Quality Assurance Project Plan

Similkameen River and Palmer Lake Investigation of Arsenic in Fish Tissue

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December 2006

303(d) Listings Addressed in this Study: None

Waterbody Numbers: Similkameen River (WA-49-1030) and Palmer Lake (WA-49-9270)

Project Code: 07-104

Approvals

Approved By:	December 2006
Mark Peterschmidt, Client, Water Quality Program Central Regional Office (CRO)	Date
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Jon Merz, Unit Supervisor, Water Quality Program, CRO	Date
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Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved By:	December 2006
Bill Kammin, Ecology Quality Assurance Officer	Date

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Abstract

This Quality Assurance Project Plan describes a study by the Washington State Department of Ecology for measuring arsenic in fish from the portion of the Similkameen River in Washington State and also from Palmer Lake. Field work will be conducted in the fall of 2006.

Previously, the Department of Ecology has documented high levels of arsenic in the Similkameen River.

Data from the study will be provided to the Washington State Department of Health for determination of the risk to human health through consumption of fish from the Similkameen River and Palmer Lake.

Background

The Similkameen River has been listed by Washington State under Section 303(d) of the federal Clean Water Act for non-attainment of the U.S. Environmental Protection Agency (EPA) human health criteria for arsenic in the water column. As a result of the listing, a Total Maximum Daily Load (TMDL) assessment was conducted on the river in 2001 (Johnson, 2002). The TMDL and associated detailed implementation plan (Peterschmidt, 2005) established water quality targets for arsenic and recommended several monitoring actions. One of these actions was to analyze arsenic in Similkameen River and Palmer Lake fish for use in assessing the potential human health risk of consuming these fish.

This study will assess current levels of arsenic in fish from the Similkameen River and Palmer Lake and provide data to the Washington State Department of Health for determination of risk to human health from consuming fish from these areas. The study will be conducted by the Washington State Department of Ecology (Ecology), Environmental Assessment Program, Toxics Studies Unit.

Similkameen River Watershed Description

The Similkameen River originates in the Cascade Mountains along the international border between British Columbia, Canada, and Washington State. The river flows north out of Manning Provincial Park, and then it turns south to cross the border and meet the Okanogan River at the city of Oroville (Figure 1). The Similkameen River is approximately 72 miles long, with the last 27 miles being in Washington (Johnson, 2002).

The Similkameen drains 3,600 square miles, over 90% of which is in British Columbia. Peak flows normally occur in April to July as a result of snowmelt. Streamflow during the winter generally stays low due to freezing weather that maintains or contributes to the snowpack; exceptions occur when mild weather and heavy rain combine to cause flooding. The annual discharge (measured at Nighthawk, WA) is 2,300 cubic feet per second (cfs), and the average is 609 cfs (Johnson, 2002).

Downstream of the international border, the Similkameen flows through farmlands and arid sagebrush typical of north-central Washington. Six miles below the border the river meets Palmer Lake outlet, sometimes called Palmer Creek. A unique hydrologic feature of their juncture is that, during times of high flow, the Similkameen can cause Palmer Creek to reverse direction so that the river flows into the lake instead of out of it. Other than Palmer Lake, Washington tributaries to the Similkameen are dry most of the year, except at higher elevations (Johnson, 2002). Sinlahekin Creek is the major tributary to Palmer Lake. It drains into Palmer Lake from the south.

The Similkameen watershed is sparsely populated in Washington. Nighthawk, just downstream of Palmer Lake, is the largest community with approximately 26 people. Enloe Dam, about nine miles below Nighthawk, was built in 1920 to generate electricity, but the dam has not been used for power since 1958. Currently, the dam blocks fish passage (Johnson, 2002).

