

# Klamath Water Quality Quarterly Sampling

# **Quality Assurance Project Plan**

U.S. Bureau of Reclamation, Mid-Pacific Region Environmental Monitoring Branch, MP-157

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# Klamath Water Quality Quarterly Sampling

# **Quality Assurance Project Plan**

Project Manager	Date
Quality Assurance Team Project Manager	Date
Data Management Team Project Manager	Date

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# Project Management

## I. Project/Task Organization

The Klamath Water Quality program (KWQ) monitors the Klamath Project. This program is administered and conducted by Jessica Asbill.

Project management is overseen by Jessica Asbill. Field operations and interpretation/assessment of analytical data are the responsibility of Jessica Asbill. Laboratory oversight and quality assurance tasks are performed by the Quality Assurance Team (QAT). Chemical analyses are performed by contract laboratories. Data management tasks are performed by the Data Management Team (DMT). Specific personnel assignments are listed in Table 1; laboratory assignments are listed in Table 2.

Task	Responsible Parties
Review and revision of Quality Assurance Project Plan	Jessica Asbill (KBAO) Melanie Lowe (QAT) Satpal Kalsi (DMT)
Sample collection and physical measurement	Jessica Asbill (KBAO)
Maintenance and operation of field equipment	Jessica Asbill (KBAO)
QA Incorporation	Melanie Lowe (QAT)
Sample transport to analytical laboratories	Jessica Asbill (KBAO)
Sample analysis	Basic Laboratory
Review and validation of analytical data	Melanie Lowe (QAT)
Writing and editing of Data summary	Eva Grey (DMT)
Program overview:	
Environmental Affairs Branch management Program management Environmental monitoring management Quality assurance management Data management	John Fields Jessica Asbill Jessica Asbill Victor Stokmanis Satpal Kalsi

Table 1Program Responsibilities

Parameter	Laboratory	Project Manager	Phone Number
As, B, Hg, Ammonia as N, Nitrate as N, TKN, Total phosphorous, Ortho-phosphorous, alkalinity, TDS	Basic Laboratory	Melissa Hawley	530-243-7234

 Table 2
 Assigned Analytical Laboratories and Lab Contacts

# II. Problem Definition/Background

Water quality issues affecting endangered fish in the watershed are a special concern. The low concentration of dissolved oxygen and high water temperature has impaired this watershed. High turbidity and nutrient loading correlate to water degradation. The hardness of the water influences the toxicity of cadmium, chromium, copper, lead, nickel, silver, and zinc to aquatic life.

This program provides baseline information on main stem and tributary contributions on the Klamath River (KR) and the Lost River (LR) for a representative suite of physical and chemical water quality constituents. These constituents will be used to characterize water quality in the main stem KR and LR and identify water quality constituents of concern within selected reaches. To achieve these objectives selected physical and chemical constituents will be measured quarterly.

# III. Project/Task Description

#### Sample Sites and Programs

This program is designed to monitor main stem KR and LR, and major tributary water quality from Malone Dam near Lorella to the Strait's Drain. Two sampling sub-programs are included within this program; Table 1 identifies site locations:

- Quarterly grab samples (Grab)
- Single Point Measurements with water quality probes (Sonde)

l able 1	Sample Sites	
Station codes	Location	Location Description
K-1	Pumping Plant F	KSD @ Hwy 97
K-2	Klamath Straits Drain (KSD) @ Stateline	KSD @ Stateline Rd.
K-3	Pumping Plant D	KSD just north of Township Rd.
K-4	Anderson-Rose Dam	Anderson-Rose Reservoir upstream of dam
K-5	Lost River Diversion Dam	Wilson Reservoir upstream of dam
K-7	Malone Diversion Dam	Malone Reservoir upstream of dam
K-8	Miller Creek Below Diversion Dam	Miller Creek downstream of North Canal Diversion Dam
K-10	Klamath River @ Hwy 140 Bridge	Klamath River @ Hwy 140 Bridge

Table 1	Sample	Citoo
Table 1	Sample	Siles

# IV. Quality Objectives and Criteria

Water quality is not evaluated in accordance with any regulatory standards.

Reporting limits for inorganic chemicals and physical parameters are listed in Table 4.

