3.0 METHODS

This section describes the field and laboratory methods used to implement the 2013-2014 Monitoring Program.

The core monitoring program was conducted in compliance with the monitoring protocols set forth by the 2001 Permit's monitoring program. Water quality samples were collected from seven watersheds. The seven watersheds included Ballona Creek, Malibu Creek, Los Angeles River, Coyote Creek, San Gabriel River, Dominguez Channel, and Santa Clara River. Collection and analysis of stormwater runoff during wet weather conditions and ambient (dry) weather runoff were performed at the MES and tributary locations.

The 2001 Permit's monitoring program required sample collection at MES locations for a minimum of three storm events (including the first storm event of the season) and two dry events. Due to the dry conditions that prevailed during the 2013-2014 season, only two samples were collected during wet weather at the Malibu Creek MES (S02) and only one dry weather sample was collected at the San Gabriel River MES (S14).

At the tributary stations located in the Malibu Creek Watershed, sample collection was required under the 2001 monitoring program for a minimum of four storm events (including the first storm event of the season) and one dry event. Due to the dry conditions, only two samples were collected during wet weather at each of tributary stations (TS25, TS26, TS27, TS28, TS29, and TS30). Insufficient sample was collected to complete all chemical analyses during the first wet weather event at each of the tributary stations except Medea Creek (TS28) and Liberty Canyon (TS29) due to equipment malfunction. Stormwater samples and dry weather samples were analyzed for chemical constituents, indicator bacteria, and toxicity to bioassay test organisms.

3.1 Precipitation and Flow Monitoring

3.1.1 Precipitation Monitoring

Precipitation monitoring was conducted at or near each MES using the various automatic rain gauges that LACFCD operates throughout Los Angeles County. A minimum of one automatic tipping bucket (intensity measuring) rain gauge was located nearby or within the tributary watershed for each MES. In some cases, large watersheds used multiple rain gauges to accurately characterize the rainfall. Existing gauges near the monitored watersheds were also used in stormwater runoff calculations and are essential in developing runoff characteristics for these watersheds.

3.1.2 Flow Monitoring

Because the monitoring program requires flow-weighted composites for many constituents, flow monitoring equipment was used to trigger the automated samplers. Flows were determined from water elevation measurements as described below.

The water elevation of an open channel was measured by the stage monitoring equipment, and the flow rate was derived from a previously established site-specific rating table or calculated with an equation (e.g., Manning's Equation). The LACFCD uses rating tables generated from open channel, cross-section analysis and upstream/downstream flow characteristics. Previous flow measurement efforts indicated that all stations require multiple events to gather the data necessary for calibration of the measurement devices. The automatic samplers used pressure transducers as the stage measurement device. At the Santa Clara MES, the leaf technique was employed to measure stream discharge. Stadia rods were used to measure depth, whereas stream velocity was estimated by timing floating objects as they traveled between rods set a fixed distance apart.

3.2 Wet Weather and Dry Weather Monitoring

3.2.1 Wet Weather Sample Collection Methods

During the 2013-2014 monitoring season, analyses of stormwater samples consisted of field measurements, grab samples, and composite samples in accordance with the methods described below.

Field Measurements – Field measurements, which included pH, dissolved oxygen (DO), conductivity, turbidity, and temperature, were conducted using calibrated YSI or similar meters at the Malibu MES and its tributary stations.

Grab Sample - A grab sample is a discrete, individual sample taken within a short period of time, usually less than 15 minutes. This method is used to collect samples for constituents not amenable to composite sampling due to short holding times and specific collection or preservation needs. Grab samples were analyzed for indicator bacteria and for conventional pollutants.

Grab Sample Constituents	
Conventional Constituents/Parameters	**Indicator Bacteria**
▪ Oil & grease ▪ Total phenols ▪ Cyanide ▪ Dissolved oxygen (DO) ▪ pH ▪ Total petroleum hydrocarbons (TPH) ▪ Methyl tertiary butyl ether (MTBE) ▪ 2-Chloroethyl vinyl ether	▪ Total coliforms ▪ Fecal coliforms ▪ Fecal streptococci ▪ Fecal enterococci ▪ *E. coli*

Analytical methods, detection limits, and holding times for these constituents are provided in Table 3-1.