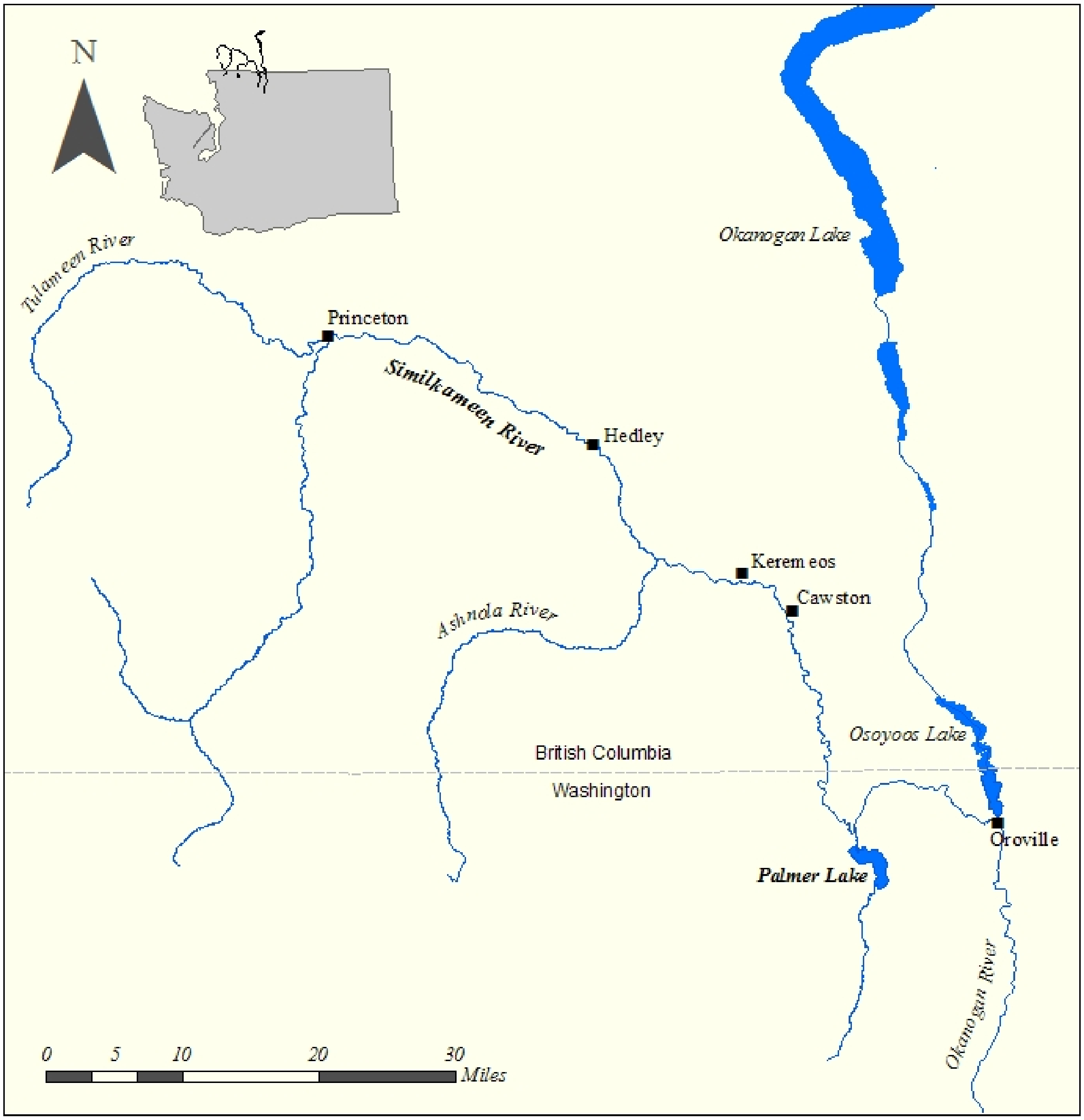

Figure 1. Similkameen River Drainage

Mining, forestry, agriculture, and recreation are the major land-use activities in the Similkameen watershed. The watershed has a history of mining, although there are currently no active large scale operations. Past mining activities in the watershed have been identified as the major source of arsenic to the river (Johnson, 2002). Notable among these are the mining operations in the vicinity of Hedly, B.C. and the Kaaba, Texas mine near Nighthawk in Washington (Peterschmidt, 2005). Other sources identified in Washington were: 1) Palmer Lake, likely arising from periodic flooding by the Similkameen River and perhaps inputs from the Sinlahekin Creek, and 2) resuspension of contaminated sediments (Johnson, 2002).

Arsenic in the Environment and Human Health

Arsenic is an element that is widely distributed in the Earth's crust. High concentrations of arsenic in the environment are a concern because of potential human health effects. The arsenic concentrations in the Similkameen River are unusually high when compared to other rivers in Washington.

