

The calibration standards were within 20% relative standard deviations (RSD) for all target analytes and 35% for all the labeled reference compounds (Internal Standards).

All calibration verification standard recoveries were within QC limits of 70% to 130% for target analytes and 50% to 150% for the labeled reference compounds.

All the ion abundance ratios and relative retention times were within QC criteria.

Internal Standard Recoveries

Recoveries for these samples were all within the method specified QC limits of 25% to 150% for all labeled compounds with several exceptions. Congener results that use the affected labeled compounds for quantification as in Table 2 of method 1668A have been qualified. Analytes showing a possible low bias have been qualified with "J" for detected analytes and "UJ" for non-detects. Congeners that may have been biased high have been qualified with "J" when the affected congener was detected.

Ion abundance ratios

Each congener reported as detected met the isotopic abundance ratio and retention time criteria for positive identification with several exceptions; results for which have been qualified "N" or "NJ". The values reported for these congeners are not included in the totals for the corresponding homolog.

On-going Precision and Recovery (OPR)

Target analyte recoveries were within quality control limits of 50 to 150%. Labeled compound recoveries were within quality control limits of 30 to 140%.

Data Qualifier Codes

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

SAMPLE RECEIPT FORM / CHEMICAL ANALYSIS FORM

FILE #: PR70261

CLIENT: WA Dept. of Ecology
Manchester Laboratory
7411 Beach Drive East
Port Orchard WA 98366-8204
USA

Phone – 360-871-8829
Email: KFED461@ecy wa gov

RECEIVED BY: P. Aceveda **DATE/TIME:** February 23, 2007 (10:45 a.m.)

CONDITION: okay, temperature 10 °C

# of Containers	Sample Type	Sample (Client Codes)	Lab Codes	Test Requested
1	water	074180	PR70261	PCB congeners
1	water	074181	PR70262	PCB congeners
1	water	074182	PR70263	PCB congeners
1	water	074183	PR70264	PCB congeners
1	water	074184	PR70265	PCB congeners
1	water	074185	PR70266	PCB congeners
1	water	074186	PR70267	PCB congeners
1	water	074187	PR70268	PCB congeners
1	water	074188	PR70269	PCB congeners
1	water	074189	PR70270	PCB congeners
1	water	074190	PR70271	PCB congeners

STORAGE: Stored at 4 °C
ANALYTES: HRGC/HRMS analysis for 209 congener PCB

SPECIAL INSTRUCTIONS: PQL: 10 pg/L

METHODOLOGY
Reference Method: PCB: SOP LAB02, EPA Method 1668a

Data summarized in Data Report Attached

Report sent to: Karin Feddersen Date: March 20, 2007

Case Narrative – PCBs

Sample Preparation
Samples were analyzed in one batch commencing on February 26, 2007. The batch consisted of eleven samples, a blank and a spike (LCS). Approximately 1 L of water was spiked with 2 ng each of 27 carbon-13 labelled PCB surrogates and extracted with 3 x 100 mL dichloromethane. The extract was collected in a 500 mL boiling flask and concentrated to 1 mL by rotary evaporator. The sample was reconstituted in 5 mL of hexane and placed in a vial to which 10 mL of concentrated H_2SO_4 is added. Clean-up standard is added at this time (2 ng). It is vigorously shaken and left sit overnight to allow the layers to separate. The extract is then cleaned up in a mixed bed silica gel column (basic, neutral and acidic silica gel). If color persists on the column it is repeated. Final cleanup is with basic alumina. The eluate from the alumina column is concentrated by rotary evaporator to 2 mL and final reduction to 20 µL is by a gentle stream of nitrogen. Recovery standard (2 ng) is added and the final volume made up to 20 µL.

Instrument Calibration
All samples were analysed on a Micromass Ultima "M" series high resolution mass spectrometer coupled with an HP5890 Series II gas chromatograph. The column used was a 60 m DB5-MS, 0.25 µm, 0.25 mm i.d.

