Quality Assurance Project Plan

Lake Spokane Phosphorus Input II

Water Quality Grant Number: WQC-2016-StCoCD-00178

Prepared by: Rich Sheibley Unites States Geological Survey

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Prepared for: Washington State Department of Ecology

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For:

Lake Spokane Phosphorus Input II WQC-2016-StCoCD-00178

Date: August, 2016

Prepared by:

Rich Sheibley Charlie Kessler

U.S. Geological Survey Stevens County Conservation District

Prepared for:

Karin Baldwin Washington State Department of Ecology

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1.0/2.0 Title Page/TOC/Abstract

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Lake Spokane Phosphorus Input II

June 2016

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2.0 Abstract

In recent decades, Lake Spokane has experienced water-quality problems associated with eutrophication, and phosphorus was identified as the limiting nutrient that regulates the growth of aquatic plants in the lake. Phosphorus is delivered to Lake Spokane from municipal and industrial point-source inputs to the Spokane River upstream of Lake Spokane, but is also conveyed by groundwater and surface water from nonpoint-sources including septic tanks, agricultural fields, and wildlife. In response, the Washington State Department of Ecology listed Lake Spokane on the 303(d) list of impaired water bodies for low dissolved oxygen levels and developed a Total Maximum Daily Load (TMDL) for phosphorus in 1992, which was revised in 2010 after continued algal blooms and water-quality concerns. Between 1992 and 2010, point sources of phosphorus were reduced and now groundwater inputs have been identified as a potential substantial source of phosphorus to Lake Spokane. Current estimates of phosphorus loading to Lake Spokane from discharging groundwater are not well defined, but are needed to facilitate management and reduction of sources of phosphorus to the lake and its biota. The objective of this study is to estimate the groundwater input of phosphorus, including seasonal variations, to Lake Spokane by measuring the concentration of phosphorus in groundwater and estimating groundwater discharge rates. Quarterly groundwater-quality measurements and groundwater-discharge rate estimates will be used to estimate seasonal variations in groundwater inputs of phosphorus.

3.0 Background

In recent decades, Lake Spokane has experienced water-quality problems associated with eutrophication. Consumption of oxygen from the decomposition of aquatic plants that have proliferated due to high nutrient concentrations has led to seasonally low dissolved oxygen levels in the lake. Of nitrogen and phosphorus, the two primary nutrients necessary for aquatic vegetation growth, phosphorus was previously identified as the limiting nutrient (Soltero and others, 1973; GeoEngineers Inc, 2011) that regulates the growth of aquatic plants, and thus dissolved oxygen levels, in Lake Spokane. Phosphorus is delivered to Lake Spokane from municipal and industrial point-source inputs to the Spokane River upstream of Lake Spokane, but is also conveyed by groundwater and surface water from nonpoint-sources including septic tanks, agricultural fields, and wildlife. In response, the Washington State Department of Ecology listed Lake Spokane on the 303(d) list of impaired water bodies for low dissolved oxygen levels and developed a Total Maximum Daily Load (TMDL) for phosphorus in 1992, which was revised in 2010 after continued algal blooms and water-quality concerns.

Since the late 1970s, after advanced waste treatment at the Spokane treatment plant went online, significant progress has been made to reduce point-source inputs of phosphorus to the Spokane River upstream of Lake Spokane. Despite these reductions in point sources, eutrophication is still a problem so attention has turned to non-point source phosphorus input to the lake, such as groundwater and on-site septic systems. Phosphorus from septic system effluent is partially retained by soils beneath septic system drain-field via sorption to sediments and precipitation and may be further attenuated by sorption along groundwater-flow paths. However, there is a growing concern that the retention capacity of sediments for binding phosphorus can be exceeded allowing phosphorus in septic system effluent to migrate greater distances along groundwater-flow paths and potentially discharge to surface water bodies. As a result, groundwater inputs from on-site septic systems have been identified as a potential source of phosphorus to Lake Spokane based on the very coarse textured sediments (low sorption capacity) in the area, high density of septic system use in some areas, and a theoretical analysis of phosphorus retentions capacity for this area (HDR 2007 and GeoEngineers Inc 2009, 2010, 2011).

3.1 Study area and surroundings

The impoundment of the Spokane River at Long Lake dam forms a 24-mile, 5,000-acre reservoir called Lake Spokane with 243,000 acre-feet of water and 54 miles of shoreline (fig. 1). Above Nine Mile Dam, which is immediately upstream of Lake Spokane, the Spokane River drains 5,220 square miles of northeastern Washington and northern Idaho including the cities of Spokane and Coeur d'Alene, Idaho. Several unregulated tributaries flow into Lake Spokane, the largest of which is the Little Spokane River, which enters Lake Spokane about 2 miles downstream of Nine Mile Dam. The predominant land covers surrounding Lake Spokane are undeveloped ponderosa pine forest, agriculture, and rural residential development within three unincorporated communities including Nine Mile Falls, Suncrest, and Tum. Residential development near Lake Spokane occurs along the shoreline of Lake Spokane and on 300-foot high terraces created during large outburst floods of Glacial Lake Missoula at the end of the

Pleistocene Epoch. Sewage from houses and businesses is managed by on-site septic systems throughout the area surrounding Lake Spokane.

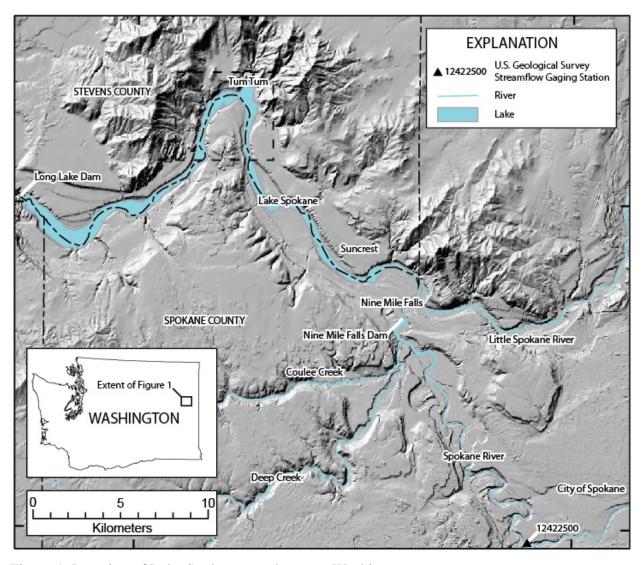


Figure 1. Location of Lake Spokane, northeastern Washington

Discharge of the Spokane River is regulated at Long Lake dam, which was completed in 1915, for hydroelectric power generation by Avista Utilities. Mean monthly discharge measured from Water Year 1892 to 2014 at the Spokane River at Spokane, Washington [U.S. Geological Survey (USGS) streamflow-gaging station 12422500] ranges from a high of 17,700 cfs in May during snowmelt to a low of 1,690 cfs in August during summer baseflow. The pool elevation of Lake Spokane is held at approximately 1535 feet above mean sea level for most of the year except for short periods of 10-foot drawdown during the winter intended to manage pervasive aquatic plants by exposing them to freezing conditions in shallow areas of the lake. Lake Spokane is shallowest at the outlet of Nine Mile Dam and becomes increasingly deeper towards Long Lake Dam where maximum water depths approach 180 feet.

3.2 Logistical problems

A similar set of samples was collected at Lake Spokane in 2014, therefore access to sample locations have already been verified. New sample locations will be determined in cooperation with contacts made through the Stevens County Conservation District. Boat launches needed for sampling the nearshore have already been identified.

3.3 History of study area

There is a long history of water quality studies of Lake Spokane. Water quality impairment has been an issue for decades, although the cause of the impairment has shifted over the years. Prior nutrient enrichment was attributed to phosphorus in effluent from the City of Spokane Wastewater Treatment Facility and a series of reports to characterize water quality of the lake were published through the 1970s and 80s. The reports spanned a time period when advanced wastewater treatment measures were installed at the Spokane plant and documented the large reduction of phosphorus loading from the Spokane River and subsequent improvement in the trophic status of the lake (Soltero and others 1981). Recently, it has been suggested that phosphorus loading from groundwater is more important than the past and further study is warranted.

3.4 Contaminants of concern

The contaminants of concern for this study are dissolved nutrients in groundwater. These include ammonia-nitrogen, nitrite-nitrogen, nitrate-nitrogen, and orthophosphate.

3.5 Results of previous studies

A similar, but limited study of shallow groundwater nutrient chemistry was completed by the U.S. Geological Survey in 2015 (Gendaszek and others, 2016). In this study, shallow groundwater was sampled in March and April 2015 from 30 piezometers driven into the near-shore area of Lake Spokane. Nitrate plus nitrite concentrations in groundwater discharging to Lake Spokane downgradient of undeveloped areas were significantly lower than those measured downgradient of both near-shore and terrace residential development. Orthophosphate concentrations in groundwater were not significantly different with respect to upgradient land use. A summary of this data is provided in Table 1.

