Quality Assurance Project Plan Addendum 4

Spokane River Toxics Reduction Strategy Study

Prepared for:
Spokane River Regional Toxics Task Force

DRAFT

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APPROVALS

Quality Assurance Project Plan – Addendum 4

May 16, 2017

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Abstract

This Addendum to the Quality Assurance Project Plan (QAPP) corresponds to a continuation in 2017 of the work described in the original QAPP for 2014 (LimnoTech, 2014a), the 2015 QAPP Addendum 1 (LimnoTech, 2015a) and the 2016 QAPP Addendums 2 (LimnoTech, 2016a) and 3 (Ecology, 2016). The objectives of the 2017 Technical Activities are to:

- Conduct a homolog-specific mass balance analyses to determine the presence of groundwater PCB sources.
- Identify, compile and assess all relevant groundwater PCB.

The 2014 QAPP, 2015 QAPP Addendum 1, 2016 QAPP Addendums 2 and 3, and the Sampling and Analysis Plan (SAP) (approved by Ecology and SRRTTF) are still applicable. The revisions contained in this Addendum consist of:

- Affirming that the quality objectives for the ~~Conducting~~ homolog-specific PCB mass balance analyses remain the same as for when these analyses were conducted using total PCB concentations.
- Defining quality objectives for the ~~I~~identification~~ying~~, compilation~~ing~~ and assessment~~sing~~ ~~all relevant~~ of groundwater PCB data.

Introduction

The Spokane River Regional Toxics Task Force (SRRTTF) has developed a comprehensive plan (LimnoTech, 2016b) to reduce toxic pollutants in the Spokane River, specifically polychlorinated biphenyls (PCBs). The comprehensive plan identified specific management actions that can be undertaken to control pollutant loads such that water quality objectives can ultimately be attained. Comprehensive plans of this type require data capable of describing individual sources and site-specific processes that drive resulting concentrations. LimnoTech (2014b) described the overall data collection strategy for a first year of monitoring, based on the work conducted to identify key gaps in the existing data set and issues addressed at a December 2013 monitoring workshop.

A Synoptic Survey was conducted in 2014 to identify potentially significant dry weather sources of PCBs to the Spokane River between Lake Coeur d'Alene and Nine Mile Dam. The results of this study showed the strong likelihood of a groundwater PCB source between Barker Road and the Trent Avenue Bridge, and the potential of an additional groundwater PCB source between the Trent Avenue Bridge and the Spokane USGS gage (LimnoTech, 2015b). The SRRTTF Technical Track Work Group recommended, and the Task Force as a whole approved (SRRTTF, 2015a, 2015b), conducting a 2015 Synoptic Survey to confirm the findings of the 2014 Synoptic Survey over a narrower spatial scope. This work was conducted in August 2015 in accordance with the 2015 QAPP Addendum 1.

In 2016, monthly water quality sampling was conducted to determine the seasonal variability in PCB concentrations in the Spokane River, to the extent that measured concentrations exceed laboratory blanks. Concurrent collection of flow data allowed for a semi-quantitative assessment of loading. The field monitoring program included six monthly sampling events. QAPP Addendum 2 was prepared to document the procedural and analytical requirements of the 2016 water quality monitoring.

Also in 2016, the Department of Ecology, in collaboration with Spokane County, collected groundwater data from a select set of Spokane Valley-Rathdrum Prairie aquifer wells and springs located adjacent to the Spokane River. The objectives of the study were to 1) characterize PCB concentrations in groundwater at the Idaho-Washington state line, and groundwater inputs to the river upstream of Kaiser Aluminum in Spokane

Valley, 2) evaluate groundwater concentrations of PCB in the aquifer near gaining reaches, 3) correlate groundwater measurements with 2015 in-river synoptic studies and mass balance determinations, 4) check for potential sources of PCB contamination in groundwater that might reach the river, and 5) characterize PCB concentrations of source water for the Spokane Fish Hatchery, which discharges to the Little Spokane River. Up to 20 environmental samples were collected in three sampling periods, representative of the Spokane River's three major flow regimes. QAPP Addendum 3 was prepared by the Department of Ecology to document the procedural and analytical requirements of the 2016 groundwater monitoring.

