2.0 METHODS

This section provides a synopsis of activities, including sample collections and analyses, that were conducted during the 2013-2016 MNR sampling program.

2.1 SEDIMENT

Operations for collecting cores are described below.

2.1.1 Shelf-Wide Sample Grid

Figure 2-1 shows the locations of sediment cores planned for the 2013 shelf-wide sampling event. As described in the Field Sampling Plan (FSP; ITSI Gilbane, 2014), these locations were collocated with EPA's baseline program conducted in 2009. For both events, EPA used a subset of the Sanitation Districts' stations typically used for the JWPCP National Pollutant Discharge Elimination System (NPDES) compliance programs for sediment sampling (California Regional Water Quality Control Board, Los Angeles Region [Water Board], 2017). The Sanitation Districts have established shore-normal Transects 0 through 10, numbered north to south. Transect 0 is located north of Palos Point near Bluff Cove (Figure 1-1), and Transect 10 is located near Point Fermin at San Pedro. Transect 8 is aligned along the White Point outfalls. Along these transects, the Sanitation Districts have established stations along the following main isobaths (water depths): A (305-m); B (150-m); C (60-m); and D (30-m). For locations between main isobaths, the convention is to combine the names of the two nearest isobaths (e.g., isobath BC is at a depth of 100 m, and DC is at a depth of 40 m). For EPA's 2013 MNR shelf-wide program, primary cores were planned for 34 locations using Transects 1 through 10 and along the B, BC, C, and DC isobaths. Replicate cores were planned for locations 2B, 4C, and 5B (Figure 2-1).

2.1.2 Outfall Area Sample Grid

In addition to the shelf-wide locations, EPA planned a grid 35 of core locations for the outfall area (OA) near the Sanitation Districts' outfall diffusers (Figure 2-2). Twenty-five locations were collocated with OA cores used for EPA's 2009 sampling event (ITSI Gilbane, 2014). The locations had been selected based on historical data including: historical concentrations of COCs; erodibility of the sediment; penetration depths of sediment profile imaging (SPI) cameras from a 2004 survey (SAIC, 2005b); and the reported thickness of the EA bed.

For the 2013 sampling event, ten additional OA cores were collected to address concerns that "hot spot" areas may have been missed in 2009. Seven OA locations were selected for single replicates. The spacing between adjacent core locations ranged from approximately 0.1 km to 1.2 km. Figure 2-2 shows the OA sample grid. All core locations within the OA boundary were within 1.5 km of a diffuser section of the Sanitation Districts' four outfall pipes.

2.1.3 Mapping, Bathymetry, and Vessel Positioning

For this sediment sampling event, ArcView by ESRI, Redlands, California, was used as the software platform for mapping. The mapping coordinate system was the Geographic Coordinate System (GCS) of 1983, based on the Greenwich Meridian and the 1983 North American Datum (NAD 83), as provided by ESRI. Coordinates were reported in degrees-decimal minutes, in conformance to previous work at PV Shelf. Seabed bathymetry was based on the low-resolution bathymetric data from multi-beam sonar surveys of the Los Angeles Margin (Point Dume [Malibu] to Dana Point [Orange County]) that were conducted by the United States Geological Survey (USGS) from 1996 to 1999.

Coring operations were conducted on the Sanitation Districts' research vessel (RV), the 20-m *Ocean Sentinel*. Ship positioning for each core drop was based both on the planned ocean depth and latitude and longitude coordinates. To navigate and position the vessel, a commercial marine navigation software product from Nobeltec, Beaverton, Oregon, was used with a differential global positioning system (DGPS). A fathometer was used to measure the ocean depth at the time of core collection. During each core drop, the vessel position was logged (i.e., a navigation fix was recorded) at the exact time that the coring device reached the ocean floor. For replicate samples, collected in the same location as the initial (primary) sample, the vessel was repositioned to the original planned coordinates for the primary sample. To avoid damage to the Sanitation Districts' infrastructure during operations near the Sanitation Districts' outfalls, the ship captain used sonar to monitor the locations of the outfall pipes and supporting ballast. The captain operated the DGPS, and manually recorded in a daily navigation log all significant events and any problems encountered.

