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State of Washington

Quality Assurance Project Plan

Okanogan River Tributaries 303(d) pH Listings Verification Study

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Quality Assurance Project Plan

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September 2015

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EAP: Environmental Assessment Program

1.0 Table of Contents

	Page
1.0 Table of Contents	2
2.0 Abstract	5
3.0 Background	6
3.1 Study area and surroundings	6
3.1.1 Logistical problems	8
3.1.2 History of study area	8
3.1.3 Parameter of concern	8
3.1.4 Results of previous studies	8
3.1.5 Regulatory criteria or standards	11
4.0 Project Description	13
4.1 Project goals	13
4.2 Project objectives	13
4.3 Information needed and sources	13
4.4 Target population	14
4.5 Study boundaries	14
4.6 Tasks required	14
4.7 Practical constraints	14
4.8 Systematic planning process	14
5.0 Organization and Schedule	15
5.1 Key individuals and their responsibilities	15
5.2 Special training and certifications	15
5.3 Organization chart	15
5.4 Project schedule	15
5.5 Limitations on schedule	16
5.6 Budget and funding	16
6.0 Quality Objectives	17
6.1 Decision Quality Objectives (DQOs)	17
6.2 Measurement Quality Objectives	17
6.2.1 Targets for Precision, Bias, and Sensitivity	18
6.2.2 Targets for Comparability, Representativeness, and Completeness	18
7.0 Sampling Process Design (Experimental Design)	20
7.1 Study Design	20
7.1.1 Field measurements	20
7.1.2 Sampling location and frequency	20
7.1.3 Parameters to be determined	21
7.2 Maps or diagram	21
7.3 Assumptions underlying design	23
7.4 Relation to objectives and site characteristics	23
7.5 Characteristics of existing data	23
8.0 Sampling Procedures	24

8.1	Field measurement and field sampling SOPs	24
8.2	Containers, preservation methods, holding times	24
8.3	Invasive species evaluation	24
8.4	Equipment decontamination	25
8.5	Sample ID	25
8.6	Chain-of-custody, if required.....	25
8.7	Field log requirements	25
8.8	Other activities	25
9.0	Measurement Methods.....	26
9.1	Field procedures table/field analysis table	26
9.2	Lab procedures table	26
9.3	Sample preparation method(s)	26
9.4	Special method requirements	26
9.5	Lab(s) accredited method(s)	26
10.0	Quality Control (QC) Procedures	27
10.1	Table of field QC required.....	27
10.2	Corrective action processes.....	27
11.0	Data Management Procedures	28
11.1	Data recording/reporting requirements	28
11.2	Laboratory data package requirements	28
11.3	Electronic transfer requirements	28
11.4	Acceptance criteria for existing data.....	28
11.5	EIM/STORET data upload procedures	28
12.0	Audits and Reports.....	29
12.1	Number, frequency, type, and schedule of audits	29
12.2	Responsible personnel	29
12.3	Frequency and distribution of report.....	29
12.4	Responsibility for reports.....	29
13.0	Data Verification.....	30
13.1	Field data verification, requirements, and responsibilities	30
13.2	Lab data verification	30
13.3	Validation requirements, if necessary	30
14.0	Data Quality (Usability) Assessment.....	31
14.1	Process for determining whether project objectives have been met	31
14.2	Data analysis and presentation methods	31
14.3	Treatment of non-detects	31
14.4	Sampling design evaluation	31
14.5	Documentation of assessment.....	31
15.0	References.....	32
16.0	Figures.....	33
17.0	Table	33
18.0	Appendix.....	34
	Glossaries, Acronyms, and Abbreviations.....	34

List of Figures and Tables

Page

Figures

Figure 1. Study area for Okanogan River Tributaries 303 (d) pH listing verification study showing the location of the sites with category 5 pH listings.	7
Figure 2. Time-series plot of all pH measurements made by the Okanogan Conservation District for the grant project – Grant Number G000225, in comparison to pH criteria of 6.5 to 8.5.	9
Figure 4. Proposed sites for verification of pH impairments within the Okanogan River basin.	22

Tables

Table 1. Land use in the Okanogan River Basin (Washington State portion of watershed).	8
Table 2. 303(d)-listed tributaries for pH impairment (by segment) ranked in order of having higher pH measurements during the 2000-03 monitoring project. Highlighted segments are proposed for re-monitoring for the verification project.	10
Table 3. Okanogan River tributary segments with pH listing on the 2012 303(d) list.	11
Table 4. Washington State water quality criteria for pH in Okanogan River and its tributaries.	12
Table 5. Organization of project staff and responsibilities.	15
Table 6. Proposed schedule for completing field work, data entry into EIM, and reports.	16
Table 7. Summary of Hydrolab datalogger parameter accuracy, resolution, and range.	17
Table 8. Measurement quality objectives for Hydrolab post-deployment bias checks.	17
Table 9. Proposed sites within the Okanogan River basin for the pH Verification Study.	21
Table 10. Field sampling and measurement methods and protocols.	24
Table 11. Measurement Methods (field).	26

2.0 Abstract

Ecology will conduct an assessment of pH in select tributaries to the Okanogan River during summer months to verify pH 303(d) listings.

Data loggers with pH sensors will be used to continuously measure pH for 24-hour periods. Data collection is planned for July 2015 to May 2016.

3.0 Background

Eighteen tributaries sites in the Okanogan River basin are included on the 2012 Washington State 303(d) list of the federal Clean Water Act of impaired water bodies, because they did not meet surface water quality criteria for pH.

The 303(d) listings are based on pH measurements made by the Okanogan County Conservation District during a 3-year grant project (2000 to 2003) to assess water quality in the Okanogan basin. A review of the collected pH measurement data shows a potential bias over the project period. Ecology would like to verify the pH impairments before conducting a more intensive TMDL study.

Streamflows during 2015 are expected to be critically low because of a declared drought in Washington. Verification measurements made in the summer and fall months of 2015 will be ideal for monitoring critical pH conditions.

