SECTION 11
QUALITY ASSURANCE/ QUALITY CONTROL (QA/QC)

The quality of analytical data is dependent on the ways in which samples are collected, handled and analyzed. To ensure that data meet project data quality acceptability limits or objectives (DQOs,) a Data Quality Evaluation Plan (DQEP), which includes QA/QC review procedures for both field and laboratory measures, should be included in the sampling and analysis plan (SAP) prior to implementing the stormwater monitoring program (see ***Sections 6*** and ***13***).

The three major categories of QA/QC checks are accuracy, precision, and contamination. Accuracy is assessed by measuring percent recovery of a known quantity of analyte (e.g. via a matrix spike or laboratory control spike) and comparing it against prescribed acceptability limits. Precision is assessed by calculating the relative difference between analytical results for duplicate samples and comparing the relative percent difference (RPD) against prescribed acceptability limits. Contamination is assessed using blank samples to identify sources of contamination.

Improved control of data quality is achieved by incorporating the following elements of a typical stormwater monitoring QA/QC program into the sample collection effort:

KEY TOPICS

- **Duplicate Samples**
- **Blank Samples**
- **Matrix Spikes/Matrix Spike Duplicate Samples**
- **QC Sample Schedule**

Each of these types of samples and the relevant responsibilities of monitoring field personnel are described below, followed by a discussion of recommended minimum frequencies for the various types of QC samples.

The results of the field QC samples are then used to evaluate the quality of the reported data (data evaluation is discussed in ***Section 13***).

➤ DUPLICATE SAMPLES

Analytical precision is a measure of the reproducibility of data and is assessed by analyzing two samples that are intended to be identical. Any significant differences between the samples indicate an unaccounted-for factor or a source of bias. There are typically two types of duplicate samples that require special sampling considerations: field duplicates and laboratory duplicates.

Once duplicate samples have been analyzed by the laboratory, the results are evaluated by calculating the RPD between the two sets of results for each constituent. This serves as a measure of the reproducibility, or "precision" of the sample collection and analysis. Calculation of RPD is discussed further in the QA/QC data evaluation section of this document (***Section 13***).

Field Duplicates

Field duplicates are used to assess variability attributable to collection, handling, shipment, storage and/or laboratory handling and analysis. The procedures for collecting field duplicate samples will depend upon the sampling method being used, and should simulate the actual sampling protocols. For example, if collecting grab samples, duplicate samples may be collected by filling two grab sample bottles at the same location either by holding both bottles in the middle of the water flow to be sampled. If bailers or other intermediate devices are used in grab sampling, all field protocols should be exactly duplicated with duplicate sets of equipment, to collect the duplicate sample simultaneously with or immediately following collection of the environmental sample. When collecting duplicate composite samples, the following procedures should be used:

- ✓ Collect enough sample for both environmental sample analysis and field duplicate analysis (amount will be specified by the analytical laboratory; see ***Section 12***) in one or more composite bottles.

- ✓ Splitting the composite samples is discussed in detail in ***Section 10***. Field duplicate samples should be split in the same manner as the environmental samples, and are taken in random order along with the environmental samples to assess the variability introduced during splitting and laboratory analysis.

Field duplicate samples should be submitted to the laboratory "blind" (i.e. not identified as a QC sample, but labeled with a different site identification than the regular sample).

Laboratory Duplicates

Laboratory duplicates (also called laboratory splits) are used to assess the precision of the analytical method and laboratory handling. For the laboratory duplicate analysis one sample will be split by the analytical laboratory into two portions and each analyzed.

When collecting samples to be analyzed for laboratory duplicates, typically double the normal sample volume is required. This requires filling a larger size sample bottle, or filling two normal size sample bottles, labeling one with the site name and the second with the site name plus "laboratory duplicate". Laboratory duplicate samples are collected, handled, and delivered to the analytical laboratory in the same manner as environmental samples.

➤ BLANK SAMPLES

Blanks are prepared to identify potential sample contamination occurring during field collection, handling, shipment, storage, and laboratory handling and analysis. Blanks are evaluated during various stages of the sampling and analytical process to determine the level of contamination, if any, introduced at each step. The collection and uses of the types of blank samples associated with typical stormwater monitoring field procedures are described below. "Blank water" refers to contaminant-free water provided by the laboratory performing the environmental and blank analyses. Typically, this water is the laboratory's reagent water that is used in the analytical or cleaning processes, as well as for their method blanks. The analytical laboratory should be consulted when selecting theselecting the source of the blank water.

Method Blanks

For each batch of samples, method blanks (also called control blanks) should be run by the laboratory to determine the level of contamination associated with laboratory reagents and glassware. Method blanks are prepared by the laboratory by analysis of laboratory reagent or blank water. Results of the method blank analysis should be reported with the sample results. At a minimum, the laboratory should report method blanks at a frequency of 5% (one method blank with each batch of up to 20 samples).