2.1.4 Coring Procedure

Sediment cores were collected in October 2013, using the Sanitation Districts' standard gravity core sampler. Figure 2-3 is a schematic of the gravity coring device used for this program. The

coring device had a cutting head about 100 cm in length with an effective sampling length of about 90 cm. At the start of the operation, the core sampler was attached to a winch cable; the winch was supported by a small crane mounted on the stern of the RV. Lead weights attached to the top of the cylinder provided added driving force for penetration of the soft EA bed; for the ocean depths at PV Shelf, a top assembly was attached to the main coring device, and 9-kilogram (kg) rings were added to give a total weight of about 125 kg. The total length of the coring device with cutting head and weighted top assembly was about 135 cm.

To address concerns regarding the possibility of "blow-off" of the surface layer of the sediment bed during coring and the angle of penetration of the corer into the sediment bed, Sanitation Districts' staff modified the coring assembly to mount a digital video camera and an inclinometer (Photographs 001 and 002 in Appendix A). The camera was used for cores collected at depths of 60 m or less, except at BA4DC. At this location, three attempts to collect core were unsuccessful; the fourth attempt was made without the camera and was successful. Video also is not available for BA3DC due to an issue with the captured electronic file. The inclinometer was used for all cores.

For each core collection, a clean acetate liner was placed into the core barrel prior to each drop. The crew then used a high-speed winch to drop the corer into the ocean. As the corer travelled downward through the water column, the hinged cap at the top remained open. When the coring device hit the bottom, a trigger mechanism (weighted bar) closed the hinged cap, providing a suction seal that helped retain the sediment core in the metal tube. When the boat crew noted slack in the winch cable, the winch was reversed to pull the corer to the surface. The cutting head at the bottom of the corer had a passive retainer (an array of sheet metal "fingers") designed to maintain core integrity during retrieval upward through the water column. After the retrieved corer was placed on the deck, the core was inspected for acceptance or rejection. Criteria used for rejection included:

- Heavy disturbance of surface sediment, indicated by muddy water at the top of the core liner;
- Water leakage out of the sides of the corer, causing the core to slump;
- Formation of a "heel" on the bottom of the core;
- Unusually short cores in comparison to historical data;

- Rocky conditions at the ocean floor; or
- Damage to the coring device (possibly due to a rocky ocean floor).

Each accepted core was retrieved from the corer with the acetate liner intact. The liner ends were sealed with plastic bags. Strapping tape was applied in a spiral around the bag and the entire length of the core to maintain core integrity. The core length was measured (Photo 003 of Appendix A) and recorded, and the core liner was marked with indelible ink to record the core location name, core length (in cm), and sampling date. Approximately 1 liter (L) of liquid nitrogen was applied to each end of the galvanized steel (GS) sleeve to provide quick freezing, and the sleeved core was then and immediately stored vertically in one of two shipboard wooden cold boxes (Photo 004 of Appendix A). Each cold box had been previously stocked with dry ice and equipped with supports to hold nine cores. The cores were transported to JWPCP for storage in a deep freezer, sometimes daily if the cold boxes were full or near-full.

2.1.5 Core Processing

Core cutting events occurred in November and December 2013 at the Sanitation Districts' Water Quality Laboratory (WQL) at the JWPCP. Core cutting was conducted by Sanitation Districts' staff (see Photo 005 of Appendix A). Cutting techniques conformed to WQL's *Sediment Core Cutting Procedure, Method 500C* (see FSP; ITSI Gilbane, 2014); these techniques were used to create sediment slices, each with an approximate thickness of 2 cm. Cuts were made on each core until the bottom remaining material was less than 2 cm thick, and this remainder was discarded.

To generate samples after the cores were cut, the outer ring of each frozen core slice initially was trimmed using a ring punch to remove potentially smeared material generated during bed penetration. The remaining slice then was broken into chunks while still frozen and partitioned into four portions of approximately equal volume. The weight of the portions ranged from approximately 60 grams (g) to 120 g, with an average of about 90 g. The portions of each slice were distributed into three containers (4-ounce amber glass jars with Teflon-lined caps) as follows: one portion for chemical testing; two portions for geotechnical testing; and one portion for archiving (deep-freeze; Photo 006 of Appendix A). As agreed between EPA and the Sanitation Districts, archived samples were sent to the Sanitation Districts' sediment archive for storage.

2.1.6 Testing of Sediment Samples

Sediment samples generated from the core cutting events were transported from JWPCP to GMU Geotechnical, Inc. (GMU), Rancho Santa Margarita, California, for geotechnical testing, and to Eurofins Calscience (Eurofins CS), Garden Grove, California, for testing of chemistry parameters and MC.

