

2009/10 DATA QUALITY EVALUATION PLAN

This data quality evaluation plan (DQEP) describes the process by which data produced by the Sacramento Stormwater Monitoring Partnership are evaluated. Data quality evaluation is a multiple step process used to identify any errors, inconsistencies, or other problems potentially associated with monitoring program data. A data quality evaluation plan provides a reference point from which a program-consistent quality assurance/quality control (QA/QC) evaluation can be performed. The plan described here generally follows the program implemented and reported during the 1995-2010 monitoring period.

The overall data evaluation process includes three major components. The initial screening step occurs promptly when the data are received from the laboratory. This step is intended to identify sample handling and analysis problems that can still be corrected within analytical hold times. The technical data evaluation step includes a detailed assessment of reported QA/QC data including both externally (field-initiated) and internally (lab-initiated) generated data. This detailed, task-intensive step includes the evaluation components in **Figures 1** (lab-initiated data) and **Figure 2** (field-initiated data). The DQEP is a detailed description of this technical review and is based on EPA guidance documents¹ and requirements set forth by the monitoring program management team. The acceptance criteria for some of the QA/QC checks (allowable spike recovery, maximum relative percent difference, etc.) are program “constants” each monitoring year. The final element of the overall process is the data reporting step. All data collected throughout the monitoring year are reported in an annual data report and in the annually updated database.

Once the data quality evaluation has identified any chronic or significant QA/QC inconsistencies, a request to verify and explain the inconsistencies is sent to the laboratory. These issues are also reviewed and discussed in a narrative form in the QA/QC section of the annual data report.

¹ Environmental Protection Agency. October 2004. *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. (EPA-540-R-04-004)

Environmental Protection Agency. June 2001. *USEPA Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review* (EPA-540-R-00-006)

Environmental Protection Agency. April 1995. *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring* (EPA-821-B-95-002)

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.

TECHNICAL DATA EVALUATION

The QA/QC process flow chart, **Figures 1** and **Figure 2**, depicts the checks necessary to completely assess data quality. 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.

The criteria used for each of these components are listed in **Tables 1** through **6** at the end of this section, for each method and type of constituent analyzed. Each table contains a field for constituent name, reporting limit, acceptable spike range, maximum allowable relative percent difference (MAV RPD), and holding time.

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, **Appendix B** 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.