Gendaszek and others (2016) provided some important background data on shallow groundwater nutrient concentrations, however, that study did not quantify groundwater flux (flow) into the lake from the nearshore areas where these samples were collected. In addition, samples were collected during a single season (spring 2015) so temporal variability in shallow groundwater concentrations are unknown. The current project proposed under this QAPP builds on the work of Gendaszek and others (2016) by expanding the spatial and temporal scope of nutrient sampling and by estimating groundwater flow into the lake in order to calculate nutrient loads to Lake Spokane.

Summary of nutrient concentrations for sampled land-use covers in Lake Spokane.

Up-Gradient Land Cover	Number of Samples	Mean DIN (μg/L) ± SD	Mean Orthophosphate (μg/L) ± SD
Near-shore residential development (NSRD)	10	2,373 ± 1,160	53 ± 41
Terrace residential development (TRD)	10	$2,007 \pm 1,798$	48 ± 26
Eastern Undeveloped (EUND)	10	655 ± 501	69 ± 74

DIN = dissolved inorganic nitrogen and is the sum of ammonia, nitrite and nitrate

3.6 Regulatory criteria or standards

There are currently no water quality criteria set for phosphorus in groundwater in Washington. For nitrate, there is a limit of 10 mg/L (WAC 173-200-040). Oxygen criteria have been set for the study area and are summarized below.

Designated aquatic life uses and dissolved oxygen criteria protected by this TMDL as defined in the 2006 water quality standards.

1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	ne 2000 water quarty standards.							
Portion of Study Area	Aquatic Life Uses	Dissolved Oxygen Criterion						
Spokane River (from Nine Mile Bridge to the Idaho border)	Migration/ Rearing/ Spawning	Dissolved oxygen shall exceed 8.0 mg/L. If "natural conditions" are less than the criteria, the natural conditions shall constitute the water quality criteria.						
Lake Spokane (from Long Lake Dam to Nine Mile Bridge)	Core Summer Habitat	No measurable (0.2 mg/L) decrease from natural conditions.						
Spokane Arm of Lake Roosevelt (from confluence of Columbia River and Spokane River to Little Falls Dam – outside of TMDL compliance point)	N/A	Dissolved oxygen shall not be less than 8.0 mg/L. ^b						

a Washington water quality standards (WAC 173-201A-020) define "natural conditions" or "natural background levels" as "surface water quality that was present before any human-caused pollution. When estimating natural conditions in the headwaters of a disturbed watershed, it may be necessary to use the less disturbed conditions of a neighboring or similar watershed as a reference condition."

In addition, the Spokane River has the following specific water quality criteria, per WAC 173-201A-130, from Long Lake Dam (RM 33.9) to Nine Mile Bridge (RM 58.0). Special conditions:

(a) The average euphotic zone concentration of total phosphorus (as P) shall not exceed 25 µg/L during the period of June 1 to October 31.

b Spokane Tribe of Indians Surface Water Quality Standards (Resolution 2003-259

4.0 Project Description

Current phosphorus loading to Lake Spokane from groundwater discharge to the lake has not been well defined. Previous work by the USGS showed there was phosphorus present in groundwater but estimates of phosphorus loads from groundwater are currently unknown. Groundwater discharge is one of many pathways that phosphorus can enter the lake and estimates are needed to facilitate management and reduction of this source of phosphorus to the lake.

4.1 Project goals

The goal of this project is to estimate the nearshore groundwater input of phosphorus, including seasonal variations, to Lake Spokane downgradient of varying residential land uses. Current estimates of phosphorus loading to Lake Spokane from discharging groundwater are not well defined, but are needed to facilitate management and reduction of sources of phosphorus to the lake and its biota.

4.2 Project objective

Collection of shallow groundwater samples for nutrients will be analyzed to ascertain characteristic seasonal concentrations potentially entering the lake. These concentrations will be combined with estimates of groundwater flux from manual (seepage meters) and automated (continuous temperature profiles) methods to determine seasonal groundwater loading of phosphorus to Lake Spokane from residential areas on the lakeshore.

4.3 Information needed and sources

This project will be addressing a large data gap in what we know about groundwater inputs into the lake. However, we will be putting our data into context by reviewing the nutrient budget work on Lake Spokane by Soltero and others (1992). In addition, we will compare our data to the current wasteload allocations outlined in the Lake Spokane dissolved oxygen TMDL (Moore and Ross, 2010).

4.4 Target population

The target population for this project will be to characterize shallow nearshore groundwater nutrient chemistry downgradient of a range of residential land uses.

4.5 Study boundaries

The study area lies within Lake Spokane (fig. 1) a 24-mile, 5,000-acre reservoir formed by Nine Mile Dam and Long Lake Dam. Shallow groundwater sampling will focus on rural residential development within unincorporated communities of the north shore including Suncrest and Tum Tum (fig.1) as well as areas with undeveloped near shore land uses.

4.6 Tasks required

The following tasks, and proposed time window for each, for the current project are listed below:

- Task 1 Site selection and planning (June-Sept, 2016)
- Task 2 Quarterly water quality sampling (July 2016 June 2018)
 - o Install temperature loggers for long term data collection
- Task 3 Estimates of groundwater discharge to the lake (July 2016 June 2018)
- Task 4 Estimate groundwater loads to the lake from varying residential land uses (July 2016 June 2018)
- Task 5 Data analysis and report publication (April 2018 September 2018)

4.7 Practical constraints

Access to the lake shore will be primarily by boat; however in some cases we will need landowner permission and/or access to sample sites. Landowner contacts from previous work in this area (Gendaszek and others, 2016) will be used in addition to establishing new local contacts. However, the success of the project is not expected to be impacted by the lack of access to sample sites.

4.8 Systematic planning process used

Not applicable for the current QAPP.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Karin Baldwin, Washington State Department of Ecology (Ecology): Will oversee the management of the project to ensure that activities are conducted in accordance with Department of Ecology guidelines and standards.

Charlie Kessler, Stevens County Conservation District (SCCD): Provide technical management of the project to ensure that activities are conducted in accordance with the centennial grant application between SCCD and Ecology. Will provide logistical support to field crews including coordination of local sampling activities and be a reviewer on all project documents. Will facilitate scheduling of public meetings.

Rich Sheibley, USGS Washington Water Science Center: As project chief, will implement project objectives including coordination of field sampling, processing, transport of samples for shallow groundwater and groundwater discharge rates. Analyze data and provide interpretive findings to SCCD. Ensure that the project is conducted according to USGS guidelines and standards including quality assurance and quality control standards.

Hydrologic technicians, USGS Washington Water Science Center: One to two hydrologic technicians will assist the project chief in all aspects of field investigations. Duties include assistance collecting shallow groundwater chemistry, estimates of groundwater discharge, and report writing.

Analytical Laboratory

All water chemistry sampled will be analyzed by the USGS National Water Quality Laboratory (NWQL) in Lakewood, CO. Samples will be preserved and shipped overnight according to established protocols (National Field Manual, variously dated).

5.2 Organization chart

This section was left intentionally blank. Project is not complex enough to warrant an organizational chart.

5.3 Project schedule

A summary of the project schedule is provided below. This project begins in quarter 3 (Q3) of the federal fiscal year (FY) 2016 and continues until Q1 FY 2019. The federal fiscal year begins on October 1st and ends on September 30th.

Project timeline

	FY 2016			FY 2017			FY 2018			FY 2019			
	Oct-	Jan-	Apr-	Jul-	Oct-	Jan-	Apr-	Jul-	Oct-	Jan-	Apr-	Jul-	Oct-
	Dec	Mar	Jun	Sep	Dec	Mar	Jun	Sep	Dec	Mar	Jun	Sep	Dec
Task 1: Site selection and planning.			X	X									
Task 2: Quarterly Water- Quality Sampling				X	X	X	X	X	X	X	X		
Task 3: Seepage Estimates				X	X	X	X	X	X	X	X		
Task 4: Phosphorus Flux Estimates								X	X	X	X		
Prepare report											X	X	
Report review and publication												X	X

5.4 Limitations on schedule

We do not anticipate any limitations on the scheduling of this project. With just quarterly sampling taking place, there will be time to work around unforeseen changes in staffing, weather, and other unexpected events.