1. All LOC/Toxic CBs are calibrated as per EPA 1668a §10.4.

An initial six point calibration (CS-LO, CS-1 to CS-5) consisting of the first and last eluting congener in for each homolog plus the twelve toxic PCBs was run covering the range of 0.2 ng/mL to 2000 ng/mL. Surrogate and recovery standards are kept at a constant 100 ng/mL.

- CS-5 was run and data is submitted as a CalVer. With the exception of the MoCB, it meets all requirements of a CalVer, therefore it can be assumed that the instrument is linear to the CS-5 level (2000 ng/mL). It should be noted that no analyte exceeds CS-4 levels.
- Internal standards were quantified relative to the Recovery Standard in the same function as follows:
  - Function 1: no recovery standard in this function therefore use PCB-009L as per method.
  - Function 2: use PCB-009L as per method for PCB004L and PCB015L
  - Function 3: use PCB-052L as per method for PCB019L, PCB037L and PCB054L. Also use for PCB104L.
  - Function 4: use PCB-101L as per method for PCB123L, PCB118L. Also use for PCB081L, PCB077L and PCB155L.
  - Function 5: use PCB-138L as per method for PCB167L, PCB156L, PCB157L, PCB169L and PCB188L. Also use for PCB114L, PCB105L, PCB126L and PCB202L
  - Function 6: use PCB-194L as per method for PCB189L, PCB205L, PCB206L, PCB208L and PCB209L

2. All other CBs are calibrated by internal standard as per EPA 1668a §10.5 with the following exceptions:

- DiCB were calibrated using a single ion rather than the sum of two ions as specified in the method. There are three possible ions to monitor for DiCB, in a sensitivity ratio of 10:3:1. The less sensitive windows had too much background noise to make quantification useful, therefore they were not used.
- All other CBs are to be calibrated against the average response for all internal standards in a given LOC. OpusQuan only allows for two Internal Standards to be averaged, whereas the method lists three for the TeCBs, six of the PeCBs and five for the HxCBs. Factors to convert from two IS to multiple IS were determined, firstly within the cali table, and then for the samples. The two factors were combined and then used to recalculate the data. All factors are listed on the OpusQuan sheets.
- Concentrations for natives and internal standards are as follows:
    - MoCB, DiCB and TriCB @ 25 ng/mL
    - TeCB, PeCB, HxCB and HpCB @ 50 ng/mL
    - OcCB, NoCB @ 75 ng/mL
    - All internal standards @ 100 ng/mL

Calibration Verification

The calibration was verified at the beginning and ending of every run or every 12 hours with a mid-point standard (CS-3, 50 ng/mL). All CalVer's were acceptable

Mass Resolution

The high resolution mass spectrometer was operated at a resolution of >10,000. This resolution was checked every 12 hours and documented in hardcopy.

Results

Data could not be quantified in one pass with OpusQuan (quantification program) because of the limitation of analytes in a run table (72). Therefore five separate quantification programs were used as follows:

- P2091, MoCB and DiCB
- P2092, TrCB and TeCB
- P2093, PeCB
- P2094, HxCB
- P2095, HpCB, OcCB, NoCB and DeCB.

For the purpose of this data, Reporting Limits/Detection Limits were set at 10 pg/L (PQL) for all analytes except the dioxin-like PCBs where the limit was set at 2-3 pg/L. All data between 2-10 pg/L was "J" flagged.

Any data that failed to meet acceptable ion ratios has been flagged with an N.

Standard Recoveries

Recoveries were acceptable (25-150%) for the samples with the following exceptions:

- Low recoveries are noted for volatile CBs. These are likely lost during the concentration steps Only one labelled CB in any given level of chlorination is low.
    - PR70267 (074186) – PCB015L, PCB019L, PCB054L
    - PR70269 (074188) – PCB001L, PCB015L
    - PR70270 (074189) – PCB001L, PCB015L
- High recoveries (>150%) are noted for PCB-209L. The CalVers bracketing the samples range from +6.8% to -15 0% which may indicate a matrix interference.
    - PR70261 (074180) – 150.4%
    - PR70264 (074183) – 210 6%
    - PR70265 (074184) – 172.4%

All clean-up standards met acceptable recoveries (30-135%) for samples.