The objective of the 2017 Technical Activities is to conduct a homolog-specific mass balance analyses to determine the presence of other PCB sources. Given the very low PCB concentrations in Spokane that are near levels observed in laboratory blanks, this work (like all previous phases) will be semi-quantitative in nature. All previously defined data quality objectives remain applicable. In addition, all relevant Method 1668 groundwater PCB data will be identified, compiled and assessed using the same data quality objectives.

Project Organization

Each of the organizations included in the project team has established an organizational structure for providing technical direction and administrative control to accomplish quality-related activities for the development of the project.

Key project personnel and their corresponding responsibilities are listed in Table 1 below and shown in Figure 1.

Table 1. Project Team Responsibilities/Distribution List

Name/Affiliation	Project Title/Responsibility
SRRTTF	**Oversight and direction** Secure funding for project activities Review and utilize project results Facilitate communications and provide public access to information Develop recommendations for controlling and reducing sources Develop comprehensive plan
Bud Leber – SRRTTF-ACE	**SRRTTF ACE President** Manage contracts: review and approve project specifications Ensure project is completed in timely manner Receive deliverables and reports Manage data on behalf of SRRTTF Communicate with SRRTTF Communicate quality assurance issues with SRRTTF Ensure access to project information on the SRRTTF website Facilitate upload of data to EIM
David Dilks - LimnoTech	**Project Manager** General oversight Review/approval of all work products prior to delivery to SRRTTF-ACE Ensures that work is done in accordance with QAPP and SAP
Adriane Borgias – Department of Ecology	**Advisor** Reviews/approves QAPP
Bob Betz - LimnoTech	**Project Quality Assurance Officer** Performs systematic evaluation of data quality Receives notices, initiates investigation, and documents nonconformance with DQOs Manage the Project QA/QC file
Robert Steed – Idaho DEQ	**Advisor** Reviews/approves QAPP
Shea Hewage – AXYS Analytical Services	**Laboratory Operations Director** Sample analysis Manages laboratory Quality Assurance systems Final review and validation of data and field systems Initiates corrective actions for nonconformance
Richard Grace – AXYS	**Laboratory Project Director** Oversight of all laboratory commercial and technical project specifications
Sean Campbell – AXYS Analytical Services	**Laboratory Project Manager** Serves as main point of contact for laboratory Assists Laboratory Operations Director with management of laboratory QA systems Communicates with Project Manager
Dale Hoover-AXYS Analytical Services	**Laboratory QA/QC Managers** Manages Laboratory QA/QC activities Reviews and verifies field records, laboratory records and laboratory data Addresses nonconformance and carries out corrective actions at the laboratory.

The lines of reporting for the organizations in the project are shown in the organization chart (Figure 1). Each team member has responsibility for performance of assigned quality control duties in the course of accomplishing identified activities. The quality control duties include:

- Completing the assigned task on or before schedule and in a quality manner in accordance with established procedures; and
- Ascertaining that the work performed is technically correct and meets all aspects of the QAPP.