The 0-to-8-cm layer of the sediment bed at PV Shelf has been recognized as the biologically active zone where a majority of the benthic biological activity occurs (SAIC, 2005a). At both laboratories, the four 2-cm-thick slices of each core, representing the bed-depth interval of 0-8 cm, were tested separately. For the portions of each core representing bed intervals at depths greater than 8 cm, two-way composite samples were prepared by combining slices representing two successive sample intervals (e.g., the slices corresponding to bed depth intervals of 8-10 cm and 10-12 cm). For cores with an odd number of slices, the slice remaining after two-way compositing, i.e., the deepest slice, was not used.

2.1.6.1 Geotechnical Tests

At GMU, samples were stored in a freezer until they were prepared for analysis. Sample preparation began with opening the sample containers and examining the frozen chunks. Where no compositing was required, samples were thawed and analyzed by the test methods listed below. For testing the two-way sample composites for BD_w, the two individual samples were first examined independently while still frozen; the largest single chunk was selected as being representative of the composite and, while still frozen, was tested for BD_w. For the other geotechnical tests (i.e., grain size and SG), where sample compositing was required, laboratory staff removed thawed equal portions from each of the two individual sample containers and placed them into a clean glass beaker. The material then was mixed using a stainless steel spoon or spatula to create a visually homogeneous mixture. The mixture was then tested for the parameters listed below.

- For grain size, GMU used ASTM D422-63: *Standard Test Method for Particle-Size Analysis of Soils*. Following this standard, GMU used sieves to determine the grain size distribution for particles 75 microns (um; #200 sieve) and larger, and a hydrometer to measure the distribution of particle sizes smaller than 75 um.
- For BD_w, GMU used ASTM D7263-09: *Standard Test Method for Laboratory Determination of Density (Unit Weight) of Soil Specimens, Method A (direct measurement)*.

- For SG (the ratio of the weight of a sample to the weight of an equal volume of water), GMU used techniques for moist soil as described in ASTM D854-98, *Standard Test Method for Specific Gravity of Soil*.

2.1.6.2 Chemistry Tests

Eurofins CS tested sediment samples for MC, TOC, and COCs. Eurofins CS is certified as an environmental testing laboratory under the Environmental Laboratory Accreditation Program (ELAP) administered by the California State Water Resources Control Board (SWRCB). Gilbane selected Eurofins CS as the chemistry testing laboratory after rigorous vetting, including performance evaluation (PE) tests (see Section 4.1.1.1).

At Eurofins CS, samples were accepted from the courier and stored in a freezer until they were prepared for analysis. Sample preparation steps included thawing the frozen samples and mixing them in the original sample containers using a stainless steel utensil. When two samples were composited, laboratory staff removed aliquots of equal weight from each of the two sample containers and placed them into a certified-clean container. The aliquots then were mixed using a stainless steel spoon or spatula to create a visually homogeneous mixture. All utensils were thoroughly cleaned between sample preps.

After compositing, a total of 1,220 samples was generated. Sample counts were as follows: 523 samples were generated for the shelf-wide primary cores; 44 samples were generated for the shelf-wide replicate cores; 541 samples were generated for the OA primary cores; and 112 samples were generated for the OA replicate cores.

Tests of the sediment samples were conducted in accordance with the requirements specified in the guidance documents listed below.

- Test Methods for Evaluating Solid Waste, SW-846 Physical/Chemical Methods (EPA, 2007a)
- ASTM Standard D2216-05, 2005, *Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass*
- Final Sampling and Analysis Plan for Sediment Sampling, Part 1 - Quality Assurance Project Plan (ITSI Gilbane, 2014)

Specific analytical methods used for this project are listed below.

- TOC using EPA Method 9060, a water method modified for sediment (includes an acidification step)
- MC (in percent moisture) using Eurofins CS standard operating procedure (SOP) M700, based on ASTM D2216-05, (EPA Method 160.3/SM 2540 B), *Determination of Moisture or Solids Content*
- DDTs and PCBS using EPA Method 8270SIM

During sediment testing in 2009, a procedural improvement for preparing DDT samples was proposed by Eurofins CS and reviewed and approved by EPA, as follows: implement a secondary cleanup step using a solid-phase extraction cartridge (in addition to the primary cleanup using solvent exchange) to remove interfering organic matter from samples. This step was an attempt to reduce the rate of DDT degradation (breakdown to DDE and DDE) observed occurring in the injection port liner of the gas chromatography/mass spectrometry (GC/MS) instrument during sample analysis. Eurofins CS demonstrated that this secondary cleanup process allowed for a reduction in the frequency of cleaning the injection port, thereby enhancing the stability and performance of the GC/MS instrument, and ultimately resulting in improved data accuracy. This same procedure was used for the 2013 sediment testing. A detailed description of this approach is provided in the *Revised Final Data Report for the Fall 2009 Sediment Sampling Program* (ITSI Gilbane, 2013b).