QC Samples

Blanks

One blank carried through the extraction and clean-up procedure. PC06653B showed trace amounts of a number of CBs. Analytes are "B" flagged if the data point is <10x the level found in the blank

Spikes

One litre of lab water was spiked with 1 ng each of 72 PCB congeners and carried through the extraction and clean-up procedures. Recoveries of all toxic PCBs and window defining PCBs were within the acceptable range of 50-150%. All of the other PCBs were also within that range.

David Hope, CEO

Pacific Rim Laboratories Inc #103, 19575-55A Avenue, Surrey, BC V3S 8P8
Tel: + 604 532 8711 Fax: + 604 532 8712 Email: info@pacificrimlabs com
www.pacificrimlabs.com

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative

April 25, 2007

Subject: General Chemistry Walla Walla WWTP PCB - 15

Project No: 131506

Officer: Brandi Lubliner

By: Dean Momohara

Summary

The samples were analyzed by the following methods: Standard Methods (SM) 2540D for total suspended solids (TSS) and SM2510B for conductivity.

All analyses requested were evaluated by established regulatory quality assurance guidelines.

Sample Information

Samples were received by Manchester Environmental Laboratory on 04/13/07. All coolers were received within the proper temperature range of 0°C - 6°C. All samples were received in good condition. Four (4) samples were received and assigned laboratory identification numbers 154184, 154185, 154187 and 154188.

Holding Times

All analyses were performed within established EPA holding times.

Calibration

Conductivity instrument calibrations and calibration checks were performed in accordance with the appropriate method. All initial and continuing calibration checks were within control limits. Oven temperatures were recorded before and after each analysis batch and were within acceptable limits.

Method Blanks

No analytically significant levels of analyte were detected in the method blanks associated with these samples.

Matrix Spikes

NA

Replicates

All associated duplicate relative percent differences of samples with concentrations greater than 5 times the reporting limit were within the acceptance range of 0% - 20%

Laboratory Control Samples

All laboratory control sample recoveries were within the acceptance limits of 80% - 120%

Other Quality Assurance Measures and Issues

U - The analyte was not detected at or above the reported result.

Bold - The analyte was present in the sample. (Visual Aid to locate detected compounds on report sheet.)

Please call Dean Momohara at (360) 871-8808 to further discuss this project.

cc: Project File

Manchester Environmental Laboratory

7411 Beach Drive East, Port Orchard Washington 98366

July 6, 2007

Subject:	**Walla Walla WWTP – Part III**
Samples:	07- 154180 through 154190
Project ID:	1315-07
Laboratory:	Pacific Rim Laboratories, Inc.
Project Officer:	Brandi Lubliner
By:	Karin Feddersen KF

Data Review for PCB Congener and PCB Equivalent Analysis

Summary

Data from these analyses were reviewed for qualitative and quantitative precision and bias following EPA method 1668A.

Samples were prepared and analyzed according to EPA method 1668A

Results have been reported in picograms per Liter (pg/L).

Several groups of congeners coelute. The reported value is a sum total of all the coeluting congeners.

Holding Times

EPA method 1668A allows storage of samples for one year from the date of collection if stored in the dark at 0-4 °C. Extraction and analysis took place within this time frame. The samples were verified to be at the proper temperature upon receipt at the contract lab, and were subsequently stored at 4 °C.

Blanks

Low levels of certain target compounds were detected in the laboratory blanks. These congeners were also detected in the samples. If the concentration of a congener in a sample was less than ten times that of the corresponding method blank, a "UJ" qualifier was added to the result; and "J" for totals of each corresponding homolog. In cases where the sample concentration for a congener was greater than ten times that of the blank, the blank result is considered insignificant relative to the native concentration detected in the sample. No qualification is warranted in these situations.

Calibration

The calibration standards were within 20% relative standard deviations (RSD) for all target analytes and 35% for all the labeled reference compounds (Internal Standards).