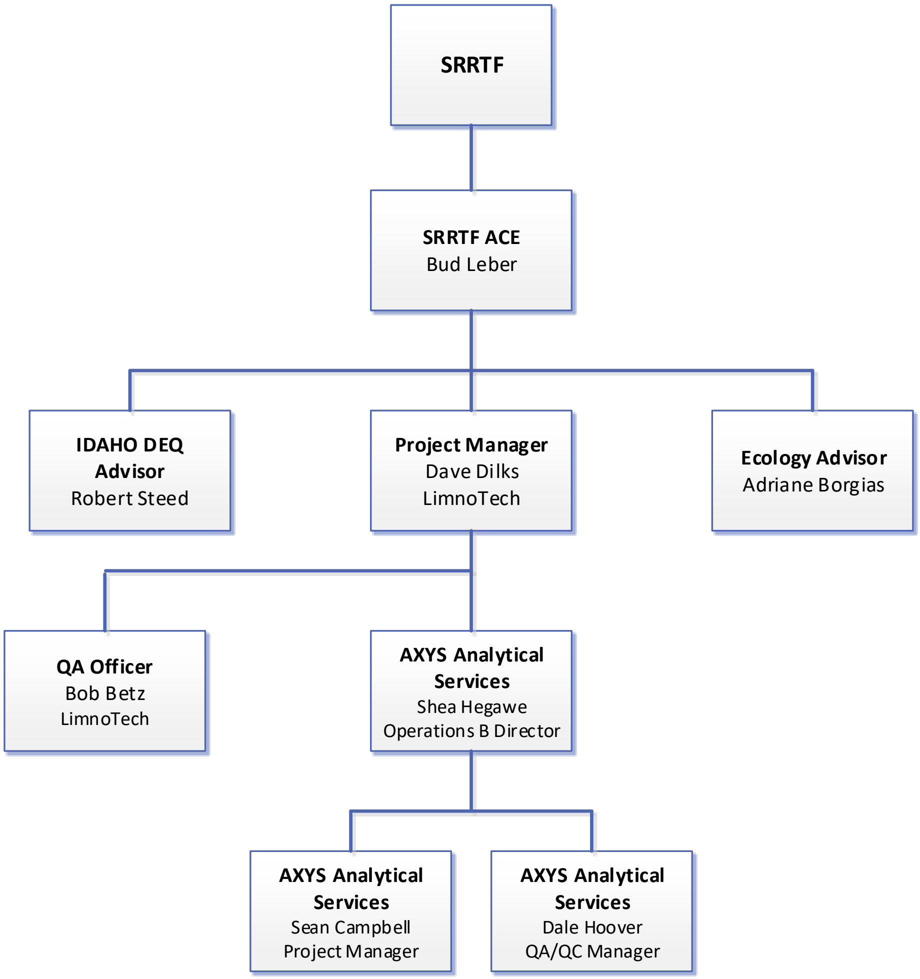

Figure 1. Project Team Organization

LimnoTech's role is to ensure that the project is conducted in accordance with the requirements of the QAPP/QAPP Addendum 4. LimnoTech is responsible for preparation of the QAPP addendum and conducting Tasks 1 and 2 (homologue mass balance/groundwater data compilation), as described below. As Project Manager, David Dilks (LimnoTech) is responsible for general oversight of the project, including review and approval of all work products prior to delivery to SRRTTF-ACE.

Budget

The total budget for this project is $33,800.

Background

The Spokane River Regional Toxics Task Force (SRRTTF) has developed a comprehensive plan to reduce PCB inputs to the Spokane River and bring it into compliance with applicable water quality standards for PCB. The Spokane River and Lake Spokane exceed the water quality standard (170 pg/L – based on fish consumption rate of 6.5 g/day) for polychlorinated biphenyls (PCBs) in several segments. Fifteen waterbody segments of the Spokane River and Lake Spokane (also known as Long Lake) and one segment of the Little Spokane River are on the 2008 303 (d) list for exceeding human health water quality criteria for PCBs. The Spokane Tribe of Indians have water quality standards for PCBs in the Spokane River below Lake Spokane (also known as the Spokane Arm of Lake Roosevelt) that are more than 95% lower than State standards (1.3 pg/L), based on a higher fish consumption rate (865 g/day) than the general population (Spokane Tribe of Indians, 2010). PCBs are not listed in Idaho.

PCB monitoring data for the Spokane River watershed available when the SRRTTF was formed provided an estimate of the amount of PCBs entering the Spokane River from contributing source area categories (e.g. stormwater, WWTPs). Based on the Spokane River PCB Source Assessment 2004-2007 (Serdar et al, 2011), only 43% of the PCB source loading to the river between Stateline (RM 96.1) and Long Lake Dam (RM 33.9) could be identified. This is due in part to the uncertainty of the analyses and the high variability in the data. Those data indicated that sources of PCBs are very diffuse throughout the watershed, such that more data were needed to support development of a management plan with targeted control actions (LimnoTech, 2013). Two studies were conducted in 2014, the Confidence Interval Testing and the Synoptic Survey. An additional Dry Weather Survey was conducted in 2015 and monthly water quality sampling was conducted in 2016 to determine the seasonal variability in PCB concentrations in the Spokane River. Groundwater monitoring was also conducted in 2016. Results of the monitoring identified multiple potential groundwater PCB sources. These findings were incorporated into a Comprehensive Plan to reduce polychlorinated biphenyls (PCBs) in the Spokane River (LimnoTech, 2016b), which called for further analysis to identify homolog patterns of suspected groundwater sources and compare these to homolog patterns in Spokane area groundwater. This work is designed to carry out those specific aspects of the Comprehensive Plan.