Data Quality Objectives were selected to meet precision, accuracy, and contamination limits set by Environmental Monitoring QA protocol and are discussed in detail in section XI.

Table 4 Acquireu i	LS IOI INDIYANIC A	nu physical monitori	
Analyte	Acquired RL (µg/L)	Analyte	Acquired RL (µg/L)
Chemical Properties		Physical Properties	
Arsenic	0.5	Specific conductance (µS/cm)	N/A
Boron (total)	10.0	рН	N/A
Mercury	0.20	Temperature (°C)	N/A
Ammonia as N	50	Turbidity (NTU)	N/A
Nitrate as N	50		
TKN	200		
Total Phosphorous	50		
Ortho-phosphorous	50		
Alkalinity	5000		
TDS	6000		

 Table 4
 Acquired RLs for inorganic and physical monitoring constituents

\* RLs are subject to change due to: dilutions, Method Detection Limit (MDL) studies, or different laboratories analyzing the samples.

# V. Special Training/Certifications

No special training or certifications are required for this project.

## VI. Documentation and Records

#### **Field Sheets**

Field sheets are carried in the field and entries are made by staff at the time of sample collection. Field sheet entries document the following information:

- Project name
- Site name
- Sample collection date
- Sample collection start times
- Weather conditions
- Sample identifiers (IDs) and associated QA designations for QA samples
- Values obtained from physical property measurements
- Brief explanation of sampling methods

- Parameters and matrices collected
- Notes explaining any sampling irregularities
- Signature of field sampler (attesting that all data entered in the field sheet is accurate and complete)

After returning from the field, field sheets are stored in the Environmental monitoring manager's office (Table 5).

Table 5 Docu	ment Locations		
Document Age:	generated within the last month	generated within the last six months	generated more than three years ago, less than 10 years ago
Field Sheet	Environmental monitoring manager's office	Environmental monitoring manager's office	Denver Archives
Instrument Calibration Sheet	White data binders stored on bookshelf in the Hydrologic Technician's office	White data binders stored on bookshelf in the Hydrologic Technician's office	Denver Archives
Chain of Custody Sheet	Environmental monitoring manager's office	Environmental monitoring manager's office	Environmental monitoring manager's office
Spike Book	File holder on walls outside of EMT/QA cubicles	QA staff member's cubicle	QA team leader's cubicle
Laboratory analytical report & case narrative	White data binders s across from EMT cub	White data binders stored in x 2's, just inside the east door	
Program-related correspondence	Environmental mo off	Environmental monitoring manager's office	
DMT report	Computer I drive		

# Table 5 Document Locations

#### Chain of Custody

Chain of Custody (COC) forms document the chain of legal custody of samples from the time samples are collected to the time they are delivered to the laboratory. Field personnel initiate COC documentation while in the field. COCs document the following information:

- Project name
- Project manager
- Title and signature of sample collector
- Name of the designated analytical laboratory
- List of sample IDs
- Sample collection date
- Sample matrix type
- Number of containers per sample ID
- Analyses requested
- Point of contact phone number
- Date, time, and signatures of all parties responsible for receiving and relinquishing the samples from the time of collection to the time of delivery to the laboratory

Upon return from the field, COCs are filed in the Environmental monitoring manager's office (Table 5). KBAO personnel send the COCs to the laboratory with the samples. A copy of the COC is returned to MP-157 by the laboratory and then filed with the field sheets in the MP-157 office. COCs greater than two years old are stored at the MP-157 El Camino Plaza Laboratory (Table 5).

#### Spike Book

The QA specialist is responsible for documenting the necessary information pertaining to the QA samples in the spike book. A spike book is a bound notebook that contains spike worksheets. The following information is documented on the spike worksheet:

- Project name
- Number of samples
- Collection date
- Batch identification numbers(laboratory assigned)
- Range of sample ID numbers within each lab batch
- Sampling site name(s)
- Types of QA samples incorporated
- Field IDs that correspond to the QA samples
- Source IDs for reference material used
- Historical parameter concentrations
- Parameter reporting limits
- Dated initials of QA personnel incorporating the QA samples

Spike books are stored in the MP-157 office when not in use (Table 5).

#### Data Assessment / Data Tables

The Data Management Team (DMT) maintains a running data table for inclusion in water quality reports.