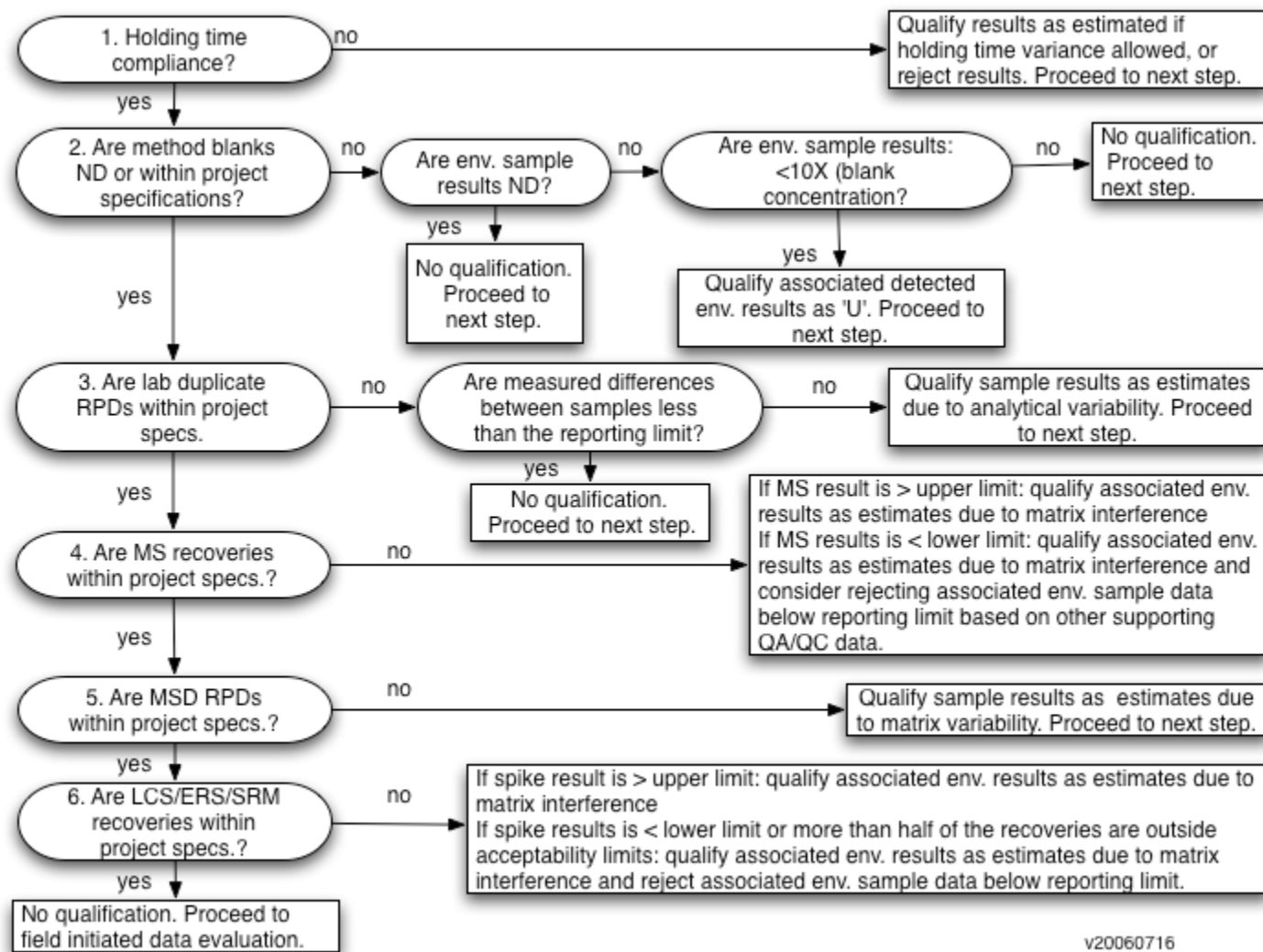


Figure 1. Technical Data Evaluation for Lab-Initiated QA/QC Samples

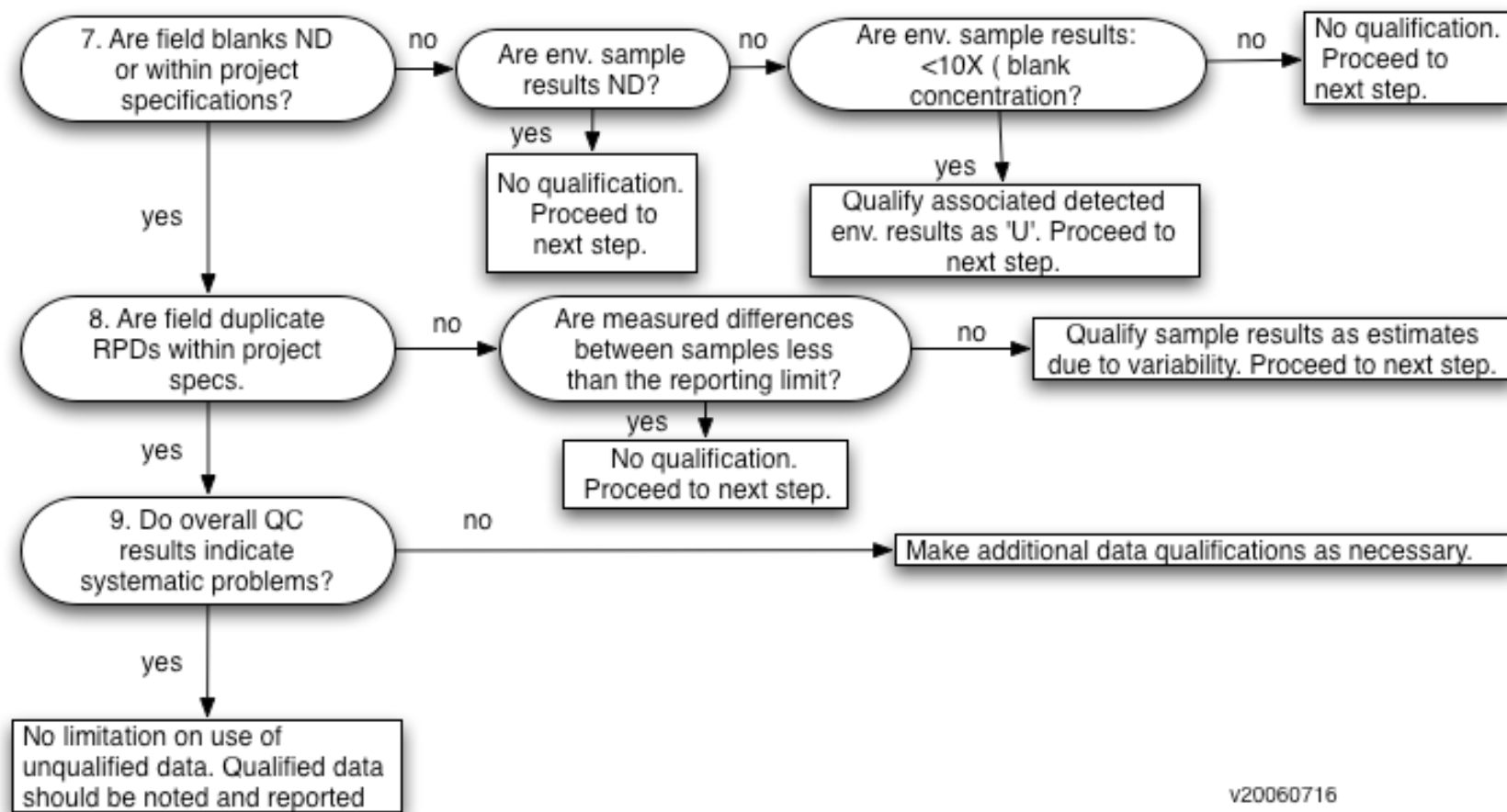


Figure 2. Technical Data Evaluation for Field-Initiated QA/QC Samples

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 **Figure 1**, 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:

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

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.

**Table 1. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Metals (µg/L)
(Total Recoverable & Dissolved)**

Constituent	Method	Reporting Limit	LCS Recovery		Matrix Spike Recovery		MAV RPD	Holding Time [1]
			LL	UL	LL	UL		
Arsenic	HG-AFS	1	75	125	75	125	25	6 months
Arsenc	ICP-MS	1	85	115	85	115	20	6 months
Cadmium	ICP-MS	0.25	85	115	85	115	20	6 months
Chromium	ICP-MS	0.5	75	125	75	125	25	6 months
Copper	ICP-MS	0.5	85	115	85	115	20	6 months
Copper	200.8	0.5	85	115	85	115	20	6 months
Iron	Color	100	75	125	75	125	25	6 months
Iron	200.8	100	85	115	85	115	20	6 months
Lead	ICP-MS	0.5	75	125	75	125	25	6 months
Lead	200.8	0.5	85	115	85	115	20	6 months
Nickel	ICP-MS	1	85	115	85	115	20	6 months
Zinc	ICP-MS	1	85	115	85	115	20	6 months
zinc	200.8	1	85	115	85	115	20	6 months
Aluminum	ICP-MS	100	75	125	75	125	25	6 months
Antimony	ICP-MS	0.5	75	125	75	125	25	6 months
Beryllium	ICP-MS	0.5	75	125	75	125	25	6 months
Hex. Chromium	SW846 7196A	5	75	125	75	125	25	24 hours
Selenium	ICP-MS	1	75	125	75	125	25	6 months
Silver	ICP-MS	0.25	85	115	85	115	20	6 months
Silver	200.8	0.25	85	115	85	115	20	6 months
Thallium	ICP-MS	1	75	125	75	125	25	6 months

[1] Dissolved samples should be filtered and preserved ASAP and within 2 days of sample collection.

Table 2. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Conventional, Grab Sampled & Miscellaneous Constituents