Grab samples were collected during the initial portion of the storm event (i.e., on the rising limb of the hydrograph), placed on ice, and taken directly to the laboratory. Samples were collected from the horizontal and vertical center of the channel if possible and kept clear from uncharacteristic floating debris. Because oil and grease and other petroleum hydrocarbons tend to float, oil and grease grab samples were collected at the air–water interface unless flows did not allow for the safe collection of samples. In these cases, grab samples were collected using the automated samplers. Bacteria samples were collected in a sterile sample bottle and then placed on ice for transport to the laboratory for analysis within 8 hours of collection.

Composite Sample - A composite sample is a mixed or combined sample created by combining a series of discrete samples (aliquots) of specific volume, collected at specific flow-volume intervals. Composite sampling is ideally conducted over the duration of the storm or other monitoring event. Composite samples were analyzed for 150 constituents, including conventional constituents, general minerals, nutrients, metals, semivolatile organics, base neutral, chlorinated pesticides, polychlorinated biphenyls (PCBs), organophosphate pesticides, and herbicides. In addition, all storm events resulting in at least 0.25 inch of rainfall were monitored for total suspended solids (TSS) at all MES equipped with automatic samplers. The additional TSS analysis was not conducted where manual sampling was required (Santa Clara River MES). Additionally, samples from the MES were analyzed for toxicity as described in Section 3.3.1.

Composite Sample Constituents	
▪ General ▪ Nutrients ▪ Metals ▪ Semivolatile organics ▪ Base/neutral	▪ Chlorinated pesticides ▪ Polychlorinated biphenyls ▪ Organophosphate pesticides ▪ Herbicides

Specific composite analytes, analytical methods, detection limits, and holding times for these constituents are provided in Table 3-1.

Most flow-weighted composite storm samples were obtained using an automated sampler programmed to collect samples at flow-paced intervals. Because it is not feasible to install an automatic sampler at the Santa Clara River station, composite samples were obtained at this location by sampling discretely from the river at 20-minute intervals for the first three hours of the storm (or the duration of the storm if it was less than three hours). The discrete samples were then mixed in the laboratory in proportion to the estimated flow rates (i.e., a flow-weighted composite).

During the storm season, the automated samplers were programmed to start automatically when the water level in the channel or storm drain exceeded a minimum predetermined level above base flow or prevailing pre-storm flow. This practice was developed based on years of monitoring experience in local watersheds. It was particularly useful when automated samplers needed to be reset to capture storms occurring a little over 24 hours apart and it was not possible to wait for flows to return to base flow conditions.

A sample was collected each time a set volume of water had passed the monitoring point. This volume is referred to as the pacing volume or trigger volume. Samples were stored in glass containers within the sampler. An 8-liter minimum sample volume was required to conduct the necessary laboratory analyses. The automated sampler was deactivated by field personnel within 48 hours after the end of each storm event. Samples were retrieved from the automated samplers as soon as possible to meet laboratory analysis holding time requirements. As samples were collected, rainfall discrete sample times and runoff data were logged and stored for transfer to the office.

3.2.2 Dry Weather Sample Collection Methods

Dry weather monitoring protocols were similar to those used for wet weather monitoring, except that samples were collected as time-weighted composites over a 24-hour period, and automated samplers were programmed to start at a specified time.

3.2.3 Field Quality Assurance / Quality Control

Quality assurance (QA)/quality control (QC) is an essential component of the monitoring program. *Evaluation of Analytes and QA/QC Specifications for Monitoring Program* (Woodward-Clyde, 1996) describes the procedures used for bottle labeling, chain-of-custody (COC) tracking, sampler equipment checkout and setup, sample collection, field blanks to assess field contamination, field duplicate samples, and transportation to the laboratory. An important part of the QA/QC plan is the continued education of field personnel. Field personnel were trained from the onset and were informed regarding new or revised stormwater sampling techniques on a continual basis. Field personnel also evaluated the field activities required by the QA/QC plan, and the plan was updated if necessary. Accurate data were obtained by proper monitoring station setup, water sample collection, sample transport, and laboratory analyses.