# **Data Generation and Acquisition**

# VII. Sampling Process Design

This program is divided into two different sub-programs; each designed to provide an overall assessment of the Klamath Project.

- <u>Quarterly Grab Samples</u>: Water quality grab samples are collected four times a year from stations K-1, K-2, K-3, K-4, K-5, and K-10. Water quality grab samples are collected twice a year in summer and fall from stations K-7 and K-8. The TDS, alkalinity, nutrients and metals are measured. The turbidity is measured using a portable instrument when the grab sample is collected. Three QA samples are added to the production samples to document lab accuracy, precision and contamination. Entries into field sheets and chain of custody (COC) are completed in the field. Samples are stored in ice-chests containing ice at 4° C. The completed COC is placed in a zip-lock plastic bag in the ice-chest and mailed or delivered to lab. The sample site locations are listed in Table 1.
- <u>Single Point Measurements with Water Quality Probes</u>: Physical parameters are measured with YSI 600xlm at all sites (see Table 1). Parameters include temperature, dissolved oxygen, pH, and specific conductance.

If a site is inaccessible for sampling the field crew will use professional judgment to obtain a representative sample at a nearby location. If an alternate sampling site is not available then the sample will not be obtained. No constituents would require re-sampling if results were unacceptable. The data collected is for monitoring and informational purposes.

# VIII. Sampling Methods

For field sampling protocol, the "Klamath Project Water Quality Standard Field Sampling Operating Procedure" is being used. This document is included in the appendix.

All water samples will be collected using the grab-sample method. A *churn splitter or sample bottle* will be used to collect water from the shore. A van Dorn will be used to collect water from places where shore is unobtainable. Before use, the churn splitter is rinsed three times with environmental water and water is run through the push valve. The van Dorn is also rinsed in the environmental water three times before use. The Field SOP instructs how the monitoring and sampling will be performed and associated procedures for documenting the field activities. Water samples designated as "dissolved" (filtered) are first pumped through a 0.45um filter. A YSI 600xlm will be used to measure the physical parameters (pH, specific conductance, dissolved oxygen, turbidity and water temperature) of the environmental water. A turbidity meter will be used to obtain this physical measurement.

# IX. Sample Handling and Custody

The size of high-density polyethylene (HDPE) bottles required is listed in Table 6 for each constituent. The sample bottles used for trace metals and mercury will be "level 1" certified to ensure bottle contamination does not affect analytical results. Water samples are preserved according to EPA, Standard Methods, or other approved analytical methodology. Samples collected in the field will be labeled with the following information:

- sample identification
- preservatives used
- constituent analyses required
- date and time sampled
- samplers initials

Sample volume is based on analytical requirements and listed in Table 6. Upon collection in the field, water and biological samples are placed in ice chests with a temperature of 4° C. All samples collected in the field require a chain of custody sheet and a field sheet. The chain of custody sheet and the field sheet will clearly document all the samples collected during that sampling period, their associated sample identification numbers--which is KWQ(four digit year)-(two-digit sample number in numerical order) ex: KWQ2008-01--and the date and time of collection for each sample. The COC is placed in the ice chest in a zip-lock plastic bag. A custody seal is attached to the ice chest by the field sampler. A commercial package carrier or laboratory courier transports the ice chests. The original COC sheet will be kept on file at the laboratory and other copy returned to the Regional Office.

Test	Filtered	Container	Preservatives	Hold Time
Trace Metals (total) and Mercury	No	500 ml "level 1"	4°C, HNO <sub>3</sub>	6 months TM 28 days Hg
NH4, (NO2+NO3)N, TKN, total P	No	1,000 ml	4°C, H <sub>2</sub> SO <sub>4</sub>	28 days
Ortho Phosphate	No	500 ml	4°C, none	48 hours
Total Alkalinity	No	500 ml	4°C, none	14 days
TDS	Yes	500 ml	4°C, none	14 days

Table 6Sample Bottles

## X. Analytical Methods

The laboratories follow the protocols for preparation, analysis, and corrective actions stated in the analytical methods and the laboratory Standard Operating Procedures (SOP). Approximate turn around times for analysis is 3 weeks. The following analytical methods will be used (Table 7):

