SECTION 13
QA/QC DATA EVALUATION

All data reported by the analytical laboratory must be carefully reviewed to determine whether the project's data quality acceptability limits or objectives (DQOs) have been met. This section describes a process for evaluation of all laboratory data, including the results of all QA/QC sample analysis.

Before any results are reported by the laboratory, the deliverable requirements should be clearly communicated to the laboratory, as described in the "Laboratory Data Package Deliverables" discussion in ***Section 12***.

The current section discusses QA/QC data evaluation in the following two parts:

KEY TOPICS

- **Initial Data Quality Screening**
- **Data Quality Evaluation**

The initial data quality screening identifies problems with laboratory reporting while they may still be corrected. When the data reports are received, they should be immediately checked for conformity to chain of custody requests to ensure that all requested analyses have been reported. The data are then evaluated for conformity to holding time requirements, conformity to reporting limit requests, analytical precision, analytical accuracy, and possible contamination during sampling and analysis. The data evaluation results in rejection, qualification, and narrative discussion of data points or the data as a whole. Qualification of data, other than rejection, does not necessary exclude use of the data for all applications. It is the decision of the data user, based on specifics of the data application, whether or not to include qualified data points.

➢ INITIAL DATA QUALITY SCREENING

The initial screening process identifies and corrects, when possible, inadvertent documentation or process errors introduced by the field crew or the laboratory. The initial data quality control screening should be applied using the following three-step process:

1. *Verification check between sampling and analysis plan (SAP), chain of custody forms, and laboratory data reports*: Chain of custody records should be compared with field logbooks and laboratory data reports to verify the accuracy of all sample identification and to ensure that all samples submitted for analysis have a value reported for each parameter requested. Any deviation from the SAP that has not yet been documented in the field notes or project records should be recorded and corrected if possible.

Sample representativeness should also be assessed in this step. The minimum acceptable storm capture parameters (number of aliquots and percent storm capture) per amount of rainfall are specified in ***Section 10***. Samples not meeting these criteria are generally not analyzed; however, selected analyses can be run at the Caltrans task manager's discretion. If samples not meeting the minimum sample representativeness criteria are analyzed, the resulting data should be rejected ("R") or qualified as estimated ("J"), depending upon whether the analyses were approved by Caltrans. Grab samples should be taken according to the timing protocols specified in the SAP. Deviations from the protocols will result in the rejection of the data for these samples or qualification of the data as estimated. The decision to reject a sample based on sample representativeness should be made prior to the submission of the sample to the laboratory, to avoid unnecessary analytical costs.

2. *Check of laboratory data report completeness*: As discussed in ***Section 12***, the end product of the laboratory analysis is a data report that should include a number of QA/QC results along with the environmental results. QA/QC sample results reported by the lab should include both analyses requested by the field crew (field blanks, field duplicates, lab duplicates and MS/MSD analysis), as well as internal laboratory QA/QC results (method blanks and laboratory control samples).

There are often differences among laboratories in terms of style and format of reporting. Therefore, it is prudent to request in advance that the laboratory conform to the style and format approved by Caltrans as shown in ***Section 14***. The Caltrans data reviewer should verify that the laboratory data package includes the following items:

- A narrative which outlines any problems, corrections, anomalies, and conclusions.
- Sample identification numbers.
- Sample extraction and analysis dates.
- Reporting limits for all analyses reported.
- Results of method blanks.
- Results of matrix spike and matrix spike duplicate analyses, including calculation of percent recovered and relative percent differences.
- Results of laboratory control sample analyses.
- Results of external reference standard analyses.
- Surrogate spike and blank spike analysis results for organic constituents.
- A summary of acceptable QA/QC criteria (RPD, spike recovery) used by the laboratory.

Items missing from this list should be requested from the laboratory.

3. *Check for typographical errors and apparent incongruities*: The laboratory reports should be reviewed to identify results that are outside the range of normally observed values. Any type of suspect result or apparent typographical error should be verified with the laboratory. An example of a unique value would be if a dissolved iron concentration has been reported lower than 500 µg/L for every storm event monitored at one location and then a value of 2500 µg/L is reported in a later event. This reported concentration of 2500 µg/L should be verified with the laboratory for correctness.