3.1 Study area and surroundings

The Okanogan River basin is a sub-watershed of the Columbia River Watershed and extends into Canada. The Okanogan River watershed portion located in north central Washington encompasses approximately 2,600 square miles (Bard, 2003).

The watershed is flanked on the western edge by the North Cascade Mountains. The eastern boundary is dominated by the North Okanogan Highlands. This watershed area generally receives varied precipitation with as little as 9 inches in some areas. The northern boundary for the study area for this project is the US-Canada border. The drainage of the watershed is generally from north to south with tributaries flowing to the Okanogan River from the east and the west. The land within the Okanogan River Basin is split almost evenly between public, private, and tribal ownership (Bard, 2003).

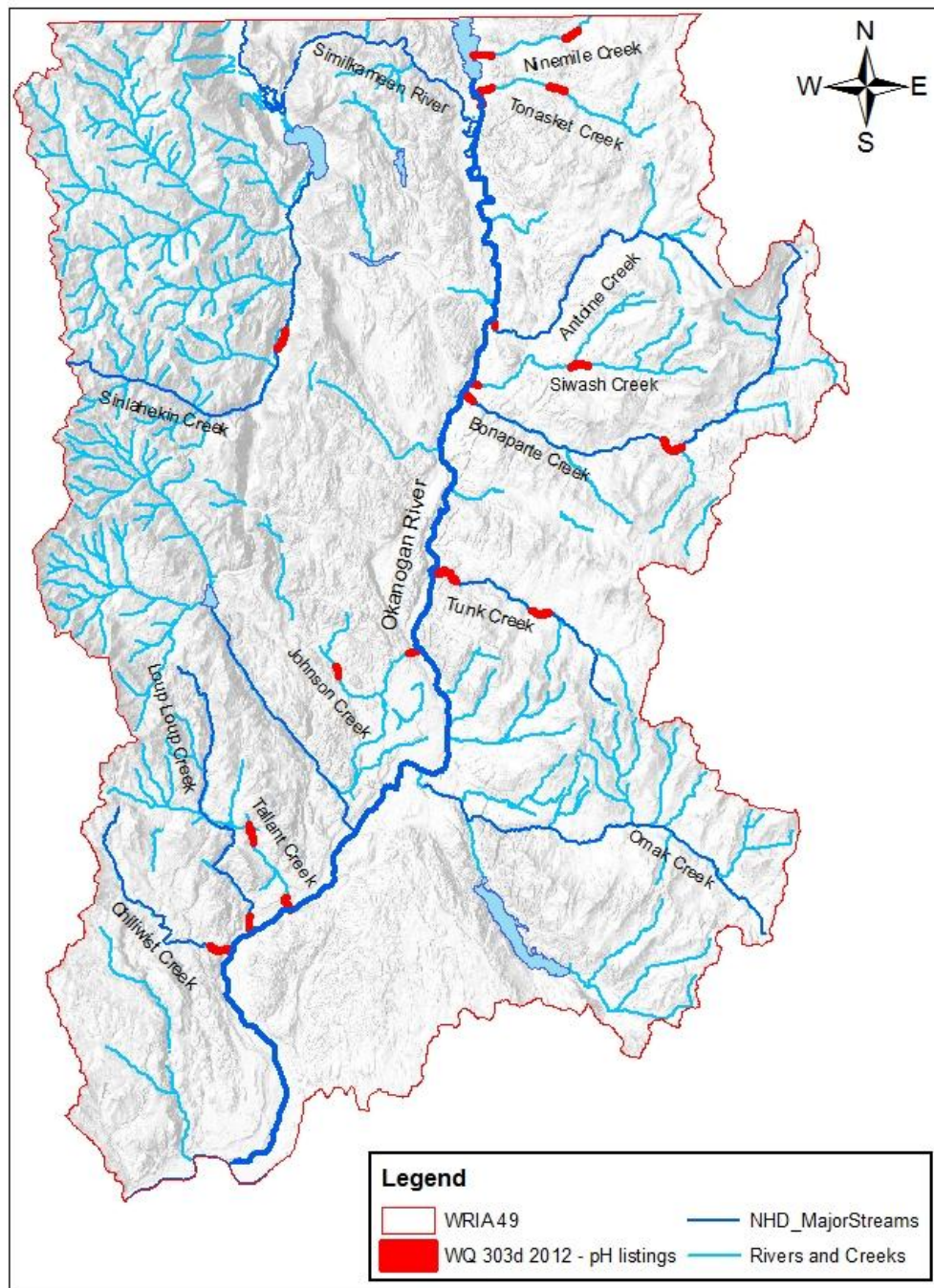


Figure 1. Study area for Okanogan River Tributaries 303 (d) pH listing verification study showing the location of the sites with category 5 pH listings.

3.1.1 Logistical problems

The following logistical issues could occur:

- Inability to measure pH or access locations during low flow. At times, some locations might be dry due to extremely low flow. If pH measurements cannot be taken, it will be noted on our field forms, and if possible, monitoring work may be rescheduled.
- Denial of access to private property. If permission to access is not granted at certain sites, alternate locations will be sought to replace the monitoring site.
- Scheduling conflicts, vehicle or equipment problems, or the limited availability of personnel or equipment may interfere with monitoring. These will be dealt with as they occur.

3.1.2 History of study area

Land ownership within the Okanogan River Basin is a mixture of public, private, and tribal ownership (OCD, 2000), and is dominated by rangeland and forest land uses. Table X presents the approximate distribution of land use (OCD, 2000).

Table 1. Land use in the Okanogan River Basin (Washington State portion of watershed).

Land Use	Approximate Acres
Forest	787,070
Range	754,996
Cropland	101,930
Urban	5,737
Other	18,065
Total Land Area	1,667,798

3.1.3 Parameter of concern

The parameter of interest for this monitoring study is pH.

3.1.4 Results of previous studies

The Okanogan Conservation District (OCD) received a grant to conduct water quality monitoring in tributaries to the Okanogan River from the spring of 2000 to spring of 2003.

