SEPTEMBER 2012

Data Quality Evaluation Plan (DQEP)

Sacramento Stormwater Quality Partnership

Prepared by

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Overview

This Data Quality Evaluation Plan (DQEP) describes the quality assurance requirements for the Monitoring and Reporting Program (Order No. R5-2008-0142, NPDES No. CAS082597) plan (MRP) for the County of Sacramento and the Cities of Citrus Heights, Elk Grove, Folsom, Galt, rancho Cordova and Sacramento (Permittees). The Permittees' project managers are Delia McGrath with the City of Sacramento and Ken Ballard with the County of Sacaramento. The Permittees' monitoring program is managed by Larry Walker Associates (LWA). The monitoring program manager is Brian Laurenson of LWA, and is responsible for maintaining the approved QAPP. The project quality assurance (QA) manager for the project is Brian Laurenson of LWA.

Sample collection and analysis will be performed by the following agencies and subcontractors:

- CDM Smith, Sacramento, CA
- Sierra Environmental Sampling, Camino, CA
- Pacific EcoRisk, Fairfield, California
- Caltest Analytical Laboratory, Napa, California
- Frontier Global Sciences, Bothell, Washington
- Sacramento Regional County Sanitation District, Freeport, California
- PHYSIS Environmental Laboratories INC., Anaheim, California

Additional contractors will be selected as required to successfully implement the monitoring program described in the MRP and this QAPP. The contractors selected to perform sampling and laboratory analyses provide the precision, accuracy, detection and reporting limits, and meet the quality control criteria necessary to satisfy the data quality objectives described in this document.

This DQEP follows the procedures set forth in the Surface Water Ambient Monitoring Program (SWAMP). All agencies and subcontractors that participate in this program will abide by SWAMP's data collection and processing requirements.

PARAMETERS MONITORED

Parameters to be monitored are determined as specified in the Permittees MRP (Order No. R5-2008-0142, NPDES No. CAS082597). The required parameters and their MLs are in **Table 1**. Field measurements will be conducted and the following parameters will be measured:

- Dissolved Oxygen
- Temperature
- pH
- Electrical Conductivity (EC)

The following constituents will be monitored using laboratory methods:

- Physical and conventional parameters in water
- Nutrients in water
- Pathogen indicator organisms in water
- Trace metals in water
- Pesticides in water and sediment
- Semi- and non-volatile organics in water
- Water column and sediment toxicity

Table 1 MRP Constituents and Required MLs

CONSTITUENTS	MLs
Field/Lab Measurements	
Date	mm/dd/yyyy
Sample Time	hr:min (regular time)
Weather	degrees F
Water Temperature	degrees C
pH	0-14
Dissolved Oxygen	Sensitivity to 5 mg/L
Turbidity	0.1 NTU
Electrical Conductivity (EC)	µmhos/cm
Bacteria	
Fecal coliform	<20mpn/100ml
E. coli (fresh waters)	<20mpn/100ml
General	**mg/L**
Total Petroleum Hydrocarbons	5
Total Suspended Solids	2
Total Dissolved Solids	2
Total Organic Carbon	1
Dissolved Organic Carbon	1
Biochemical Oxygen Demand	2
Chemical Oxygen Demand	20-900
Total Kjeldahl Nitrogen	0.1
Alkalinity	2
Nitrate-Nitrite	0.1
Total Phosphorus	0.05
Total Hardness	2
Methylmercury	0.05 ng/L
Metals	**µg/L**
Copper, Dissolved	0.5
Copper, Total	0.5
Iron, Total	100
Lead, Dissolved	0.5
Lead, Total	0.5
Mercury, Total	0.5 ng/L
Zinc, Dissolved	1
Zinc, Total	1