   Besides apparent out-of-range values, the indicators of potential laboratory reporting problems include:

   - Significant lack of agreement between analytical results reported for laboratory duplicates or field duplicates.
   - Consistent reporting of dissolved metals results higher than total or total recoverable metals.
   - Unusual numbers of detected values reported for blank sample analyses.
   - Inconsistency in sample identification/labeling.

   If the laboratory confirms a problem with the reported concentration, the corrected or recalculated result should be issued in an amended report, or if necessary the sample should be re-analyzed. If laboratory results are changed or other corrections are made by the laboratory, an amended laboratory report should be issued to update the project records.

➢ DATA QUALITY EVALUATION

The data quality evaluation process is structured to provide systematic checks to ensure that the reported data accurately represent the concentrations of constituents actually present in stormwater. Data evaluation can often identify sources of contamination in the sampling and analytical processes, as well as detect deficiencies in the laboratory analyses or errors in data reporting. Data quality evaluation allows monitoring data to be used in the proper context with the appropriate level of confidence.

QA/QC parameters that should be reviewed are classified into the following categories:

- ➢ Reporting limits
- ➢ Holding times
- ➢ Contamination check results (method, field, trip, and equipment blanks)
- ➢ Precision analysis results (laboratory, field, and matrix spike duplicates)
- ➢ Accuracy analysis results (matrix spikes, surrogate spikes, laboratory control samples, and external reference standards)

Each of these QA/QC parameters should be compared to data quality acceptability criteria, also known as the project's data quality objectives (DQOs). The key steps that should be adhered to in the analysis of each of these QA/QC parameters are:

1. Compile a complete set of the QA/QC results for the parameter being analyzed.
2. Compare the laboratory QA/QC results to accepted criteria (DQOs).
3. Compile any out-of-range values and report them to the laboratory for verification.
4. Prepare a report that tabulates the success rate for each QA/QC parameter analyzed.

This process should be applied to each of the QA/QC parameters as discussed below.

Reporting Limits

Stormwater quality monitoring program DQOs should contain a list of acceptable reporting limits that the lab is contractually obligated to adhere to, except in special cases of insufficient sample volume or matrix interference problems. The reporting limits used should ensure a high probability of detection. Table 12-1 provides recommended reporting limits for selected parameters.

Holding Times

Holding time represents the elapsed time between sample collection time and sample analysis time. Calculate the elapsed time between the sampling time and start of analysis, and compare this to the required holding time. For composite samples that are collected within 24-hours or less, the time of the final sample aliquot is considered the "sample collection time" for determining sample holding time. For analytes with critical holding times (≤48 hours), composite samples lasting longer than 24-hours require multiple bottle composite samples. Each of these composite samples should represent less than 24 hours of monitored flow, and subsamples from the composites should have been poured off and analyzed by the laboratory for those constituents with critical holding times (***see Section 12***). It is important to review sample holding times to ensure that analyses occurred within the time period that is generally accepted to maintain stable parameter concentrations. Table 12-1 contains the holding times for selected parameters. If holding times are exceeded, inaccurate concentrations or false negative results may be reported. Samples that exceed their holding time prior to analysis are qualified as "estimated", or may be rejected depending on the circumstances.

Contamination

Blank samples are used to identify the presence and potential source of sample contamination and are typically one of four types:

1. ***Method blanks*** are prepared and analyzed by the laboratory to identify laboratory contamination.

2. ***Field blanks*** are prepared by the field crew during sampling events and submitted to the laboratory to identify contamination occurring during the collection or the transport of environmental samples.
3. ***Equipment blanks*** are prepared by the field crew or laboratory prior to the monitoring season and used to identify contamination coming from sampling equipment (tubing, pumps, bailers, etc.).
4. ***Trip blanks*** are prepared by the laboratory, carried in the field, and then submitted to the laboratory to identify contamination in the transport and handling of volatile organics samples.
5. ***Filter blanks*** are prepared by field crew or lab technicians performing the sample filtration. Blank water is filtered in the same manner and at the same time as other environmental samples. Filter blanks are used to identify contamination from the filter or filtering process.