	Method	Units	Reporting Limit	LCS Recovery		Spike Recovery		MAV RPD	Holding Time
				LL	UL	LL	UL		
CONVENTIONAL AND MISCELLANEOUS CONSTITUENTS									
BOD ₅	EPA 405.1	mg/L	2	85	115	NA	NA	20	48 hours
Hardness as CaCO ₃	EPA 130.2/ SM 2340C	mg/L	2	90	110	80	120	10	6 months
Nitrate + Nitrite as N	EPA 353.2	mg/L	0.1	90	110	80	120	10	28 days
Phosphorus	EPA 365.3	mg/L	0.02	80	120	80	120	20	28 days
Phosphorus	EPA 365.2	Mg/L	0.02	90	110	90	110	20	
TDS	EPA 160.1	mg/L	2	80	120	NA	NA	20	7 days
TSS	EPA 160.2	mg/L	2	80	120	NA	NA	20	7 days
DOC	EPA 415.1	mg/L	1	80	120	80	120	20	28 days
TOC	EPA 415.1	mg/L	1	80	120	80	120	20	28 days
TKN	EPA 351.3	mg/L	0.1	90	110	90	110	20	28 days
Turbidity	EPA 180.1	NTU	1	90	110	NA	NA	20	
COD	HA 8000	mg/L	5	NA	NA	NA	NA	20	
COD	EPA 410.4	Mg/L	5	90	110	NA	NA	20	28 days
Cyanide	EPA 335.2	µg/L	5	80	120	80	120	20	14 days
Total Phenols	EPA 420.2	µg/L	100	80	120	80	120	20	28 days
Fluoride	EPA 300.0	mg/L	100	80	120	80	120	15	28 days
GRAB SAMPLED CONSTITUENTS									
Total Coliform	SM 9221B	MPN/100 mL	2	---	---	---	---	100 [1]	6 hours
Fecal Coliform	SM 9221E								
Escherichia coli	SM 9221F								
Methyl Mercury [1]	EPA 1631 CV-AFS	µg/L	0.00005	75	125	70	130	25	6 months
Mercury	CV-AFS	µg/L	0.0001	80	120	75	125	25	6 months
MTBE	EPA 8020A	mg/L	1	80	120	80	120	20	14 days

Note:

[1] Bacteriological measurements are highly variable in urban runoff and are often as low as 200 MPN/100 mL and as high as 20,000,000 MPN/100 mL. This variability is most likely due to the effect of macroscopic debris and a “clumping” effect. For this reason the listed RPD is used to determine only if a result requires additional investigation.

Table 3. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: PAHs (EPA 8270/625)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
1-Methylnaphthalene	0.005	55	105	30	7	40
1-Methylphenanthrene	0.005	70	130	30	7	40
2,3,5-Trimethylnaphthalene	0.005	70	121	30	7	40
2,6-Dimethylnaphthalene	0.005	70	114	30	7	40
2-Methylnaphthalene	0.005	50	124	30	7	40
Acenaphthene	0.005	70	116	30	7	40
Acenaphthylene	0.005	70	115	30	7	40
Anthracene	0.005	70	112	30	7	40
Benzo(a)anthracene	5	70	130	30	7	40
Benzo(a)pyrene	2	70	130	30	7	40
Benzo(b)fluoranthene	10	70	130	30	7	40
Benzo(e)pyrene	1	70	130	30	7	40
Benzo(ghi)perylene	5	70	130	30	7	40
Benzo(k)fluoranthene	2	70	130	30	7	40
Biphenyl	1	50	118	30	7	40
Chrysene	0.005	70	114	30	7	40
Dibenzo(a,h)anthracene	0.1	70	130	30	7	40
Fluoranthene	0.005	70	130	30	7	40
Fluorene	0.005	70	122	30	7	40
Indeno(1,2,3-cd)pyrene	0.005	70	130	30	7	40
Naphthalene	0.005	50	109	30	7	40
Perylene	0.005	70	130	30	7	40
Phenanthrene	0.005	70	127	30	7	40
Pyrene	0.005	70	130	30	7	40
Total Detectable PAHs	[a]	50	150	30	7	40

Notes:

[a] "Total detectable PAHs" refers to the summation of the reported results for all PAHs (i.e., it is a mathematical calculation derived from analytical results, and is not a direct analytical result).