Semi-Quantitative Mass Balance

LimnoTech has conducted a semi-quantitative mass balance of PCBs in the Spokane River using the data described above. The general conceptual approach of the mass balance assessment was to determine the presence of unmonitored loads (presumably from groundwater sources) by comparing the amount of mass passing through the Spokane River at two locations where flow and concentration measurements are available. The magnitude of the unmonitored load can be determined as the difference in monitored load at the downstream and upstream locations, as depicted below in Figure 2 and Equation 1. Q_u and Q_d represent the river flow at the upstream and downstream stations, respectively, while C_u and C_d represent the upstream and downstream PCB concentrations.

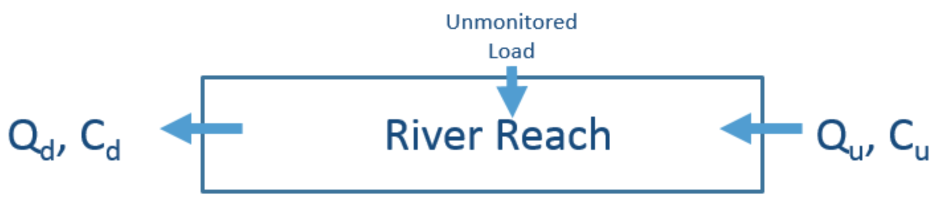

Figure 2. Simplified Description of Mass Balance Approach

The approach is described mathematically in Equation 1.

$$\text{Unmonitored load} = \text{Downstream load} - \text{Upstream load} \quad (1)$$

where:

Downstream load = Flow at downstream location (Q_d) x Concentration at downstream location (C_d)

Upstream load = Flow at Upstream location (Q_u) x Concentration at upstream location (C_u)

Equation 1 is based upon the assumption that environmental loss processes affecting PCBs are relatively insignificant between the two monitoring locations. This assumption was verified using low-flow hydraulic results from model of the Spokane River, observed data on suspended solids concentrations, and literature values for coefficients related to solids partitioning and volatilization.

The potential for confounding groundwater interactions is depicted in Figure 3, which indicates that the river alternates between stretches where water is lost from the river to the aquifer (i.e. losing reaches) and stretches where water is delivered to the river from the aquifer (i.e. gaining reaches~~.~~).