Based on the results of the monitoring, 18 out of 25 sites were listed for pH impairments on the 303(d) list. The 18 sites are on 11 different tributaries, with 7 tributaries having 2 segments

(upper site and lower site) with pH impairments. Ecology is required to address the pH impairments with a Total Maximum Load Study (TMDL).

Prior to conducting a planned, intensive pH TMDL, Ecology reviewed the pH measurements from the OCD monitoring. Anomalies in the pH data concerned Ecology and triggered the current verification study. Figure 2 presents a time series plot of the pH data collected by the OCD from the spring of 2000 to the spring of 2003. Darker shaded measurements are from the 11 tributary segments (highlighted in Table 2) that Ecology plans to re-monitor for pH.

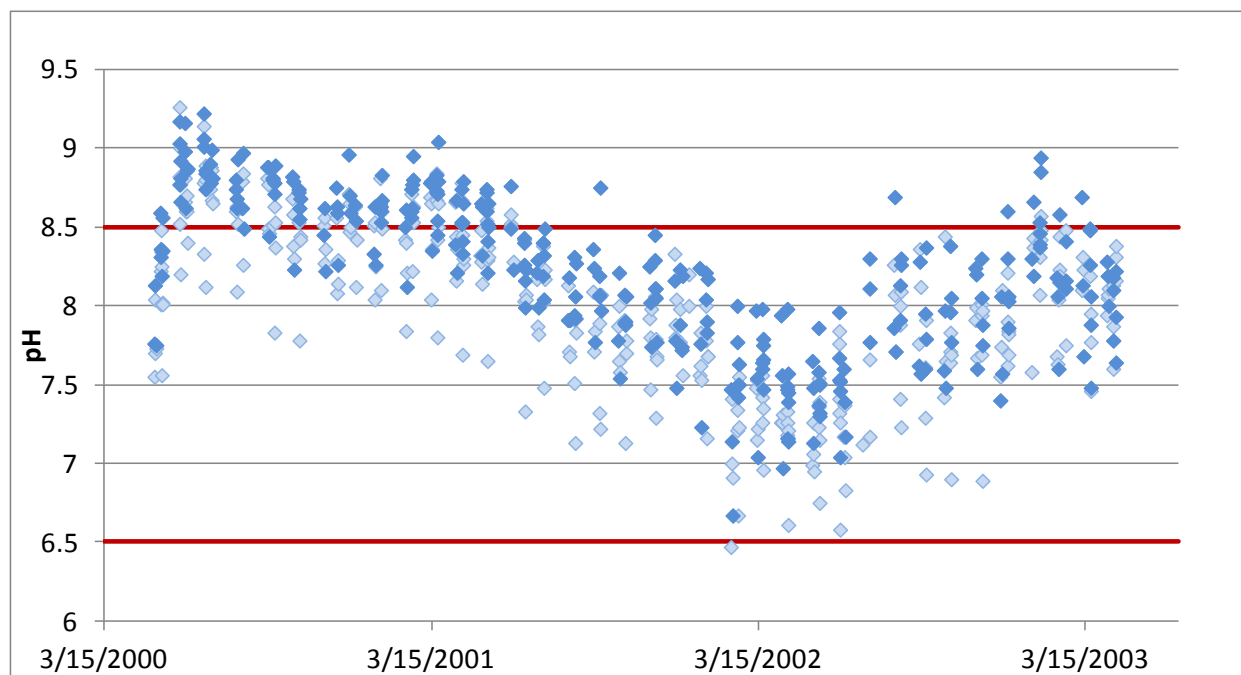


Figure 2. Time-series plot of all pH measurements made by the Okanogan Conservation District for the grant project – Grant Number G000225, in comparison to pH criteria of 6.5 to 8.5.

The pH data show that the relative range of pH measurements from all sites for each monthly survey was about the same: ≈ 1 to 1.5 pH units. This might indicate that the measurements show the same precision for each monitoring event.

However, there appears to be a meandering bias throughout the project monitoring period. For example, from June of 2000 to May 2001, pH measurements were higher, with many of the sites exceeding 8.5 pH units. The pH measurements from this period of the monitoring project are the basis for most of the 303(d) pH listings. Then, from June 2001 to December 2002—the next 18 months of monitoring—almost all sites were below 8.5 pH units.

There was not a change or difference in measurement time of year (seasonality), time of day, stream temperature, or streamflow to explain the meandering bias shifts in pH over the period of the project.

The OCD monitoring was conducted under a Quality Assurance Project Plan (OCD, 2000). The QAPP cited the District's Water Quality Monitoring SOP (OCD, 1999) in regards to sampling protocols and instrument calibration. The QAPP and SOP were reviewed by Ecology as part of the grant approval. Both documents were deemed in good standing and complete for the purposes of collecting water quality data.

The District's SOP lists pre-calibration procedures for the pH meter, as well as quality control measures to be performed throughout the sample day. Even though the QAPP stated that a quality assurance summary would be presented in the final report, the OCD final summary report (Bard, 2003) has no quality assurance section or discussion. As significant time has lapsed, the OCD no longer has quality assurance records pertaining to the monitoring project, so Ecology does not have documentation of quality assurance for their pH monitoring activities from the 2000-03 monitoring project.

Ecology proposes to re-monitor all 11 tributaries that are on the 303(d) list for verification. For the tributaries that had more than one segment with pH impairment, the top-ranked segment of the two (most likely to have higher pH based on earlier monitoring) will be re-monitored. Regardless of the time period or any potential bias, some segments consistently had higher pH measurements than other segments during each monthly survey of the previous monitoring project. Table 2 presents a ranking of the segments by the tendency to have a higher pH.

Table 2. 303(d)-listed tributaries for pH impairment (by segment) ranked in order of having higher pH measurements during the 2000-03 monitoring project. Highlighted segments are proposed for re-monitoring for the verification project.

