

Memorandum

From: Cathy Whiting, Dave Dilks

Date: June 28, 2013

Project: SRRTTF

To: SRRTTF

SUBJECT: Review of Standard Operating Procedures for PCB Data Collection and Analysis

Summary

The Spokane River Regional Toxics Task Force is developing a comprehensive plan designed to bring the Spokane River into compliance with water quality standards for PCBs, and has hired LimnoTech to serve as a technical advisor. Task 3 of LimnoTech's scope calls for a review of standard operating procedures for data analysis and collection, designed to ensure comparability of analytical data used during this project. This document presents the results of our review of all available Quality Assurance Project Plans (QAPPs) and Sampling and Analysis Plans (SAPs) for data analysis and collection currently employed by those agencies collecting data. Results of the review are as follows:

- Several agencies do not have documented SAPs or QAPPs.
- The SAPs or QAPPs that do exist are largely consistent with acceptable practices.
- The QAPPs for several agencies list a generic EPA Method 1668 rather than the specific version of the method (e.g. 1668A, 1668C). This was done to provide flexibility to use the latest acceptable version as the method is updated and to allow the use of either 1668A or 1668C.

Three areas were identified where there was variability in procedures among agencies that may potentially be of concern:

- Laboratory reporting limits vary across the documents reviewed.
- The number of quality control samples (e.g. duplicates, blanks) vary across the documents reviewed.
- The method used to assess blank contamination varies across documents, including some documents that provided no assessment procedures.

Further discussion is required to determine whether any of the above items merit changes to existing standard operating procedures.

Quality Assurance Project Plans/ Sampling and Analysis Plans Reviewed

Based on information provided by Ecology, the Quality Assurance Project Plans (QAPP) and Sampling and Analysis Plans (SAP) for PCB data collection and analysis were requested from the agencies listed in Table 1. Several of these agencies did not have documented quality assurance plans or procedures as shown in the table.

Table 1. Available QAPP/SAP Documentation

Agency	Contact	QAPP/SAP Documentation
Washington Department of Ecology	Arienne Fernandez	Yes
Idaho DEQ *	Dan Redline	No
City of Coeur d'Alene	H. Sid Fredrickson	No
City of Post Falls	Mike Neher	No
City of Spokane	Dale Arnold	Yes
Hayden Area Regional Sewer Board	Paul A. Klatt, P.E.	No
Spokane County	Bruce Rawls	Yes
Liberty Lake Water and Sewer District	Bijay Adams	Yes
Inland Empire Paper	Doug Krapas	No
Kaiser Aluminum (SAP only)	Bud Leber	Yes

*Idaho DEQ does not collect samples for PCB analysis

The available QAPPs and SAPs related to PCB data collection and analysis are listed in Table 2. These documents were then reviewed to determine the variability between procedures used by each of the entities collecting PCB data that could potentially be used by the SRRTTF.

Table 2. Reports Received for Review

AGENCY	REPORT	DATE	STUDY OBJECTIVE	Sample Matrix
Washington Department of Ecology	SAP/QAPP for the Liberty Lake Source Trace Study Regarding PCBs, PBDEs, Metals, and D/Fs	June 2008	Conduct toxics trace study in the Liberty Lake drainage system to find sources of PCBs	stormwater sanitary wastewater
	Spokane Basin SAP/QAPP for the Spokane River Source Trace Study	May 2009	Conduct toxics trace study in the Spokane Basin to find sources of PCBs	CSO stormwater
	Manchester Lab - SOP for Reviewing Contract Lab Data	June 2012	Verify data that has been analyzed by contract laboratories	---
City of Spokane	City of Spokane QAPP for NPDES Permit Required Study of PCBs, PBDFs, and 2,3,7,8 TCDD	April 2012	Riverside Park Water Reclamation Facility NPDES permit requirement for sampling/analysis of PCBs to develop source control programs	WWTP influent WWTP effluent
	SAP/QAPP for the City of Spokane Catch Basin Sediment Sampling		Gather data to aid in the identification of likely PCB sources to stormwater	catch basin sediment
	SAP/QAPP for the City of Spokane PCB Adaptive Management Plan	2012	Gather data to aid in the identification of likely PCB sources to stormwater	stormwater
Spokane County	Spokane Co. Regional Water Reclamation Facility QAPP Receiving Water Study: Toxic Parameters	October 2012	Spokane County Regional Water Reclamation Facility NPDES permit requirement for sampling/analysis of PCBs to develop source control programs	WWTP influent WWTP effluent
Liberty Lake Water and Sewer District	QAPP for Liberty Lake Water Reclamation Facility Regarding PCBs, PBDEs, and 2,3,7,8 TCDDs	October 2011	Liberty Lake Water Reclamation Facility NPDES permit requirement for sampling/analysis of PCBs to develop source control programs	WWTP influent WWTP effluent
Kaiser Aluminum	Field Procedures Work Plan PCB Sampling Protocols	July 2011	Conducted to satisfy a requirement of Amended Order No. 2868 - evaluate the usefulness of different sampling methodologies	Industrial WWTP Effluent
	Sampling Plan PCB Sampling Protocols - Outfall 001	August 2012	Determination of residual sources of PCBs in the southern portion of the industrial wastewater system	Industrial WWTP Effluent



Results of Review

The results of the QAPP/SAP documentation review are summarized in Table 3. The information found in the documents was largely consistent with acceptable practices, with some discrepancies between agencies related to detection limits number of QA/QC samples, and assessment of blank contamination.