Trip Blanks

Trip blanks are used to determine whether sample contamination is introduced during sample transportation and delivery. Trip blanks are prepared at the analytical laboratory, by filling the sample bottle with deionized water and securing the bottle lid. Trip blanks are transported to and from the sampling site with normal sample bottles. Trip blanks are analyzed like normal samples.

Equipment Blanks

Before using sampling equipment for sample collection activities, blanks should be collected to verify that the equipment is not a source of sample contamination. Stormwater monitoring programs normally include equipment blanks to check sample tubing and strainers, and sample bottles, especially composite bottles. Equipment blanks are usually prepared at the beginning of the monitoring season, and are collected by passing blank water through clean equipment. Equipment blanks are collected using clean techniques, prior to on-site sample collection, before the equipment has been contaminated by environmental sample water or other sources. Equipment blank collection normally requires a two-person field crew. After collection, equipment blanks are capped, placed in an ice chest with fresh ice or frozen refreezable ice packets, and delivered to the analytical laboratory in the same manner as environmental samples.

If using manual collection methods (i.e. bailers), fill the bailer or other collection device with blank water in the field and pour the water into clean sample bottle(s). If an automatic sampler is being used, place the cleaned strainer on the end of the clean tubing, and install the tubing through the sampler. Do not install the tubing and strainer into the pipe or channel, but leave the tubing coiled up beside the sampler. Prevent the strainer or exposed tubing end from contacting anything other than the inside of a new plastic bag during this process. Then insert the strainer into the bottle containing the blank water and pump forward through the clean suction tubing, into clean composite bottle(s) and/or grab sample containers.

Equipment blanks are analyzed using the same methods as those used for normal sample analysis and submitted to the analytical laboratory "blind" (disguised as a regular environmental sample by labeling with a pseudonym).

To account for any contamination introduced by sampling containers, blanks must be collected for composite bottles and laboratory bottles used for sample storage for metals analysis. A sampling container blank is prepared by filling a clean container with blank water and measuring the concentrations of selected constituents (typically metals and trace organics for composite bottles; metals analysis only for metals storage bottles). These blanks may be submitted “blind” to the laboratory by field personnel or prepared internally by the laboratory. Collection of sample container blanks may not be required if certified pre-cleaned bottles are used. The manufacturer can provide certification forms that document the concentration to which the bottles are “contaminant-free”; these concentrations should be equivalent to or less than the program reporting limits. If the certification level is above the program reporting limits, 2% of the bottles in a “lot” or “batch” should be blanked at the program detection limits with a minimum frequency of one bottle per batch. A batch is a group of samples that are cleaned at the same time and in the same manner; or, if decontaminated bottles are sent directly from the manufacturer, the batch would be the lot designated by the manufacturer in their testing of the bottles.

Field Blanks

Field blanks are necessary to evaluate whether contamination is introduced during field sampling activities. Field blanks are prepared by the field crew, under normal sample collection conditions, at some time during the collection of normal stormwater samples. Field blanks are prepared by filling a large carboy or other appropriate container with blank water, transporting the container to the field and processing the water through the same sampling procedures to be used for sample collection. If grab sample collection is required, grab sample field blanks should be prepared by pouring a sample directly from the bottle of blank water, into the grab sample containers. Grab sample blanking should imitate environmental sampling as closely as possible by using grab poles, clean intermediate containers, and other clean equipment in the same manner. For composite field blanks, pour the blank water directly into clean composite bottles at the sampling site, label as an environmental sample, and submit “blind” to the laboratory. The filled

blank sample bottles should be sealed and sent to the laboratory to be analyzed for the required constituents.

In addition to the minimum field blank collection requirements indicated in Table 11-1, it is important that field blanks are collected at a frequency no less than once per field sampling team per sampling season. Additional blanks should be collected when there is a change in sampling personnel, equipment, or procedures. It may also be desirable to prepare field blanks prior to any actual sampling events as an advance check of the overall sampling procedures.

In addition, if any filtration of samples is performed in the field, some field blanks should be filtered before being transported back to the laboratory. Filtered blanks help to ensure that contamination is not attributable to filtration equipment, such as hoses, housing, filters, and technique, whereas unfiltered blanks check for contamination from containers and preservatives.

➤ MATRIX SPIKES/MATRIX SPIKE DUPLICATE SAMPLES

Matrix spike (MS) and matrix spike duplicate (MSD) analyses are used to assess the accuracy (MS) and precision (MSD) of the analytical methods in the sample matrix. The analytical laboratory prepares matrix spike samples by splitting off three aliquots of the environmental sample and adding known amounts of target analytes to two of the three environmental sample aliquots. The results of the analysis of the unspiked environmental sample are compared to the MS analysis results, and "percent recovery" of each spike is calculated to determine the accuracy of the analysis. The results of the MS analyses are compared to calculate RPD as an additional measure of analytical precision.