Rank	303(d)-Listed Stream Segment for pH Impairment
1	Siwash Creek (lower)
2	Tonasket Creek (lower)
3	Antoine Creek (lower)
4	Johnson Creek (lower)
5	Tunk Creek (lower)
6	Bonaparte Creek (lower)
7	Tonasket Creek (upper)
8	Ninemile Creek (upper)
9	Tallant Creek (upper)
10	Chiliwist Creek (lower)
11	Tunk Creek (upper)
12	Bonaparte Creek (upper)
13	Ninemile Creek (lower)
14	Siwash Creek (upper)
15	Johnson Creek (upper)
16	Tallant Creek (lower)
17	Loup Loup Creek (lower)
18	Sinlahekin Creek (upper)

3.1.5 Regulatory criteria or standards

Table 3 lists the study area's category 5 pH listings on the 2012 303(d) list.

Table 3. Okanogan River tributary segments with pH listing on the 2012 303(d) list.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Bonaparte Creek	41280	1194456487053	1.18	0.00
Chiliwist Creek	41286	1197369482463	2.55	0.48
Johnson Creek	41288	1195057485045	1.06	0.00
Siwash Creek	41289	1194384487121	0.77	0.07
Ninemile Creek	41326	1194333489670	2.18	0.52
Antoine Creek	41827	1194112487614	0.77	0.00
Loup Loup Creek	41828	1197043482804	1.67	0.00
Tonasket Creek	41831	1194229489371	1.64	0.00
Siwash Creek	50591	1194384487121	13.88	12.07
Tonasket Creek	50595	1194229489371	8.90	7.34
Bonaparte Creek	50600	1194456487053	24.66	22.11
Tunk Creek	50601	1194868485618	2.91	0.58
Tunk Creek	50602	1194868485618	13.58	11.63
Johnson Creek	50604	1195057485045	12.21	11.21
Tallant Creek	50615	1196594482977	1.46	0.00
Tallant Creek	50616	1196594482977	10.06	7.90
Ninemile Creek	51195	1194333489670	10.92	9.52
Sinlahekin Creek	51200	1196463487988	19.30	17.20

Designated and Beneficial Uses

Water Quality Standards for Surface Waters of the State of Washington (WAC 173-201A-200) establish beneficial uses of waters and incorporate specific numeric and narrative criteria for parameters such as water temperature. The criteria are intended to define the level of protection necessary to support the beneficial uses. Washington Administrative Code (WAC) 173-201A-600 and WAC 173-201A 602 list the use designations for specific areas (WAC 173-201A-600 and WAC 173-201A-602).

For the Okanogan River and its tributaries, the designated uses of the waters in this specific area are:

- *Aquatic Life Use*: Salmonid Spawning, Rearing and Migration.
- *Recreation*: Primary Contact Recreation.
- *Water Supply*: Domestic, Industrial, Agricultural, and Stock Watering.
- *Miscellaneous Uses*: Wildlife Habitat, Harvesting, Commerce/Navigation, Boating, and Aesthetics.

pH Criteria

The pH criteria used to protect for salmonid spawning, rearing, and migration are outlined in Table 4 and described in further detail below.

Table 4. Washington State water quality criteria for pH in Okanogan River and its tributaries.

Parameter	Criteria
pH	To protect the designated aquatic life uses of “Salmonid Spawning, Rearing, and Migration,” pH must be kept within the range of 6.5 to 8.5, with a human-caused variation within the above range of less than 0.5 units.

The pH of natural waters is a measure of acid-base equilibrium achieved by the various dissolved compounds, salts, and gases. pH is an important factor in the chemical and biological systems of natural waters. pH both directly and indirectly affects the ability of waters to have healthy populations of fish and other aquatic species. Changes in pH affect the degree of dissociation of weak acids or bases. This effect is important because the toxicity of many compounds is affected by the degree of dissociation. While some compounds (e.g., cyanide) increase in toxicity at lower pH, others (e.g., ammonia) increase in toxicity at higher pH.

While there is no definite pH range within which aquatic life is unharmed and outside which it is damaged, there is a gradual deterioration as the pH values are further removed from the normal range. However, at the extremes of pH lethal conditions can develop. For example, extremely low pH values (<5.0) may liberate sufficient CO₂ from bicarbonate in the water to be directly lethal to fish.

The state established pH criteria in the state water quality standards primarily to protect aquatic life and to protect domestic water supply sources. Water supplies with either extreme pH or that experience significant changes of pH even within otherwise acceptable ranges are more difficult and costly to treat for domestic water purposes. pH also directly affects the longevity of water collection and treatment systems, and low pH waters may cause compounds of human health concern to be released from the metal pipes in distribution systems.

4.0 Project Description

4.1 Project goals

This study will verify pH impairments for tributaries to the Okanogan River.

The goals of this study are to:

1. Collect pH diel data from select tributaries that are representative of having impaired pH waters based on historical monitoring.
2. Use the collected pH data to determine if pH impairments are still present.
3. Write a summary report that recommends appropriate follow-up actions.

4.2 Project objectives

The objectives of this study are to:

1. Measure diel pH in 11 tributaries that are listed for pH impairments based on previous monitoring.
2. Ensure that representative stream pH measurements are obtained throughout the desired monitoring period (April–October).
3. Use quality assurance and quality control procedures to ensure the reliability of the monitoring data, relying primarily on the pre- and post-deployment calibration checks of the pH loggers.
4. Evaluate the quality of the pH data and publish the data in Ecology’s EIM database.
5. Publish a report that summarizes the data quality, data results, and recommendations regarding the verification of the pH listings in the Okanogan River tributaries.

4.3 Information needed and sources

Exact sampling locations used by the Okanogan Conservation District (OCD) and access points for the deploying the pH data loggers will have to be determined by communication and possibly site visits with the OCD.

Ecology would like to review the calibration notes from the earlier monitoring performed by the OCD, if they are available.

4.4 Target population

Monitoring is targeting pH of water in the Okanogan River basin tributaries.

4.5 Study boundaries

The study area is located in the Okanogan River basin. A map of the study area is provided in Figure 1.

