

11 QUALITY ASSURANCE

CHRISTOPHER GARDUÑO¹

¹ Quality Assurance Specialist, U.S. Bureau of Reclamation, Mid Pacific Region, Sacramento, California 95825. Email: cgarduno@usbr.gov

DATA QUALITY OBJECTIVES

The Data Collection and Reporting Team (DCRT) use the laboratory data from this project to support the determination as to whether selenium levels in the Grassland Bypass exceed regulatory compliance levels. Because individuals use the data generated by this program for regulatory compliance and baseline monitoring purposes, the data must be of the highest degree of validity. Sample collection of different environmental media and analytical methods performed by the laboratories must adhere to the guidelines established in the Quality Assurance Project Plan (QAPP).

QUALITY ASSURANCE PROJECT PLAN

On August 22, 2002, the U.S. Bureau of Reclamation (USBR) and the DCRT completed and released the QAPP for Phase II of the use and operation of the Grassland Bypass Project (GBP). USBR initiated a review and revision of the QAPP in 2005. The QAPP was reviewed and revised from 2005 through 2006; an updated version was issued November 20, 2006. The QAPP provides the protocols for documenting the Quality Assurance/Quality Control (QA/QC) activities carried out by the agencies responsible for the separate components of the Compliance Monitoring Program (CMP II). The QAPP describes the organization and membership of the project participants and defines the data quality objectives (DQOs) for CMP II. This plan describes the QA/QC activities associated with each agency's monitoring program, provides the QA/QC protocol of each laboratory participating in the program, provides acceptance criteria for data validation procedures, and describes corrective actions to be taken when the data fail to meet such criteria. The QAPP addresses both quantitative goals, including precision, accuracy, and completeness, and qualitative goals, including representativeness and comparability.

The QAPP follows the format described in the May 1994 Guidelines for Preparing Quality Assurance Project Plans, published by the State of California Department of Water Resources. The QAPP includes all the requirements identified in the August 1994 Draft Interim Final, U.S. EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations, EPA QA/R-5.

The QAPP will be updated and revised when a new Waste Discharge Requirement (WDR) is issued. The new Waste Discharge Requirement was tentatively scheduled to be enacted in October 2014. As of May 2015, the WDR has not been finalized.

Quality Assurance Oversight

QA/QC oversight for CMP II is the responsibility of a QA/QC oversight manager (QAQCOM) working for USBR. The QAQCOM oversees the implementation of commitments, guidelines, practices, and protocols outlined in the QAPP in compliance with the goals and objectives of the project. The QAQCOM uses guidelines, protocols, and criteria established in the QAPP to monitor and validate data collected by USBR personnel and to audit the data collection and validation processes used by the other participating agencies, including the U.S. Environmental Protection Agency (EPA), U.S. Fish and Wildlife Service (USFWS), U.S. Geological Survey (USGS), California Department of Fish and Game (CDFG), California Regional Water Quality Control Board (CRWQCB), and San Luis Delta-Mendota Water Authority (SLDMWA). When the QAQCOM identifies a noncompliance issue, the appropriate QA Officer is notified, and the responsible agency implements corrective actions to resolve the problem. The QAQCOM brings any unresolved issues between the QAQCOM and a participating agency's QA Officer to the attention of the DCRT for resolution. USBR QA personnel conduct audits of all participating analytical laboratories and review the data collection activities of the participating agencies for adherence to protocol. Additionally, USBR QA personnel conduct field audits on agencies participating in CMP II by evaluating sampling methods in the field.

Laboratory Performance and System Audits

During 2012, 2013 and 2014, USBR conducted performance and system audits on laboratories that perform work in support of the Grassland Bypass Project (**Table 1** and **Table 2**). The laboratories performed well and provided acceptable corrective actions for any deficiencies noted during the audits.

Laboratories are audited by USBR every three to four years. The audit consists of performing a documentation review, submitting performance evaluation (PE) samples to the laboratory, and conducting an on-site system audit of the laboratory.