Organophosphate Pesticides	ng/L
Chlorpyrifos	10
Diazinon	50
Malathion	50

Semi- and Non-Volatile Organics	ng/L
Perylene	5
Benz[a]anthracene	5
Chrysene	5
Fluorene	5
Benzo[b]fluoranthene	5
Benzo[e]pyrene	5
Benzo[k]fluoranthene	5
Benzo[a]pyrene	5
Indeno[1,2,3-c,d]pyrene	5
Dibenz[a,h]anthracene	5
Benzo[g,h,i]perylene	5
Pyrene	5
Acenaphthylene	5
Acenaphthene	5
Naphthalene	5
2-Methylnaphthalene	5
1-Methylnaphthalene	5
2,6-Dimethylnaphthalene	5
2,3,5-Trimethylnaphthalene	5
Fluoranthene	5
Phenanthrene	5
Anthracene	5
1-Methylphenanthrene	5

Pyrethroid Pesticides in Water [1,2]	Target Reporting Limit ppb (ng/L)[3]
Bifenthrin	2
Cyfluthrin	4
Cypermethrin	4
Deltamethrin/Tralomethrin	4
Esfenvalerate/Fenvalerate	2
Fenpropathrin	4
Lambda-cyhalothrin	2
Permethrin	5

Pyrethroid Pesticides in Sediment	Target Reporting Limit (ng/g)[3]
Bifenthrin	2
Cyfluthrin	4
Cypermethrin	4
Deltamethrin/Tralomethrin	4
Esfenvalerate/Fenvalerate	2
Fenpropathrin	4
Lambda-cyhalothrin	4
Permethrin	8

[1] Analysis for pyrethroid pesticides in water would only be required if monitoring results from the studies investigating the Pelagic Organism Decline in the Delta indicate these concentrations are present and of concern in Sacramento Permittee discharges

[2] Unfiltered, grab sample using glass jars

[3] Acceptable method should generally be able to meet the minimum level target, however, the method detection limit (MDL) reported should be equal to or less than the listed target

Data Evaluation Procedures

INITIAL SCREENING

The initial screening process occurs when the laboratory reports are received, following each monitoring event, and after the pre-season QA/QC sampling. It is important to check the reported data as soon as possible after the storm event to identify gross errors committed in the sampling, analysis, or reporting process. To ensure that the corrective measures are completed before the holding time has elapsed the laboratory must report results in a timely fashion and these results must be reviewed immediately upon receipt to allow for re-analysis of questionable (out-of-range) results. The initial screening includes the following checks:

√ Completeness. All laboratory analyses specified in the sampling plan should be requested on the chain of custody forms. All laboratory analyses should likewise be performed as specified in the chain of custody forms. QA/QC analyses should also be checked for completeness. A review of chain of custody forms is necessary to check that this documentation was properly filled out by the field crew and the laboratory check-in attendant.

√ Reporting Limits. Reporting limits should meet or be lower than the levels agreed upon prior to laboratory submission.

√ Reporting Errors. On occasion laboratories commit typographical errors or send incomplete results. Reported concentrations that appear out of range or inconsistent are indicators of laboratory reporting problems that should be investigated when detected. Examples of this would be a dissolved concentration greater than the corresponding total recoverable concentration or a constituent concentration orders of magnitude different than the same constituent for other events.

Irregularities found in the initial screening process should immediately be reported to the laboratory for clarification or correction. The initial screening process can identify and correct errors that would otherwise cause problems further along in the data evaluation process, or later if the data are used for higher-level analyses. Moreover, reanalysis of out-of-range values can increase confidence in the integrity of questionable data.

QUALITY CONTROL

Quality control (QC) is achieved by collecting and/or analyzing a series of duplicate, blank, spike, and spike duplicate samples to ensure that analytical results are within the specified QC objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results. The internal QC components of a sampling and analyses program will ensure that data of known quality are produced and documented. The internal QC samples, frequency, acceptance criteria, and corrective action must meet the minimum requirements presented in the following sections.

For basic water quality analyses, quality control samples prepared in the contract laboratory will typically consist of method blanks, laboratory control samples, laboratory duplicates, matrix spikes and duplicates, and surrogate compounds added to each sample (organic analysis). The minimum required samples and frequency for QC analyses are provided in Table 2.