All calibration verification standard recoveries were within QC limits of 70% to 130% for target analytes and 50% to 150% for the labeled reference compounds, and all the ion abundance ratios and

relative retention times were within QC criteria with one exception. The ion abundance ratios were low for one calibration verification standard, (most likely due to matrix interference), causing the analyte recoveries to be high. The associated samples were reanalyzed; however the ending calibration verification standard now had low recoveries due to high ion abundance ratios. The sample results were unchanged between the two analyses. Therefore, only the results from the first analysis were reported.

Internal Standard (IS) Recoveries (referred to as "surrogates in Pacific Rim's narrative)

Recoveries for these samples were all within the method specified QC limits of 25% to 150% for all labeled compounds with one exception in several samples.

The lock mass issues mentioned in Pacific Rim's case narrative may cause a high bias for results which use in their calculation. However none of these analytes were detected in the associated samples, so no qualification was required. PCB-15L could not be quantitated at all due to interference in sample 154191; the result has been qualified as "NC".

Ion abundance ratios

Each congener reported as detected met the isotopic abundance ratio and retention time criteria for positive identification with several exceptions; results for which have been qualified "N". The values reported for these congeners are not included in the totals for the corresponding homolog.

On-going Precision and Recovery (OPR)

Target analyte recoveries were within quality control limits of 50 to 150%. Labeled compound recoveries were within quality control limits of 30 to 140%. Analytes showing a possible low bias have been qualified with "J" for detected analytes and "UJ" for non-detects. Congeners that may have been biased high have been qualified with "J" when the affected congener was detected. Non-detect results are unaffected in these cases.

Data Qualifier Codes

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".

NC - Not calculated.

Case Narrative – PCBs

Sample Preparation
Samples were analyzed in two batches commencing on April 30th and May 1st, 2007. Each batch consisted of nine samples, a blank and a spike (LCS). Approximately 1 L of water was spiked with 2 ng each of 27 carbon-13 labelled PCB surrogates and extracted with 3 x 100 mL dichloromethane. The extract was collected in a 500 mL boiling flask and concentrated to 1 mL by rotary evaporator. The sample was reconstituted in 5 mL of hexane and placed in a vial to which 10 mL of concentrated H_2SO_4 is added. Clean-up standard is added at this time (2 ng). It is vigorously shaken and left sit overnight to allow the layers to separate. The extract is then cleaned up in a mixed bed silica gel column (basic, neutral and acidic silica gel). If color persists on the column it is repeated. Final cleanup is with basic alumina. The eluate from the alumina column is concentrated by rotary evaporator to 2 mL and final reduction to 20 µL is by a gentle stream of nitrogen. Recovery standard (2 ng) is added and the final volume made up to 20 µL.

Instrument Calibration
All samples were analysed on a Micromass Ultima "M" series high resolution mass spectrometer coupled with an HP5890 Series II gas chromatograph. The column used was a 60 m DB5-MS, 0.25 µm, 0.25 mm i.d.

1. All LOC/Toxic CBs are calibrated as per EPA 1668a §10.4.

An initial six point calibration (CS-LO, CS-1 to CS-5) consisting of the first and last eluting congener in for each homolog plus the twelve toxic PCBs was run covering the range of 0.2 ng/mL to 2000 ng/mL. For MoCB and DiCB, CS-5 saturated the detector and was eliminated from the calibration. Surrogate and recovery standards are kept at a constant 100 ng/mL.

- Internal standards were quantified relative to the Recovery Standard in the same function as follows:
  - Function 1: no recovery standard in this function therefore use PCB-009L as per method.
  - Function 2: use PCB-009L as per method for PCB004L and PCB015L.
  - Function 3: use PCB-052L as per method for PCB019L, PCB037L and PCB054L. Also use for PCB104L.
  - Function 4: use PCB-101L as per method for PCB123L, PCB118L. Also use for PCB081L, PCB077L and PCB155L.
  - Function 5: use PCB-138L as per method for PCB167L, PCB156L, PCB157L, PCB169L and PCB188L. Also use for PCB114L, PCB105L, PCB126L and PCB202L.
  - Function 6: use PCB-194L as per method for PCB189L, PCB205L, PCB206L, PCB208L and PCB209L.