QA/QC for sampling processes included proper collection of the samples to minimize the possibility of contamination. Samples were collected in clean sample bottles, sterilized by the laboratory. Sampling personnel were trained according to the field sampling SOPs. Additionally, the field staff was made aware of the significance of the project’s detection limits and the requirement to avoid contamination of samples.

3.2.3.1 Field Setup Procedures

Automated field sampling stations were at fixed locations, with the sampler placed on a public road or flood control right-of-way. Inspection of visible hoses and cables was performed to ensure proper working conditions according to the station design. Inspection of the intake tube, pressure transducer, and auxiliary pump was performed during daylight hours in normal (i.e., non-storm) conditions.

For stormwater sample collection, the automated samplers were programmed prior to the event based upon weather forecast information. The automated samplers were checked at the beginning of the storm to ensure proper working conditions and to determine whether flow composite samples were being collected properly. Grab samples were taken during the rising limb of the hydrograph.

For dry weather, following the initial sample collection, field staff prepared the sampler to collect subsequent samples (dry weather mode) until the entire set had been completed for that station. Manual samples were generally collected by field staff at the time they pre-programmed the auto sampler to begin collecting at each station. Dry weather collection techniques were similarly performed for both grab samples and 24-hour composite samples.

When a complete set of samples had been collected for a given event, the bottles were removed from the sampler and packed with ice and foam insulation inside individually marked ice chests. COC forms were completed by field staff before transporting the samples to the laboratory. Under no circumstances were samples removed from the ice chest during transportation from the field to the laboratory.

3.2.3.2 Bottle Preparation

A minimum of three sets of bottles were prepared for each monitoring station so that change-outs could be made quickly between closely occurring storms. Bottle labels included the following information:

- LACFCD's Field Sample Identification (FSID) number.
- Station (site) number.
- Station (site) name.
- Laboratory analysis requested.
- Date (written at time of sampling).

Bottles were cleaned at the laboratory prior to use, labeled, and stored in sets. Each station was provided with the same number, type, and size bottles for each rotation, unless special grab samples were required. Clean composite sample bottles with sterile stoppers were placed in the automated sampler when samples were collected. This practice ensured readiness for the next storm event. All bottles not in use at the time of sampling were stored in clean dry conditions for later use. Composite sample bottles were limited to a maximum of 2.5 gallons each, to ensure ease of handling.

3.2.3.3 Chain-of-Custody Procedure

COC procedures (Woodward-Clyde, 1996) were used for all samples throughout the collection, transport, and analytical process. Samples were considered to be in custody if they were: (1) in the custodian's possession or view (2) retained in a secured place (under lock) with restricted access, or (3) placed in a container and secured with an official seal to prevent the sample from being reached without breaking the seal. COC records, field logbooks, and field tracking forms were the principal documents used to identify samples and to document possession. The COC procedures were initiated during sample collection. A COC record was provided with each sample or group of samples. Each person with sample custody signed the form and ensured the samples were not left unattended unless properly secured. Documentation of sample handling and custody included the following:

- Bottle label information (i.e., the LACFCD FSID number, station [site] number, station [site] name, laboratory analysis requested, and date [written at time of sampling]).
- Time (written at time of sampling).
- Number of bottles.
- Temperature of sample.
- Sampler(s), laboratory and sampler/courier signatures, and time(s) sample(s) changed possession (completed upon sample transfer(s)).

3.2.3.4 New Zealand Mud Snails

Due to concern about the spread of New Zealand Mud Snails, additional decontamination of monitoring equipment between Malibu MES and tributary monitoring stations was conducted. A designated set of sampling equipment (exclusive of temperature and pH field meters) was used for each of the stations in the Malibu watershed (Malibu MES and tributary stations), and was decontaminated before and after each event. Decontamination procedures as described by the California Department of Fish and Game (Hosea and Finlayson, 2005) were employed and included immersion of sampling equipment in Sparquat 256.