Analyte	Method	Analyte	Method
Arsenic	EPA 200.8	TKN	EPA 351.2
Boron	EPA 200.8	Ammonia as N	EPA 350.1
Mercury	EPA 7470	Nitrate+Nitrite as N	EPA 353.2
Alkalinity	SM 2320B	Total Phosphorous	SM 4500P-BE
TDS	SM 2540C	Ortho-phosphorous	SM 4500P-E

Table 7 Analytical methods

#### XI. Quality Control

Quality Control requirements are fully documented in the Environmental Monitoring Branch's *Standard Operating Procedures for Quality Assurance*, January 2005. Following is a brief summary of the QA activities that pertain to this project.

#### **External Quality Assurance Samples**

External QA samples for inorganic analytes are incorporated into the sample batches for all samples that are submitted to the laboratory. These (blind) QA samples are used by the QAT to assess the laboratory's ability to process samples with an acceptable level of precision and accuracy without introducing contamination to the sample. If any of the QA samples do not meet the criteria stated in section IV, all samples are reanalyzed. If the laboratory is unable to confirm the original result upon reanalysis, a bracket of samples or the entire batch of samples are submitted for reanalysis. The following external QA samples are incorporated:

#### Accuracy

To assess accuracy, matrix spike samples are incorporated for metals and nutrients, and reference samples are incorporated for alkalinity and TDS. Accuracy check samples are incorporated at a rate of 10% of the production samples. If less than 10 production samples are collected, at least one matrix spike/reference sample is incorporated. Accuracy is assessed using percent recovery:

$$PR = \left(\frac{(S-R)orF}{MPVorMPN}\right) (100)$$

PR	=	Percent Recovery
S	=	Spiked Sample Result
R	=	Regular Sample Result
F	=	Reference Sample Result

MPV	=	Most Probable Value
MPN	=	Most Probable Number

#### Precision

Duplicate samples are incorporated to assess precision. They are incorporated at a rate of 10% of the production samples. If less than 10 production samples are collected, at least one duplicate sample is incorporated. Precision is assessed using relative percent difference (RPD):

$$RPD = \frac{|R-D|}{\left(\frac{(R+D)}{2}\right)} (100)$$

RPD	=	Relative Percent Difference
R	=	Regular Sample Result
D	=	Duplicate Sample Result

#### Contamination

DI water blank samples are incorporated to assess laboratory contamination. They are incorporated at a rate of 5% of the production samples. If less than 20 production samples are collected, at least one blank sample is incorporated.

#### Laboratory Quality Control Samples

The laboratory incorporates QC samples at the frequency specified in the laboratory SOP and/or analytical method. Results for the QC samples are assessed based on the acceptance criteria in the analytical method and the laboratory SOP. If any laboratory QC samples do not meet the established acceptance criteria, the laboratory follows the corrective action protocol detailed in the analytical methods and/or laboratory SOP.

#### **Holding Times**

The date of the sample processing/analysis is compared to the date the sample was collected to ensure the sample was processed and analyzed within the holding time. If the holding times are exceeded, the program manager determines if re-sampling is required. If re-sampling is not required, the QA specialist qualifies the data as necessary.

#### **Historical Outliers**

When the QAT receives the analytical report, the results for the production samples from each site are entered into an Excel spreadsheet. The Excel

spreadsheets have been developed to flag any result that is an outlier. If a result is flagged, the QAT will use the guidelines in the QASOP to determine if the sample needs to be reanalyzed for the parameter.

#### Completeness

Since samples will be collected quarterly over multiple years, there is no completeness criterion for this program.

# XII. Instrument/Equipment Testing, Calibration, Inspection, and Maintenance

#### Field

Portable (hand held) instruments are calibrated according to manufacturer protocol. For each sampling episode (whether taking place in one day, or over a number of days), instruments are calibrated up to one day before any measurements are taken; calibrations are verified with calibration standards up to one day after sampling has been completed. These calibrations follow the Klamath YSI Calibration Protocol in the appendix. Field personnel will record YSI calibrations on calibration sheets, which will be filed at the Klamath Basin Area Office.

#### Laboratory

Maintenance procedures for contract laboratories are detailed in the contract laboratory's QA manual. Instrument calibration procedures are specified in the analytical methods section for each parameter.