The Water Resource Inventory Area (WRIA) of the Okanogan River Basin is designated as WRIA 49. The eight-digit Hydrologic Unit Code (HUC) number is 17020000.

4.6 Tasks required

Brief summary of tasks required to complete this project:

- Do pre-calibration checks on pH loggers.
- Deploy loggers at selected monitoring sites.
- Collect pH data for 24 hours at 15-minute intervals.
- Collect flow measurements at tributaries.
- Retrieve, download, and do post-calibration checks of all loggers.
- Quality assurance check of the collected data.
- Submit data to Ecology's EIM database.
- Write a summary report.

4.7 Practical constraints

See section 3.1.1.

4.8 Systematic planning process

This QAPP represents the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 5. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Heather Simmons Water Quality Program Central Regional Office Phone: 509-454-7207	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Jim Carroll Eastern Operations Section Phone: 360-407-6196	Project Manager/ Principal Investigator	Writes the QAPP. Oversees field deployment of pH loggers and field activities. Writes data summary report.
Eiko Urmos-Berry Eastern Operations Section Phone: 509-575-2397	Assistant Investigator	Helps collect field information and audit data collection and QA review. Conducts QA review of data and enters accepted data into EIM database for publication on the Ecology website.
Tom Mackie Eastern Operations Section Phone: 509-454-4244	Section Manager for the Project Manager	Reviews the project scope, tracks progress, reviews the draft QAPP, and approves the final QAPP. Approves the initiation of field work.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP. Approves the initiation of field work.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

5.2 Special training and certifications

The field lead and assistants for each survey are trained in and experienced with the SOPs being used.

5.3 Organization chart

See Table 5.

5.4 Project schedule

Field work for data collection is expected to be completed between July 2015 and May 2016. Table 6 presents the proposed schedule for this project.

Table 6. Proposed schedule for completing field work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	May 2016	Jim Carroll
Environmental Information System (EIM) database		
EIM Study ID	JICA0003	
Product	Due date	Lead staff
EIM data loaded	June 2016	Eiko Urmos-Berry
EIM data entry review	July 2016	Jim Carroll
EIM complete	July 2016	Eiko Urmos-Berry
Final technical report		
Author lead	Jim Carroll and Eiko Urmos-Berry	
Schedule		
Draft due to supervisor	August 2016	
Draft due to client/peer reviewer	September 2016	
Draft due to external reviewer(s)	September 2016	
Final (all reviews done) due to publications coordinator	October 2016	
Final report due on web	November 2016	

5.5 Limitations on schedule

Field-related logistical issues are addressed in section 3.1.1.

Work load of project manager, lead, and assistant will determine if work products can be followed as scheduled.

5.6 Budget and funding

No laboratory budget is needed for this project. Travel and staff time are the only expected expenses.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

All of the pH data collected for this project must meet the measurement quality objectives (MQO) to be used for the project goals. If monitoring data does not meet the MQOs then monitoring sites will be re-monitored.

6.2 Measurement Quality Objectives

Field sampling procedures have associated uncertainty, which results in data variability. Measurement quality objectives (MQOs) state the acceptable data variability for a project. Precision and bias are data quality criteria used to indicate conformance with MQOs.

The accuracy and instrument bias MQO of each pH logger is verified through both pre- and post-deployment calibration checks following the procedures described in the Standard Operating Procedures for Hydrolab data loggers (EAP033, 2010).

The procedures require the pH loggers be calibrated and tested with certified pH standard buffer solutions that bracket the expected monitoring range (from 7.0 to 10.0 pH units). Post calibration pH readings measuring certified pH standard buffer solutions will determine the measurement quality of the data.

Table 7. Summary of Hydrolab datalogger parameter accuracy, resolution, and range.

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range
Water Quality Measurements							
pH	Hydrolab®	See Table 7	± 0.2 s.u.	± 0.2 units	0.01 s.u.	0 to 14 s.u.	6 to 10 s.u.
Water velocity	Marsh McBirney	±0.05 ft/s ^e	n/a	±2%	0.01 ft/s	-0.5 to +20 ft/s	0.01 to 10 ft/s

Table 8. Measurement quality objectives for Hydrolab post-deployment bias checks.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8

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. Precision for field replicate measurements of pH will be expressed as the difference of duplicate pairs (Table 7). If they are taken, two pH loggers will be placed side-by-side.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Bias will be measured by post-deployment calibration checks used to document logger bias and performance (Table 8).

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. It is commonly described as detection limit. The detection limit for field measurement of pH is 0.1 pH units.

6.2.2 Targets for Comparability, Representativeness, and Completeness

6.2.2.1 Comparability

To ensure comparability, field measurements will follow approved Environmental Assessment Program (EAP) SOPs. These are listed in section 8.1.

6.2.2.2 Representativeness

The study is designed to have enough monitoring sites and sufficient monitoring frequency to meet study objectives of characterizing daily maximum pH in the target tributaries.

6.2.2.3 Completeness

Completeness is a measure of the amount of valid data needed to meet the goals defined for the uses of the data. The goals for the collected data will be to:

- Verify if pH impairments are occurring in 11 of the Okanogan River 303(d)-listed tributaries for pH impairment.

The target for this study is to correctly monitor, record, and analyze 100% of the time intervals pre-set to record by the pH loggers at all sites. Completeness will be acceptable if pH monitored at each site allows the daily maximum pH to be evaluated for each survey date.

Problems which can occasionally arise during data collection which need to be avoided if possible include: loss of pH loggers by vandalism, loss of valid pH monitoring due to water levels dropping below logger installations, malfunctioning of loggers, and site access problems.

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design

The project objectives will be met by re-monitoring all 11 tributaries to the Okanogan River that are on the 303(d) list for verification of pH impairment. For the tributaries that had more than one segment with pH impairment, the top-ranked segment of the two (most likely to have higher pH, based on earlier monitoring) will be re-monitored (see section 3.1.4). Continuous pH data collection with a pH logger at these 11 sites will be used to determine the daily minimum and maximum pH at each site. Three monitoring events will be spread out over the expected critical conditions time period to meet minimum requirements for 303(d) list assessment requirements.