For the 2013 sediment program, the PCB list was expanded to include the 46 congeners used during previous EPA fish studies at PV Shelf (Innovative Technical Solutions, Inc. [ITSI], 2011). Table 2-1 lists the individual chemistry analytes (eight DDT compounds and 46 PCB congeners) used for the chemistry tests of sediment samples, with the associated RLs. Table 2-2 lists various congener lists commonly used by research institutions including NOAA and the World Health Organization (WHO) that are concerned with PCBs in the general environment. EPA's expanded list includes all 21 congeners from NOAA's list (NOAA, 1998), and the twelve congeners recognized by WHO as dioxin-like (WHO, 2006), in addition to other congeners of interest.

2.1.7 Geostatistical Modeling of Sediment Data

As was done for EPA's 2009 sediment data set, Mining Visualization System (MVS) software (C Tech Development Corporation, Bellingham, Washington) was used as the geostatistical modeling platform to characterize the sediment bed. To duplicate the previous approach at PV

Shelf, the MVS model was set up using a rectilinear three-dimensional (3D) grid aligned roughly parallel to the shore, in the general direction of the recognized dominant transport pathway for sediment at PV Shelf (Sherwood et al., 2006). The model extent encompassed all core locations (Figure 2-1); the total modeled area was 29.8 km^2.

The MVS model used two-dimensional (2D) kriging for geological surfaces and 3D kriging for geotechnical and chemistry data. The kriging approach considered proximities of samples both in the areal and vertical directions (corrected from elevation to bed depth), as well as the heterogeneity of the data set being analyzed.

The model was used to derive values for various characteristics of the sediment bed at PV Shelf, including the mean (average) OC normalized concentrations and total masses of COCs for both the entire modeled grid and for the 0-8-cm sediment layer (see Section 3.1.6). Appendix C presents a detailed discussion of the MVS modeling effort and software parameters, and provides a contextual analysis of input/output parameters and values.

2.2 WATER COLUMN SAMPLING

To directly support the MNR component, Gilbane conducted high resolution grab sampling of the water column during 2015. This was the first EPA-sponsored event to use high resolution grab sampling at PV Shelf. A round of water sampling using PSDs was also conducted in 2013. (EPA had sponsored a previous PSD sampling event at PV Shelf in 2010 [Fernandez et al., 2012]). The high resolution event and the 2013 PSD event are described below.

2.2.1 High Resolution Grab Water Sampling

2.2.1.1 High Resolution Water Sampling Grids

Figure 2-4 shows the grid for the high resolution grab samples. As described in the QAPP for high resolution sampling (Gilbane, 2014), the sample locations were generally selected to match the locations from the Sanitation Districts' standard benthic sediment sampling program (Section 2.1.1). The sampling depths in the water column were selected generally to match EPA's PSD water sampling events (Section 2.2.2). Five locations (W1 through W5) were selected at deep-water locations near the edge of the PV Shelf or past the shelf break on the continental slope. Sample location T11 is far southeast of the PV Shelf contaminated zone, on the 60-m isobath.

This location has been used during PSD events as a background reference location, and was again used during the high resolution grab sampling.

2.2.1.2 Sampling Locations, Depths, and Vessel Positioning

The latitude and longitude coordinates for each water sample location were referenced to the Greenwich Meridian and NAD 83, and were reported in degrees-decimal minutes. To navigate and position the vessel, commercial marine navigation software products (including Nobeltec on the *Ocean Sentinel*) were used with a DGPS. For each sampler deployment, an accurate digital cable length counter was used to measure sampling depths; however, due to ocean swells and drift away from the vertical, the sample depth error is estimated as ±1.5 m.

Target sampling depths at 23 locations were: 5 m below the ocean surface; mid-column; and 5 m above the ocean floor. At 17 other locations, a sample was also collected 2 m above the ocean floor. These four-tiered locations were collocated with previous PSD deployments.

2.2.1.3 Water Sampling Procedure

During the 2015 water sampling program, a grab sampler device developed by Kinnetic was used. The sampler held a 2.5-L sample bottle; this approach allowed adequate sample volume to be collected during a single "drop". Other features of the sampler were a spring-loaded stopper and rope trip-line system; a removable base plate to allow the quick loading and release of sample bottles; and a mounted digital video camera allowing review of each drop (Photo 007 in Appendix A).