2. All other CBs are calibrated by internal standard as per EPA 1668a §10.5 with the following exceptions:

- All CBs are to be calibrated against the average response for all internal standards in a given LOC. OpusQuan only allows for two Internal Standards to be averaged, whereas the method lists three for the TeCBs, six of the PeCBs and five for the HxCBs. Factors to convert from two IS to multiple IS were determined, firstly within the cali table, and then for the samples. The two factors were combined and then used to recalculate the data. All factors are listed on the OpusQuan sheets.

- Concentrations for natives and internal standards are as follows:
  - MoCB, DiCB and TriCB @ 25 ng/mL
  - TeCB, PeCB, HxCB and HpCB @ 50 ng/mL
  - OcCB, NoCB @ 75 ng/mL
  - All internal standards @ 100 ng/mL

Calibration Verification

The calibration was verified at the beginning and ending of every run or every 12 hours with a mid-point standard (CS-3, 50 ng/mL). All CalVer's were acceptable with the exception of $^{13}C_{12}$-MoCB in HRMS file UT03874s1, which gave an ion ratio about half of the expected. The samples associated with this CalVer were reanalyzed a few days later, however there were also problems with the CalVer run immediately following the samples. This time the ratio for the $^{13}C_{12}$-MoCB was high by 10-15%. The data was not repeated a third time.

Mass Resolution

The high resolution mass spectrometer was operated at a resolution of >10,000. This resolution was checked every 12 hours and documented in hardcopy

Results

Data could not be quantified in one pass with OpusQuan (quantification program) because of the limitation of analytes in a run table (72). Therefore five separate quantification programs were used as follows:

- P2091, MoCB and DiCB
- P2092, TrCB and TeCB
- P2093, PeCB
- P2094, HxCB
- P2095, HpCB, OcCB, NoCB and DeCB.

For the purpose of this data, Reporting Limits/Detection Limits were set at 10 pg/L for all analytes except the dioxin-like PCBs where the limit was set at 2 pg/L. The PQL is calculated 4 pg/L. All data between 2-4 pg/L was "J" flagged.

Any data that failed to meet acceptable ion ratios has been flagged with an N.

Five samples were rerun on the HRMS due to failed $^{13}C_{12}$-MoCB ratios. The ratios failed in the rerun samples as well, however the standard recoveries increased dramatically. Therefore, data is reported from the 2nd run for MoCBs only.

Standard Recoveries

Recoveries were acceptable (25-150%) for the samples with the following exceptions:

- Low recoveries are noted for volatile CBs. Usually these are lost during the concentration steps. However, in the two cases noted, the instrument "lock mass" has been suppressed, probably by coextractives. This will cause the acquisition mass to shift, meaning in this case, the instrument is no longer locked on the DiCB masses. Sample PR70470 was rerun 4 times in an attempt to acquire data for all CBs, however we were unable to eliminate the lock mass issues for PCB015L.
  - PR70466 (154185) – PCB015L
  - PR70470 (154191) – PCB015L

All clean-up standards met acceptable recoveries (30-135%) for samples.

QC Samples

Blanks

Two blanks were carried through the extraction and clean-up procedure. Both showed trace amounts of a number of CBs. Analytes are "B" flagged if the data point is <10x the level found in the blank.

Spikes

Two 1 L samples of lab water were spiked with 1 ng and 0 4 ng each of 72 PCB congeners and carried through the extraction and clean-up procedures. Recoveries of all toxic PCBs and window defining PCBs were within the acceptable range of 50-150% except as noted.