Arsenic enters the air, water, and land from natural processes such as erosion, leaching of soil and rocks, and volcanic eruptions. Arsenic also enters the environment from human activities such as mining and smelting, coal-fired power plants, and incinerators.

Arsenic is usually found combined with other elements such as oxygen, chlorine, and sulfur. These forms are called inorganic arsenic. Arsenic combined with carbon and hydrogen is referred to as organic arsenic. Inorganic forms are generally considered to be more toxic to humans than organic forms (ATSDR, 2005).

Inorganic arsenic compounds were once used in pesticides primarily applied to cotton fields and orchards. Some organic arsenic compounds are still used in pesticides, animal feed, metal mixtures, and lead-acid batteries (ATSDR, 2005).

Arsenic has been acknowledged as a human poison for centuries. Ingestion of arsenic has been linked with skin, liver, bladder, and prostate cancer. Humans are exposed to arsenic by eating food, drinking water, and breathing air. Food is usually the largest source of arsenic.

Marine organisms, especially shellfish, are known to contain relatively high concentrations of arsenic, while arsenic concentrations in freshwater organisms are much more variable (Cullen and Reimer, 1989). Most of the arsenic in marine species is found in an organic form called arseobetaine that is much less toxic than inorganic arsenic (ATSDR, 2005). Historically the toxic arsenic species of most concern in fish and shellfish include inorganic arsenic, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA), all of which are minor constituents.

Quantitative data on inorganic arsenic in freshwater fish is sparse, and the toxicity to humans of fish tissue containing arsenic has not been well studied. This is a data gap acknowledged by the scientific community.

Project Description

As recommended by the 2001 TMDL arsenic study (Johnson, 2002), fish will be collected from the Similkameen River and Palmer Lake and analyzed for total arsenic, inorganic arsenic, and other arsenic species.

The objectives of the 2006 Similkameen River fish tissue study will be to:

1. Assess current levels of total arsenic, inorganic arsenic, and other arsenic species in fish tissue from the Similkameen River and Palmer Lake.
2. Provide data to the Washington State Department of Health (WDOH) to evaluate potential risks to human health from fish consumption.

Organization, Schedule, and Laboratory Budget

Organization

Name	Ecology Affiliation	Role	Phone
Mark Peterschmidt	Water Quality Program, Central Regional Office	Client	509.454.7843
Brandee Era-Miller	Toxics Studies Unit, Environmental Assessment Program	Project Lead	360.407.6771
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Stuart Magoon	Manchester Laboratory	Director	360.871.8801
Karin Feddersen	Manchester Laboratory	Lab Contracting	360.871.8829
Pam Covey	Manchester Laboratory	Sample Scheduling/ Receipt	360.871.8827
Bill Kammin	Environmental Assessment Program	Quality Assurance Officer	360.407.6964

Schedule

Field and Laboratory Schedule	
Fish Collection	October - November 2006
Fish Processing	December 2006
Laboratory Analysis Complete	February 2007
Data Review	February 2007
Environmental Information System (EIM) Data Set	
EIM Data Engineer	Brandee Era-Miller
EIM User Study ID	BERA0004
EIM Study Name	Similkameen River and Palmer Lake Investigation of Arsenic in Fish Tissue
EIM Completion Due	June 2007
Final Report	
Report - Author Lead	Brandee Era-Miller
Schedule	
Report - Supervisor Draft Due	April 2007
Report - Client/Peer Draft Due	May 2007
Report - Final Due (Original)	June 2007

The data will be sent to WDOH in March 2007. A completion date for their human health assessment has yet to be determined.

Lab Budget Estimate

Table 1. Lab Budget Estimate.

Analysis	No. of Samples[1]	Cost per Analysis	Cost Subtotals
Total Arsenic	28	$ 81	$ 2,268
Inorganic Arsenic	28	$127	$ 3,556
MMA & DMA	28	$ 144	$ 4,032
25% MEL surcharge for contract analysis			$ 2,464
		Total	$ 12,320

[1] Includes one field (split) replicate. Cost for quality control samples is included.

MMA – Monomethylarsonic acid
DMA – Dimethylarsinic acid
MEL – Manchester Environmental Laboratory

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality and quantity so that the data can be used by WDOH and others to determine potential harm to human health from consumption of fish from the Similkameen River and Palmer Lake. The data should also be comparable to other similar studies. These objectives will be achieved through careful sampling, measurement, and quality control procedures described in this plan.