The grab sampler was attached to a winch cable supported by a small crane mounted on the stern of the vessel (Photo 008 in Appendix A). Detachable lead weights hanging below the sampler provided counter-weight for the buoyancy of the empty sample bottle, and resistance to trip the stopper against the spring closing mechanism. The maximum counterweight for the deepest (200-m) samples was approximately 136 kg. The total length of the grab sampler was about 1.5 m.

A clean 2.5-L amber sample bottle was placed into the sampler prior to each deployment. The bottle cap was removed and stored in a clean plastic bag during the sampler deployment. To initiate a sampling deployment, the vessel was piloted to the selected sample location using the

DGPS. The crew then used a high-speed winch to lower the sampler into the ocean. As the sampler was lowered through the water column, the spring-loaded stopper remained closed. When the sampler reached the selected water depth, the stopper trip rope was pulled and upward pressure maintained for approximately 30 seconds for the bottle to fill. When the crewman released the trip rope, the stopper closed, and the winch was reversed to pull the sampler to the surface.

After the grab sampler was retrieved and placed on the deck of the vessel, the sample bottle was inspected for acceptance or rejection. Criteria used in evaluating whether water samples should be rejected (and the sample re-collected) included:

- Visible sediment in the sample bottle, indicating that the sampler had contacted the ocean floor and stirred up the sediment (this criterion was adopted because visible sediment could interfere with the sample filtering efficiency at the laboratory); and
- The O-ring on the bottle stopper entering the sample bottle (for initial drops conducted during the pilot test, silicone O-rings were found in several deep samples due to the tremendous pressure of the initial water flow into the bottle – the O-ring/stopper was re-designed).

The digital video of each sampling deployment was reviewed to ensure that the trip line had not snagged and opened the sample stopper prematurely; to assess possible sediment disturbance (for the deepest samples); and to assess tidal drift during sampling. Each acceptable water sample bottle was released from the sampler, some water was poured out of the bottle, and the original bottle cap was hand tightened to seal the sample. The bottle was dried with a paper towel, and a pre-printed sample label with the sample identification, date, and sample time added in indelible ink, was affixed to each bottle.

Use of this sampler greatly reduced the need for equipment decontamination between samples, because the only reusable components in contact with the sample water were the bottle stoppers. Six stoppers were used throughout the project and they were decontaminated in batches using a soapy water wash; several deionized water rinses; a laboratory-grade acetone wash; and a final rinse using high-purity reverse osmosis (RO) water from the testing laboratory (Photo 009 in Appendix A). Periodically, a final rinsate sample was collected for chemical testing. The clean (decontaminated) bottle stoppers were stored in a clean, sealed plastic bag until deployment.

Each sample and rinsate bottle was wrapped in bubble wrap and stored upright in a large marine cooler on a bed of ice and within a heavy garbage bag that was later sealed to contain melt water. All sample coolers were shipped overnight to ALS Life Sciences (ALS), Burlington, Ontario, Canada, the testing laboratory (Photo 010 in Appendix A).

2.2.1.4 Sample Preservation, Filtration, and Extraction

Water samples collected during each sampling event were transported to ALS in Canada. This required ALS to send a cross-border courier to a FedEx depot in Cheektowaga, New York, to receive shipments and accept samples. ALS is accredited in California under the ELAP administered by SWRCB, and in Canada by the Canadian Association for Laboratory Accreditation.

All samples were stored by ALS in a refrigerator at less than 6 degrees Celsius (^{o}C). Samples were filtered prior to extraction to isolate dissolved-phase DDTs and PCBs in the water samples. All glassware and filters were cleaned appropriately for ultra-trace analyses. High purity RO water generated by ALS was used for the field equipment blanks and for all laboratory blanks and quality control (QC) samples.

Samples were filtered gravimetrically through glass-fiber filters with a nominal pore size of 0.7 um. The resulting filtrate was defined as the dissolved fraction, in accordance with a previous study (Zeng, 1999). During filtration and storage awaiting extraction, the funnels and flasks were covered with aluminum foil to avoid possible sample contamination by dust. The sample bottle was not solvent- or water-rinsed, to minimize re-mobilization of particulates through the filter, and to reduce filtering times. Because of possible losses of dissolved targets during the filtration process, all spiking of samples was done after filtration. This included native target spiking for laboratory control samples (LCSs) and the spiking of carbon isotope 13 (C-13)-labeled extraction standards during extraction.