Field meters utilize sensitive osmotic membranes for use in measurement of pH. Therefore, the use of freezing or Sparquat 256 as a decontamination method was not employed. Field meters were visually inspected after use at each location; and all snails, mud, algae, and debris were removed. The meters were then thoroughly rinsed on-site with tap water and allowed to dry completely. Visual inspection of the field meters was completed prior to departure from the station and before use at the next monitoring location.

3.3 Laboratory Analyses

The 2001 Permit specified a suite of analyses and associated minimum levels (MLs) for samples collected at the MES and tributary locations, as detailed in Table 3-1. The laboratory methods used for analyzing stormwater samples are approved by the California Department of Public Health (CDPH) and conform to EPA-approved methods.

The Los Angeles County Department of Agricultural Commissioner Weights and Measures (ACWM) Environmental Toxicology Laboratory provides water quality laboratory and related services to LACFCD. The ACWM Laboratory is state certified to perform the water quality analyses and maintains a laboratory analysis program that includes QA/QC protocols consistent with the monitoring program. The ACWM subcontracts toxicity testing with Aquatic Bioassay Consulting Laboratories, Inc. (ABC) of Ventura, California. This laboratory is accredited by the State of California’s Environmental Laboratory Accreditation Program (ELAP; certificate number 1907) for whole effluent toxicity of wastewater testing as well as for other types of analyses.

Several storm events were monitored with the assistance of an environmental consulting firm, Weston Solutions, Inc. (WESTON®). Grab and composite samples collected by WESTON were sent to ACWM. Toxicity samples collected by WESTON were analyzed by ABC Laboratories.

3.3.1 Toxicity Analysis

Toxicity testing was performed on flow-weighted composite samples collected from the MES locations concurrently with the water chemistry analyses during two wet weather events. Toxicity testing was also performed on time-weighted composite samples during two dry weather events at the MES locations, with the exception of San Gabriel River MES, where one dry weather sample was collected due to the dry conditions.

Toxicity testing is an effective tool for assessing the potential impact of complex mixtures of unknown pollutants on aquatic life in receiving waters. Rather than performing chemical analysis on a sample for a host of compounds potentially toxic to aquatic life, toxicity testing provides a direct measure of the toxicity of the sample to laboratory test organisms. Interactions among the complex mixture of chemicals and physical constituents inherent to environmental samples can lead to additive or antagonistic effects, potentially causing an individual compound to become either more or less toxic than it would be if it were isolated. Although the potential effects of these interactions cannot be derived from simple chemical measurements, they are directly accounted for in toxicity tests. If toxicity is identified in a given sample, toxicity identification evaluations (TIEs) can be used to help characterize and identify the constituent(s) responsible for the toxicity. Toxicity testing can provide information on both potential short-term (i.e., acute) effects as well as longer-term (i.e., chronic) effects.

Toxicity analysis was performed using the following methods:

- *Ceriodaphnia dubia* 7-day (chronic) survival and reproduction tests.
- *Strongylocentrotus purpuratus* (sea urchin) (chronic) fertilization test.

The tests were performed using multiple sample concentrations ranging from 0% (N-control) to 100%, such that the desired toxicity endpoints could be adequately observed. Based on the endpoints of reproduction and survival, the no-observed-effect concentrations (NOEC), inhibitory concentrations (IC), effective concentrations (EC), and toxicity units (TU) were calculated and reported for each test. Toxicity units are calculated by dividing 100 by the calculated median test response value (e.g., IC_{50}). The *C. dubia* and *S. purpuratus* tests were conducted under guidelines prescribed in *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms* (EPA, 2002) and *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms* (EPA, 1995), respectively. Water quality measurements (i.e., temperature, pH, DO, conductivity, salinity, hardness, and alkalinity) were recorded for each sample at the beginning and throughout each test. These measurements were performed to ensure that there were no large variations in water quality, which can affect the accuracy of the toxicity tests.