Table 4. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Acid & Base/Neutral Extractables (EPA 8270/625)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
Acid Extractables						
2,4,6-Trichlorophenol	10	37	144	30	7	40
2,4-Dichlorophenol	1	39	135	30	7	40
2,4-Dimethylphenol	2	32	119	30	7	40
2,4-Dinitrophenol	5	0	191	30	7	40
2-Chlorophenol	2	23	134	30	7	40
2-Methyl-4,6-dinitrophenol	5	0	181	30	7	40
2-Nitrophenol	10	29	182	30	7	40
4-Chloro-3-methylphenol	1	22	147	30	7	40
4-Nitrophenol	5	0	132	30	7	40
Pentachlorophenol	2	14	176	30	7	40
Phenol	1	5	112	30	7	40
Base/Neutral Extractables						
1,2,4-Trichlorobenzene	1	44	142	30	7	40
1,2-Dichlorobenzene	1	32	129	30	7	40
1,3-Dichlorobenzene	1	0	172	30	7	40
1,4-Dichlorobenzene	1	20	124	30	7	40
2,4-Dinitrotoluene	5	60	140	30	7	40
2,6-Dinitrotoluene	5	50	158	30	7	40
2-Chloronaphthalene	10	60	118	30	7	40
3,3-Dichlorobenzidine	5				7	40
4-Bromophenyl phenyl ether	5				7	40
4-Chlorophenyl phenyl ether	5				7	40
Azobenzene	0.2	50	150	30	7	40
Bis(2-chloroethyl)ether	1	12	158	30	7	40
Bis(2-chloroisopropyl)ether	2	36	166	30	7	40
Bis(2-ethylhexyl)phthalate	1	8	158	30	7	40
Bis(2-chloroethoxy)methane	5				7	40
Butyl benzyl phthalate	10	0	152	30	7	40
Di-n-butyl phthalate	10	1	118	30	7	40
Diethyl phthalate	2	0	114	30	7	40
Dimethyl phthalate	2	0	112	30	7	40
Di-n-octyl phthalate	10	4	146	30	7	40
Hexachlorobenzene	1	0	152	30	7	40
Hexachlorobutadiene	1	24	116	30	7	40
Hexachlorocyclopentadiene	5	50	150	30	7	40
Hexachloroethane	1	40	113	30	7	40
Isophorone	1	21	196	30	7	40
Nitrobenzene	1	35	180	30	7	40
Benzidine	5				7	40
N-Nitroso-dimethyl amine	5				7	40
N-Nitroso-diphenyl amine	1				7	40
N-Nitroso-di-n-propyl amine	5	60	140		7	40

Table 5. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Carbamate Pesticides (EPA 8321)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
Aldicarb	0.4	44	132	25	7	40
Aminocarb	0.4	[a]	[a]	25	7	40
Barban	3.5	[a]	[a]	25	7	40
Benomyl (Carbendazim)	0.4	[a]	[a]	25	7	40
Carbaryl	0.07	68	112	25	7	40
Carbofuran	0.07	54	155	25	7	40
Chlorpropham	3.5	[a]	[a]	25	7	40
Methiocarb	0.4	63	123	25	7	40
Methomyl	0.07	34	125	25	7	40
Mexacarbate	0.8	[a]	[a]	25	7	40
Oryzalin	0.4	[a]	[a]	25	7	40
Oxamyl	0.4	[a]	[a]	25	7	40
Propham	3.5	[a]	[a]	25	7	40
Propoxur	0.4	[a]	[a]	25	7	40

[a] Constituent not used for spike. MAV RPD based on other constituents.

Table 6. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Organophosphate Pesticides (EPA 8141)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
Azinphosmethyl	1	36	189	25	7	40
Bolstar	0.1	55	119	25	7	40
Chlorpyrifos [b]	0.01	61	125	25	7	40
Coumaphos	0.2	60	124	25	7	40
Def	0.1	60	118	25	7	40
Demeton	0.2	21	85	25	7	40
Diazinon [c]	0.05	64	122	21	7	40
Dichlorvos	0.2	59	136	25	7	40
Dimethoate	0.1	68	149	25	7	40
Diphenamid	0.1	[a]	[a]	25	7	40
Disulfoton	0.1	29	90	22	7	40
EPN	0.1	57	133	25	7	40
EPTC	0.1	39	133	25	7	40
Ethion	0.1	59	118	20	7	40
Ethoprop	0.1	65	125	25	7	40
Ethyl Parathion	0.1	62	123	25	7	40
Fensulfothion	0.5	54	150	25	7	40
Fenthion	0.1	50	118	25	7	40
Malathion	0.05	64	125	25	7	40
Merphos	0.1	54	114	25	7	40
Methidathion	0.1	33	152	25	7	40
Methyl Parathion	0.1	53	137	25	7	40
Methyl Trithion	0.2	[a]	[a]	25	7	40
Mevinphos	0.7	61	141	25	7	40
Naled	0.5	10	67	25	7	40
Phorate	0.1	45	101	24	7	40
Phosalone	0.1	[a]	[a]	25	7	40
Phosmet	1	0	162	25	7	40
Prometon	0.1	50	143	25	7	40
Prowl	0.1	63	129	25	7	40
Ronnel	0.1	53	114	25	7	40
Simazine	0.5	49	114	25	7	40
Stirophos	0.1	65	146	25	7	40
Sulfotep	0.1	49	119	25	7	40
Tokuthion	0.1	61	123	25	7	40
Trichloronate	0.1	53	113	25	7	40
Trifluralin	0.1	44	117	25	7	40

[a] Constituent not used for spike. MAV RPD based on other constituents.