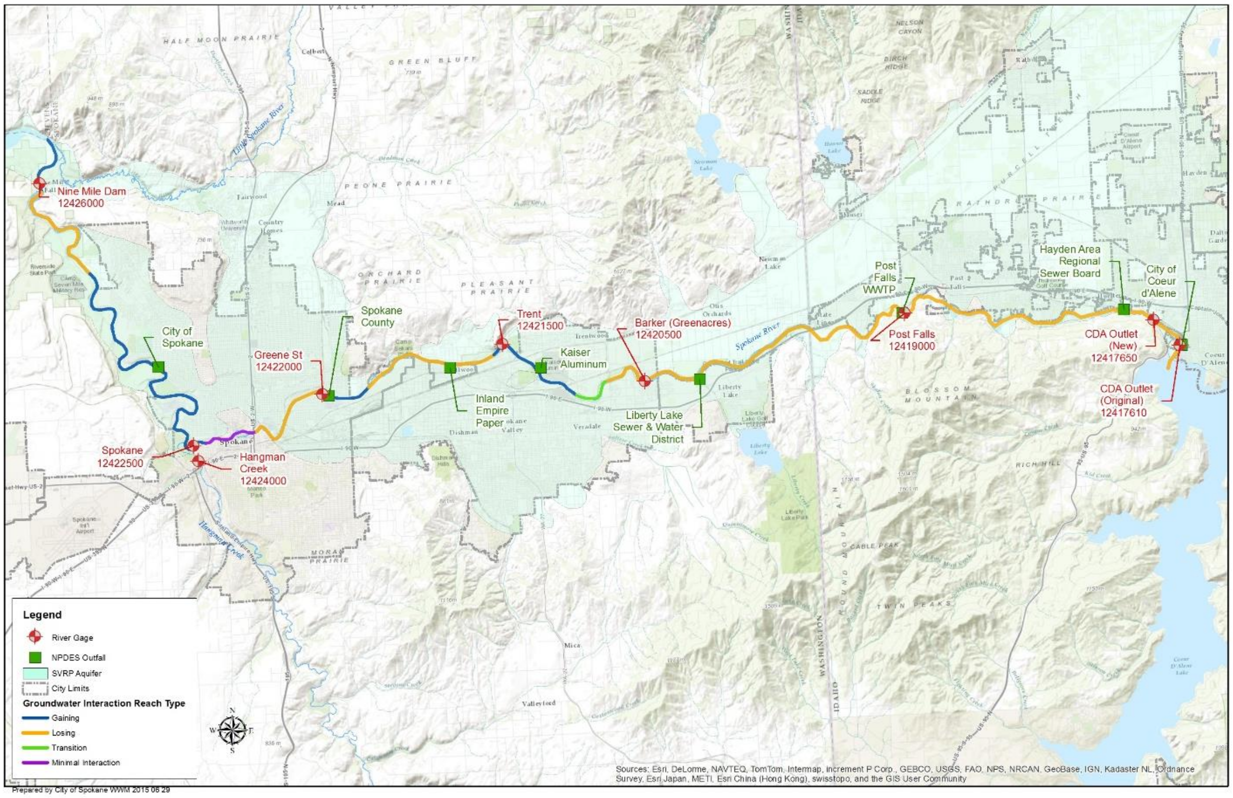

Figure 3. Map of Groundwater Interactions throughout Study Area

2017 Technical Activities

The 2017 technical activities include the following:

1. ***Reach by Reach Homolog-Specific Mass Balance Calculations (Comprehensive Plan Section 5.14.1)***

The general conceptual approach of the mass balance assessment is to determine the presence of unmonitored loads (presumably from groundwater sources) by comparing the amount of mass passing through the Spokane River at two locations where flow and concentration measurements are available. The magnitude of the unmonitored load can be determined as the difference in monitored load at the downstream and upstream locations.

Mass balance analyses on total PCB concentrations as described in the 2014 and 2015 Technical Activities Reports (LimnoTech, 2015c and 2016a), were sufficient to identify the presence of a groundwater PCB source to the Spokane River between Barker Road (47.677397, -117.152148) and Trent Avenue/Plante's Ferry (47.697117, -117.244098) (Figure 2). Subsequent mass balance analyses conducted on a homolog-specific basis identified a potential additional groundwater PCB source below Plante's Ferry. These semi-quantitative low-flow mass balances were conducted using the data collected by SRRTTF in 2014 and 2015. These data were collected in accordance with the project QAPP (LimnoTech, 2014a) and QAPP Addendum 1 (LimnoTech, 2015a), and were subsequently validated and determined sufficient for the objective.

The purpose of this task is to conduct homolog-specific mass balance analyses on the remaining river reaches to determine the presence of other potential sources, and to calculate homolog distributions for any identified sources. The mass balance analyses will be semi-quantitative and will be conducted similar to those contained in the 2014 and 2015 Technical Activities Reports (LimnoTech, 2015c and 2016a), using the validated data collected by SRRTTF. ~~but~~The mass balance assessment will be modifiedy ~~those analyses~~ to provide results by reach on a homolog-specific basis rather than the total PCB basis contained in the prior analyses. The homolog distributions calculated for the inferred groundwater loads will be compared to homolog distributions observed in groundwater and calculated as part of the task outlined below. This task will include processing all of the 2014 data to generate blank-corrected homolog distributions for river and effluent samples (blank-corrected homolog distributions have already been generated for the 2015 data).