If no contamination is present, all blanks should be reported as "not detected" or "non-detect" (e.g., constituent concentrations should not be detected above the reporting limit). Blanks reporting detected concentrations ("hits") should be noted in the written QA/QC data summary prepared by the data reviewer. In the case that the laboratory reports hits on method blanks, a detailed review of raw laboratory data and procedures should be requested from the laboratory to identify any data reporting errors or contamination sources. When other types of blanks are reported above the reporting limit, a similar review should be requested along with a complete review of field procedures and sample handling. Often times it will also be necessary to refer to historical equipment blank results, corresponding method blank results, and field notes to identify contamination sources. This is a corrective and documentative step that should be done as soon as the hits are reported.

If the blank concentration exceeds the laboratory reporting limit, values reported for each associated environmental sample must be evaluated according to USEPA guidelines for data evaluations of organics and metals (USEPA, 1991; USEPA, 1995) as indicated in Table 13-1.

Table 13-1. USEPA Guidelines for Data Evaluation

Step	*Environmental Sample*	*Phthalates and other common contaminants*	*Other Organics*	*Metals*
1.	Sample > 10X blank concentration	No action	No action	No action
2.	Sample < 10X blank concentration	Report associated environmental results as "non-detect" at the reported environmental concentration.	No action	Results considered an "upper limit" of the true concentration (note contamination in data quality evaluation narrative).
3.	Sample < 5X blank concentration	Report associated environmental results as "non-detect" at the reported environmental concentration.	Report associated environmental results as "non-detect" at the reported environmental concentration.	Report associated environmental results as "non-detect" at the reported environmental concentration.

Specifically, if the concentration in the environmental sample is less than five times the concentration in the associated blank, the environmental sample result is considered, for reporting purposes, "not-detected" *at the environmental sample result concentration* (phthalate and other common contaminant results are considered non-detect if the environmental sample result is less than ten times the blank concentration). The laboratory reports are not altered in any way. The qualifications resulting from the data evaluation are made to the evaluator's data set for reporting and analysis purposes to account for the apparent contamination problem. For example, if dissolved copper is reported by the laboratory at 4 µg/L and an associated blank concentration for dissolved copper is reported at 1 µg/L, data qualification would be necessary. In the data reporting field of the database (see ***Section 14***), the dissolved copper result would be reported as 4 µg/L***)***, the numerical qualifier would be reported as "<", the reporting limit would be left as reported by the laboratory, and the value qualifier would be reported as "U" ("not detected above the reported environmental concentration").

When reported environmental concentrations are greater than five times (ten times for phthalates) the reported blank "hit" concentration, the environmental result is reported unqualified at the laboratory-reported concentration. For example, if dissolved copper is reported at 11 µg/L and an associated blank concentration for dissolved copper is reported at 1 µg/L, the dissolved copper result would still be reported as 11 µg/L.

Precision

Duplicate samples provide a measure of the data precision (reproducibility) attributable to sampling and analytical procedures. Precision can be calculated as the relative percent difference (RPD) in the following manner:

$$RPD_i = \frac{2 * |O_i - D_i|}{(O_i + D_i)} * 100\%$$

where:

RPD_i = Relative percent difference for compound i

O_i = Value of compound i in original sample

D_i = Value of compound i in duplicate sample

The resultant RPDs should be compared to the criteria specified in the project's DQOs. The DQO criteria shown in Table 13-2 below are based on the analytical method specifications and laboratory-supplied values. Project-specific DQOs should be developed with consideration to the analytical laboratory, the analytical method specifications, and the project objective. Table 13-2 should be used as a reference point as the least stringent set of DQO criteria for Caltrans monitoring projects.

Laboratory and Field Duplicates

Laboratory duplicates are samples that are split by the laboratory. Each half of the split sample is then analyzed and reported by the laboratory. A pair of field duplicates is two samples taken at the same time, in the same manner into two unique containers. Subsampling duplicates are two unique, ostensibly identical, samples taken from one composite bottle (see ***Section 10***). Laboratory duplicate results provide information regarding the variability inherent in the analytical process, and the reproducibility of analytical results. Field duplicate analysis measures both field and laboratory precision, therefore, it is expected that field duplicate results would exhibit greater variability than lab duplicate results. Subsampling duplicates are used as a substitute for field duplicates in some situations and are also an indicator of the variability introduced by the splitting process.