If any of the 11 tributaries show no pH impairment for all 3 monitoring periods, then Ecology will be satisfied that the entirety of that tributary is not impaired for pH, including segments listed for pH impairment on those tributaries that were not re-monitored. A recommendation will be made for delisting all segments attributed to those tributaries.

If a re-monitored segment shows pH impairment only once or twice during the verification monitoring, then Ecology will have to evaluate how impaired these specific sites are and if they are representative of the overall condition of the whole tributary or are singly impaired for other reasons. Ecology may recommend more monitoring to characterize the potential impairment.

If a re-monitored segment shows pH impairment during all 3 verification monitoring events, then Ecology will most likely determine that there is an overall potential for pH impairment in the entirety of that tributary and a TMDL study will be recommended for that tributary.

7.1.1 Field measurements

The sampling design will use a fixed network of 11 tributary monitoring sites. Each will be monitored for 24-hour periods, with continuous pH loggers. Each site will be monitored twice between July and October 2015 and once in April or May 2016.

Also, instantaneous discharge measurements will be made during these visits.

7.1.2 Sampling location and frequency

Data monitoring will occur between July 2015 and May 2016. Table 9 lists the proposed locations.

Table 9. Proposed sites within the Okanogan River basin for the pH Verification Study.

Site ID in EIM	Station Description	Latitude	Longitude
LOWERSIWASHCR	Siwash Creek (lower)	48.71158	-119.436
LOTONASKETCR	Tonasket Creek (lower)	48.94322	-119.413
LOWERANTOINECR	Antoine Creek (lower)	48.75903	-119.409
LOWERJOHNSONCR	Johnson Creek (lower)	48.50214	-119.505
LOWERTUNKCR	Tunk Creek (lower)	48.55248	-119.465
LOBONAPARTECR	Bonaparte Creek (lower)	48.70033	-119.439
UPNINEMILECR	Ninemile Creek (upper)	48.98149	-119.316
UPPERTALANTCR	Tallant Creek (upper)	48.35772	-119.704
LOCHILIWISTCR	Chiliwist Creek (lower)	48.26689	-119.734
LOLOUPLOUPCR	Loup Creek (lower)	48.28342	-119.708
UPSINLAHEKINCR	Sinlahekin Creek (upper)	48.75284	-119.662

Continuous pH measurement collection:

- Data loggers will be deployed to log every 30 minutes in locations where representative pH data may be measured in the tributary segment.

7.1.3 Parameters to be determined

Primary target parameter is the daily maximum pH of water.

7.2 Maps or diagram

See a map of the study area (Figure 1) in Section 3.1. Figure 3 has a map of the proposed sites.

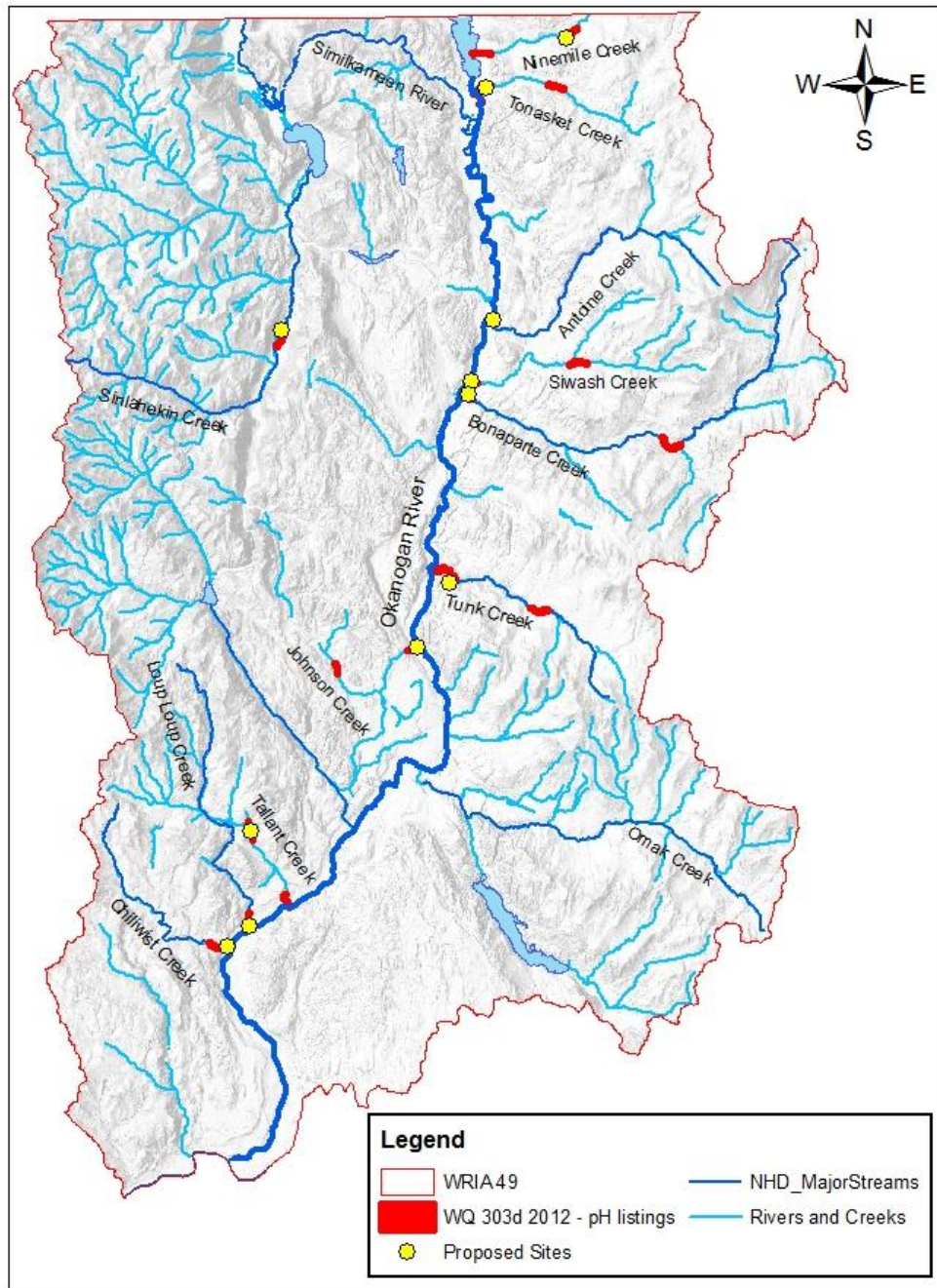


Figure 3. Proposed sites for verification of pH impairments within the Okanogan River basin.