5.5 Budget and funding

The Stevens County Conservation District has \$150,000 to contribute towards this project. The USGS has a match of \$100,000.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

This project is to gather information about nutrient content (nitrogen and phosphorus) and loading of groundwater entering Lake Spokane. To improve the water quality, and increase dissolved oxygen in the lake, information to assess the most effective means by which to control phosphorus loading is needed. This includes refining the information we have from prior studies with respect the range of phosphorus concentrations discharging from groundwater to the lake, and identifying the locations or land uses that are correlated with those concentration ranges. The data will be used by the Washington State Department of Ecology inform future water quality modeling of the lake and may be used to help implement the Spokane River and Lake Spokane Dissolved Oxygen TMDL.

6.2 Measurement Quality Objectives

Measurement quality objectives for the sampling of shallow groundwater chemistry described here are to obtain and analyze sufficient numbers of high quality samples to meet the goals and objectives of this program. Data quality indicators include precision, bias, sensitivity, representativeness, comparability, and completeness (defined in Appendix A).

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error and is expressed as the relative percent difference (RPD) between two samples. For this project, three field replicates for shallow groundwater nutrients will be collected quarterly for two years. Replicates will be collected sequentially from the same piezometer and will result in approximately 24 replicates. This will result in approximately 10% of all environmental samples having a replicate over the course of the project as suggested in the National Field Manual, Chapter A4 (U.S. Geological Survey, variously dated) and Wagner and others (2007). For nutrient samples, the threshold for RPD of field replicates is $\leq 20\%$ for all parameters (table 4).

For field parameters, measurements of temperature, dissolved oxygen, pH, and specific conductivity will be determined using a YSI 6280 V2 sonde or similar multi-parameter sonde. Precision limits for the sondes are:

• Water temperature between -5 and 50 °C, resolution 0.01 °C \pm 0.15 °C

- Dissolved oxygen between 0 and 50 mg/L, resolution 0.01 mg/L \pm 0.1 mg/L or 1%, whichever is greater
- pH between 0 and 14 units, resolution 0.01 unit ± 0.2 unit
- Specific conductance between 0 and 100 mS/cm, resolution 0.001 mS/cm $\pm 0.5\%$ of reading

The analytical laboratory (NWQL) will conduct laboratory blank, laboratory control samples (LCS), and laboratory control replicates according to their quality assurance and control plan (with every batch of approximately 20 samples). In addition, laboratory replicates and matrix spikes (MS) of environmental samples from this project will be requested at approximately a 10% frequency.

Precision of groundwater discharge flux using manual seepage meters will be assessed by examining the variation of flux estimates across 10 seepage meters co-located at a designated field site. Information on the variability of flux estimates will be used to calculate a 95% confidence interval around the mean groundwater flux value.

Measurement Quality Objectives: Laboratory Analyses of Water Samples

Parameter	Check Standard (LCS)	Duplicate Samples	Matrix Spikes	Matrix Spike- Duplicates	Surrogate Standards	Lowest Concentrations of Interest
	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Units of Concentration
Nitrogen, ammonia	90-110	≤ 20	80-120	≤ 20	NA	0.01 mg/L
Nitrogen, nitrite	90-110	≤ 20	80-120	≤ 20	NA	0.001 mg/L
Nitrogen, nitrite + nitrate	90-110	≤ 20	80-120	≤ 20	NA	0.01 mg/L
Phosphorus, orthophosphate	90-110	≤ 20	80-120	≤ 20	NA	0.004 mg/L

NA = not applicable, these types of quality control samples are not typically collected for nutrients.

6.2.1.2 Bias

Bias is the closeness of agreement between an observed measurement value to the expected value or to the most-probable value. The multi-parameter sonde used for discrete measurements of temperature, pH, dissolved oxygen, and specific conductivity will be calibrated in the field on the day of each sampling event. Calibration records will be maintained and preserved throughout the project. Furthermore, all field personnel will be assessed annually through the USGS National Field Quality Assurance (NFQA) program. The NFQA program sends laboratory prepared samples to all USGS offices for analysis of field parameters (pH,

conductivity) and compares results from each individual to the known values. Field personnel not receiving a passing score will be asked to resubmit samples.

For nutrient analyses, bias of the NWQL data will be assessed through the inorganic blind sample program administered by the Branch of Quality Systems (BQS) of the USGS. The BQS is a group independent from NWQL and oversees regular (biannual) testing of NWQL (and multiple other national labs) for a suite of parameters, including dissolved and total nutrients. Results from these assessments are available online and will be tracked throughout the duration of this project to ensure bias is minimized. In addition, field blanks (once per quarter) and equipment blanks samples (once annually) will be collected. The field blank will be lab-provided inorganic-free water transported from the WAWSC in its original container and processed onsite identically to environmental samples and analyzed for dissolved nutrients. The equipment blank is the same as a field blank but it is processed in the laboratory. Annual equipment blanks are required as part of USGS sampling protocols (Horowitz and others, 1994; Wagner and others 2007) and will be analyzed more frequently if sample equipment is replaced or changed during the project. Detections within these blank samples will indicate if there is any bias in our field samples as a result of equipment cleaning and field collection/processing of samples.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. For nutrient samples, sensitivity is described as the method detection limit (MDL). The MDLs for dissolved nutrients are provided in table 3. Results from the field and equipment blanks (described above) will indicate if the equipment cleaning, sampling collection, handling, and processing procedures introduce contamination that could increase the low reporting limits.

For groundwater flux estimates, the ability to measure a value of flux is dependent on the environmental conditions at the sample location. For manual seepage measurements, flux is determined from the change in water volume over time in a flexible capture bag attached to the top of a 55-gal drum inserted into the lakebed. If flux is small, the deployment time can be extended to increase chances of detecting a volume change. For the automated temperature methods, flux is modeled based on changes in temperature with depth. Temperature will be measured at up to 6 locations within the lake bed, allowing for a number of possible combinations of temperature. This will ensure that under most conditions, an estimate of groundwater flux will be possible.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Comparability expresses the confidence with which one data set can be compared to another. For this project, comparability will be achieved through the use of standard U. S. Environmental Protection Agency approved laboratory methods. In addition, standard techniques to collect and analyze representative water quality samples will be used (U.S. Geological Survey, variously dated). The methods used for this current project are based on similar work examining groundwater discharge of nitrogen in the intertidal zone of Hood Canal, WA (Simonds and

others, 2008). In addition, estimates of groundwater flux employ procedures used by a wide variety of studies and included in a multiple reports for the analysis of groundwater/surfacewater interactions published by the USGS (Stonestrom and Constantz, 2003; Rosenberry and Labaugh, 2008).

6.2.2.2 Representativeness

Representativeness expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. For this project, representativeness will be determined by the sample location selection, timing of the sampling events, sample collection methods, acceptance criteria, and sample handling and storage (U.S. Geological Survey, variously dated). To ensure samples for chemical analysis are representative, they will be collected:

- From a location along the nearshore of varying upland land uses
- Quarterly to assess annual variability
- Across multiple years to estimate any inter-annual variability
- Across a range of lake stage to determine how stage influences the amount of groundwater entering the lake

To ensure groundwater flux estimates are representative of nearshore conditions throughout the lake, they will be collected:

- From a location along the nearshore of varying upland land uses
- Seepage meters and temperature rods will be placed along the shore and perpendicular to the shore to determine how much of the lakebed is seeing groundwater discharge.
- Quarterly to assess annual variability
- Across multiple years to estimate any inter-annual variability
- Across a range of lake stage to determine how stage influences the amount of groundwater entering the lake.

6.2.2.3 Completeness

Completeness is a measure of the amount of acceptable analytical data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Target completeness values are 95% for nutrient analyses of water. Target completeness for estimating groundwater discharge at each site is also 95%.

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design

Field measurements will be made quarterly for 2 years from temporary piezometers and seepage meters. Piezometers will extend up to three feet into the lake bed. Approximately 30 piezometers will be installed along a variety of near shore development (relatively undeveloped,

near shore development, and terraced development). Approximately 5 to 10 seepage meters and 1 to 2 long term sediment temperature profilers will be used at each type of near shore development. Additional details are described below.

7.1.1 Sampling location and frequency

Groundwater samples will be collected from shallow (less than 1 meter depth), temporary piezometers. Samples will be taken in the nearshore along the northern shore of the lake located within Stevens County. We will target three levels of nearshore land use; high residential development, low residential development, and undeveloped and will include locations of Suncrest and Tum Tum. During each sample trip, 10 samples will be collected in the nearshore downgradient of each these differing land uses for a total of 30 samples per field trip. Sample trips will take place quarterly beginning in July 2016 through June 2018 for a total of 8 sample trips during the two year period.

Groundwater flux estimates will be made at each location using manual seepage meters and continuous lakebed temperature profilers. These two approaches will allow for short term (~ hours) to long term (~months) estimates of groundwater flux entering the lake.