Documentation Review

Prior to the audit, the laboratory's QA Manual and a copy of the last three years of approved round-robin performance study results are reviewed. Any deficiencies in the QA manual, performance study results, or corrective actions for unacceptable values on PE samples are addressed in the audit report.

Performance Evaluation Samples

Prior to the on-site audit, PE samples are submitted by USBR to the laboratories for a more direct evaluation of the laboratory's performance. The purpose of the PE samples is to evaluate the laboratory's ability to generate accurate data. The parameters selected for the PE samples correspond to those analyzed by the laboratories in support of the Grassland Bypass Project. Unacceptable PE sample results are addressed in the audit report. The results of the PE samples submitted by USBR to the laboratories are presented in **Table 2**.

On-Site System Audit

An on-site system audit is conducted to assess the laboratory's expertise in performing sample analyses, their capability for producing valid data, their ability to effectively support the data,

and the integrity of their QA/QC practices. During the on-site audit, the QA Officer, analysts, and other key laboratory personnel are questioned to determine their overall understanding of the methods and laboratory procedures. Documentation practices are also reviewed. In general, the auditors are ensuring that laboratory procedures follow the laboratory's QA manual guidelines and the analytical method protocols. Any deviations are addressed in the audit report.

Audit Report

The auditors send a report identifying deficiencies found during the audit to the laboratory with a time frame for the laboratory to respond to the findings and to implement and document the corrective actions.

Sample Collection System Audits

The sample collection system audits focus on the quality of the environmental samples collected and the ability of field personnel to adequately support and document the sample collection process. The purpose of the sample collection system audits is to identify and prevent problems in the field that could compromise sample integrity. On August 08-09, 2012, USBR conducted a field audit of Stacy Brown who collects samples in support of the Grassland Bypass Project. All aspects of the sample collection process were audited including equipment calibration and use, equipment decontamination, sample collection protocol, and documentation practices. Any deviations were addressed in the audit report.

Data Validation and Review Audit

The QAQCOM is responsible for ensuring the participating agencies properly validated their analytical data, identified problems, and contacted their respective laboratories to initiate corrective actions. The QAQCOM is also responsible for ensuring the participating agencies properly calibrated their instruments and documented their field work. To accomplish this, USBR reviewed and audited the laboratory and field data generated by the participating agencies as discussed below. Any deviations from the QAPP were provided in writing to the agencies.

Laboratory Data

USBR did not audit other agency's laboratory data in 2012, 2013, or 2014. Most analytical work is handled by USBR. If other agency data is available, USBR will assess the validity of the analytical results by comparing QC sample results to acceptance criteria identified in Table 10 of the QAPP. The guidelines in the QAPP address both internal and external QC sample results. The QAPP defines internal QC samples as those check samples incorporated by the laboratories performing the work and defines external QC samples as those check samples submitted to the laboratories by the participating agencies. During the data review, validation, and audit process, USBR will perform the following:

- verify that agencies are correctly incorporating external QC samples (i.e., spikes, references, duplicates, blanks) into batches of field samples
- bring laboratory QC summary report issues to the attention of each agency's QA Officer
- check data packages to ensure laboratories are documenting the details of their corrective actions
- check to ensure the laboratories are analyzing project samples within required holding times
- identify possible outliers (analytical results that are outside of the established range)

Field Data

In August 2012, USBR personnel conducted an audit on field data generated by Stacy Brown and in September 2014, USBR personnel conducted two audits on field data generated by Terry Falaschi with Panoche Water District and Larry Marques with San Luis Delta Mendota Water Authority.

These reviews were performed to ensure proper documentation was in place to support instrument calibration and sample collection procedures.

Deficiencies were noted during the Panoche Water District audit that required a change in sample collectors from Panoche Water District to USBR at the Site A autosamplers. A review of the data at Site A after two months showed no significant change in data quality.