Table 2. Quality Control Samples and Frequency

QC Sample Type	Minimum Frequency	
	Chemical Analyses	Microbiological Analyses
Field blank	One per event	One per event
Equipment blanks	Optional	Optional
Field duplicate or Lab Duplicate	One per event	One per event
Matrix spike (MS) and matrix spike duplicate (MSD)	One per event	N/A
Laboratory control spike (LCS), and duplicate (LCSD)	One per analytical batch	N/A
Laboratory blank	One per analytical batch	N/A

TECHNICAL DATA EVALUATION

The technical data evaluation procedure will follow the QA/QC process flow chart, **Figures 1** and **Figure 2**, and use the SWAMP measurement quality objectives in **Table 3**. The entire set of QA/QC data necessary for a complete technical data evaluation is provided by the laboratories. Certain elements are available by special request as they are not part of a laboratory's standard report deliverables. The technical QA/QC review process is established in the DQEP, in part, for consistency, however, the data evaluator must rely on professional judgment for consideration of "special cases" where data evaluation information apparently conflict. Such cases are documented in the narrative discussion included in the annual data report.

Detection limits for this project are reported by the laboratories as a method detection limit (MDL), minimum level (ML), and a reporting limit (RL). The MDL is performed according to the protocol established in 40 CFR, Part 136 and should be reported only when the laboratory is performing calibration curves at levels in the range of the reported MDL. The ML is the concentration of the lowest calibration curve used by the lab. The RL is a more general laboratory defined detection level term. It is calculated as a multiple of the MDL based on the laboratory's comfort level and historical performance. In other words, the RL is a limit that the principal analyst feels can be achieved on a routine basis for a specific type of matrix.

Table 3. SWAMP Quality Control Objectives and Desired Completeness

Quality Control	Measurement Quality Objective	Completeness
Conventionals		
Lab Blank	<RL for target analyte	95%
Field Blank	<RL for target analyte	95%
Lab Control Sample	80-120% recovery	95%
Matrix Spike	80-120% recovery	95%
Lab Control Sample + Matrix Spike Duplicate	80-120% recovery RPD<25% for duplicates	95%
Lab Duplicate + Field Duplicate	RPD<25% (n/a if native concentration of either sample <RL)	95%
Pathogens		
Lab Blank	No growth on filter	95%
Field Blank	Blanks<RL for target analyte	95%
Lab Duplicate + Field Duplicate	RPD<25% (n/a if native concentration of either sample <R; coliforms: within 95% confidence interval as defined by IDEXX Labs)	95%
Inorganics		
Lab Blank	<RL for target analyte	95%
Field Blank	Blanks<RL for target analyte	95%
LCS	75-125% recovery (70-130% for MMHg)	95%
Matrix Spike	75-125% recovery (70-130% for MMHg)	95%
Lab Control Sample + Matrix Spike Duplicate	75-125% recovery (70-130% for MMHg); RPD<25%	95%
Lab Duplicate + Field Duplicate	RPD<25% (n/a if native concentration of either sample <RL), unless otherwise specified by method	95%
Volatile Organic Compounds		
Lab Blank	<RL for target analyte	95%
Field Blank	<RL for target analyte	95%
LCS	70-130% recovery if certified; otherwise 50-150% recovery	95%
Matrix Spike	50-150% recovery, or based on 3x the standard deviation of laboratory's actual method recoveries	95%
Lab Control Sample + Matrix Spike Duplicate	RPD<25%	95%
Lab Duplicate + Field Duplicate	Per method	95%

Sediment		
Lab Blank	<RL or <30% of lowest sample	95%
Field Blank	<RL or <30% of lowest sample	95%
Lab Duplicate + Field Duplicate	RPD<25% (n/a if native concentration of either sample <RL)	95%
Lab Duplicate + Field Duplicate	Per method	95%