7.1.2 Parameters to be determined

Shallow groundwater will be analyzed for dissolved nutrients. These parameters include: nitrogen, ammonia (NH₃), as N, nitrogen, nitrite (NO₂), as N, nitrogen, nitrite plus nitrate (NO₂+NO₃), as N, and phosphorus, orthophosphate (PO₄), as P. In addition, shallow groundwater will be analyzed in the field for temperature, dissolved oxygen, pH and specific conductivity using a field multimeter.

Groundwater fluxes will be expressed in units of volume per time from the manual and automated temperature methods.

7.1.3 Field measurements

Field measurements at each piezometer will be made for temperature, dissolved oxygen, specific conductivity, and pH. Field measurements will be made using an YSI 6920 V2 multiparameter data sonde. Operation, maintenance, and calibration of all equipment will follow established USGS protocols (U.S. Geological Survey, variously dated).

7.2 Maps or diagram

The study area is shown in Figure 1. The general locations of the sampling sites are indicated in this figure and include residential areas of Suncrest, and Tum Tum, as well as undeveloped areas west of Tum Tum. Specific sampling locations will be established once site reconnaissance and sampling begins.

7.3 Assumptions underlying design

It is assumed that groundwater discharge is occurring at each of the field locations and the rate of discharge is relatively constant over seasonal time scales.

7.4 Relation to objectives and site characteristics

This sample design will allow for the estimation of groundwater nutrient flux downgradient of the several residential and undeveloped areas. The design will take into account seasonal and inter-annual variability and allow for sufficient resolution of the variation of groundwater along the north shore of Lake Spokane.

7.5 Characteristics of existing data

Shallow groundwater chemistry was recently sampled in this region by Gendaszek and others (2016). In this study, nutrient content at three areas along the lake shore was evaluated. This previous data will help put the new data collection into context to ensure that our samples are representative of general shallow groundwater conditions. However, a relationship between land use, groundwater flow, or hydrogeologic environment and nutrient concentrations detected in groundwater was not established previously (Gendaszek and others, 2016). In addition to assessing the nutrient loading rates by location over the course of the current proposed study, the factors contributing to the loading will be evaluated where applicable.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

Field measurements for temperature, dissolved oxygen, pH and conductivity, will follow standard operating procedures (SOPs) provided by the USGS (U.S. Geological Survey, variously dated) and the following SOPs developed by Ecology:

- EAP011 Instantaneous Measurements of Temperature in Water (Nipp, 2006)
- EAP031 Collection and Analysis of pH Samples (Ward, 2014a)
- EAP032 Collection and Analysis of Conductivity Samples (Ward, 2014b)

Installation and monitoring water quality using hand-driven piezometers will follow USGS methods in Rosenberry and LaBaugh (2008) and Ecology SOP EAP061 – Installing, Monitoring, and Decommissioning Hand-Driven In-water Piezometers (Sinclair and Pitz, 2016).

A set of 10 hand-driven piezometers will be installed at each sample site to characterize shallow ground water chemistry. Field parameters will be collected from hand driven piezometers using a YSI multi-meter and flow through cell. Several piezometer volumes will be pumped to flush the system and readings will be recorded after all parameters are stable. After field readings are recorded, tubing will be used to fill bottles for nutrient samples. Containers, preservation methods and hold times are provided in section 8.3. In addition to nutrient

sampling, estimates of vertical hydraulic gradient (VHG) will be made at each piezometer following procedures in Rosenberry and LaBaugh (2008). The VHG will be determined with a manometer board to measure the difference in pressure head inside the piezometer and the lake surface (fig. 2). Positive VHG indicates potential for groundwater discharge into the lake, where negative VHG shows potential for groundwater recharge (flow from surface into the lakebed).

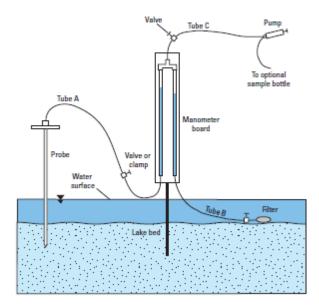


Figure 2. A portable field manometer board used to determine vertical hydraulic gradients in monitoring piezometers (from Rosenberry and LaBaugh, 2008).

Groundwater flux estimates will be made at each location using manual seepage meters and continuous lakebed temperature profilers. These two approaches will allow for short term (~hours) to long term (~months) estimates of groundwater flux entering the lake. These methods have been used by the USGS for decades and standard operating procedures have been established (Rosenberry and LaBaugh, 2008; Stonestrom and Constantz, 2003).

Seepage meters are devices that isolate a small area of the lakebed and measure the flow of water across that area (figure 3). A known volume of water is put into a volume capture bag, and installed onto the meter. The bag is left to sit for the collection time and a final volume recorded. The change in volume over time is calculated as the groundwater flux across the sediment-water interface.

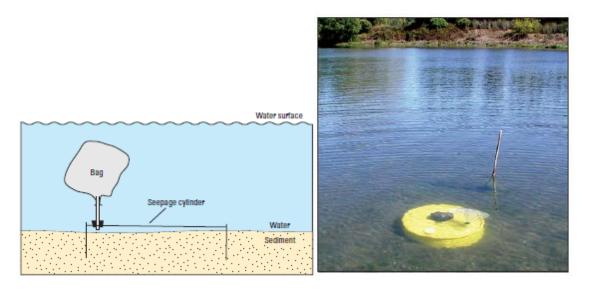


Figure 3. Full-section view of seepage meter placement in a lake showing details of placement in the sediment and photo of seepage meter placed in the field (from Rosenberry and LaBaugh, 2008)

Temperature methods for estimating groundwater flux involve numeric simulation of lakebed temperature profiles. Lakebed thermal profiles will be affected by the amount of groundwater flow through the measurement area (Stonestrom and Constantz, 2003) (Figure 4). Two to three temperature rods (about 1 meter in length) constructed out of PVC will be installed at each residential sample location (Suncrest and Tum Tum) and an undeveloped area. Temperature at up to 6 depths will be measured for the 2-year study period and data will be downloaded quarterly. Temperature profile data will be modeled using the recently updated USGS program 1DTempPro (http://water.usgs.gov/ogw/bgas/1dtemppro/) which provides a graphical user interface for the solution of a 1-dimensionl heat flux equation. Temperature profile data collected in the field is used by the model (1DTempPro) to calibrate the heat flux model. Optimization of the model fit to observed data is used to estimate vertical groundwater/surface-water exchange (figure 5) of the system.

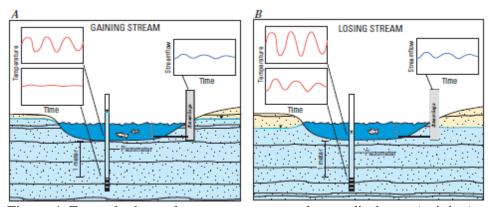


Figure 4. Example thermal responses to groundwater discharge (gaining) and recharge (losing) reach of a stream. The same concepts hold in a lakebed (from Rosenberry and LaBaugh, 2008).

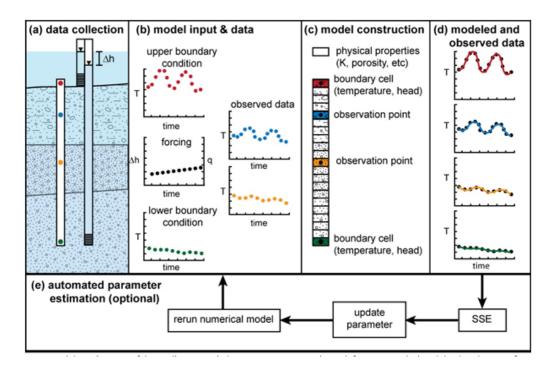


Figure 5. Procedure of estimating groundwater flux through a lakebed using the 1DTempPro model. (Adopted from http://water.usgs.gov/ogw/bgas/1dtemppro/). (a) data is collected in the field at several depths below the sediment-water interface; (b) the heat flux model uses the upper and lower temperature data as the boundary conditions for the model domain; (c) definition of sediment properties and locations of temperature boundaries provide the construct to (d) model the vertical component of groundwater flux.

8.2 Containers, preservation methods, holding times

Sample Containers, Preservation and Holding Times (Fishman, 1993)

Parameter	Matrix	Minimum Quantity Required	Container	Preservative*	Holding Time
Nitrogen, ammonia	Groundwater	10 ml	125 ml brown polyethylene bottle	Keep chilled at 4 ⁰ C	30 days
Nitrogen, nitrite	Groundwater	10 ml	125 ml brown polyethylene bottle	Keep chilled at 4 ⁰ C	30 days
Nitrogen, nitrite + nitrate	Groundwater	10 ml	125 ml brown polyethylene bottle	Keep chilled at 4 ⁰ C	30 days
Phosphorus, orthophosphate	Groundwater	10 ml	125 ml brown polyethylene bottle	Keep chilled at 4 ⁰ C	30 days

^{*}no additional preservatives (for example, H₂SO₄) for dissolved nutrients, USGS adds H₂SO₄ to samples that are digested and analyzed for total nitrogen and phosphorus only.