Sampling Design

Resident fish species will be collected from three areas in the Washington portion of the Similkameen River drainage: (1) Upper Similkameen River between the international border and Palmer Lake, (2) Palmer Lake, and (3) Lower Similkameen River between Palmer Lake and Enloe Dam. These sampling sections are shown in Figure 2. Specific collection sites may vary depending on access and location of fish.

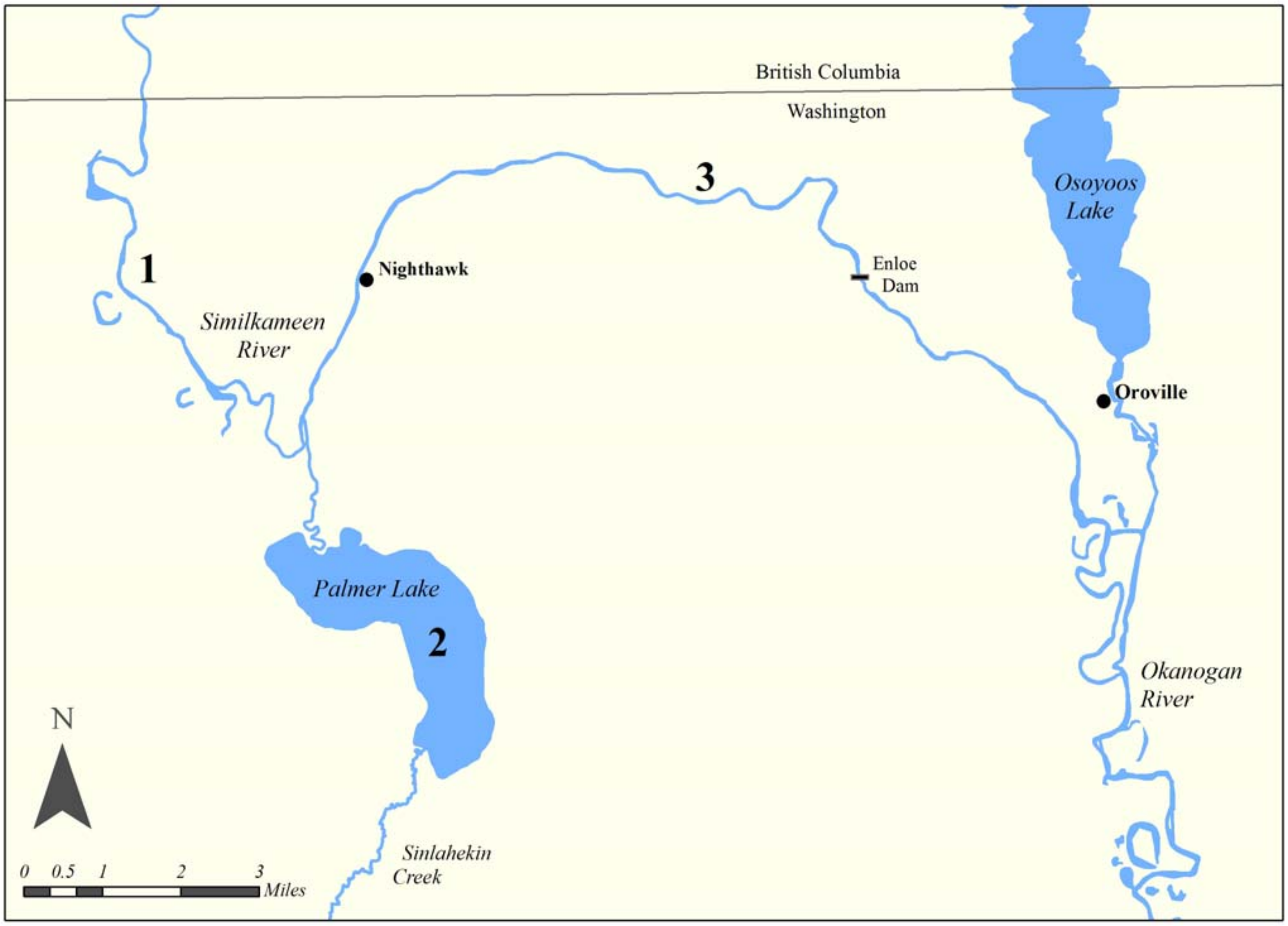

Figure 2. Simikameen River and Palmer Lake Sampling Locations.