In addition, a more refined homolog-specific analysis will be conducted for the Plante's Ferry to Greene Street (47.679059, -117.364657) segment (Figure 2), as this segment contains both gaining and losing sections. The original homolog-specific analysis considered only the net exchange of groundwater, instead of independently assessing the gaining and losing portions. That analysis demonstrated that this section of the river gained certain homologs and lost others, but was not suitable for generating a homolog pattern for the suspected new source. The refined analysis to be conducted for this task will divide the reach into two segments: 1) The losing section from Plante's Ferry to just downstream of Upriver Dam (47.685784, -117.328556), and 2) The gaining section from just downstream of Upriver Dam to Green Street. Groundwater additions and losses for these sections will be based upon flow measurements conducted by USGS below Upriver Dam for Spokane County in September, 2015 as well as results from the Ground-Water Flow Model for the Spokane Valley-Rathdrum Prairie Aquifer.

By parsing out the loss of river PCB to groundwater prior to the consideration of PCBs being added in the gaining section, this new analysis will generate a homolog distribution for the new groundwater loading source. Based on the results of this study, the gaining and losing stream reaches will be further defined and documented in the study report. This refined analysis is consistent with the work described in Section 5.14.1 of the Comprehensive Plan.

There are no anticipated impediments to completion of this task.

2. *Compilation of Available Groundwater Data and Comparison to Homolog Patterns of Suspected Groundwater Loads (Comprehensive Plan Section 5.14.1)*

This task consists of identifying, compiling, and assessing ~~all relevant~~ currently available groundwater PCB data from Kaiser, Urban Waters, SRRTTF, Ecology, and Spokane County (secondary data), with the ultimate objective of comparing homolog distributions from suspected groundwater sources to homolog patterns observed in groundwater. The secondary data will be verified and validated in accordance with the QAPP (LimnoTech, 2014a) and this QAPP addendum, using a process that controls measurement uncertainty, evaluates data, and flags or codes data against various criteria. Data from all other sources will be reviewed for the presence of a QAPP, and a comparison of those QAPPs to the SRRTTF QAPP. Only those data collected under a QAPP with quality objectives at least as rigorous of the SRRTTF QAPP will be considered for this analysis. The quality of the study is directly related to the ability of the project personnel to evaluate the quality of data and to determine the appropriate use of the data.

~~All available Spokane-area~~The groundwater PCB data ~~analyzed using Method 1668 from Kaiser, Urban Waters, Ecology, and Spokane County will be compiled, validated, and~~will be analyzed (if determined to meet the data quality objectives) to report the following features for each measurement:

- Blank Corrected Total PCB Concentrations
- Blank Corrected Congener Levels
- Blank Corrected Homologue Levels
- Collection Dates, Collection Method, Analytical Method, Location
- Ten Most Prevalent Congeners by Concentration
- D/F Like Congener Concentrations

The resulting groundwater homolog distributions will be compared to the homolog distributions for the unknown loads generated in the task above, using accepted fingerprinting techniques (e.g. cosine theta method) to identify similarities in patterns and aid in identifying which groundwater sources may be contributing to the observed increase in river concentration.

The data used for the evaluations described in Tasks 1 and 2 above, are currently available. There are no anticipated impediments to completion of this task.

Parameters

The study parameters of interest are PCB congeners, and the combination of individual congener values into homologs.

Schedule

Key milestones associated with the project are described below along with their targeted completion dates:

Task: Deliverable	Completion Date
1: Revised QAPP	May 31, 2017
2: Draft memorandum on homolog-specific mass balance analyses	June 28, 2017
2: Presentation to Task Force on homolog-specific mass balance analyses	June 28, 2017
2: Final memorandum on homolog-specific mass balance analyses	July 26, 2017
3: Draft memorandum comparing homolog patterns in unknown loads to homolog patterns in groundwater sources.	July 26, 2017
3: Presentation to Task Force on comparison of homolog patterns in unknown loads to homolog patterns in groundwater sources	July 26, 2017
3: Final memorandum comparing homolog patterns in unknown loads to homolog patterns in groundwater sources.	August 30, 2017

There are no known limitations on the schedule.