8.3 Invasive species evaluation

Field staff will follow the procedures described in Ecology SOP EAP070 – Minimizing the Spread of Invasive Species (Parsons and others, 2012). The study area for this project is not located within areas of extreme concern. However, it is common practice for field personnel in the Washington Water Science Center to decontaminate field gear with a 1% Virkon solution to ensure invasive species are not spread from site to site. Boats used to access field sites will be inspected after use on boat ramps and cleaned accordingly.

8.4 Equipment decontamination

Standard field and laboratory cleaning procedures for all sample equipment (tubing, sample bottles) will follow standard procedures outlined in the National Field Manual (U.S. Geological Survey, variously dated). This includes rinsing with tap or DI water, scrubbing and soaking in liquinox, soaking in 5% HCl solution for 30 minutes, followed by copious rinsing with ultra-pure DI water.

8.5 Sample ID

Sample IDs for groundwater will be based on the site location followed by a piezometer ID number (i.e., Suncrest001). In addition, the USGS assigns site IDs a unique 15 digit number based on the piezometer latitude and longitude location.

8.6 Chain-of-custody, if required

The USGS uses a standard Analytical Service Request (ASR) form for all samples sent to the NWQL. An Example ASR is provided in Appendix B. Samples are shipped overnight to the NWQL and upon receiving, samples are logged in, and an automatic email generated and sent to the project chief to confirm status of all samples received. This ASR is scanned and kept as part of the permanent record during the life cycle of the sample at the lab.

8.7 Field log requirements

All field sampling activities will be recorded in standard USGS water quality field sheets (Appendix C). Information on these sheets includes, but is not limited to:

- Environmental conditions
- Date, time, location, ID, and description of each sample
- Instrument calibration procedures
- Field measurement results
- Identity of QC samples
- Unusual circumstances that may affect interpretation of results

In addition, a field log will be maintained by each sampler that will contain additional information. This field log will be a bound, waterproof notebook used with permanent,

waterproof ink for entries. It will use a single strikethrough (one line) to correct information and all corrections will be initialed and dated. The field log will include:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes to plan
- Unusual circumstances that may affect interpretation of results

8.9 Other sampling-related activities

Not applicable. Necessary activities are detailed in other sections of this QAPP.

9.0 Measurement Methods

9.1 Lab Measurement Methods Table.

Field and Laboratory measurement methods

Analyte	Sample Matrix	Samples [Number/ Arrival Date]	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Water	Shallow	30 samples	$5 - 15 {}^{\circ}\text{C}$	NA	None,	Multimeter:
temperature	groundwater	quarterly			measured	thermistor
		July 2016 to			on raw	
		Jun 2018			sample	
Dissolved	Shallow	30 samples	2.0 - 12.0	NA	None,	Multimeter:
oxygen	groundwater	quarterly	mg/L		measured	optical sensor
		July 2016 to			on raw	
		Jun 2018			sample	
pН	Shallow	30 samples	5 - 8 pH units	NA	None,	Multimeter:
	groundwater	quarterly			measured	probe
		July 2016 to			on raw	
		Jun 2018			sample	
Specific	Shallow	30 samples	0 - 1000	NA	None,	Multimeter:
conductance	groundwater	quarterly	uS/cm		measured	probe
		July 2016 to			on raw	
		Jun 2018			sample	
Nitrogen,	Shallow	30 samples	< 1.0 mg N/L	0.01 mg/L	0.45 micron	EPA method
ammonia	groundwater	quarterly	_		filter	350.1
		July 2016 to				
		Jun 2018				

Analyte	Sample Matrix	Samples [Number/ Arrival Date]	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Nitrogen, nitrite	Shallow groundwater	30 samples quarterly July 2016 to Jun 2018	< 1.0 mg N/L	0.001 mg/L	0.45 micron filter	Enzymatic reduction; Patton and Kryskalla (2011)
Nitrogen, nitrite + nitrate	Shallow groundwater	30 samples quarterly July 2016 to Jun 2018	< 1.0 mg N/L	0.01 mg/L	0.45 micron filter	Enzymatic reduction; Patton and Kryskalla (2011)
Phosphorus, orthophosphate	Shallow groundwater	30 samples quarterly July 2016 to Jun 2018	< 1.0 mg P/L	0.004 mg/L	0.45 micron filter	EPA method 365.1

Method range and resolution presented in Section 6.2

9.2 Sample preparation method(s)

Field measurements (temperature, DO, pH, conductivity) of shallow groundwater will be determined with a multimeter data sonde equipped with a flow-through cell to avoid exposure to the atmosphere. Values will be recorded after a minimum of 3 well volumes are flushed through the cell and readings have stabilized. Shallow groundwater nutrient samples will be filtered in the field through 0.45 micron disk filters and chilled at 4°C until analysis according to procedures outlined in the USGS National Field Manual (Chapter 5.2.1; USGS, variously dated). Briefly, filters are rinsed with 50 milliliters of inorganic blank water or laboratory DI water in the field. Prior to sample collection, 20-40 milliliters of the environmental sample are run through the filter to condition the filter. Ideally, the collection of the environmental sample should take place right after the filter is rinsed with DI water, however, if this is not possible, DIrinsed filters need to be kept on ice until they are used (within a few hours).

9.3 Special method requirements

Not applicable, there are no special method requirements for this project.

9.4 Field procedures table field analysis table

A table summarizing the field methods and procedures is provided in Table 6.

9.5 Lab(s) accredited for method(s)

The USGS National Water Quality Lab in Denver will be used for this project and is accredited through the National Environmental Laboratory Accreditation Program, or NELAP.

10.0 Quality Control (QC) Procedures

10.1 Table of lab and field QC required

Field QC procedures for measurements of temperature, pH, and conductivity will follow the SOPs listed in Section 8.1. Table 7 provides the field and laboratory QC procedures required for this study.

QC Samples, Types and Frequency

	Fie	eld	Laboratory				
Parameter	Blanks	Replicates	Check	Method	Analytical	Matrix	
		1	Standards	Blanks	Duplicates	Spikes	
Nitrogen, ammonia	1/quarter (3% of samples)	3/quarter (10% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	
Nitrogen, nitrite	1/quarter (3% of samples)	3/quarter (10% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	
Nitrogen, nitrite + nitrate	1/quarter (3% of samples)	3/quarter (10% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	
Phosphorus, orthophosphate	1/quarter (3% of samples)	3/quarter (10% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	1/batch (5% of samples)	

For the NWQL, each batch is approximately every 20 samples. Guidelines for QC sample frequency from Maloney (2005) and Mueller and others (2015).

10.2 Corrective action processes

The project manager will work closely with the NWQL to review the data as it becomes available. If nutrient data falls out of the QC criteria (Table 3) or data shows anomalous results, a rerun of the samples will be requested within the sample hold times. If a concentration value is quantifiable but less than the method detection limit, it will be qualified with an "E" code for an estimated value. Review of data is an ongoing process throughout the project and data rejected as needed.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

All field data and observations will be recorded on waterproof paper kept in field notebooks. Staff will transfer information contained in field notebooks to Excel spreadsheets after they return from the field. Data entries will be independently verified for accuracy by another member of the project team. Field data (temperature, dissolved oxygen, pH, and specific conductance) from each sample trip will be entered into the USGS's National Water Information System (NIWS) database. Laboratory data is automatically uploaded into NWIS from NWQL.

This data will be provided to Stevens County Conservation District for upload into Ecology's EIM database.

All relevant components of the 1DTempPro model application will be archived according to the USGS guidelines for the archival of surface-water, groundwater, and water quality models (OWQ memo 2015.01). The model archive will fully describe and contain the model boundaries, input parameters, and statistical results to allow for reproduction of the model results, in accordance to the USGS Fundamental Science Practices and USGS Office of Water Quality Technical Memorandum 2015.01. Input files and model output will be stored in ScienceBase (https://www.sciencebase.gov/catalog/).

11.2 Lab data package requirements

The NWQL provides electronic data packages to the Washington Water Science center 2 times a week with water chemistry results for all projects in the center. The Center's database manager and water quality specialist forward the results to each project manager for review. After reviewing the data package from NWQL, the project manager will determine if reruns are necessary and request the lab to do so. If QC data fall outside of expected ranges, corrective actions will be taken prior to the next sample trip.