The RPDs resulting from analysis of both laboratory and field duplicates should be reviewed during data evaluation. Deviations from the specified limits, and the effect on reported data, should be noted and commented upon by the data reviewer. Laboratories typically have their own set of maximum allowable RPDs for laboratory duplicates based on their analytical history. In most cases these values are more stringent than those listed in Table 13-2. Note that the laboratory will only apply these maximum allowable RPDs to laboratory duplicates. In most cases field duplicates are submitted "blind" (with pseudonyms) to the laboratory.

Environmental samples associated with laboratory duplicate results greater than the maximum allowable RPD (when the numerical difference is greater than the reporting limit) are qualified as "J" (estimated). When the numerical difference is less than the RL, no qualification is necessary. Field duplicate RPDs are compared against the maximum

allowable RPDs used for laboratory duplicates to identify any pattern of problems with reproducibility of results. Any significant pattern of RPD exceedances for field duplicates should be noted in the data report narrative.

Corrective action should be taken to address field or laboratory procedures that are introducing the imprecision of results. The data reviewer can apply "J" (estimated) qualifiers to any data points if there is clear evidence of a field or laboratory bias issue that is not related to contamination. (Qualification based on contamination is assessed with blank samples.)

Laboratories should provide justification for any laboratory duplicate samples with RPDs greater than the maximum allowable value. In some cases, the laboratory will track and document such exceedances, however; in most cases it is the job of the data reviewer to locate these out-of-range RPDs. When asked to justify excessive RPD values for field duplicates, laboratories most often will cite sample splitting problems in the field. Irregularities should be included in the data reviewer's summary, and the laboratory's response should be retained to document laboratory performance, and to track potential chronic problems with laboratory analysis and reporting.

Accuracy

Accuracy is defined as the degree of agreement of a measurement to an accepted reference or true value. Accuracy is measured as the percent recovery (%R) of spike compound(s). Percent recovery of spikes is calculated in the following manner:

$$\%R = 100\% * [(C_s - C) / S]$$

where:

- %R = percent recovery
- C_s = spiked sample concentration
- C = sample concentration for spiked matrices
- S = concentration equivalent of spike added

Accuracy (%R) criteria for spike recoveries should be compared with the limits specified in the project DQOs. A list of typical acceptable recoveries is shown in Table 13-2. As in the case of maximum allowable RPDs, laboratories develop acceptable criteria for an allowable range of recovery percentages that may differ from the values listed in Table 13-2.

Percent recoveries should be reviewed during data evaluation, and deviations from the specified limits should be noted in the data reviewer's summary. Justification for out of range recoveries should be provided by the laboratory along with the laboratory reports, or in response to the data reviewer's summary.

Laboratory Matrix Spike and Matrix Spike Duplicate Samples

Evaluation of analytical accuracy and precision in environmental sample matrices is obtained through the analysis of laboratory matrix spike (MS) and matrix spike duplicate

(MSD) samples. A matrix spike is an environmental sample that is spiked with a known amount of the constituent being analyzed. A percent recovery can be calculated from the results of the spike analysis. A MSD is a duplicate of this analysis that is performed as a check on matrix recovery precision. MS and MSD results are used together to calculate RPD as with the duplicate samples. When MS/MSD results (%R and RPD) are outside the project specifications, as listed in Table 13-2, the associated environmental samples are qualified as "estimates due to matrix interference". Surrogate standards are added to all environmental and QC samples tested by gas chromatograph (GC) or gas chromatography-mass spectrometer (GC-MS). Surrogates are non-target compounds that are analytically similar to the analytes of interest. The surrogate compounds are spiked into the sample prior to the extraction or analysis. Surrogate recoveries will be evaluated with respect to the laboratory acceptance criteria to provide information on the extraction efficiency of every sample.