Data Validation and Review Activities

The following routine data validation, review, and audit activities were performed in 2012, 2013, and 2014 to ensure data validity as stated in the QAPP:

TYPE OF DATA	REVIEW AND VALIDATION GROUP
Laboratory and field data from USBR (sediment and water)	USBR
Laboratory data from Block Environmental Services (water)	Block Environmental Services
Laboratory and field data from USFWS and CDFG(biota)	USFWS

QA ISSUES

In September 2012, California Laboratory Services (CLS) notified USBR that they would no longer be able to perform total organic carbon analysis for the Grassland Bypass Project sediment samples due to instrument malfunction. They also stated it would not be possible to continue this analysis in the future. Samples were picked up from CLS and delivered to TestAmerica, Inc. TestAmerica analyzed one round of samples; however their reporting limit was higher than required. In an effort to find a laboratory with a lower reporting limit, a performance evaluation sample for total organic carbon was submitted to Calscience Environmental Laboratories, Inc. Calscience successfully analyzed the PE samples, meeting USBR's acceptance limits. In addition, Calscience's reporting limit for total organic carbon was acceptable. Samples requiring total organic carbon analysis will be submitted to Calscience.

In 2012, South Dakota Agricultural Laboratories, the laboratory providing selenium analysis of water samples, changed facilities causing samples to become backlogged although no samples were held longer than their 6 month holding time. An on-site system audit was conducted at their new facility.

In July of 2013, Block Environmental Services (BES) closed their bioassay testing section. BES was the laboratory responsible for water toxicity analysis for the Grassland Bypass Program. Pacific Ecorisk, an environmental toxicology laboratory in Fairfield, CA, will perform future water toxicity testing. USBR plans to audit and submit performance evaluation samples to Pacific Ecorisk in 2014.

At the end of 2013, USBR performed an audit of the California Department of Fish and Wildlife Water Pollution Control Laboratory (CDFW-WPCL). A range of deficiencies were discovered, mostly affecting the legal defensibility of their data. It is important to note that CDFW-WPCL performed acceptably on the performance evaluation samples for selenium analysis on a variety of matrices (**Table 2**); selenium data analyzed by the CDFW-WPCL in support of the GBP should be regarded as accurate and valid. But due to a perceived lack of funding and staffing, it is USBR's assessment that CDFW-WPCL is incapable of producing highly defensible results on par with other contract laboratories from USBR's approved laboratory list. CDFW-WPCL will no longer analyze samples in support of the GBP.

A field audit of Terry Falaschi with the Panoche Water District in September of 2014 collecting samples at Site A, determined that insufficient sample collection techniques were being followed. Sample collection responsibility was transferred to USBR personnel for the Site A Autosampler.

At the end of 2014, USBR identified a possible site identification error being made by SLDMWA in collection of the Grassland Bypass Toxicity samples. The error was corrected, and a field audit was performed to ensure that proper sample collection techniques were being utilized. The same error occurred again in March of 2015. USBR facilitated coordination between the laboratory and SLDMWA to ensure the error would be eliminated.

UNCERTAINTY ASSOCIATED WITH ENVIRONMENTAL MEASUREMENTS

A degree of uncertainty accompanies all quantitative measurements. This is especially true for environmental data where measurement error may be introduced in the sample collection as well as in the laboratory preparation and analysis. Program participants and the public should understand that values presented in laboratory reports are not absolute, but rather represent values with associated precision and accuracy as defined in Table 10 of the QAPP. In addition, as the concentration of the parameter approaches the limit of detection for a particular analytical method, the level of uncertainty of the result increases significantly as shown in Figure 4 of the QAPP. The data user should understand the degree of uncertainty or the confidence limits associated with the data.

SUMMARY

In support of the Grassland Bypass project, USBR conducted audits of project laboratories and field personnel responsible for collecting samples. In addition, USBR validated, reviewed, and audited the data collected. USBR also performed comparison studies to find replacement laboratories for total organic carbon analysis in sediment samples and performed performance evaluation and system audits on South Dakota Agricultural Laboratories, Calscience Environmental Laboratories, Inc., and Block Environmental Services. In performing QA oversight, USBR seeks to ensure all participating agencies are operating in accordance with established QAPP protocols. Adherence to the QAPP ensures the reliability of the data collected and provides the necessary documentation to support the accuracy of the measurements.