Sample extractions were performed on the same work shift as the filtrations. The extractions were performed using 2-L separatory funnels. Transfer occurred in approximately two-thirds and one-third aliquots, using the appropriate volumes of dichloromethane extract, with each extraction repeated three times. The combined extracts were collected in a single 500-milliliter

(mL) flask. The raw sample extract was then split in half for DDTs and PCBs analysis, and spiked with the appropriate C-13-labeled cleanup standards.

The DDT portion of the extract was first cleaned by gel-permeation chromatography (GPC) to help remove intractable biological interferences and improve performance of the gas chromatography (GC), and then by silica column chromatography (activated silica gel), a cleanup designed to remove earlier eluting hydrocarbon/organic fractions. The PCB portion of the extract was cleaned by acidified silica column chromatography, followed by activated alumina column cleanup.

2.2.1.5 Testing of High Resolution Grab Water Samples

ALS tested the water samples in accordance with the requirements specified in the documents listed below.

- EPA Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, EPA-820-R-10-005 (EPA, 2010)
- EPA Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, EPA-821-R-08-001 (EPA, 2007)
- Final Quality Assurance Project Plan - Water Sampling Program, Remedial Action – Monitored Natural Recovery Component, Palos Verdes Shelf, Los Angeles County, California (QAPP; Gilbane, 2014)

The specific analytical methods used for water testing are listed below.

- Organo-chlorine pesticides (OCPs/DDTs) by HRGC/HRMS, EPA Method 1699
- PCBs by HRGC/HRMS, EPA Method 1668C

Table 2-3 lists the individual chemistry analytes, including eight DDT compounds and 46 PCB congeners, along with the associated RLs used for the chemistry tests. For the uncommon analytes DDMU and DDNU, ALS performed method detection limit (MDL) studies and surrogate recovery limit studies.

2.2.2 PSD Water Sampling

The PSD collection program was set forth in the PSD QAPP (Fluen Point Environmental, 2013). Appendix D includes the complete report of the results. Salient details of the PSD sampling program are described below.

2.2.2.1 PSD Water Sampling Grid, Locations, and Depths

Figure 2-4 shows the sample grid for the 2013 PSD event. PEDs were deployed at 16 stations on the PV Shelf and at one background station T11. SPMEs were co-deployed with PEDs on the same mooring lines at five stations on the PV Shelf (4C, 7C, 8C, 9C, W3) and at the background station T11. As in the 2010 sampling program, samplers were deployed at three depths at each station: 5 m below the surface (near-surface); mid-column; and 5 m above the sediment-water interface (near-bottom). Discrete water samples were collected at depth using a Niskin bottle, and DOC readings were measured with a field meter.

2.2.2.2 PSD Water Sampling Procedures

PE samplers were prepared by impregnating them with the following performance reference compounds (PRCs): ^{13}C-4,4'-DDT, ^{13}C-4,4'-DDE, ^{13}C-4,4'-DDD, ^{13}C-PCB28, ^{13}C-PCB52, ^{13}C-PCB118, and ^{13}C-PCB128. For the PEDs, this step was accomplished by soaking each sampler in an aqueous solution of the PRCs in a 1-L amber glass jar for at least 20 weeks before deployment. SPME samplers were also fortified with PRCs: ^{13}C-4,4'-DDE, PCB 50, ^{13}C-PCB 52, PCB 98, ^{13}C-PCB 128, PCB 155, and PCB 184. The pre-cleaned SPME samplers were immersed in the PRC solution for 4 hours in a dark temperature-controlled room after which they were dried and stored at -20^{o} C until use. After preparation, both types of samplers were deployed in triplicate at each station/depth. Water temperature and conductivity were measured using conductivity-temperature-depth meter casts at the time of retrieval. The problem of PED loss during deployment, encountered during the 2010 sampling event was addressed by using stainless steel wire for threading of sampler polymer to the deployment gear, although some losses of samplers still occurred (as further discussed in Appendix D).

2.2.2.3 PSD Sample Preservation and Extraction

All retrieved PSDs (PEDs and SPMEs) were transported on ice to the analytical laboratory at the Southern California Coastal Water Research Project (SCCWRP) facility in Costa Mesa, California, for analysis. SCCWRP's ongoing mission is to provide a scientific foundation for managing marine and coastal resources in Southern California. As part of that mission, SCCWRP organizes and participates in collaborative regional monitoring programs, such as the Southern California Bight Regional Monitoring Program. Samplers were frozen at the laboratory until analysis.