External Reference Standards

External reference standards (ERS) are artificial certified standards prepared by an external agency and added to a batch of samples. ERS's are not required for every batch of samples, and are often only run quarterly by laboratories. Some laboratories use ERS's in place of laboratory control spikes with every batch of samples. ERS results are assessed the same as laboratory control spikes for qualification purposes (see below). The external reference standards are evaluated in terms of accuracy, expressed as the percent recovery (comparison of the laboratory results with the certified concentrations). The laboratory should report all out-of-range values along with the environmental sample results. ERS values are qualified as biased high" when the ERS recovery exceeds the acceptable recovery range and "biased low" when the ERS recovery is smaller than the recovery range.

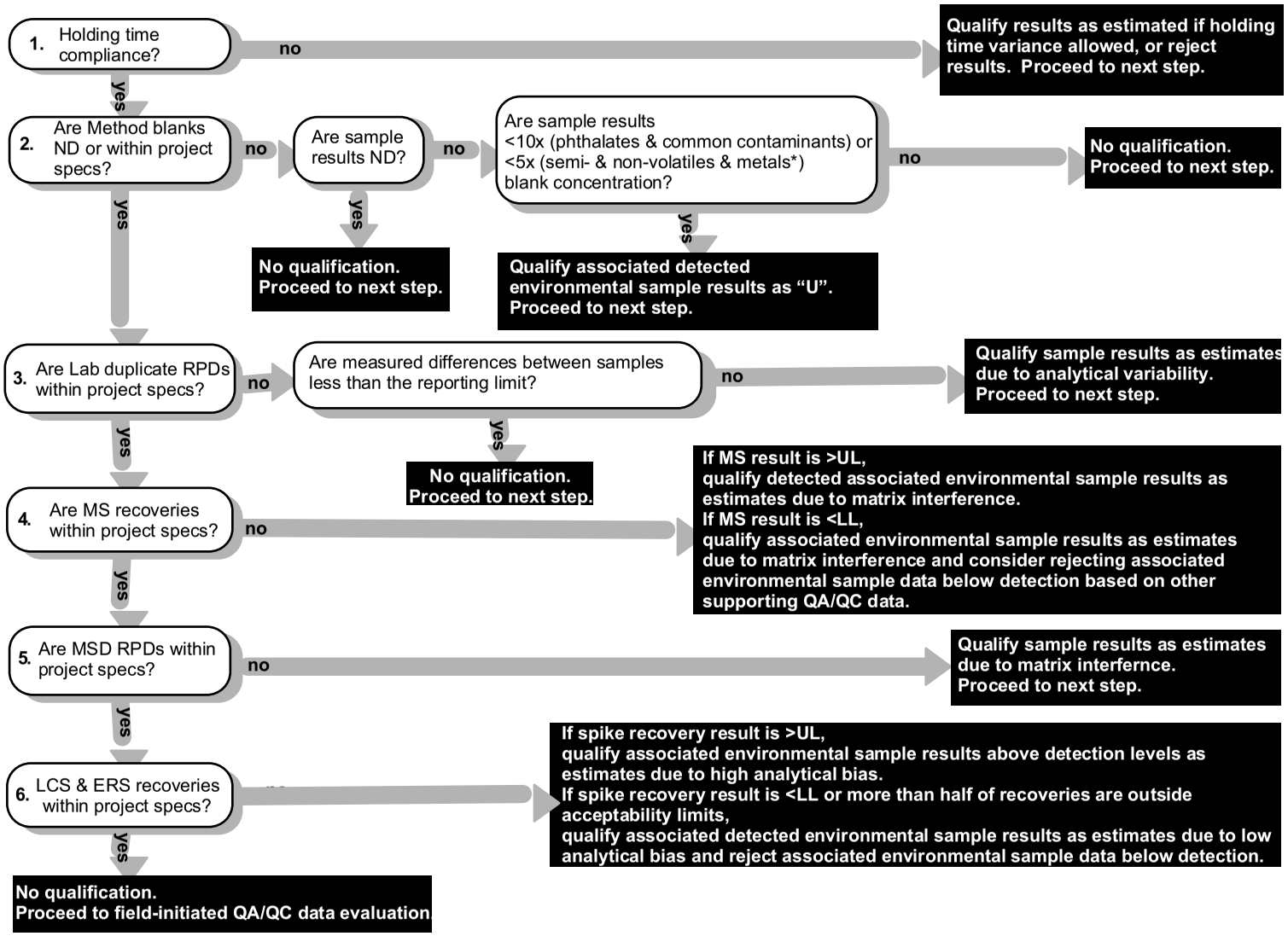
Laboratory Control Samples