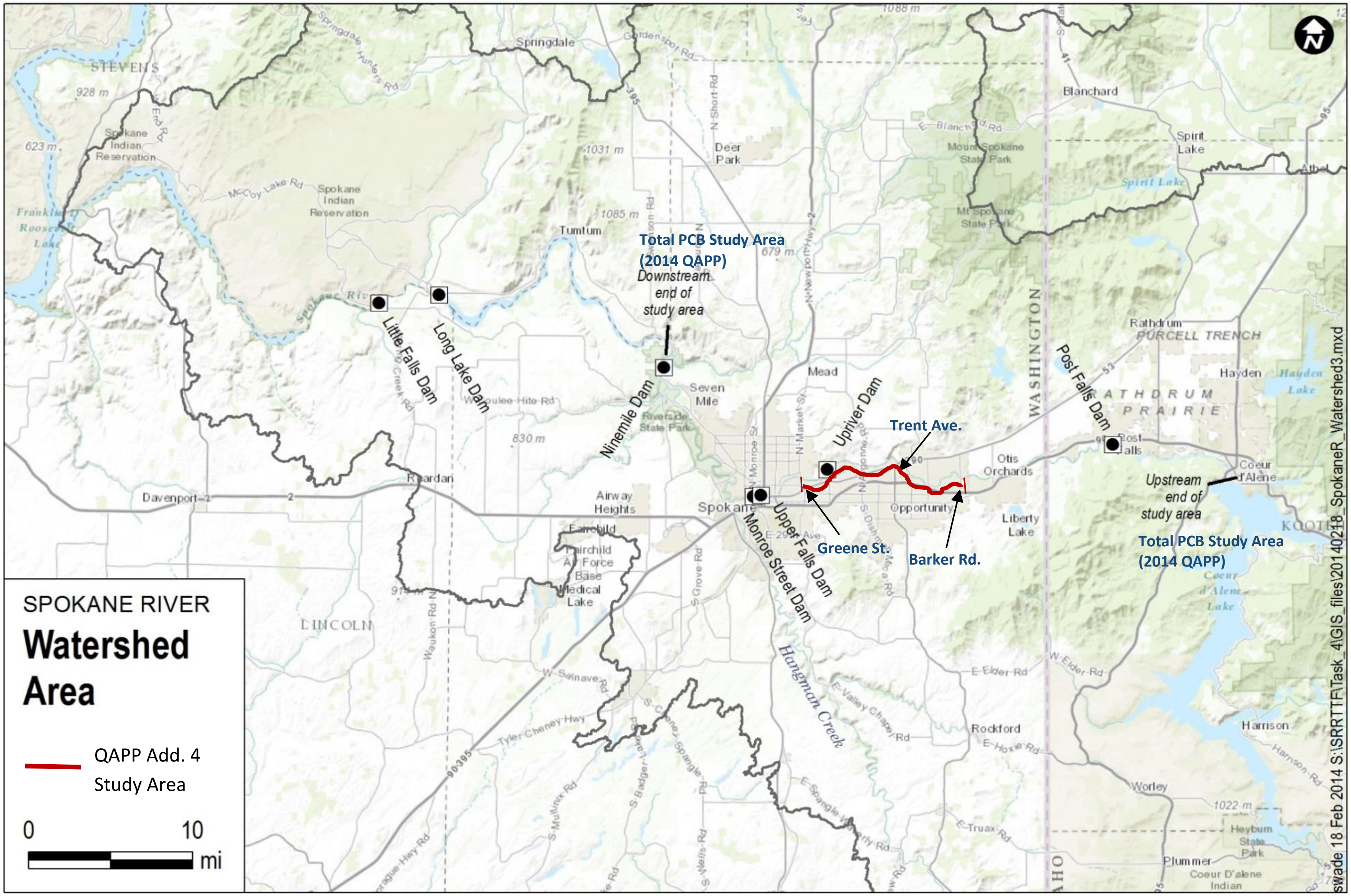

Figure 4. Spokane River Study Area

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Quality Objectives and Criteria

The data quality objectives are intended to clarify the study's technical and quality objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of the data needed to support decisions. The data quality objectives for this study were developed in order to ensure that the data collected were of acceptable quality and support the objectives of the project. The data quality objectives are described in Section 1.4 of the 2014 QAPP (LimnoTech, 2014a).