Prior to extraction, the PEDs were wiped to remove adhering particles and biofilms, and cut into small pieces. The PEDs were then spiked with recovery surrogates and extracted three times by sonicating in methylene chloride. The solvent was concentrated to a small volume and exchanged to hexane, at which point internal standards were added in preparation for analysis. SPME fibers required no extraction, but were manually injected on the instrument for analysis.

2.2.2.4 Testing of PSD Samples

The SCCWRP laboratory tested the water samples using gas chromatography/mass spectrometry in selective ion mode in accordance with the requirements specified in the PSD QAPP (Fluen Point, 2013). The specific analytical methods used for water testing are listed below.

- SCCWRP SOP Chapter 24 – Determination of DOC and Total Nitrogen (TN) in Water Samples
- SCCWRP SOP Chapter 27 – Construction, Deployment, Retrieval, and Analysis of SPME Samplers
- SCCWRP SOP Chapter 35 – Use of Polyethylene Devices (PEDs)

Table 2-4 lists the individual analytes along with the associated RLs used for the chemistry tests performed on the PSDs at SCCWRP's analytical laboratory.

2.3 FISH

The fish collection program was set forth in the fish QAPP (Gilbane, 2016a). Salient details on the fish sampling program are described below.

2.3.1 Design of Sample Collection

The MNR fish collection areas and numbers of samples were derived by consensus during a scoping discussion at the PVSTIEG meeting held January 2014. Seven collection areas were selected, each 1 km x 5 km. They are as follows (from north to south): Ventura Flats; Redondo Flats; three areas within the Sanitation Districts' NPDES bioaccumulation zones (EPA Zones 1, 2, and 3); an area near the breakwater of Los Angeles Harbor; and Huntington Flats (Figure 2-5). These areas are described as follows:

- Ventura Flats is situated approximately 110 km northwest of the Sanitation Districts' outfall diffusers; it is the collection area farthest from the diffusers and serves as a reference area for assessing spatial variability of contaminants in WC.
- Redondo Flats is located north of the Palos Verdes Peninsula and the deep ocean Redondo Canyon, which is regarded as an impediment to fish migration along the coast;

it is about 25 (shoreline) km north of the Sanitation Districts' outfalls. BSB and WC collections were planned for this area. The resulting analytical data would be used to assess the spatial variability of contaminants in both species in the northward direction from the outfalls.

- EPA Zones 1, 2, and 3 are subareas within the respective boundaries of the Sanitation Districts' three Fish Tissue Bioaccumulation Sampling Zones used in the JWPCP NPDES compliance programs for fish. The EPA zones were located along the 60-m isobath, where the Sanitation Districts' outfall diffusers, the former source of release of COCs to the environment, are located. BSB and WC collections were planned for each of these three EPA zones.
- The Breakwater collection area is located on the ocean side of the breakwater at Los Angeles Harbor and is approximately 10 km east of the Sanitation Districts' outfall diffusers. BSB and WC collections were planned for this area. Analytical data for fish caught at the breakwater would be used in assessing spatial variability of contaminants in both species.
- Huntington Flats is located approximately 25 km east-southeast of the Sanitation Districts' outfalls and is a known spawning area for BSB. Analytical data for BSB caught in this area are of interest to study spatial variability of contaminants in the fish and the possible effects of cyclic loading on spawning fish.

Other features of the collection areas are indicated on Figure 2-5 and described below.

- The Zone 1 and Zone 2 collection areas are within the commercial catch ban area for WC established by CDFW (CDFW, 1990).
- The Zone 3, Breakwater, and Redondo Flats collection areas are within the "red zone" published in guidelines from the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA); the public is advised to not consume BSB or WC caught in this zone (CalEPA/OEHHA, 2009).
- The Huntington Flats collection area is within CalEPA/OEHHA's "yellow zone"; the public is advised to limit consumption of BSB and WC caught in this zone (CalEPA/OEHHA, 2009).
- The Ventura Flats collection area is outside CDFW's WC catch ban area and CalEPA's fish advisory zones.

Table 2-5 presents the number of fish planned for each area. As indicated, the number of specimens generally planned for each fish species for each collection area was 30. This value is generally accepted as a sample population that provides a statistically supportable representation of the distribution of contamination in the populations of fish sampled (NOAA/EPA, 2007). The number of BSB specimens planned for the Zone 2 collection area was limited to 10 by the JWPCP NPDES permit. For Ventura Flats, collections of only WC were planned. For

Huntington Flats, collections of only BSB were planned, as that area is a known BSB spawning ground.