LCS analysis is another batch check of recovery of a known standard solution that is used to assess the accuracy of the entire recovery process. LCSs are much like ERS's except that a certified standard is not necessarily used with LCSs, and the sample is prepared internally by the laboratory so the cost associated with preparing a LCS sample is much lower than the cost of ERS preparation. LCSs are reviewed for percent recovery within control limits provided by the laboratory. LCS out-of-range values are treated in the same manner as ERS out-of-range values. Because LCS and ERS analysis both check the entire recovery process, any irregularity in these results supersedes other accuracy-related qualification. Data are rejected due to low LCS recoveries when the associated environmental result is below the reporting limit.

A flow chart of the data evaluation process, presented on the following page as Figures 13-1 (lab-initiated QA/QC samples) and 13-2 (field initiated QA/QC), can be used as a general guideline for data evaluation. Boxes shaded black in Figures 13-1 and 13-2 designate final results of the QA/QC evaluation.

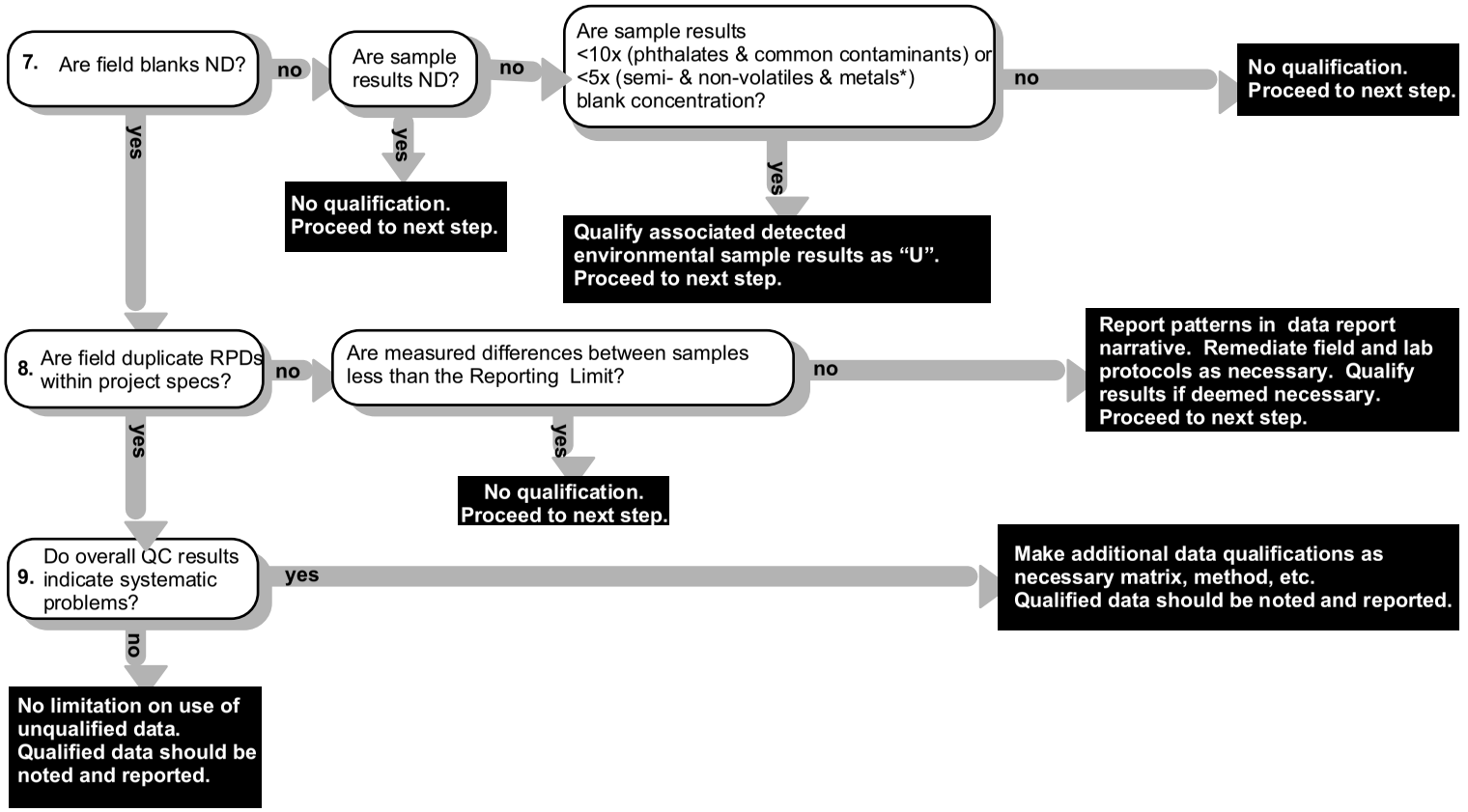
Table 13-2. Typical Control Limits for Precision and Accuracy for Analytical Constituents

