

# **FIRST MONITORED NATURAL RECOVERY REPORT**

## ***Data Collections 2013–2016***

**PALOS VERDES SHELF  
OPERABLE UNIT 5 OF THE MONTROSE CHEMICAL CORPORATION  
SUPERFUND SITE  
LOS ANGELES COUNTY, CALIFORNIA**

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## EXECUTIVE SUMMARY

A sampling and analysis program was conducted at Palos Verdes Shelf (PV Shelf), Los Angeles County, California, in support of monitored natural recovery (MNR), a component of the interim remedy set forth in EPA's 2009 Interim Record of Decision (IROD) for PV Shelf. PV Shelf is Operable Unit (OU) 5 of the Montrose Chemical Company Superfund Site, located in Los Angeles, California.

### *Background*

Montrose OU 5 addresses risks to human health and the environment related to a bed of contaminated solids (sediment) on PV Shelf off the coast of the Pacific Ocean in southern California. In regions south of Los Angeles through the 1950s and 1960s, chemical producers (notably the DDT producer Montrose), discharged industrial wastes to the sanitary sewer system operated by the Sanitation Districts of Los Angeles County (Sanitation Districts). As a result, wastewater contaminated with DDTs and PCBs reached the Sanitation Districts' Joint Water Pollution Control Plant (JWPCP) in Carson, California. The contaminants were transported in the treated wastewater stream (JWPCP effluent) through tunnels under the Palos Verdes Hills to the JWPCP ocean outfall system, and were released to the ocean through the outfall diffusers. The diffusers are located about 2 kilometers (km) offshore, in water depths of about 60 meters (m). Suspended solids emitted from the diffusers formed a bed of "effluent affected" (EA) sediment on PV Shelf. The EA bed is contaminated with DDTs and PCBs. It is encountered at water depths of about 40 m to more than 100 m, and it extends along PV Shelf, parallel to the shore, for about 16 km. The DDTs have spread through the environment and impacted marine animals including fish and birds. DDTs have not been detected in the JWPCP waste stream since 2002, and PCBs have not been detected since 1985. However, these persistent substances remain as chemicals of concern (COCs) for Montrose OU 5.

### *Interim Record of Decision*

In addition to MNR, the IROD set forth two other components of the interim remedy for Montrose OU 5: (1) continuation of the PV Shelf Institutional Controls (ICs) program that includes: public outreach and education to increase awareness and understanding of the existing fish consumption advisories and fishing restrictions; monitoring to evaluate and track contaminant concentrations in fish (primarily white croaker [WC] – a fish known to be impacted by DDTs) caught at or near the site

as well as those sold in retail fish markets and served in restaurants; and enforcement of existing commercial and recreational restrictions on WC fishing established by the California Department of Fish and Wildlife (CDFW); and (2) placement of an isolation cap (layer of clean sand) over the most contaminated and erosive area of sediment at PV Shelf. The IROD also promulgated cleanup objectives for the interim cap, and cleanup goals for sediment, for ocean water, and for WC.

#### *Monitored Natural Recovery Program*

The objectives of the MNR program included: (1) gathering data to establish the current condition of the sediment bed and compare findings to IROD cleanup levels; (2) supporting the possible remedial design (RD) of the interim isolation cap; (3) gathering data on current conditions of the water column and comparing findings to IROD cleanup levels; and (4) gathering data on current conditions of two COC-impacted fish species, barred sand bass (BSB) and WC, caught in the vicinity of PV Shelf, and comparing COC concentrations in fish tissue (skin-off filets) to IROD cleanup levels and to levels in fish caught far away from PV Shelf. The MNR sampling program included the elements described below.