7.3 Assumptions underlying design

Seven segments on the 303(d) list for pH impairments will not be re-monitored because there will be another segment re-monitored on the same tributary (alleged to have higher pH, based on earlier monitoring data). This sampling design assumes that by re-monitoring the segments that were most likely to have high pH measurements in the past, the tributary will be fully characterized for pH impairment currently. Ecology will recommend delisting all segments on those tributaries in these cases.

7.4 Relation to objectives and site characteristics

All segments that will be re-monitored are on the 303(d) list for pH impairment. If there are two segments on the same tributary, then the segment with higher pH values in the past will be re-monitored.

7.5 Characteristics of existing data

See section 3.1.4.

8.0 Sampling Procedures

Field measurement protocols will follow Standard Operating Procedures (SOP) developed by the Environmental Assessment Program. Table 10 shows the parameter and SOP that will be used to collect the data.

Field measurements for pH will be collected using a calibrated Hydrolab® multi-probe data logger (Datasonde or Minisonde).

Where possible, flow measurements in tributaries will be made using a cross-sectional method.

Table 10. Field sampling and measurement methods and protocols.

Parameter	Measurement/ Sample Type	Lab Method	Standard Operating Field Protocol #
pH	Hydrolab® multi- parameter data logger	n/a	EAP033 (Swanson, 2010)
Flow	Instantaneous	n/a	EAP024 (Kardouni, 2013)

8.1 Field measurement and field sampling SOPs

To insure comparability, field measurements will follow approved EAP SOPs (Ecology, 2014):

- EAP033 - Standard Operating Procedure for Hydrolab®, DataSonde®, and MiniSonde® Multiprobes
- EAP024 - Standard Operating Procedure for Estimating Streamflow
- EAP070 - Standard Operating Procedures to Minimize the Spread of Invasive Species

8.2 Containers, preservation methods, holding times

Not Applicable.

8.3 Invasive species evaluation

The study area is not in an area of concern for invasive aquatic species; however, as mentioned in Section 8.1, we will follow SOP EAP070, Standard Operating Procedures to minimize any chance of spreading of invasive species.

8.4 Equipment decontamination

Not Applicable.

8.5 Sample ID

Not Applicable.

8.6 Chain-of-custody, if required

Not Applicable.

8.7 Field log requirements

A field notebook will be maintained by the field lead and used during monitoring events. Observations and measurements will be recorded waterproof paper in field notebooks. They will contain:

- Name of location and site ID
- Date and time
- Field staff
- Field measurement results
- Instrument IDs
- Pertinent observations
- Any data logger information
- Comments

8.8 Other activities

No other activities expected.

9.0 Measurement Methods

9.1 Field procedures table/field analysis table

There will only be field procedures associated with this study. Table 11 shows the field measurement methods required to meet the goals and objectives of this project.

Table 11. Measurement Methods (field).

Analyte	Sample Matrix	# of measurements	Expected Range of Results	Method	Method Detection Limit
pH	water	≈ 500 logged intervals	6.5 – 10 s.u	Hydrolab MiniSonde®	0.1 s.u.
Velocity	water	≈ 11 flow cross sections	<0.1 – 10 ft/s	Marsh-McBirney	0.01 ft/s

9.2 Lab procedures table

Not Applicable. See Section 9.1.

9.3 Sample preparation method(s)

Not Applicable. See Section 9.1.

9.4 Special method requirements

Not Applicable. See Section 9.1.

9.5 Lab(s) accredited method(s)

Not Applicable. See Section 9.1.

10.0 Quality Control (QC) Procedures

Field measurements will follow quality control protocols described in Ecology's field sampling protocols (Table 10).

The accuracy and instrument bias of each pH logger is verified through both pre- and post-deployment calibration checks.

Prior to each synoptic survey, field staff will pre-calibrate the Hydrolabs by:

- For pH, using a two-point calibration with NIST-certified pH 7 and pH 10 standards.

Following the monitoring surveys where the loggers are deployed, field staff will post-check deployed data loggers against NIST-certified pH standard buffers within 24 hours of returning from the survey.

Marsh-McBirney FlowMate® will be zeroed at the beginning of the field week to ensure accurate measurements.

10.1 Table of field QC required

See Tables 7 and 8 in Section 6.2.

10.2 Corrective action processes

QC results may indicate problems with monitoring data during the course of the project. Options for corrective actions might include:

- Recheck pre- and post-calibration checks.
- If possible, re-sample sites.
- Qualify or reject results.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

Staff will record all field notes in a field notebook. Before leaving each site, staff will check field notebooks for missing information. Staff will download field-generated logger data into Microsoft (MS) Excel® spreadsheets as soon as practical after they return from the field. The field lead will check data entry against the field notebook data for errors and omissions.

Data from loggers that meet the calibration check accuracy requirement are generally graphed using MS Excel® to report and present the data.

11.2 Laboratory data package requirements

Not applicable.

11.3 Electronic transfer requirements

Not applicable.

11.4 Acceptance criteria for existing data

Not applicable.

11.5 EIM/STORET data upload procedures

All continuous and field data that meet the data quality objectives will be input into Ecology's Environmental Information Management (EIM) Database. All EIM entries will follow all existing Ecology business rules and the EIM User's Manual for loading, data quality checks, and editing.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

Audits are not planned for this project.