Analytical Method

The documents reviewed indicated that samples would be analyzed using EPA Method 1668, Method 1668A and 1668B. EPA Method 1668 was published in 1997 to specifically determine the 12 PCB congeners designated as toxic by the World Health Organization. The method was expanded for analysis of all 209 congeners and published in 1999 as EPA Method 1668A (Revision A). EPA published Method 1668B in 2009. Method 1668B revises EPA Method 1668A to replace single-laboratory quality control (QC) acceptance criteria with inter-laboratory criteria, along with other changes. Method 1668C was published in 2010 and revises the quality control acceptance criteria in Method 1668B to allow the upper recovery limit for some congeners to be above 100 percent. Method 1668B is rarely used and Ecology and the SRRTTF previously agreed that Method 1668B would not be used due to the limitations created by the quality assurance boundaries making comparability difficult.

The Ecology QAPP referred to Method 1668B, but this method was subsequently never used by Ecology, with EPA Methods 1668A and 1668C used instead. The City of Spokane, Spokane County, and Liberty Lake all identified EPA Method 1668 as the analytical method. This was done to provide flexibility to use the latest acceptable version as the method is updated and to allow the use of either 1668A or 1668C.

Reporting Limits

The reporting limit is the lowest concentration at which an analyte can be detected in a sample and its concentration can be reported with a reasonable degree of accuracy and precision. Each of the QAPPs required reporting limits for Method 1668/A/B ranging from 7 pg/L to 400 pg/L. The 400 pg/L was from the Ecology Liberty Lake study in 2008, which is the oldest QAPP reviewed. Table 3 shows that the majority required reporting limits ranging from 10 pg/L to 50 pg/L. Task 8 of LimnoTech's scope of work will provide guidance on maximum acceptable reporting limits, although discussions on this topic can begin sooner if desired.

Collection Methods

Due to the very low concentrations of PCBs in the samples collected, the collection method is important. EPA Methods 1668A and 1668C require the following:

- Amber glass containers
- Screw cap lined with fluoropolymer
- Containers detergent water washed with a solvent rinse before use
- Samples stored in the dark at less than 6°C
- Automatic samplers – must use glass containers, tubing must be fluoropolymer, must be rinsed with methanol then reagent water



The collection methods specified in the QAPP documents were from Ecology guidance, guidance in Method 1668 and EPA Method 1669. EPA Method 1669 is the ultra clean sampling procedure and was specified in the Liberty Lake QAPP. The collection methods were mentioned in all the documents or in designated SAPs with varying levels of detail.

QA/QC Samples

The most variable information category among the documents reviewed was the field QA/QC sample collection, corresponding to equipment blanks, travel blanks, and duplicates. The frequency of QA/QC samples described in the plans reviewed ranged from not described, to one per year, to one per ten samples. There are no official guidelines regarding the required number of QA/QC samples, but some guidance documents (e.g. EPA, 2008) suggest collecting one duplicate in 10 samples and one field or equipment blank in 20 samples. For all but the studies conducted by Ecology, the number of blanks and duplicates is lower than this frequency or not specified.

In addition, Ecology provides guidance on assessing blank contamination. The QAPPs/SAPs reviewed mentioned blank contamination in varying levels of detail, from no mention to providing detailed procedures.

References

- EPA. 2002. Guidance for Quality Assurance Project Plans (EPA/240/R-02/009).
- EPA. 2008. Waste Management System; Testing and Monitoring Activities; Notice of Availability of Final Update IV of SW-846.
- EPA. 2012. Draft - Guidance on Quality Assurance Project Plans (CIO 2106-G-05 QAPP).
- WDOE. 2002. How to do Stormwater Sampling –A Guide for Industrial Facilities.
- WDOE. 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies.
- WDOE. 2009. Standard Operating Procedures for Automatic Sampling for Stormwater Monitoring.