11.3 Electronic transfer requirements

Lab data is automatically uploaded to NWIS for permanent storage. Field parameters are entered in manually and uploaded to NWIS by project staff.

11.4 Acceptance criteria for existing data

Shallow groundwater data collected during the 2015 study (Gendaszek and others, 2016) will be used if it meets the MQOs outlined above. This will help increase the statistical power for our estimates of groundwater nutrient loads to Lake Spokane in the targeted near shore residential areas. This assessment of previous data will take place prior to the start of new sample collection.

11.5 EIM data upload procedures

All water quality data collected for this project will be archived in the USGS National Water Information System (NWIS). This is a publically available database (http://nwis.usgs.gov/) for retrieval of data. In addition, field and lab data will be formatted and uploaded to EIM at the end of the project.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

No audits are planned specifically for this project. See section 6.2.1. Internal laboratory audits of the NWQL are conducted by the USGS Branch of Quality Systems.

12.2 Responsible personnel

See section 5.1 and 13.0.

12.3 Frequency and distribution of report

A final USGS series report will be completed by December 31st, 2018. A draft report will be available for review prior to this date. This report will be made available to the public in PDF format at the USGS publications warehouse (https://pubs.er.usgs.gov/).

12.4 Responsibility for reports

The project manager will be the lead author and responsible for publishing the final report.

13.0 Data Verification

Field data verification, requirements, and responsibilities

All field data and notes will be verified by field personnel and double checked by the project manager after each sample trip. Field parameters recorded on field sheets will be uploaded to NWIS within 48 hours of returning from the field and verified by the project manager.

13.2 Lab data verification

Data verification, examination of results to ensure that quality assurance criteria have been met, will be conducted by the project manager. A second check of all data in NWIS will be performed by the hydrologic technicians who collected the field samples. All other laboratory verification procedures ae covered earlier in this QAPP.

13.3 Validation requirements, if necessary

Independent data verification is not necessary for this project.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

After the project data have been reviewed and verified, the principal investigator/project manager will determine if the data are of sufficient quality to make determinations and decisions for which the study was conducted. The data from the laboratory's QC procedures will provide information to determine if MQOs have been met. Laboratory and QA staff familiar with assessment of data quality may be consulted. In addition, the project manager will ensure the

criteria of completeness, representativeness, and comparability have been met. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted and qualified accordingly.

14.2 Data analysis and presentation methods

One of the goals of this project is to characterize nutrient chemistry in shallow groundwater. Summary statistics (range, mean, median, and interquartile range) will be determined for nutrient data at each sample location. In addition, Wilcoxon Rank Sum tests will be performed to assess the difference in nutrient chemistry across sample locations. Significant differences between locations will be determined with 95% confidence.

14.3 Treatment of non-detects

If nutrient data are below the method detection limits, they will be censored with a less than symbol. Statistical methods that can incorporate censored values while generating summary statistics will then be employed (see for example Helsel, 2005).

14.4 Sampling design evaluation

The approach used here to estimate groundwater nutrient loads into Lake Spokane is a first cut at determining this important nutrient pathway. The final report will clearly state the limitations of this study and provide recommendations for future work. In addition, we will be able to estimate upper and lower bounds on the amount of groundwater nutrients entering the lake which should be put into context with previously published nutrient budgets for the lake (Soltero and others, 1992).

14.5 Documentation of assessment

Documentation of assessment will occur in the final report.

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16.0 Figures

The figures in this QAPP are inserted after they are first mentioned in the text.

17.0 Tables

The tables in this QAPP are inserted after they are first mentioned in the text.

18.0 Appendices

Appendix A -- Glossary, Acronyms, and Abbreviations

Quality Assurance Glossary

Accreditation - A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)...that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy - the degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

Analyte - An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e. g. fecal coliform, Klebsiella, etc. (Kammin, 2010)

Bias - The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

Blank - A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

Calibration - The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

Check standard - A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator. (i. e. CRM, LCS, etc.) [Kammin, 2010; Ecology, 2004])

Comparability - The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

Completeness - The amount of valid data obtained from a data collection project compared to the planned amount. Completeness is usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Data Quality Indicators (DQI) - Data Quality Indicators (DQIs) are commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

Data Quality Objectives (DQO) - Data Quality Objectives are qualitative and quantitative statements derived from systematic planning processes that clarify study 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 data needed to support decisions. (USEPA, 2006)

Dataset - A grouping of samples, usually organized by date, time and/or analyte. (Kammin, 2010)

Data validation - An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the dataset.

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier, data is usable for intended purposes
- J (or a J variant), data is estimated, may be usable, may be biased high or low
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004)

Data verification - Examination of a dataset for errors or omissions, and assessment of the Data Quality Indicators related to that dataset for compliance with acceptance criteria (MQO's). Verification is a detailed quality review of a dataset. (Ecology, 2004)

Detection limit (limit of detection) - The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

Duplicate samples - two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

Field blank - A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

Initial Calibration Verification Standard (ICV) - A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

Laboratory Control Sample (LCS) - A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

Matrix spike - A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

Measurement Quality Objectives (MQOs) - Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

Method - A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (EPA, 1997)

Method blank - A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

Method Detection Limit (MDL) - This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

Parameter - A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene, nitrate+nitrite, and anions are all "parameters". (Kammin, 2010; Ecology, 2004)

Population - The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

Precision - The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

Quality Assurance (QA) - A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

Quality Assurance Project Plan (QAPP) - A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

Quality Control (QC) - The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

Relative Percent Difference (RPD) -. RPD is commonly used to evaluate precision. The following formula is used:

Abs(a-b)/((a+b)/2) * 100

Where a and b are 2 sample results, and abs() indicates absolute value

RPD can be used only with 2 values. More values, use %RSD.

(Ecology, 2004)

Replicate samples - two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

Representativeness - The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

Sample (field) – A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

Sensitivity - In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

Spiked sample - A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

Split Sample – The term split sample denotes when a discrete sample is further subdivided into portions, usually duplicates. (Kammin, 2010)

Standard Operating Procedure (SOP) – A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

Surrogate – For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or

measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

References

Ecology, 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. http://www.ecy.wa.gov/biblio/0403030.html

USEPA, 1997. Glossary of Quality Assurance Terms and Related Acronyms. http://www.ecy.wa.gov/programs/eap/qa.html

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Kammin, 2010. Definition developed or extensively edited by William Kammin, 2010.

USGS, 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf

Glossary – General Terms

Ambient: Background or away from point sources of contamination.

Baseflow: The component of total streamflow that originates from direct groundwater discharges to a stream.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Eutrophic: Nutrient rich and high in productivity resulting from human activities such as fertilizer runoff and leaky septic systems.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities. This includes, but is not limited to, atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination is considered a nonpoint source. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act is a nonpoint source.

Nutrient: Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or is likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Synoptic survey: Data collected simultaneously or over a short period of time.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standard, and are not expected to improve within the next two years.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

ASR Analytical Service Request BQS Branch of Quality Systems

e.g. For example

Ecology Washington State Department of Ecology

EIM Environmental Information Management database

EPA U.S. Environmental Protection Agency

et al. And others
i.e. In other words
FY Fiscal Year

MQO Measurement quality objective
NFQA National Field Quality Assurance
NWIS National Water Information System

NWQL National Water Quality Lab

PVC Polyvinyl Chloride QA Quality assurance

RPD Relative percent difference

SCCD Stevens County Conservation District

SOP Standard operating procedures SRM Standard reference materials

TMDL (See Glossary above)
USGS U.S. Geological Survey

WAWSC Washington Water Science Center

Units of Measurement

°C degrees centigrade cfs cubic feet per second

ft feet

g gram, a unit of mass

km kilometer, a unit of length equal to 1,000 meters.

m meter mg milligram

mg/L milligrams per liter (parts per million)

mL milliliters

ug/L micrograms per liter (parts per billion)

uS/cm microsiemens per centimeter, a unit of conductivity

Appendix B – Example of the USGS chain-of custody (Analytical Service Request) form U.S. GEOLOGICAL SURVEY - NATIONAL WATER QUALITY LABORATORY ANALYTICAL SERVICES REQUEST