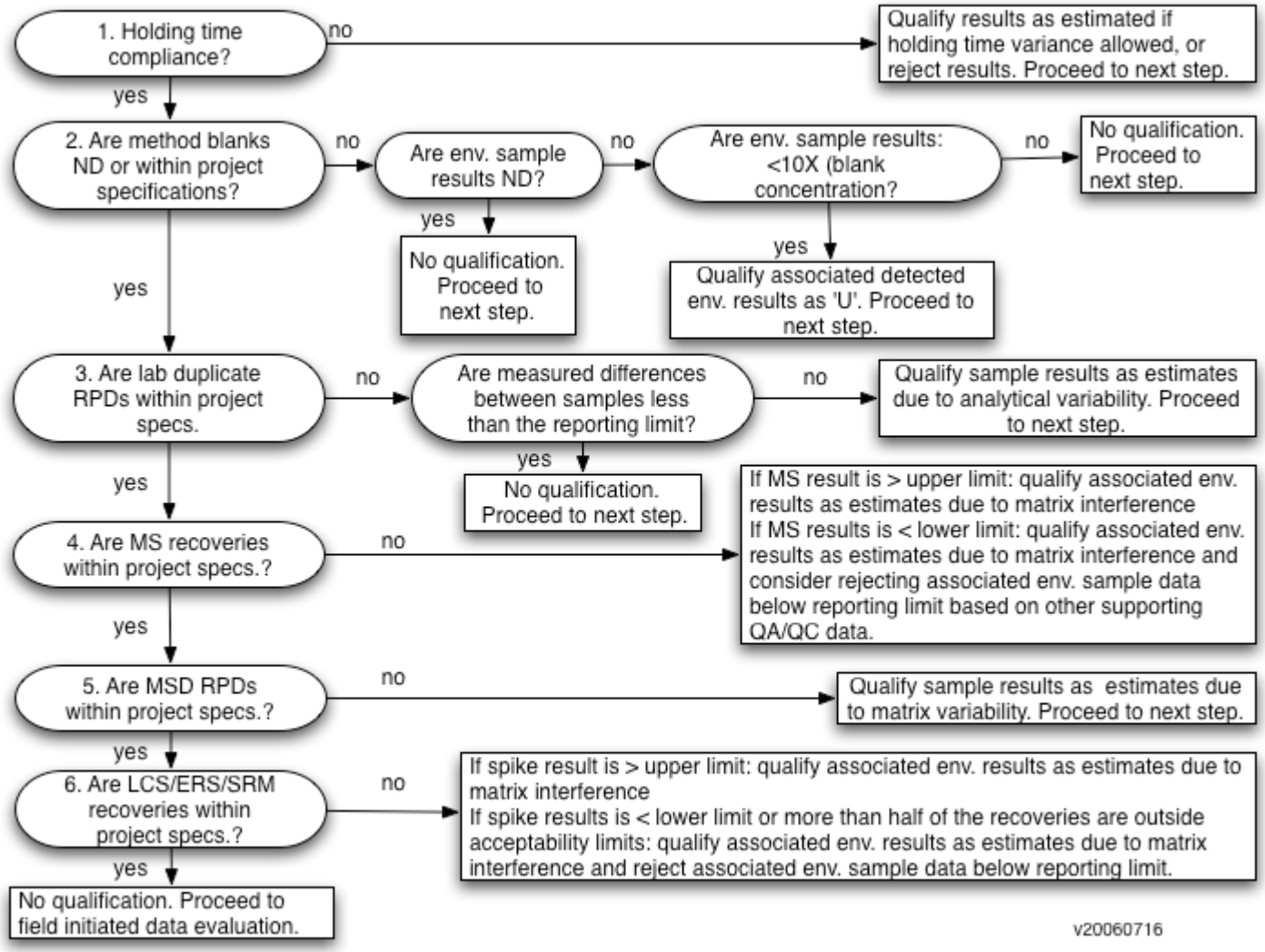

Figure 1. Technical Data Evaluation for Lab-Initiated QA/QC Samples

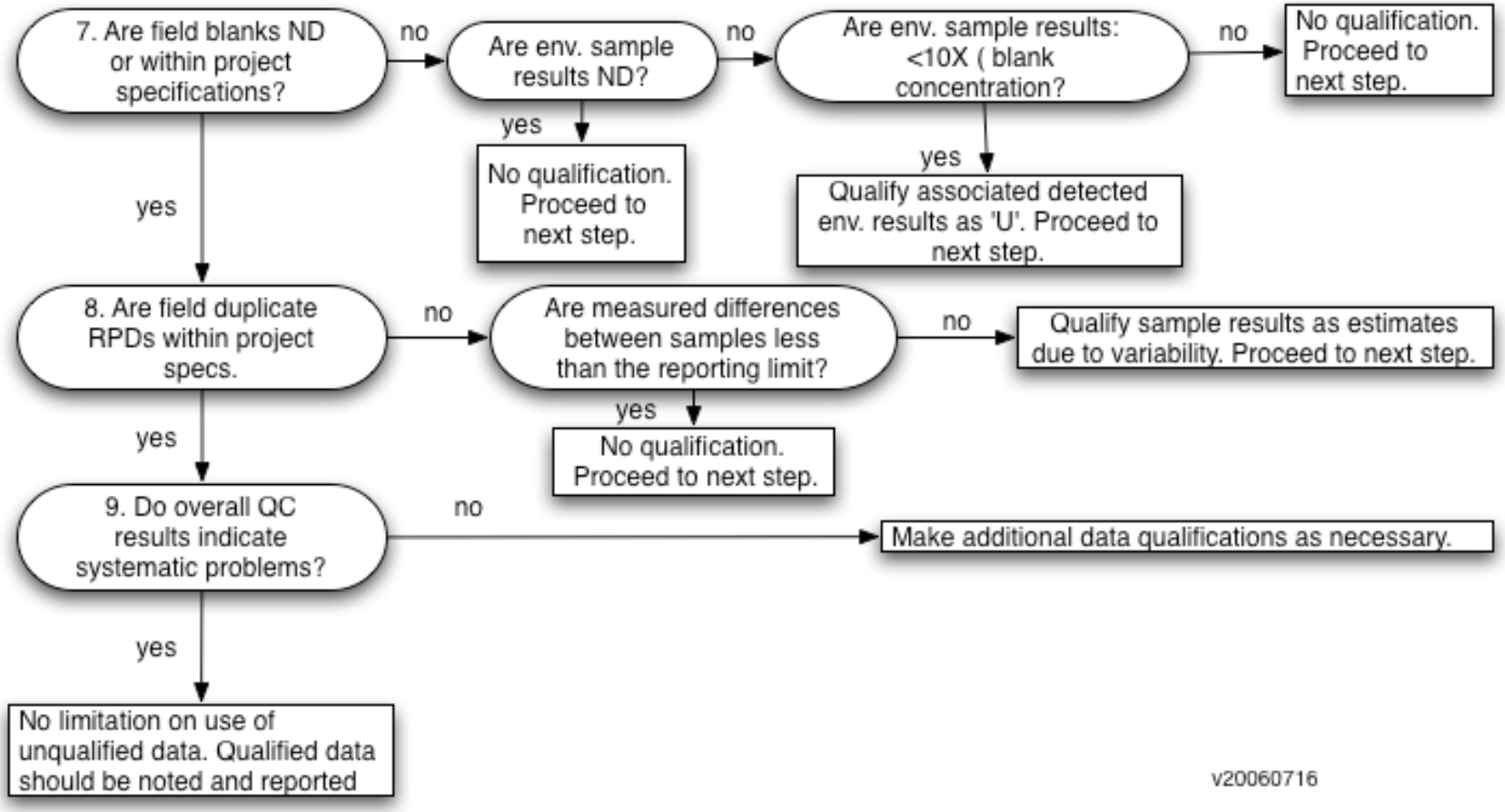

Figure 2. Technical Data Evaluation for Field-Initiated QA/QC Samples

CONTAMINATION CHECKS

Contamination of samples is assessed using method/reagent blanks (**Figure 1**, step #2) and field/equipment blanks (**Figure 2**, step #1). Blanks are prepared using reagent grade deionized water and tested using analytical procedures identical to those used for the environmental samples. The conditions under which the blanks are prepared follow, as closely as possible, the conditions in the field or laboratory, as appropriate for the type of blank.