Analyte	*EPA Method Number or Standard Method*	*Maximum Allowable RPD*	*Recovery Upper Limit*	*Recovery Lower Limit*
Conventionals				
BOD	405.1; SM 5210B	20%	80%	120%
COD	410.1; 410.4; SM 5220C; SM 5220D	20%	80%	120%
Hardness	130.2; 130.1; SM 2340B	20%	80%	120%
pH	150.1	20%	NA	NA
TOC/DOC	415.1	15%	85%	115%
TDS	160.1	20%	80%	120%
TSS	160.2	20%	80%	120%
Turbidity	180.1	20%	NA	NA
Nutrients				
NH3-N	350.2; 350.3	20%	80%	120%
NO3-N	300.0	20%	80%	120%
NO2-N	300.0	20%	80%	120%
NO3/NO2-N	353.2	20%	80%	120%
P	365.2	20%	80%	120%
Ortho-P	365.2; 365.3	20%	80%	120%
TKN	351.3	20%	80%	120%
Metals				
Ag	272.2; 200.8	20%	75%	125%
Al	200.9; 200.8	20%	75%	125%
Cd	213.2; 200.8	20%	75%	125%
Cr	218.2; 200.8	20%	75%	125%
Cu	220.2; 200.8	20%	75%	125%
Ni	249.2; 200.8	20%	75%	125%
Pb	239.2; 200.8	20%	75%	125%
Zn	289.2; 200.8	20%	75%	125%
As	206.3; 200.8	20%	75%	125%
Fe	200.9; SM 3500-Fe B	20%	75%	125%
Se	200.9; 270.3; 200.8	20%	75%	125%
Hg	1631	21%	79%	121%
Total Petroleum Hydrocarbons				
TPH (gasoline)	8015b	21%	45%	129%
TPH (diesel)		21%	45%	129%
TPH (motor oil)		21%	45%	129%
Oil & Grease	1664	18%	79%	114%
Pesticides and Herbicides				
Glyphosate	547	30%	70%	130%
OP Pesticides (esp. diazinon and chlorpyrifos)	8141; ELISA	25%	see method for constituent specific	
OC Pesticides	8081	25%		
Chlorinated Herbicides	8150; 8151	25%		
Carbamate Pesticides	8321	25%		
Miscellaneous Organic Constituents				
Base/Neutrals and Acids	625; 8270	30% to 50% (analyte dependent)	see method for constituent specific	
PAHs	8310			
Purgeables	624; 8260	20%		
Purgeable Halocarbons	601	30%	see method, Table 2	
Purgeable Aromatics	602	20%	see method for constituent specific	
Miscellaneous Constituents				
Cyanide	335.2	20%	75	125
Bacteriological				
Fecal Coliform	SM 9221E	-	-	-
Total Coliform	SM 9221B	-	-	-



*Environmental results between 5x and 10x the blank concentration are qualified as "an upper limit on the true concentration" and the data user should be cautioned.

Figure 13-1. Technical Data Evaluation for Lab-Initiated QA/QC Samples



*Environmental results between 5x and 10x the blank concentration are qualified as "an upper limit on the true concentration" and the data user should be cautioned.

Figure 13-2. Technical Data Evaluation for Field-Initiated QA/QC Samples