12.2 Responsible personnel

See Table 5 found in Section 5.1.

12.3 Frequency and distribution of report

A summary of the data collected under this project will be published in a formal, peer-reviewed report, including results, methods, and data quality assessment. The final report will be published according to the project schedule in Section 5.4, Table 6.

12.4 Responsibility for reports

Jim Carroll and Eiko Urmos-Berry will be the lead authors on the final report. See Table 5.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

The field team will verify initial pH logger calibration and settings (including date, time, logging interval, and battery state) before leaving for the field. This process involves completing a pre-calibration worksheet for each logger. Field team will verify that all pH standard buffer solutions are not expired and not contaminated; only new and unopened buffer solutions will be used for each monitoring survey. Field notebooks will record conditions and deployments of loggers. The field team will check field notes for omissions and completeness each monitoring day. If field notes are inaccurate or missing, monitoring will be repeated. After deployment, the loggers will be checked for bias or drift with post-calibration checks following protocols. Post calibration checks will be recorded on the same worksheet that the pre-calibration information is recorded on.

The project manager and report authors will verify that the quality assurance criteria have been met by examining the pre- and post- calibration worksheet and comparing the recorded pH results with the criteria listed in Table 8.

13.2 Lab data verification

Not Applicable.

13.3 Validation requirements, if necessary

Validation of data collected by this monitoring project will not be done.

After data entry tasks are completed, all field and flow data entered into the EIM system will be independently reviewed by another field assistant for errors at an initial 10% frequency. If significant entry errors are discovered, a more intensive review will be undertaken.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

After all field data are verified, the field lead or project manager will thoroughly examine the data to determine if MQOs have been met. The project manager will examine the data to determine if all the criteria for MQOs, completeness, representativeness, and comparability have been met. If the criteria have not been met, the project manager will decide if affected data should be qualified or rejected.

14.2 Data analysis and presentation methods

The analysis to determine the usability of the data will be a data quality assessment of post-calibration bias checks to determine if the pH loggers meet the quality control requirements. The data quality assessment will be documented in the final report by using graphs, tables, narration, or a combination that best represent and describe data quality standing and usability.

14.3 Treatment of non-detects

Not Applicable.

14.4 Sampling design evaluation

The sampling design is based on the data needs for assessing pH impairments in surface water. Ecology's Water Quality Program has minimum requirements for the listings of water bodies for pH impairment, which include 3 daily pH violations during the season of concern, generally May through October. Data collected during this project will be sufficient to meet project goals and objectives.

14.5 Documentation of assessment

The technical report will include a summary of the data quality assessment. This summary is usually included in the data quality section of reports.

15.0 References

Bard, E. 2003. Okanogan River Watershed Water Quality Summary Report for Grant Number G0000225, Okanogan Conservation District, Okanogan, WA.

Kardouni, J. 2013. Standard Operating Procedure for Estimating Streamflow. Washington State Department of Ecology, Environmental Assessment Program, Olympia, WA. 19 pp. with appendices. Publication No. EAP024.

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Parsons, J., D. Hallock, K. Seiders, B. Ward, C. Coffin, E. Newell, C. Deligeannis, K. Welch. 2012. Standard Operating Procedures to Minimize the Spread of Invasive Species, Version 2.0.

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Swanson, T. 2007. Standard Operating Procedure for Hydrolab DataSonde® and MiniSonde® Multiprobes. Version 1.0. Washington State Department of Ecology, Environmental Assessment Program. SOP Number EAP033. www.ecy.wa.gov/programs/eap/quality.html

WAC 173-201A-200. 2013. Washington State Administrative Code. Fresh water designated uses and criteria. <http://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A-200>

WAC 173-201A-600. 2013. Washington State Administrative Code. Use designations — Fresh waters. <http://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A-600>

WAC 173-201A-602. 2013. Washington State Administrative Code. Table 602 — Use designations for fresh waters by water resource inventory area (WRIA). <http://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A-602>

16.0 Figures

See Table of Contents for list of figures.

17.0 Table

See Table of Contents for list of tables.

18.0 Appendix

Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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.

Designated uses: Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each water body or segment, regardless of whether or not the uses are currently attained..

Reach: A specific portion or segment of a stream.

Salmonid: Fish that belong to the family *Salmonidae*. Any species of salmon, trout, or char.

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.

Thalweg: The deepest and fastest moving portion of a stream.

Total Maximum Daily Load (TMDL): A distribution of a substance in a water body 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.

1-DMax or 1-day maximum temperature: The highest water temperature reached on any given day. This measure can be obtained using calibrated maximum/minimum thermometers or continuous monitoring probes having sampling intervals of thirty minutes or less.

303(d) list: Section 303(d) of the federal Clean Water Act, requiring 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 standards and are not expected to improve within the next two years.

7-DADMax or 7-day average of the daily maximum temperatures: The arithmetic average of seven consecutive measures of daily maximum temperatures. The 7-DADMax for any individual day is calculated by averaging that day's daily maximum temperature with the daily maximum temperatures of the three days before and the three days after that date.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
et al.	And others
MQO	Measurement quality objective
QA	Quality assurance
RM	River mile
SOP	Standard operating procedures
USFS	United States Forest Service
USGS	United States Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
m	meter

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. (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, e.g., CRM, LCS. (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 project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Continuing Calibration Verification Standard (CCV): A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at ± 2 standard deviations from the mean, action limits at ± 3 standard deviations from the mean. (Kammin, 2010)

Data Integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

Data Quality Indicators (DQI): 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): 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)

Data set: A grouping of samples organized by date, time, analyte, etc. (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 data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

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 data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (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)

Measurement result: A value obtained by performing the procedure described in a method. (Ecology, 2004)

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)

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010)

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite 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:

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

where “Abs()” is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (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)

Sample (statistical): A finite part or subset of a statistical population. (USEPA, 1997)

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 blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

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: A discrete sample that 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)

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

References for QA Glossary

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

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