[b] Scan reported to MDL = 0.012 µg/L

[c] Scan reported to MDL = 0.018 µg/L

Table 7. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Organochlorine Pesticides & PCBs (EPA 8081)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
2,4,5-T	0.1	66	117	25	7	40
2,4,5-TP	0.2	65	113	25	7	40
2,4-D	0.02	69	111	25	7	40
2,4-DB	1	72	115	25	7	40
4,4'-DDD	0.05	53	122	25	7	40
4,4'-DDE	0.05	21	134	25	7	40
4,4'-DDT	0.01	18	145	25	7	40
Aldrin	0.005	11	138	25	7	40
BHC, alpha	0.01	33	111	25	7	40
BHC, beta	0.005	49	119	25	7	40
BHC, delta	0.005	12	97	25	7	40
BHC, gamma (Lindane)	0.02	40	114	25	7	40
Chlordane, alpha	0.1	44	152	25	7	40
Chlordane, gamma	0.1	51	115	25	7	40
Dalapon	1	20	140	25	7	40
Dicamba	0.1	59	119	25	7	40
Dichloroprop	0.5	66	108	25	7	40
Dieldrin	0.01	48	121	25	7	40
Dinoseb	0.25	23	117	25	7	40
Endosulfan I	0.01	50	131	25	7	40
Endosulfan II	0.02	55	128	25	7	40
Endosulfan sulfate	0.05	47	125	25	7	40
Endrin	0.01	24	143	25	7	40
Endrin aldehyde	0.01	44	132	25	7	40
Endrin ketone	0.01	47	142	25	7	40
Heptachlor	0.01	24	124	25	7	40
Heptachlor epoxide	0.01	58	109	25	7	40
MCPA	100	62	112	25	7	40
MCPP	100	60	118	25	7	40
Methoxychlor	0.01	30	163	25	7	40
Toxaphene	0.5	50	120	25	7	40
PCB 1016	0.5	50	114	15	7	40
PCB 1221	0.5	15	178	15	7	40
PCB 1232	0.5	10	215	15	7	40
PCB 1242	0.5	39	150	15	7	40
PCB 1248	0.5	38	158	15	7	40
PCB 1254	0.5	29	131	15	7	40
PCB 1260	0.5	8	127	15	7	40

Table 8. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Other Herbicides (EPA 8321 & EPA 547 - Glyphosate)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
Bromacil	0.4	54	145	25	7	40
Chloroxuron	0.4	0	9999	25	7	40
Diuron	0.4	72	124	25	7	40
Fenuron	0.4	48	117	25	7	40
Fluometuron	0.4	57	135	25	7	40
Glyphosate	4.6 [a]	70	130	25	7	40
Linuron	0.4	64	131	25	7	40
Monuron	0.4	55	129	25	7	40
Neburon	0.4	65	129	25	7	40
Propachlor	3.5	0	9999	25	7	40

Notes:

- Some MRP listed “Other Herbicide” constituents are analyzed using EPA 8081.

[a] EPA 547, listed RL is MDL

Table 9. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Triazines (EPA 8321 & EPA 547 - Glyphosate)

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
Ametryn	2	54	138	25	7	40
Atraton	2	49	141	25	7	40
Atrazine	2	48	142	25	7	40
Cyanazine	2	45	154	25	7	40
Prometon	2	50	143	25	7	40
Prometryn	2	45	143	25	7	40
Propazine	2	37	154	25	7	40
Simazine	2	49	114	25	7	40
Simetryn	2	44	144	25	7	40
Terbuthylazine	2	53	144	25	7	40
Terbutryn	2	52	135	25	7	40

Table 10. QA/QC Criteria for Laboratory Reporting of Analytical Concentrations: Pyrethroids