A *method (or reagent) blank* is prepared and analyzed for every batch of samples (typically once per event for all three discharge characterization sites). A detected concentration or "hit" is an indication of contamination in the analytical process. Such hits have frequently occurred in this project in the EPA 625 and 8270 analyses for phthalates. Phthalates are commonly associated with plasticides, a ubiquitous set of compounds in modern life and the laboratory setting. Efforts by the laboratory to identify and remediate the sources of contamination have not been completely successful and values are sometimes reported at low, but detectable concentrations.

Equipment blanks, collected prior to the monitoring year, are used to identify contamination introduced by the sampling equipment (Teflon tubing, silicone tubing, and the overall sampling unit). Blank concentrations reported above the detection limit are assessed and acted upon using the guidelines listed in the bulleted items below. Concentrations reported above the detection limit for the common organic contaminants (phthalates, benzoic acid and certain phenols) do not need to be considered further if the reported concentration is less than 10x the reporting limit. This cutoff is not statistically derived, and is used to account for analytical variability around the low detection limits reported by the laboratory and the presence of these constituents as common laboratory contaminants. Selection of this cutoff is based on a review of historical laboratory performance. Blank concentrations reported above the detection limit for the mercury samples analyzed by Frontier Geosciences do not need to be considered further if the reported concentration is less than 10x the detection limit. Blank water provided by Frontier Geosciences contains up to approximately 1 ng/L of mercury (the detection limit is typically 0.1 ng/L). Equipment blanks for metals other than mercury should be investigated further if a concentration is reported above the detection limit.

Equipment blank hits should be investigated using the actions listed below.

* Request that the laboratory confirm the reported results against lab bench sheets or other original analytical instrument output. Any calculation or reporting errors should be corrected and reported by the laboratory in an amended laboratory report.
* If the previous step does not identify improperly reported results, the laboratory should be asked to identify any possible sources of contamination in the lab.
* If no laboratory contamination is identified, a note should be introduced into the text stating that the equipment blank results indicate that the sampling equipment may have introduced contamination. When practical, remedial measures should be taken to eliminate field contamination, including tubing cleaning and replacement or introduction of new, "cleaner" equipment.

Bottle rinse blanks are performed by the laboratory, prior to the monitoring year, and should be handled, for QA/QC purposes, in the same manner as equipment blanks.

A *field blank* is prepared in the field, using procedures that simulate the actual field sampling procedures. A hit reported in a field blank indicates that contamination has occurred at some point during the field sampling or analytical procedures. When a method blank is reported as "not detected" and the corresponding field blank is reported at concentrations greater than the detection limit, the contamination has likely been introduced in the field. Additionally, if the pre-season equipment blank result for the constituent in question was reported at a concentration above the detection limit, the equipment might have introduced the contamination. Field observations and input from lab personnel can be useful in confirming contamination source identification.

ACCURACY CHECKS

The laboratory performs internal accuracy checks by analyzing a "spike" of known concentration and comparing their results with the known concentration. Laboratories calculate percent recovery using the following formula:

$$R = 100\% * \left[\frac{(C_s - C)}{s} \right] \quad \{1\}$$

where, R = percent recovery

C_s = spiked sample concentration

C = sample concentration (for spiked matrices)

s = concentration equivalent of spike added

Matrix spike analysis (**Figure 1**, step #4) involves the introduction of a known spike in the original environmental sample "matrix" (sample solution), and is a measure of the accuracy of the recovery performance of the laboratory. To perform this analysis, the laboratory generally requires an additional volume of sample. Matrix interference can lead to recovery problems and raised detection limits. Reanalysis is the first corrective action once matrix interference problems are identified, but reanalysis is only possible when sufficient sample volume is available.