When collecting samples to be specified for MS/MSD analysis, typically triple the normal sample volume is required. This will require filling a larger size sample bottle, or filling three normal size sample bottles, labeling one with the site name and the other two with the site name plus "MS/MSD". MS/MSD samples are collected, handled, and delivered to the analytical laboratory in the same manner as environmental samples. Analytical laboratories often will perform MS/MSD analyses at no charge on a specified sample when a certain minimum number of samples are submitted for analysis.

➤ QC SAMPLE SCHEDULE

Table 11-1 summarizes the minimum frequencies of QC sample collection/preparation for Caltrans stormwater monitoring programs based on EPA Guidance (EPA, 1995). These frequencies are minima and may be increased depending on the nature and objectives of the study being undertaken or if QA/QC problems (e.g. contamination) are discovered. An adequate QC sample schedule should be included in the analytical budget for the monitoring program.

Table 11-1. Recommended QC Sample Frequency

QA/QC Sample Type	*Minimum Sampling Frequency*	*Constituent Class*
Field Duplicate	Once every ten samples collected at a given site or once per sampling station per project, whichever is more frequent.	All
Lab Duplicate	Once every ten samples collected at a given site or once per sampling station per project, whichever is more frequent.	All
Equipment Blank	Equipment blanks should be collected prior to each sampling season for each piece of equipment to be used for sample collection (bailers, pumps, and carboys).	Metals and other common contaminants. [1]
Bottle Blanks	Composite and sample bottles should be blanked every batch [2]; or manufacturer or laboratory-certified to concentrations below the reporting limits used for the sampling program.	Metals and other common contaminants. [1]
Field Blank	Once every ten samples collected at a given site or once per sampling station per project, whichever is more frequent.	Metals and other common contaminants. [1]
Matrix Spike/Matrix Spike Duplicate	Once every ten samples collected at a given site or once per sampling station per project, whichever is more frequent.	Metals and other common contaminants. [1]

Notes:
[1] Other common contaminants include phthalate compounds, pesticides, organic carbon (TOC and DOC), nitrate as N, and PAHs. Analyze blanks for these constituents as appropriate for constituents monitored in specific projects.
[2] A batch is defined as the group of bottles that have been cleaned at the same time, in the same manner; or, if decontaminated bottles are sent directly from the manufacturer, the batch would be the lot designated by the manufacturer in their testing of the bottles.

A QC sample schedule should be developed, included in the SAP, and followed closely by field personnel. The project QC sample schedule should meet the minimum QC sample frequency criteria over the term of the project. In some cases, QC samples at one site may be applied to an analogous situation at another site. For example, if the same equipment and protocols are used at Site A and Site B, contamination checks at one site can be applied at both sites; if the matrices at Site Y and Site Z are the same (i.e., both urban runoff from similar types of watersheds), then the MS/MSD results at one site can be applied at both sites. The minimum frequency criteria must still be met; however, the QC sample schedule should consider the location of each QC sample to maximize coverage at all project sites. A QC sample schedule should, at a minimum, indicate the types and frequency of QC sample collection, site of QC sample collection, and QC sample pseudonyms for samples that will be submitted "blind" to the laboratory. An example of a QC sample schedule is shown in Table 11-2 below. This example schedule demonstrates the distribution of QC samples over one year of monitoring and assumes a total of ten events over a two-year period. The example QC sample frequency exceeds the minimum frequency criteria for MS/MSD and field blank samples because the variability noted in sample matrices and the consistent contamination problems

previously noted for this example project. QC sample scheduling should consider project-specific issues such as this.

Table 11-2. Example QC Sample Schedule

Site	***Pre-Season***	***Event #1***	***Event #2***	***Event #3***	***Event #4***
Site 1		MS/MSD		Field Duplicate (Site C)	Field Blank (Site B)
Site 2	Equipment Blank (Site A1)	Field Blank (Site B)	MS/MSD		Lab Duplicate
Site 3		Field Duplicate (Site C)	Field Blank (Site B)	MS/MSD	
Site 4	Equipment Blank (Site A2)		Lab Duplicate	Field Blank (Site B)	MS/MSD
Laboratory	Composite bottle blank; sample bottle blanks				

Notes:
•Equipment blanks, field blanks and field duplicates are sent to the laboratory "blind", labeled as Site A, Site B, and Site C respectively.
•This is a schedule assumes ten total events over a two-year period.

Because of unforeseen storm characteristics or equipment malfunctions, adequate volume to perform all QC sample analyses may not be available for each monitoring event. In this case MS/MSD analysis should be prioritized ahead of all other QC samples requiring environmental sample volume. If there is inadequate volume to do a complete MS/MSD analysis, duplicate analysis should be performed first. Any variations from the sampling plan should be documented and the monitoring program schedule should then be adjusted to ensure that the minimum number of QC samples are performed during the project.