THIS SECTION MANDATORY FOR SAMPLE LOGIN
LAB USE ONLY LAB USE ONLY SAMPLE ID NUMBER User Code Project Account NWQL LABORATORY ID
STATION ID 2 0
Science Center Contact Phone Number End Date (YYYYMMDD) End Time Science Center Contact Email
SITE / SAMPLE / SPECIAL PROJECT INFORMATION (Optional) State County Source Agency Analysis Hydrologic Hydrologic Chain of Code Status* Condition* Event* Custody
NWQL Proposal Number NWQL Contact Name NWQL Contact Email Program/Project
Station Name: Field ID:
Comments to NWQL:
Hazard (please explain):
ANALYTICAL WORK REQUESTS: SCHEDULES AND LAB CODES (CIRCLE A=add =delete)
SCHED 1: SCHED 2: SCHED 3: SCHED 4: SCHED 5: SCHED 6:
Lab Code: A D Lab Code:
Lab Code: A D
SHIPPING INFORMATION (Number of containers sent)
ALF CUR FCA GCV PHARM RU TBI
BGC DIC FCC HFL POCIS-SPMD RUR TBY CC DOC FCCVT HUN RA RURCV TOC
CHL FA FU MBAS RAM SAS TPCN
COD FAM FUS OXW RAR SUR UAS
NWQL Login Comments:
Collected by: Phone No Date Shipped:
FIELD VALUES
Lab/P Code Value Remark Lab/P Code Value Remark Lab/P Code Value Remark Lab/P Code Value Remark 21/00095 Specific Conductance uS/cm @ 25 deg C PH Standard Units CaCO3
USDA NWIS RECORD NUMBER
Lab Use only Form 9-3094 *MANDATORY FOR NWIS (February 2015)

Appendix C – Example of the USGS field sheets

Science for a changing world								NWIS Record No.	
Station No1211339	90	Station Name <u>Duwarr</u>	ni <u>sh River</u> a	at Golf C	ourse nr T	ukwila, V	NA.	Field ID	
Sample Date		Mean Sam	ple Time _		Ti	ime Datu	um	(eg. PST, PDT)	
								le Type: 9 (regular) 7 (replicate) 1 (spike)	
26127CL 0054CL00C427C 2547K CSCRONICS CRED. CCSCCRED.564C10. 6C		N Blank Replicate	Via Documentation	20-000-000-000-00					
		00 / GC14YG00F6EGS00	<u> </u>	Project	Name <u>G</u>	reen Riv	erToxic	Loads	
Sampling Team									
	_		FIELD	MEASU	REMENTS	3	T., ,,		
Property	Parm Code	Method Code	Result	Units	Remark Code	Value Qual.	Null Value Qual.	NWIS Result-Level Comments	
Gage Height	00065			ft					
Discharge, instantaneous	00061			cfs					
Turbidity (DTS-12)	63680	TS032		FNU					
Turbidity (hand-held)	63680	TS087		FNU					
Temperature, Air	00020	THM04 (thermister) THM05 (thermometer)		•c				†	
Temperature, Water	00010	THM01 (thermister) THM02 (thermometer)		*C	<u> </u>		T		
Specific Conductance	00095	SC001 (contacting sensor)		μS/cm					
Dissolved Oxygen	00300	MEMBR (amperometric)		mg/L					
Barometric Pressure	00025	BAROM		mm Hg					
рН	00400	PROBE (electrode)		units					
Alkalinity, filtered, incr.	39086	TT061		mg/L					
Carbonate, flt, incr.	00452	SSM01		mg/L				Advanced Speciation Method	
Bicarbonate, flt, incr.	00453	SSM01		mg/L				Advanced Speciation Method	
Suspended Sediment	80154			mg/L					
Susp. Sed., < 62.5 um	70331			%					
QC Sample Collected	99111							See Page 7 for Codes	
Type of Replicate	99105							See Page 7 for Codes	
Purpose, topical QC	99112							For Cross-Sections: Variability	
			SAMPLI	NG INFC	RMATION	N			
Parameter	Pcode		Value					Information	
Sampler Type—for suspend- ed sediment chemistry	84164	3051 DH-95 Teflon 3 3053 D-95 Teflon 3 3055 D-96 Bag Sampler 3 3058 DH-2 Bag Sampler 3	3051 DH-95 Teflon 3052 DH-95 Plastic 3053 D-95 Teflon 3054 D-95 Plastic 3056 D-96 Bag Sampler 3057 D-99 Bag Sampler 3058 DH-2 Bag Sampler 3060 Weighted-Bottle Sampler			Sam Nozz	Sampler ID: Sampler bottle/bag material: plastic teffor other Nozzle material: plastic teffor other Nozzle size: 3/16 1/4 5/16		
Sampler Type—for water chemistry and suspended sediment physical parametei	84164 ers	3051 DH-95 Teflon 3 3053 D-95 Teflon 3 3055 D-96 Bag Sampler 3	070 Grab 4TT Sampler, point, automatic Nozzle size: 044 DH-81 3045 DH-81 Teffon Sampler ID: 051 DH-95 Teffon 3052 DH-95 Plastic Sampler bott 303 D-95 Teffon 3054 D-96 Plastic Sampler bott 3059 D-96 Bag Sampler 3057 D-99 Bag Sampler 3057 D-99 Bag Sampler			pler bottle/t	rbag material: plastic (efforother		

Parameter	Pcode	Value	Information		
Sampler Type—for suspended sediment chemistry	84164	3044 DH-81 3045 DH-81 Teflon 3051 DH-95 Teflon 3052 DH-95 Plastic 3053 D-95 Teflon 3052 DH-95 Plastic 3056 D-96 Bag Sampler 3057 D-99 Bag Sampler 3058 DH-2 Bag Sampler 3060 Weighted-Bottle Sampler 3070 Grab 4115 Sampler, point, automatic	Sampler ID: Sampler bottle/bag material: plastic teflon other Nozzle material: plastic teflon other Nozzle size: 3/16* 1/4* 5/16*		
Sampler Type — for water chemistry and suspended sediment physical parameters		3044 DH-81 3045 DH-81 Teflon 3051 DH-95 Teflon 3052 DH-95 Plastic 3053 D-95 Teflon 3054 D-96 Plastic 3055 D-96 Bag Sampler 3057 D-99 Bag Sampler 3059 DH-2 Bag Sampler 3060 Weightled-Bottle Sampler 3070 Grab 4115 Sampler, point, automatic	Sampler ID: Sampler bottle/bag material: plastic (eflor) other Nozzle material: plastic (eflor) other Nozzle size: 3/16" 1/4" (5/16)		
Sampling Method—for physi- cal parameters	82398	10 EWI; 20EDI; 30 single vertical; 40 multiple vertical; 50 Point Sample; 70 Grab (dip sample)	Bottle size: pint quart 1 L bottle 1 L bag 3 L bag 6 L bag		
Transit Rate	50015	ft/sec			
Hydrologic Condition	N/A	X Not applicable; 4 Stable, low stage; 5 Falling stage; 6 Stable,	high stage; 7 Peak stage; 8 Rising stage; 9 Stable, normal stage		
Observations [Codes: 0=none; 1=mild; 2=moderate; 3=serious; 4=extreme]	2000	grease (01300) Detergent suds (01305) n. Odor (01330) Fish kill (01340)	Floating garbage (01320) Floating algae mats (01325) Floating debris (01345) Turbidity (01350)		

	COMPILED BY:	DATE	CHECKED BY:	DATE:	LOGGED INTO NWIS BY:	DATE
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Stream width:ft Notes:	SAMPLING CONDITIONS
Sediment Sampling points:	
NO NO DESCRIPTION OF THE PARTY	upstream downstream side of bridge0.8 mi below gage
Total number of sediment bottles:	A and B set?: Sediment mean time: (attach sediment field sheet)
	(ft from REW) (ft below water surface)
AP 81 0 1287	(ft from REW)(ft below water furace)
Sonde No Calibrated by:	Calibration Location: (attach calibration information)
WALL WAS DOOR TO BE AN ARROW TO BE ARROW TO BE AN ARROW TO BE AN ARROW TO BE AN ARROW TO BE AN A	S/N: ID:
Probe: make/model:	S/N: ID:
Calibration information:	
Sampling site: pool riffle open channel braided	d backwater Bottom: bedrock rock cobble gravel sand silt concrete other
10 CEA 10 10	other Stream mixing: well-mixed stratified poorly-mixed unknown other
Weather: sky- clear partly cloudy cloudy	precipitation- none light medium heavy snow sleet rain mist
	t. wind speed mph temperature - very cold cool warm hot
No. days since last significant rainfall	
Field Observations:	
Sample Comments (for NWIS; 300 characters max.	<i>)</i> :
LI A DODA TODY INFORMATION Some Soft	4 ID
LABORATORY INFORMATION Sample Set	
SAMPLES COLLECTED: If Pesticides are collect 	cted, circle Organics bottle type and Laboratory Schedule number.
Nutrients:WCAFCCFCACC Maj	or cations:FARA _ Major anions: _FU _Trace elements: _FARACU
	Lab pH/SC/ANC:RU
Mercury:FAMRAMWis. Hg Lab	
	eredunfiltered <u>X_BGCC18</u> Kansas OGRG Lab
VOC: GCV (vials)	
VOC: GCV (vials) Organics:GCC filte Suspended solids:SUSO Turbidity:TBY Phenols:PHE	eredunfiltered <u>X_</u> BGCC18 Kansas OGRG Lab
VOC: GCV (vials) Organics:GCC filte Suspended solids:SUSO Turbidity:TBY Phenols:PHE	eredunfiltered <u>X_</u> BGCC18Kansas OGRG Lab thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filts Suspended solids:SUSO Turbidity:TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filte Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	eredunfiltered <u>X_</u> BGCC18Kansas OGRG Lab thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filte Suspended solids:SUSO Turbidity:TBY Phenols:PHE Oil&Grease:OAG Met Carbon: _X_TPCNPIC filter1-vol filtered Stable isotopes:FUSRUS RadiocBODCOD Chlorophyll:CHL Ultraviolet Absorbing Substances:UAS	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filte Suspended solids:SUSO Turbidity:TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filter Suspended solids:SUSO	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCCfilt Suspended solids:SUSOTurbidity:TBY Phenols:PHEOil&Grease:OAGMet Carbon:X_TPCNPICfilter1-vol_filtered Stable isotopes:FUSRUSRadioc BODCODChlorophyll:CHL Ultraviolet Absorbing Substances:UAS Other:(Lab) O Suspended sediment:XONCS/P€INES	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filt Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filts Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filts Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filt Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filts Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	thylene Blue Active Substances:MBAS
VOC: GCV (vials) Organics:GCC filts Suspended solids:SUSO Turbidity: _TBY Phenols:PHE	thylene Blue Active Substances:MBAS