Laboratory control spike (LCS) and certified reference material (CRM) analyses (**Figure 1**, step #6), are batch checks for recovery of a known concentration of a standard solution, used to assess the accuracy of the entire recovery process from preparation of the sample to analysis. LCS samples are analyzed in the same manner as the environmental samples. SRMs are spiked samples prepared by a third party laboratory. SRMs are only necessary if chronic LCS recovery problems are noted, or if they are used by the lab in place of LCSs. Typically, laboratories perform SRMs on a quarterly basis or for constituents whose in-house preparation of spikes is difficult or expensive.

Surrogate matrix spikes, considered along with LCS spikes in **Figure1**, step #6, are used as a check on the extraction process for organic compounds. Surrogate recovery uses organic compounds other than the constituent being tested for, but with similar chemical characteristics. The surrogate used is easier to distinguish from other compounds and can be more accurately extracted and recovered.

Laboratory accuracy results and percent recovery calculations for each type of accuracy check should be delivered by the laboratory and screened by the data reviewer upon receipt.

PRECISION CHECKS

Precision is the measurement of the difference between samples (environmental and QA/QC) that are presupposed to be collected and analyzed in the same manner. The relative percent difference (RPD) is used to measure the difference between these replicate samples. The RPD is calculated from field duplicate, lab duplicate, and matrix spike duplicate data as follows:

{2}

$$RPD = 100\% * \left[\frac{(R_2 - R_1)}{((R_1 + R_2)/2)} \right]$$

where, RPD = relative percent difference

R_1 = replicate sample #1

R_2 = replicate sample #2

Laboratory duplicates (**Figure 1**, step #34) are samples split in the laboratory to measure the precision, as relative percent difference (RPD), of the laboratory analysis and the storm composite sample splitting.

Field duplicates (**Figure 2**, step #8) can be grabs or composite duplicates. Grab samples are sampled one directly after the other in the field and submitted to the laboratory as separate samples. Composite duplicates are prepared in the staging area (Sacramento County Regional Sanitation District Control Laboratory) along with the preparation of the environmental composite-based samples during splitting of the storm composite sample. Both composite-based and grab-based field duplicates provide a measure of the concentration variability introduced by field and laboratory procedures. Composite-based field duplicates also provide a measure of the precision of the storm composite sample splitting process. In combination with lab duplicates, field duplicates allow some separation of the sources of analytical variability (e.g. field and lab procedures).

Matrix spike duplicate (MSD) analysis (**Figure 1**, step #5) checks the precision of the MS recovery. Ideally, triple the normal sample volume is available for the analysis of a matrix spike and a matrix spike duplicate. As with field duplicates, the additional QA/QC volume is collected at the same time as the environmental sample. The QA/QC composite sample volume is poured from storm composite sample in the staging area, along with the environmental sample.

RPDs between duplicated samples are calculated by the data reviewer. This calculation should be done immediately following receipt of the laboratory results. Generally, laboratories will perform the reanalysis for the laboratory-initiated duplicates (laboratory and matrix spike duplicates) that are significantly out-of-range on the first analysis run. The results of the reanalysis should be presented in laboratory report form or in a case narrative prepared by the laboratory.

APPLICATION OF QUALIFICATIONS

Comparing the QA/QC data against the QA/QC acceptance criteria identifies out-of-range QA/QC samples. Translating the QA/QC results into qualifications of environmental data requires identifying the relationships of QA/QC data to the environmental sample results. These relationships are presented in **Table 7**. Beginning with the 1996/1997 monitoring year the qualification application process was completed using a "program" written in a database software system. This process was updated in 2010/2011 to reflect SWAMP data guidelines. This automated process uses the information in **Table 4**, the QA/QC database, and the constituent database, to produce the qualified constituent database which includes the qualification "codes" listed in the "SWAMP qualifier" column of **Table 4**.

Justification of these qualification application relationships is based on the design of the entire QA/QC program for the Sacramento Stormwater Monitoring Program. For instance, in an ideal world of unlimited resources all QA/QC checks would be run for every monitoring site and all constituents.