A total of 135 individual fish will be targeted for the study: 45 fish from each of the three sample locations (Table 2). Each sampling location will contain three composite samples of three different species. This sampling design was recommended by the WDOH to ensure enough data for a human health assessment.

Table 2. Number of Fish to be Collected for the Similkameen River Study.

Sampling Location	No. of composite samples	No. of fish in each composite	Total No. of Individual Fish
1. Upper River: between the international border and Palmer Lake	9	5	45
2. Palmer Lake	9	5	45
3. Lower River: between Palmer Lake and Enloe Dam	9	5	45
		Study Total:	135

The fish collection will be conducted October through November of 2006. Fish will be collected by a combination of electro-shocking, gill netting, fyke netting, set lines (for burbot only), beach seining, and hook and line.

Only legal size fish will be selected for this study. For species with no size limits, only those large enough to reasonably be retained for consumption will be taken. To the extent possible, the length of the smallest fish in a composite will be no less than 75% of the length of the largest fish.

Fisheries in the Similkameen River include a winter whitefish season (December through March) and a summer rainbow trout season (June through October).

Table 3 lists the fish species found in the Similkameen River and Palmer Lake. This information was obtained from a Washington Department of Fish and Wildlife (WDFW) warmwater fisheries survey of Palmer Lake conducted in 1999 (Osborne et al., 2003) and from Bob Jateff, WDFW fisheries biologist.

Table 3. List of Fish Species for the Similkameen River and Palmer Lake.

Sampling Location:	1. Upper River: Between International Border and Palmer Lake	2. Palmer Lake	3. Lower River: Between Palmer Lake and Enloe Dam
Common species	Possibly similar to the Lower River	Black crappie Bluegill *Kokanee* *Largescale sucker* *Northern pike minnow* Peamouth chub *Smallmouth bass* *Yellow perch*	*Largescale sucker* *Mountain whitefish* *Northern pike minnow* *Rainbow trout* Sculpin *Smallmouth bass*
Less common species	Possibly similar to the Lower River	*Burbot* *Bridgelip Sucker* *Common carp* Chiselmouth *Largemouth bass* *Mountain whitefish* Pumpkinseed *Rainbow trout* Sculpin	*Brook trout* *Common carp* Crappie *Largemouth bass*

Species preferred for the study are shown in *italics* font.

Sampling Procedures

All necessary state and federal permits have been obtained for fish collection. Fishing locations will be recorded by a Global Positioning System (GPS). Fish selected for analysis will be quickly killed with a sharp blow to the head and given an ID number, then the weight and length will be recorded. The fish will be individually wrapped in heavy aluminum foil and put in plastic bags, kept cold in coolers, and frozen immediately upon return from the field.

Preparation of fish tissue samples will follow EPA (2000) guidance and will take place at Ecology's Headquarters building in Lacey, Washington. Precautions will be taken to minimize contamination during sample processing. Persons preparing samples will wear non-talc nitrile gloves and aprons. Work surfaces will be covered with heavy grade aluminum foil. Gloves, aluminum foil, and dissection tools will be changed between composite samples.

Samples for analysis will be prepared by partially thawing the fish to remove the foil wrapper and rinsing in de-ionized water to remove adhering debris. The entire fillet from one or both sides of each fish will be removed with stainless steel knives or scalpels and homogenized in a Kitchen-Aide or Hobart commercial blender. The fillets will be scaled and analyzed skin-on, except for skin-off for burbot since the skin is not eaten.

Composite samples will be made up of equal-weight aliquots from each of the five fish. The samples will be homogenized to uniform color and consistency, then placed in jars, specifically-cleaned for arsenic analyses, and sent to the laboratories. Excess sample will be retained from each composite and stored frozen in the event that additional analysis is required by the laboratories.

All resecting instruments will be washed thoroughly with Liquinox detergent and hot tap water, followed by rinses with 10% nitric acid, de-ionized water, and acetone. Instruments will then be dried in a fume hood before use. The same decontamination procedure will be repeated between each composite sample.

The sex of each fish will be recorded during processing. Aging structures (scales, otoliths, opercles, and/or dorsal spines as appropriate for each species) will be saved for age determination by the Washington Department of Fish and Wildlife (WDFW) in Olympia. Upon request from the WDFW, fin clips may be collected for possible future DNA analysis.