- ~~PC07230S – PCB004/010 @ 156%~~ KF (repeated)

~~All of the other PCBs were also within the acceptable range of 50-150% except as noted.~~

- PC07230S – PCB004/010 @ 156%
- PC07230S – PCB005/008 @ 157%
- PC07230S – PCB018 @ 24.3%
- PC07230S – PCB056 @ 180%
- PC07236S – PCB018 @ 42.3%

David Hope, CEO

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Appendix B. Location Descriptions

Table B1. Description of Sampling Site Locations.

Location ID	Descriptive Name*	Location Details
Walla Walla WWTP		
WW Headworks	Walla Walla WWTP Influent	Sample was taken at the WWTP from the top of the headworks to the right side.
WW Effluent	Walla Walla WWTP Effluent	Sample was taken from a small access door, post UV treatment, at the WWTP.
WW Trunkline 1	Walla Walla WWTP Trunkline 1 "Deepthroat"*	The manhole accessed for this trunkline is on Walla Walla WWTP property. The depth to water is approximately 30 feet.
WW Trunkline 2	Walla Walla WWTP Trunkline 2 "Beavis"	The manhole accessed for this trunkline is located off Woodland Rd. Trunklines 2 and 3 run parallel very close to each other at this site. The first manhole is "Beavis" and the depth to water surface is shallow.
WW Trunkline 3	Walla Walla WWTP Trunkline 3 "Butthead"	The manhole accessed for this trunkline is located off Woodland Rd. Trunklines 2 and 3 run parallel very close to each other at this site. The second manhole is "Butthead" and the depth to water surface is deeper than "Beavis".
WW Trunkline 4	Walla Walla WWTP Trunkline 4 "Dirty Dog"	The manhole accessed for this trunkline is located near Canoe Winery in the middle of Cherry Street. The manhole reveals an intersection of two flows. One flow is from a juice plant and is often colored. The sample was taken from a mixed area below confluence.
WW TL4-1	Walla Walla WWTP Trunkline 4-Tracking Sample 1 "Edith"	The manhole accessed is located near the entrance of the State Penitentiary along the shoulder of 13th Street, across from Edith Street. The manhole reveals a confluence of 3 flows; only the penitentiary flow was sampled. Eventually this site links to Trunkline 4.
WW TL4-2	Walla Walla WWTP Trunkline 4-Tracking Sample 2 "Frazier"	The manhole accessed is located on Frazier Drive at the northwestern end of town on the north side of Hwy 12. Eventually this site links to Trunkline 4.
WW TL4-3	Walla Walla WWTP Trunkline 4-Tracking Sample 3 "N.Cherry"	The manhole accessed is located on W Cherry Street and is the northern manhole just 10 feet from the southern manhole that was also sampled. Eventually this site links to Trunkline 4.
WW TL4-4	Walla Walla WWTP Trunkline 4-Tracking Sample 4 "S.Cherry"	The manhole accessed is located on W Cherry Street and is the southern manhole just 10 feet from the northern manhole that was also sampled. Eventually this site links to Trunkline 4.

Location ID	Descriptive Name*	Location Details
WW TL4-5	Walla Walla WWTP Trunkline 4-Tracking Sample 5 "Cayuse"	The manhole accessed is located on Cayuse Street, just a half-block from the W Cherry Street manholes. Eventually this site links to Trunkline 4.
WW TL3-1	Walla Walla WWTP Trunkline 3-Tracking Sample 1 "Roundhouse"	The manhole accessed is located on Wallace Street, at the northeastern end of town. Eventually this site links to Trunkline 3.
WW TL3-2	Walla Walla WWTP Trunkline 3-Tracking Sample 2 "Barky"	The manhole accessed is located on the bank of Mill Creek at N Tausick Way. Eventually this site links to Trunkline 3.
College Place WWTP		
CP Headworks	College Place WWTP Influent	Sample taken at the WWTP from a manhole near the headworks.
CP Effluent	College Place WWTP Effluent	Sample taken at the WWTP just as the effluent pours over the last weir.
CP TL1-1	College Place WWTP Trunkline 1-Tracking Sample 1 "Agassi"	The manhole accessed is located on W 6th Street at the intersection with SW Evans Avenue.

* Descriptive names only used by Ecology in this study.