2.3.2 Fish Collections, Handling, and Testing

Collection methods included hook and line, spear fishing, traps, and trawls (Photos 011 and 012 in Appendix A). Caught fish were weighed and measured for standard length and total length (Figure 2-6, Photos 013 and 014 in Appendix A). BSB specimens kept for analysis met the minimum size limit (total length of 14 inches) as specified in the saltwater sport fishing regulations set by CDFW (CDFW, 2017). There are no CDFW size limits for WC.

Specimens retained for analysis were wrapped in aluminum foil, labeled, and sealed in a plastic bag for storage (Photo 015 in Appendix A). Most fish specimens were frozen onboard the respective fishing vessel, then transferred to the freezer (-20^{o} C) at the Sanitation Districts' Marine Biology laboratory in Carson, California (Photo 016 in Appendix A). Some fish collected by Seaventures in 2016 were immediately shipped on wet ice to the testing laboratory.

Prior to fish collection, Gilbane had conducted a laboratory selection effort by having candidate labs analyze a standard reference material (SRM) fish tissue sample (SRM 1946 – Lake Superior homogenate) obtained from the National Institute of Standards and Technology (NIST). Gilbane selected Vista Analytical Laboratory, Inc. (Vista), El Dorado Hills, California, as the chemical testing laboratory for the fish sampling program. Vista is accredited in California under the ELAP administered by SWRCB.

To initiate fish testing, the whole fish specimen was removed from the storage freezer and placed under a fume hood to thaw at ambient temperature. For BSB specimens, a single filet was cut and the skin was then removed. Most of the WC specimens were small and required two skin-off filets to achieve a minimum sample mass of 20 g. Each filet was cut into dorsal/ventral strips about 2 cm in width, then shuffled prior to being run through a grinder, to provide homogenization. Between samples, all grinding parts and components were thoroughly cleaned with soap and water; multiple solvent rinses; and a final organic-free water rinse.

Each homogenized sample was placed in a beaker and mixed with sodium sulfate solution to remove moisture, and stirred frequently to remove lumps. After one hour, an appropriate volume

of internal standard (IS) solution and LCS were added. The mixture was then extracted for 18 to 24 hours with a solvent solution of methylene chloride and hexane. The extract was concentrated and prepared for acid-base silica gel (ABSG) cleanup. All traces of solvent chemicals other than hexane were removed from the extract. The sample extract was transferred to an ABSG column with hexane, and the eluate was collected and concentrated for analysis for DDTs and PCBs. A small portion of the initial sample homogenate was extracted separately for lipids analysis using a chloroform-methanol solvent. The extracts were analyzed in accordance with the guidance documents listed below.

- EPA Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. EPA-821-R-08-001 (EPA, 2007)
- EPA Method 1668C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. EPA-820-R-10-005 (EPA, 2010)
- A Rapid Method of Total Lipid Extraction and Purification (Bligh-Dyer, 1959)

The specific analytical methods used for fish tissue analyses are listed below.

- Organo-chlorine pesticides (OCPs) by HRGC/HRMS, EPA Method 1699, using a ZB-50 GC column
- PCBs by HRGC/HRMS, EPA Method 1668C, using a ZB-1 GC column
- Total extractable percent lipids (Lipids) by Bligh-Dyer extraction

Table 2-6 lists the individual chemistry analytes with the associated RLs.

2.4 DATA MANAGEMENT SYSTEM

A web-based environmental data management system (eDMS) developed by Synectics, Sacramento, California, was used to manage the data received from all testing labs, including the geotechnical (sediment) and chemistry (sediment, water, and fish tissue) laboratories. The eDMS provided access to the chemistry data for the data validation step (Section 2.5) and, combined with Access software, allowed for the efficient transfer and tabulation of data.

2.5 DATA VALIDATION

The analytical data sets for sediment, water, and fish were reviewed and validated by Veridian Environmental, Inc. (Veridian), Davis, California, following procedures specified in the respective QAPPs (Gilbane, 2013a, 2014, 2016a). For sediment and fish tissue, approximately 10% of the data was subjected to full data validation, and 90% of the data was subjected to

routine data validation. For the water data set, full validation was performed on approximately 23% of the data, and 77% received routine validation. Veridian used an automated data validation system augmented by manual review of all project data. Results from the data validation procedures are discussed in Section 4.0.