Constituent	Reporting Limit (µg/L)	LCS/Spike Recovery		RPD MAV	Holding Time	
		LL	UL		Extraction	Analysis
Bifenthrin	0.002	75	131	30	7	40
Cyfluthrin	0.004	76	128	30	7	40
Cypermethrin	0.004	72	132	30	7	40
Deltamethrin	0.004	47	142	30	7	40
Esfenvalerate	0.002	50	140	30	7	40

Fenvalerate	0.002	41	146	30	7	40
L-Cyhalothrin	0.002	72	130	30	7	40
Permethrin	0.005	74	137	30	7	40
Fenpropathrin	0.004				7	40

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 1996/97 monitoring year the qualification application process was completed using a “program” written in a database software system. This automated process uses the information in **Table 10**, the QA/QC database, and the constituent database, to produce the qualified constituent database which includes the qualification “codes” listed in the “qualification” column of **Table 10**. The qualifiers developed for the Sacramento Stormwater Monitoring Program are a more detailed subset of the EPA qualifiers also listed in **Table 10**.

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. To minimize laboratory analytical costs the checks are rotated from site to site from one monitored storm event to the next based on a schedule published in the *Sampling and Analysis Plan*² before the start of the storm monitoring season.

² Larry Walker Associates. November 2005, 2005-06 *Sacramento Stormwater NPDES Monitoring Sampling and Analysis Plan*. Prepared for the Sacramento Stormwater Permittees

Table 10. Application of Qualifiers to Environmental Data Based on Out-of-Range QA/QC Checks

QA/QC Type	Out-of-Range Test Result	Database Qualification	EPA Qualifier	Qualification Application	
				Sampling Location	Constituent
METHOD BLANK	"Hit" on blank. Associated environmental sample is detected and is less than 10x the blank concentration.	"U" Result considered not detected at reported environmental concentration.	U	All	One to One (when dissolved metal blanks are not available, use TR metal blanks)
FIELD BLANK	"Hit" on blank. Associated environmental sample is detected and is less than 10x the blank concentration.	"U" Result considered not detected at reported environmental concentration.	U	All	One to One (dissolved metals can use TR metal blanks)
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).	-	-	-	-
LCS & SRM	<u>Out of range value</u> on laboratory QA/QC report. Recovery is outside of limits set forth in data quality evaluation plan. This can be set by project managers or the lab acceptable ranges can be adopted.	"LB"-Low Bias or "HB"-High Bias "R" – Reject if <LL or more than half or recoveries are outside limits and environmental sample result is ND	J or R	All	One to One
MATRIX SPIKE	<u>Out of range value</u> on laboratory QA/QC report. Recovery is outside of limits set forth in data quality evaluation plan. This can be set by project managers or the lab acceptable ranges can be adopted.	"MI" - Matrix Interference (estimated value) "RMI" – Reject considered if <LL and environmental sample result is ND.	J or R	All	One to One

Table 8 (cont'd). Application of Qualifiers to Environmental Data Based on Out-of-Range QA/QC Checks

QA/QC Type	Out-of-Range Test Result	Qualification	EPA Qualifier	Qualification Application	
				Sampling Location	Constituent
MATRIX SPIKE OR LCS DUPLICATE	<u>Relative percent difference (RPD) is greater than maximum allowable value.</u> RPD is set forth in data quality evaluation plan. This can be set by project managers or the lab acceptable ranges can be adopted.	"NRS" - Not reproducible due to laboratory spike recovery variability.	J	Site specific (MSD) All (LCSD)	One to One
LAB DUPLICATE	<u>Relative percent difference (RPD) is greater than maximum allowable value.</u> RPD is set forth in data quality evaluation plan. This can be set by project managers or the lab acceptable ranges can be adopted.	"NR" - Not reproducible due to lab variability.	J	Site specific	One to One
FIELD DUPLICATE	<u>Relative percent difference (RPD) is greater than maximum allowable value.</u> RPD is set forth in data quality evaluation plan. This can be set by project managers or the lab acceptable ranges can be adopted.	"EST" - Estimated	J	Site specific	One to One
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).	"HT" - Holding time exceedance may have compromised constituent recovery.	J or UJ when non-detect	Site specific	One to One
BACTI DUPLICATE SAMPLES	Considered as an indicator of potential out-of-range values.	-	-	-	-

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.