Measurement Procedures

The contracted laboratory (Brooks Rand) is expected to meet all the quality control requirements of the analytical methods being used for this project. Laboratory methods and parameters are shown in Table 4. The laboratory method detection limits (MDLs) shown are what the lab expects to achieve based on previous analysis and are sufficient for WDOH to determine risks to human health from fish consumption.

Table 4. Methods for Arsenic Analysis by Brooks Rand Laboratory.

Parameter	Laboratory MDL (ug/Kg ww)	Analytical Method
Total Arsenic	50	EPA 1638
Arsenic Species*		EPA 1632 Revision A
Inorganic Arsenic	3	
MMA	3	
DMA	10	

* Inorganic arsenic - $As^{+3} + As^{+5}$
MMA - monomethylarsonic acid
DMA - dimethylarsinic acid

Measurement quality objectives (MQOs) for the analytical methods are described in further detail in the EPA method references (EPA, 1996 and 2001). Because there are limited data available for arsenic species in freshwater fish, study MQOs for precision and accuracy will be based solely on laboratory quality control results.

Quality Control Procedures

Field

The field sampling and decontamination procedures described in the *Sampling Procedures* section of this Quality Assurance (QA) Project Plan will be carefully followed to avoid contamination of samples. A copy of the QA Project Plan will be taken into the field for reference.

Natural variability in arsenic concentrations between individual fish will be assessed by analyzing samples as composites and replicates as described in the *Sampling Design* section of this QA Project Plan.

One field duplicate (split sample) will be analyzed for the study. This sample will be split during fish tissue processing and submitted blind to the laboratory with a different sample number and sample name.

Laboratory

The quality control procedures followed by the contract laboratory (Brooks Rand) will be satisfactory for the purposes of this project. Laboratory quality control samples to be analyzed are shown in Table 5. The samples will be analyzed by the laboratory in two batches. The number of quality control samples shown here are for both batches combined.

Table 5. Laboratory Quality Control Samples.

Analysis	Method Blank	Lab Duplicate	Lab Control Sample	Matrix Spike	Matrix Spike Duplicate	Lab SRM[1]
Total Arsenic	6	2	2	3	3	3
Arsenic Species	6	2	2	3	3	3

[1]An in-house internal standard reference material (SRM) developed from the laboratory's historical data.

Brooks Rand will prepare and analyze three blanks with all batches. They will perform a blank correction using the mean of these blanks.

Laboratory duplicates will be used to help assess the analytical precision associated with the fish tissue data. Duplicate samples will be selected from different sampling sections.

Data Management Procedures

Field data and data from the processing of fish tissue will be recorded on printed data sheets and then carefully transferred to electronic data sheets.

The contract laboratory (Brooks Rand) will provide the data in electronic format and include a case narrative discussing any problems with the analysis, corrective action taken, and an explanation of data qualifiers. Ecology's Manchester Laboratory will review the contract data package and make any additional corrections including changes to data qualifiers prior to receipt of the data by the project manager. The project manager will then review the data to determine if project measurement quality objectives (method blanks, check standards/LCS samples, matrix spikes, and laboratory duplicates) were met.

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

Audits

The contract laboratory for the study (Brooks Rand) has been accredited through Ecology's Laboratory Accreditation Section. The accreditation process includes extensive on-site audits. More information about Ecology's accreditation process can be found in the *Procedural Manual for the Environmental Laboratory Accreditation Program* (Ecology, 2002).

Reports

The project manager will provide a data report to WDOH in March 2007. Their review and any associated formal reports will be provided by them separately from the Ecology technical report. A date for the completion of the WDOH review has yet to be determined.

The Ecology draft technical report will be provided to the Ecology client, internal Ecology reviewers, and other interested parties by May 2007. The final technical report will be published by June 2007. Data will be entered into EIM by June 2007.

Data Verification and Validation

Manchester Laboratory will review and verify laboratory results and case narratives from the contract laboratory (Brooks Rand). Formal (third party) validation of the data will not be necessary for this project.

Data Quality (Usability) Assessment

Once the data have been reviewed and verified, the project manager will determine if the quality and quantity of the data are useable for the purposes of the study. The project manager will review laboratory data by determining if study MQOs were met.

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