Table 4. Application of Qualifiers to Environmental Data Based on Out-of-Range QA/QC Checks

QA/QC Type	Out-of-Range Test Result	SWAMP Qualifier	Qualification Application	
			Sampling Location	Constituent
Pre-Season Blanks	Considered only as indicator of potential contamination problems that need to be corrected prior to the monitoring season (see discussion in text).	-	-	-
Method Blank	"Hit" on blank. Associated environmental sample is detected and is less than 10x the blank concentration.	IP	All	One to One
Field Blank	"Hit" on blank. Associated environmental sample is detected and is less than 10x (the blank concentration.	IP	All	One to One
Lab Duplicate	Relative percent difference (RPD) is greater than maximum allowable value.	IL	Site specific	One to One
Field Duplicate	Relative percent difference (RPD) is greater than maximum allowable value.	FDP	Site specific	One to One
Bacti Duplicate Samples	Considered as an indicator of potential out-of-range values.	-	-	-
Matrix Spike	Out of range value on laboratory QA/QC report. Recovery is outside of limits set forth in data quality evaluation plan.	GB	All	One to One
Matrix Spike Duplicate	Relative percent difference (RPD) is greater than maximum allowable value.	IL	Site specific	One to One
LCS & SRM	Out of range value on laboratory QA/QC report. Recovery is outside of limits set forth in data quality evaluation plan.	EUM	All	One to One
LCS Duplicate	Relative percent difference (RPD) is greater than maximum allowable value.	IL	All	One to One
Surrogate Spike	Out of range value on laboratory QA/QC report. Recovery is outside of limits set forth in data quality evaluation plan.	GN	-	-
Holding Time	The difference between the time/date of analysis and the time/date of sampling is greater than the EPA prescribed holding time (as included in QA/QC criteria tables).	H	Site specific	One to One

APPLICATION BY MONITORING SITE

Qualification is applied to all sites (batch application) when a QA/QC check done on a sample from a preselected site is outside of the acceptable criteria, and the QA/QC check involves blank or spike analysis. Data qualification is applied to the environmental data from only the site generating the QA/QC sample (one-to-one application) when the QA/QC check involves duplicate analysis. This procedure, as outlined in **Figure 1**, applies one-to-one (site-specific) data qualification for QA/QC checks that assess the sub-sampling (e.g. splitting off of samples for duplicate analysis) and applies a batch data qualification for all other QA/QC checks. The rationale for this is based on the presumption that the sub-sampling process is site dependent. The actual matrix type is similar, but the effectiveness of the sample splitting is dependent more on sample handling than on laboratory analytical performance. Spike and blank analyses represent laboratory analytical performance more generally, and should be applied to all sites as a batch. Field blank results from one monitoring site are applied to all three monitoring sites because field procedures are very similar at all three sites (same tubing type, same composite autosampler type, grab and composite samples are collected in a similar fashion, etc.).

APPLICATION BY ANALYSIS METHOD/CONSTITUENT

The constituent qualified for an out-of-range QA/QC check is the constituent that failed the check, with one exception. Concentrations of the compounds used for surrogate spikes are not reported (or of interest) in the environmental sample concentration report. Therefore, a one-to-one relationship with the environmental sample constituents is impossible. In this case, if a surrogate spike recovery is out-of-range, all constituents in that method are qualified.

Data qualification is limited to the constituents spiked in the case of organic analysis (EPA 8270/625, EPA 8321, EPA 8081, EPA 8141, MTBE, and ELISA) matrix and laboratory control sample spikes. Only a limited number of constituents from the method list are spiked into the sample for recovery. Without additional information, such as an obvious extraction problem for a sample, it is inappropriate to apply matrix or laboratory control sample spike qualification to constituents that are not actually spiked. In the case of matrix or laboratory control sample spikes, only the out-of-range constituents that were spiked are qualified.

DQEP Future Modifications

This document summarizes the process used to assess the quality of environmental concentration data reported for the Sacramento Stormwater Quality Partnership Discharge Monitoring Program and other studies within the Partnership that incorporate it. In fact, the process will change as laboratory analytical methods advance and the concentration data set grows. The QA/QC process should then be flexible enough to allow for improvements, but with enough structure to focus work effort and minimize ambiguity.