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Station	h I -			

SAMPLE TI	MES:									
Instantaneo	ous Discharge	e Measurem	ent:			Time:		Initials:		
Water Sam	ple Start Time	•:		End	Time:		_ Mean 1	Гіте:		
Suspended	Sediment Ph	ıysical Paraı	neters Start	Time:		End Tim	ie:	Mean Time:		
Suspended	Sediment Ch	nemistry Pur	ie:	Mean Time:						
From pump 1-L amber (o: glass bottle fo	or TPCN:	22 42							
1-L poly bo	ttle for TSS: _	72	<u> </u>							
3-L poly bo	ttle for SSC/P	'SD:		<u> </u>						
BED SEDIN	MENT SAMPL	ING								
Bed Sediment Sample Start Time: End Time: Mean Time:										
	ent Sample G		ns:		2.					
l	3									
				2						
					ERAL WATE					
Time	Water Temp (°C)	pН	Specific Cond. (uS/ cm)	DO (mg/L)	Turbidity (NTU)	Air Temp (°C)	Barometric Pressure (mm Hg)	Notes		
							7			
OTHER FIF	LD NOTES:									
					3	3		SW Form version 8 0		

Station	h I -			

QUALITY-CONTROL INFORMATION

PRESERVATIVE LOT NUMBE	RS				
4.5N H₂SO4 (NUTRIENTS&000	45N H ₂ SO ₄ (NJTRIENTS&DOC)	45N H₂SO4 (NuTRIENTS&BOC)	7.5N HNO ₃ (METALS&CATIONS)	7.5N HNO3 METALS&CATIONS	
1:1 HCI(voc)	Number of drops of HCL	added to lower pH to ≤ 2	(NOTE: Maximum n	umber of drops = 5)	
BLANK WATER LOT NUMBER	RS			SPIK	ES
Inorganic (99200)	2nd Inorgan	nic (99201)		Spike-sample type Field	99107 Spike-solution source 10 NWQL
Pesticide (99202)	2nd Pesticio	de (99203)	20 1	Lab	10 MWQL
VOC/Pesticide (99204)			99108 3	Spike-solution volume,	mL
TOON CONTOUR (COZOT)	210 0001		8	Spike-vial lot number_	
			200	ion Date	
FILTER LOT NUMBERS					
capsule		pore size	brand_		
142mm GFF (organics)		pore size	brand _		
25mm GFF (organic carbon)		pore size	brand _		
Sample Type NWIS Reco	Sequentia Spike Concurrer C Samples)	nt	Trip Blank Other Other		
	Commis Time Code	(Circle appropriate selection	ons) [99102 Blank-sample ty	/pe
Sample Medium Codes WS Surface water WSQ Quality-control sample OAQ Artificial 99105 Replicate-sample type 10 Concurrent 40 Split-Ci		99111 QC sample associated environmental sample 1 No associated QA data 10 Blank 30 Replicate Sample 40 Spike sample 100 More than one type of QA 200 Other		1 Source Soluti 30 Trip 40 Sampler 50 Splitter 60 Filter 70 Preservation	
20 Sequential 50 Split-Sc 30 Split 200 Other 99100 Blank-solution type 10 Inorganic grade (distilled/deionix 40 Pesticide grade (OK for organic 50 Volatile-organic grade (OK for organic carbon) 200 Other 99101 Source of blank water 10 NWQL 55 Wisconsin Mercury Lab 140 EMD Chemicals 150 Ricca Chemical Compar	zed) s and organic carbon)	99112 Purpose, Topical QC da 1 Routine QC (non-topical) 10 Topical for high bias (cont 20 Topical for low bias (recont 110 Topical for variability (field 82398 Sampling Method 10 Equal Width Increment (20 Equal Discharge Increm 30 Single Vertical 40 Multiple Verticals 50 Point Sample	amination) ery) I collection)	84164 Sampler Type 3044 US DH-81 3045 US DH-98 IN 3061 US DH-95 Pit 3062 US DH-95 Pit 3063 US D-95 Pit 3064 US D-96 Bag 3067 US D-98 Bag 3070 Grab Sample 3071 Open-Mouth 3080 VOC Hand S 8000 None 8010 Other	ith Teflon Cap And Nozzle effon Bottle satic Bottle on Bottle stic Bottle Sampler Sampler Bottle Bottle
200 Other	ıy	70 Grab Sample (Dip) 8010 Other 8030 Grab Sample At Water-			e codes can be found online at:

SW Form version 8.0



United States Department of the Interior

U.S. Geological Survey

USGS Washington Water Science Center 934 Broadway, Suite 300 Tacoma, Washington 98402 (253) 552-1600. FAX (253) 552-1581 http://wa.water.usgs.gov/

August 4, 2016

To: Karin Baldwin

WQ Program Manager, Washington State Department of Ecology, Spokane, WA

From: Rich Sheibley

Research Hydrologist, USGS WAWSC, Tacoma, WA

Subject: Response to EAP comments on Lake Spokane QAPP

Included with this memo is a cleaned up version of the QAPP for the phase 2 work to study groundwater inputs of nutrients to Lake Spokane. Most of the comments were addressed within the revised document. Below, I address comments that needed more explanation. The EAP comment is identified by the section and headings/subheadings of the QAPP where the comment was entered by the reviewer. Please feel free to contact me with any questions.

• Section 6 – Quality Objectives; Decision Quality Objectives

We did not add anything to this section. The missing parts identified by the reviewer: identify the decision, develop decision rule, and specify tolerable limits on decision errors are not applicable for this study. We discussed have already this with the Ecology Project Manager.

• Section 7 – Sampling Process Design; Study Design; Sampling location and frequency

The reviewer mentioned we will be addressing agricultural areas but these sites are not included in the sample plan, but this is not the case. The mention of agricultural areas was for the background section describing the study area and larger watershed of Lake Spokane. We are not targeting any agricultural areas in this study.

• Section 8 – Sampling Procedures; Containers, preservation, holding times

We added information to the table including a reference for USGS procedures for nutrient sampling and the temperature we chill samples. We do not add sulfuric acid to these samples that is only added to bottles where total N and P are analyzed. We added a footnote to the table to address this.

• Section 9 – Measurement Methods; Lab procedures table; analytical method

The reviewer asked for the EPA or standard method for nitrite+nitrate and nitrite but the USGS lab has developed its own method for these analyses, which was already cited in the table. The Patton and Kryskalla (2011) method uses an enzymatic reaction not cadmium reduction (EPA method) to convert nitrate to nitrite prior to analysis which greatly reduces the hazardous waste produced during the analysis process. The cited report validates the use and comparability of the newer USGS method with the EPA method.

• Section 14 – Data Quality (usability) assessment; Treatment of non-detects

The reviewer asked how non-detects will be used in the data set. This was already mentioned in the text. Values less than the method detection limit are censored with a less than symbol. For cases where data are censored we will use non-parametric statistical methods specifically designed to use with data sets that include censored values. In other words, we will not be replacing non-detects with an artificial value (zero, ½ MDL, or MDL). There are methods available to calculate summary statistics, compare medians of different groups and examine variability of data with censored values.

Enclosed:

Revised QAPP (word document)