Data collected between 2014 and 2016 has been evaluated relative to the data quality objectives outlined in the 2014 QAPP (LimnoTech, 2014a). Data quality was interpreted using the Data Quality Indicators (DQIs) which are the quantitative statistics and qualitative descriptors used to interpret the degree of acceptability of the data to the user. The DQIs include bias and precision, representativeness, completeness, comparability, and the required detection limits (sensitivity) for the analytical methods. The Data Quality Indicators (DQIs) established in the 2014 QAPP (LimnoTech, 2014a) remain unchanged for this Addendum.

The Data Quality Indicators and the measurement performance criteria for each are provided in Table 2.

It should be noted that there is no standard blank correction method, and numerous approaches are utilized, both nationally and within the Spokane River Basin. The selection of the most appropriate blank correction methodology must consider factors such as: study objectives, sample matrix, sampling methodology, expected range of results, and tolerance for biased results.

Table 2. PCB Data Quality Indicators

		BIAS	BIAS	BIAS		PRECISION	SENSITIVITY	COMPLETENESS
	Analytical Method	Daily Calibration Verification	Lab Control Sample Recovery*	Sample and Method Blank Surrogate Recovery	Method Blank	Duplicate Sample	Detection Limit (Level at which non-detects are reported)	Completeness Criteria
		% recovery limits	% recovery limits	% recovery limits	Concentration (pg/L)	RPD (valid for congeners > 10x EDL)	Concentration (pg/L)	%
PCB Congeners	EPA 1668C /AXYS Method MLA-010 Rev 11	50-145%	50-150%	25-150%*	Maximum = 127 pg/L (total) Laboratory will B-qualify congeners results < 3x the concentration in an associated blank	50%	1-20	95%

*Per AXYS Method MLA-010 Revision 11 for OPR, internal standards and labeled compounds.

Analytical Methods

The following section details the aspects of the analytical requirements, ensuring that appropriate analytical methods are employed. Table 3 summarizes the analytical methods that were used by the laboratory (AXYS Analytical Services).

Table 3. Parameters, Detection Limits, Expected Concentrations and Analytical Methods

Parameter	Matrix	Detection Limit	Expected Concentrations	Analytical Method	Laboratory
PCB (pg/L)	Water	1-20	10-10,000 total	EPA 1668C	AXYS Analytical Services

Quality Control

Analytical quality control ~~will be~~has been performed on the data collected by the SRRTTF, in accordance with the specified analytical methods and as presented in the 2014 QAPP (LimnoTech, 2014a).

Corrective Action

Corrective actions have been implemented if required to rectify problems identified during the course of normal field and laboratory operations. Possible problems requiring corrective action include:

- Equipment malfunctions;
- Analytical methodology errors; or
- Non-compliance with quality control systems.

Equipment and analytical problems that require corrective action may occur during sampling and sample handling, sample preparation, and laboratory analysis.

For non-compliance problems, steps for corrective action will be developed and implemented at the time the problem is identified. The individual who identifies the problem is responsible for immediately notifying the Project Manager and the Project QAO.

Any non-conformance with the established quality control procedures outlined in the 2014 QAPP (LimnoTech, 2014a) will be identified and corrected. The Project Manager will ensure that a Corrective Action Memorandum is issued for each non-conformance condition. All non-conformance memoranda will be discussed in the final report submitted to the SRRTTF-ACE.

Data Management

Data management will be conducted as described in the 2014 QAPP (LimnoTech, 2014a).

Reconciliation with User Requirements

Once all groundwater data have been reviewed, quality control measures assessed, and any problems addressed, the measurement and analytical data will be assessed.

The assessment of the information generated groundwater data review will be initiated by entering all analytical data and field measurement data into the project database. All of these data will be evaluated and any relationships or correlations will be noted. The compilation of all the groundwater information will be available to facilitate reconciliation with user requirements. Ultimately these data will be used to support a semi-quantitative low-flow mass balance assessment.

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