## XIII. Inspection/Acceptance for Supplies and Consumables

Certified clean bottles for sample collection, certified calibration standards for portable instrument calibration and spike preparation, and references for external QA incorporation are ordered from outside vendors. Standards and references have vendor-certified values. Spike solutions used for external QA incorporation are certified to be within 90%-110% of the expected value prior to use. All bottles and reagents are inspected prior to use. If any damage or contamination is suspected, packages are not accepted.

## XIV. Data Management

The alpha-numeric field sample identification (ID) assigned for this project is: KWQ [four digit year-*number*]. Each calendar year the ID system repeats with a new four digit year. The number portion is assigned sequentially for the year, always beginning with 01 at the start of a new year. The assigned field station ID is: KWQ\_ [*number*]. Numbers are assigned sequentially, beginning with 01. Station IDs correlate with a sample collection area.

DMT personnel enter field measurements, laboratory data into Microsoft Excel tables. Prior to releasing data or reports, data entries are secondarily reviewed.

All data are entered into the tables are in accordance with the DMT SOP. As a QC check, all data entered is secondarily reviewed by an additional DMT member and initialed. After all data has been entered into the tables, the data is signed and filed in project binders. Project binders are locked in a file cabinet in the MP-157 office and must be signed out by individuals.

# Assessment and Oversight

#### XV. Assessments and Response Actions

#### Audits

The QAT performs laboratory audits for the KWQ project. Field and documentation audits, also conducted by the QAT, are not performed for the KWQ project.

#### Laboratory

Laboratory audits are conducted every three years. The three-tier audit consists of reviewing the laboratory's QA Manual, reviewing the laboratory's performance evaluation (PE) sample results, and conducting an intensive, on-site, system audit of the laboratory. The laboratory's expertise in conducting analyses, their capability for producing valid data, their ability to effectively support the data, and the integrity of the QA/QC practices are assessed during the on-site audit. Once the audit reports are issued to the laboratory, the laboratory issues a response with corrective actions to the EMB. At that time, the QAT determines whether or not to approve the laboratory for use and communicates this decision to the laboratory with a formal letter.

#### Field

Field audits are conducted every two years on EMB staff; they include reviewing the SOP, submitting PE samples and reviewing the results, and accompanying the field sampler while they demonstrate the sample collection process. EMB personnel do not collect KWQ samples so field audits are not performed for this project.

#### **Documentation**

The biannual documentation audits are performed on a percentage of field logbook entries as well as the corresponding field sheets and field instrument calibration sheets generated by EMB staff. Documentation for KWQ is not generated by the EMB so documentation audits are not performed for this project.

#### XVI. Reports to Management

Following secondary review by DMT members quarterly data reports are submitted to Jessica Asbill.

# **Data Validation and Usability**

#### XVII. Data Review, Verification, and Validation

If all external QA samples and laboratory QC samples meet the acceptance criteria and all samples are analyzed within the holding time, all data is accepted as valid.

If a result is confirmed after reanalysis, the result is accepted as valid.

Data may be qualified if results demonstrate unacceptable QA after being reanalyzed, if the laboratory QC sample results are unacceptable, if the holding times are exceeded, or as professional judgment may require.

The data assessor determines the usability of the data.

#### XVIII. Verification and Validation Methods

The QA specialist validates the data by following the guidelines in the MP-157's *SOPs for Quality Assurance*, January 2005.

If any of the external QA sample results do not meet the acceptance criteria stated in section IV, the samples are submitted for reanalysis. If the laboratory confirms the original result, the original data is accepted based on the laboratory demonstrating that sample preparation and instrumentation was performed properly on the initial analysis. If the original result cannot be confirmed, the laboratory must analyze a bracket of samples or the entire batch of samples an additional time for the parameter. The bracket of samples or the entire batch of samples that has been analyzed an additional time is then evaluated for the parameter to see if the results meet the acceptance criteria in section IV. Professional judgment is used to decide which set of data to accept and whether or not the data should be qualified if both sets of data demonstrate unacceptable external QA sample results.

# XIX. Reconciliation with User Requirements

Following QA SOP protocol, any qualified results are noted on the "Qualified Results" form. Qualified results are flagged with a footnote on the data table.