Tables

Table 1. Laboratories Audited in 2012, 2013, and 2014

Table 2. Performance Evaluation Sample Results

TABLE 1. LABORATORIES AUDITED IN 2012, 2013, AND 2014

LABORATORY	AUDIT DATE(S)	ANALYSIS TYPE FOR GBP
South Dakota Ag. Laboratories Brookings, SD	October 23-24, 2012	Selenium in water
Block Environmental Pleasant Hill, CA	September 26-27, 2012	Water toxicity
Calscience Garden Grove, CA	February 14-15, 2012	Total Organic Carbon in sediment
WET Laboratory Sparks, NV	April 17-18, 2013	Metals and Nutrients in water
Cal. Dept. Fish & Wildlife - Pollution Control Laboratory Rancho Cordova, CA	September 19-20, 2013	Selenium in sediment and tissue
Pacific Ecorisk Fairfield, CA	January 13 - 14, 2014	Water toxicity
APPL Laboratory Clovis, CA	March 5-6, 2014	Metals and Nutrients in water
California Laboratory Services Rancho Cordova, CA	June 18 -19, 2014	Total Suspended Solids in water

TABLE 2. PERFORMANCE EVALUATION SAMPLE RESULTS

SOUTH DAKOTA AGRICULTURAL LABORATORIES						
DATE: 9/25/2012						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA925	Water	Selenium	1.73 µg/L	2.10 µg/L	82%	80% - 120%
QA926	Water	Selenium	9.53 µg/L	10.3 µg/L	93%	80% - 120%
QA927	Water	Selenium	98.8 µg/L	92 µg/L	107%	80% - 120%
QA928	Water	Selenium	1940 µg/L	1655 µg/L	117%	80% - 120%
QA929	Tissue	Selenium	1.42 mg/kg	1.63 mg/kg	87%	65% - 135%
QA930	Sludge	Selenium	ND	0.44 mg/kg	0%	65% - 135%
QA931	Vegetation	Selenium	0.0500 mg/kg	0.050 mg/kg	100%	65% - 135%
DATE: 10/18/2012						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA937	Soil	Selenium	0.568 mg/kg	0.78 mg/kg	73%	65% - 135%
QA938	Sludge	Selenium	8.78 mg/kg	16.0 mg/kg	55%	65% - 135%
QA938 - reanalysis	Sludge	Selenium	13.4 mg/kg	16.0 mg/kg	84%	65% - 135%
QA939	Soil	Selenium	1.22 mg/kg	1.52 mg/kg	80%	65% - 135%
BLOCK ENVIRONMENTAL SERVICES						
DATE: 9/07/2012						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA919	Water	Dissolved Oxygen	8.8 mg/L	8.62 mg/L	102%	80% - 120%
QA920	Water	Chlorine	1.22 mg/L	1.14 mg/L	107%	80% - 120%
QA921	Water	Hardness	366 mg/L	371 mg/L	99%	80% - 120%
QA922	Water	Alkalinity	82 mg/L	84.5 mg/L	97%	80% - 120%
QA923	Water	pH	8.1 s.u.	7.8 s.u.	104%	80% - 120%
QA923	Water	Conductivity	208 uS/cm	214 uS/cm	97%	80% - 120%
QA924	Water	Ammonia	3.0 mg/L	2.8 mg/L	104%	80% - 120%
CALSCIENCE ENVIRONMENTAL LABORATORIES, INC.						
DATE: 11/16/2012						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA940	Soil	TOC	3200 mg/kg	2520 mg/kg	127%	65%-135%

TABLE 2. PERFORMANCE EVALUATION SAMPLE RESULTS (CONT.)