Table 3. QAPP/SAP Review Summary

Agency	Contact	Report	QAPP/SAP Date	Analysis	Lab Method	Acceptance Criteria/ Measurement Quality Objectives	Reporting Limit	Laboratory	Sample Collection	Collection Protocol/Method	Sample Preservation	Decon	Field QA/QC Samples				
													Equipment Blank	Travel Blank	Duplicate	Blank Contamination Assessment	
Washington Department of Ecology	Arianne Fernandez	SAP/QAPP for the Liberty Lake Source Trace Study Regarding PCBs, PBDEs, Metals, and D/Fs	Jun-08	PCB congeners	EPA 1668A	---	RL = 400 pg/L	Manchester Lab sends to accredited lab	Grab with pole or peristaltic pump	as described in WDOE guidance and Method 1668	---	WDOE SOP	1 per 10 samples	1 per 10 samples	1 per 10 samples	assessment not mentioned	
		Spokane Basin SAP/QAPP for the Spokane River Source Trace Study	May-09	PCB congeners	Manchester Lab - EPA 8082 Contract Lab - EPA 1668B	---	Manchester Lab-RL = 3300-10,000 pg/L Contract Lab - RL = 10-500 pg/L	Manchester Lab sends to accredited lab	CSO -24 hour composite Storm - grab composite	as described in WDOE guidance and Method 1668	< 4°C	WDOE SOP	1 per 10 samples	each sampling event	1 per 10 samples	Transfer blanks will be prepared as a check for cross contamination during sampling.	
		Addendum to QAPP - Includes additional sample locations, procedures are the same as above	Oct-09														
		Manchester Environmental Lab (MEL) - SOP for Reviewing Contract Lab Data	Jun-12														
City of Spokane	Dale Arnold	City of Spokane QAPP for NPDES Permit Required Study of PCBs, PBDFs, and 2,3,7,8 TCDD	Apr-12	PCB congeners	EPA 1668	---	RL water = 20 pg/L	lab accredited by Ecology	24 hour composite	Wear gloves	< 4°C	Included in QAPP	2 per year	2 per year	1 per year	Blank contamination will be qualified- if the QC discrepancy is enough to invalidate the dataset, resampling and retesting may be required	
		SAP/QAPP for the City of Spokane PCB Adaptive Management Plan	2012	PCB congeners	EPA 1668	---	RL = 7-30 pg/L	lab accredited by Ecology	Flow weighted composite - auto sampler	wear gloves/practice clean sampling techniques	< 4°C	WDOE SOP	1 - first sampling event only	First sampling event only		Any blanks out of acceptance range will have data qualifier flag	
		SAP/QAPP for the City of Spokane Catch Basin Sediment Sampling	Undated	PCB congeners	EPA 1668	Yes	30 ng/kg	Pacific Rim or other contract	Composite samples	Detailed procedure included	< 4°C	Included in QAPP	Not applicable	Not Mentioned		Not mentioned	



Agency	Contact	Report	QAPP/SAP Date	Analysis	Lab Method	Acceptance Criteria/ Measurement Quality Objectives	Reporting Limit	Laboratory	Sample Collection	Collection Protocol/Method	Sample Preservation	Decon	Field QA/QC Samples			
													Equipment Blank	Travel Blank	Duplicate	Blank Contamination Assessment
Spokane County	Bruce Rawls	Spokane Co. Regional Water Reclamation Facility QAPP Receiving Water Study: Toxic Parameters	Jun-13	PCB congeners	EPA 1668 8082 for screening	Yes	10 pg/L	AXYS Analytical Services	24 hour composite	Detailed SOP attached to QAPP	< 4°C	SOP attached	1 per sampling event	1 per sampling event	3 per 12 month sampling period	Will evaluate based on DRBC decision rules
Liberty Lake Water and Sewer District	Bijay Adams	QAPP for Liberty Lake Water Reclamation Facility Regarding PCBs, PBDEs, and 2,3,7,8 TCDDs	Oct-11	PCB	EPA 1668	---	QL = 10 pg/L	Pacific Rim Labs	24 hour composite	EPA 1669	< 4°C	Included in QAPP	2 per year	1 per year	2 per year	Says "If there are no problems" – definition of problems not mentioned
Idaho DEQ	Dan Redline	no PCB sampling/no QAPP														
City of Coeur d'Alene	Sid Fredrickson	no QAPP														
City of Post Falls	Mike Neher	no QAPP														
Hayden Area Regional Sewer Board	Paul A. Klatt, P.E.	no QAPP														
Kaiser Aluminum (no QAPP)	Bud Leber	Field Procedures Work Plan PCB Sampling Protocols	Jul-11	PCB congeners	EPA 1668A	---	---	AXYS Analytical Services	SMPD/24 hour composite	SOP for deploying SMPD samplers	< 4°C	---	---	---	---	Assessment not mentioned
		Sampling Plan PCB Sampling Protocols - Outfall 001	Aug-12	PCB congeners	EPA 1668A	---	---	AXYS Analytical Services	SMPD/24 hour composite	---	< 4°C	---	---	---	---	Assessment not mentioned
Inland Empire Paper	Doug Krapas	no QAPP														