WET LABORATORY DATE: 3/28/2013						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA953	Water	Total Alkalinity	51 mg/L	50.4 mg/L	101%	80-120%
QA954	Water	Aluminum	2.5 mg/L	2.6 mg/L	96%	80-120%
		Barium	0.14 mg/L	0.14 mg/L	100%	80-120%
		Beryllium	0.024 mg/L	0.026 mg/L	92%	80-120%
		Boron	0.12 mg/L	0.15 mg/L	-	+/- RL (0.2 mg/L)
		Chromium	0.048 mg/L	0.051 mg/L	94%	80-120%
		Iron	0.094 mg/L	0.100 mg/L	94%	80-120%
		Manganese	0.37 mg/L	0.37 mg/L	100%	80-120%
		Molybdenum	0.091 mg/L	0.100 mg/L	91%	80-120%
		Nickel	1.0 mg/L	1.0 mg/L	100%	80-120%
		Silver	0.026 mg/L	0.026 mg/L	100%	80-120%
		Sodium	3.3 mg/L	2.8 mg/L	118%	80-120%
		Zinc	0.53 mg/L	0.51 mg/L	104%	80-120%
		Antimony	0.048 mg/L	0.051 mg/L	94%	80-120%
		Arsenic	0.050 mg/L	0.051 mg/L	98%	80-120%
		Cadmium	0.024 mg/L	0.026 mg/L	92%	80-120%
		Copper	0.051 mg/L	0.051 mg/L	100%	80-120%
		Lead	0.025 mg/L	0.026 mg/L	96%	80-120%
		Thallium	0.025 mg/L	0.026 mg/L	96%	80-120%
Uranium	0.12 mg/L	0.13 mg/L	92%	80-120%		
QA956	Water	Ammonia	0.52 mg/L	0.55 mg/L	95%	80-120%
		Total Phosphorous	0.70 mg/L	0.70 mg/L	100%	80-120%
		Nitrate + Nitrite	0.60 mg/L	0.60 mg/L	100%	80-120%
CAL. DEPT. OF FISH & WILDLIFE - WATER POLLUTION CONTROL LABORATORY DATE: 9/10/2013						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA1015	Tissue (Mussel)	Selenium	1.86 mg/kg	1.8 mg/kg	-	+/- 2xRL
QA1016	Sediment	Selenium	0.606 mg/kg	0.78 mg/kg	78%	65-135%
QA1017	Biota (plankton)	Selenium	1.68 mg/kg	1.75 mg/kg	96%	65-135%
QA1018	Tissue (Fish)	Selenium	3.64 mg/kg	3.56 mg/kg	-	+/- 2xRL

TABLE 2. PERFORMANCE EVALUATION SAMPLE RESULTS (CONT.)

APPL LABORATORY DATE: 2/12/2014						
Sample ID	Matrix	Parameter	Result	True Value	Percent Recovery	Acceptance Limit
QA1037	Water	Boron	198 ug/L	199 ug/L	99%	80% - 120%
		Calcium	1950 ug/L	2000 ug/L	98%	
		Iron	198 ug/L	199 ug/L	99%	
		Magnesium	1980 ug/L	2000 ug/L	99%	
		Potassium	3660 ug/L	3990 ug/L	92%	
		Sodium	1880 ug/L	3990 ug/L	97%	
		Aluminum	595 ug/L	598 ug/L	99%	
		Antimony	10.9 ug/L	12 ug/L	91%	
		Arsenic	11.4 ug/L	12 ug/L	95%	
		Barium	31.7 ug/L	31.9 ug/L	99%	
		Beryllium	6.2 ug/L	6.0 ug/L	103%	
		Chromium	11.2 ug/L	12 ug/L	93%	
		Manganese	82.6 ug/L	87.7 ug/L	94%	
		Molybdenum	2.8 ug/L	3.0 ug/L	93%	
		Nickel	221 ug/L	239 ug/L	92%	
		Zinc	119 ug/L	120 ug/L	99%	
QA1038	Water	Bromide	1.7 mg/L	1.42 mg/L	120%	80% - 120%
		Chloride	22.6 mg/L	23.6 mg/L	96%	
		Fluoride	0.91 mg/L	0.96 mg/L	95%	
		Sulfate	13 mg/L	14.6 mg/L	89%	
		Alkalinity	48.8 mg/L	50.4 mg/L	97%	
		TDS	119 mg/L	128 mg/L	93%	
QA1075	Water	Mercury	4.3 ug/L	3.61 ug/L	119%	80% - 120%
CALIFORNIA LABORATORY SERVICES DATE: 5/16/2014						
QA1080	Water	TSS	47 mg/L	51.2 mg/L	92%	80% - 120%