- Sediment sampling program. Using sampling approaches and techniques similar to EPA's 2009 baseline sediment assessment, sediment cores were collected in October 2013 using a gravity coring device. Sixty-nine primary cores and 10 replicate cores were collected and processed to yield 1,025 samples and 150 replicate samples. Samples were tested for physical parameters including grain size and bulk density, and for chemical parameters including DDTs, PCBs, moisture content (MC), and organic carbon (OC).
- Water sampling using passive sampling devices (PSDs). PSDs including polyethylene devices (PEDs) and solid-phase microextraction devices (SPMEs) were prepared and then deployed at 17 locations along PV Shelf and at one reference location (at 3 or 4 depths per location). The devices were deployed in September 2013 and retrieved in October 2013, then tested for COCs at an analytical laboratory. A total of 207 PSD samples were tested.
- Water sampling for high resolution testing. Grab samples were collected at depth directly into sample bottles from locations along PV Shelf and from one reference location. The bottles were retrieved and sent to an analytical laboratory for testing of COCs using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The high resolution water study generated 137 primary samples and 11 replicates from 40 locations (at 3 or 4 depths per location).
- Fish collection for high resolution testing. Specimens of BSB and WC were caught from several collection areas extending from Ventura in the north to Huntington Flats in the south. The fishing period ran from June 2014 through August 2016; specimens were sent to an analytical laboratory for processing and testing. The catch yielded 301 samples of fish tissue

(skin-off filets; 143 BSB and 158 WC) that were tested for COCs using HRGC/HRMS, and for lipids.

Chemistry testing of all samples was done in conformance with EPA-approved quality assurance project plans (QAPPs). For each medium, COC chemistry results were organized into groupings as follows:

- Total DDTs – the summation of the o,p'- and p,p'- isomers of DDD, DDE, and DDT
- Total DDT Compounds – the summation of Total DDTs plus p,p'-DDMU and p,p'-DDNU
- Total PCBs (short list) – the summation of 29 individual PCB congeners (used for sediment goals in the IROD)
- Total PCBs (expanded list) – the summation of 46 individual PCB congeners
- OC normalization – for sediment, COC test results were also normalized for OC, in conformance with IROD cleanup goals.
- Bioactive layer – for sediment, COC test results for the 0-8-cm bed-depth interval were analyzed and processed (in addition to the results for the total EA bed), because that interval has been demonstrated to be the bioactive layer at PV Shelf.

For sediment, C Tech's Mining Visualization System was used to estimate average COC concentrations (both dry-weight values and OC normalized values) and total mass, both for the entire EA bed and for the 0-8-centimeter (cm) sediment bed-depth interval.

### *Results of the MNR Program*

For each medium, maximum values were reported for samples collected near or just down-current (northwest) of the diffuser sections of the Sanitation Districts' ocean outfalls, along the 60-m isobath.

#### **Maximum Values of Concentrations of COCs by Medium**

<i>Medium</i>	<i>Total DDTs</i>	<i>Total DDT Compounds</i>	<i>Total PCBs (expanded list)</i>
Sediment in 0-8-cm bed-depth interval (milligrams per kilogram [mg/kg])	76 (1,400)	81 (1,500)	6.2 (140)
Sediment in total bed (mg/kg)	310 (6,840)	350 (7,320)	35 (450)
Water using passive sampling devices (PSDs) (nanograms per kilogram [ng/L])	11	13	0.31
Water using high resolution analyses (ng/L)	1.6	3.3	0.19
Fish (micrograms per kilogram [ug/kg])	2,400	3,200	260

Notes

1. The 0-8-cm bed-depth interval in the sediment bed is the bioactive zone at PV Shelf.
2. Units of concentrations match the units used for cleanup goals in the IROD.
3. For sediment, values in parentheses are OC normalized, and may be for different sediment samples.

Sediment results indicated that widespread deposits of DDT and PCB contamination still exist at PV Shelf. For the 0-8-cm bed-depth interval, a DDT hot spot (an area with dry-weight concentrations exceeding 20 milligrams per kilogram [mg/kg]) remains near the center of the diffuser array. A PCB hot spot (an area with dry-weight concentrations exceeding 1 mg/kg) is also present at the same location. Other observations based on the results of the MNR program are:

- In all three media (sediment, water, and fish), p,p'-DDE and p,p'-DDMU are the dominant isomers of DDT. In sediment, these two chemicals accounted for 50% and 30%, respectively, of the mass of Total DDT Compounds.
- Significant amounts of COCs remain in the sediment bed. Patterns of distribution of COCs in the sediment bed at PV Shelf do not appear to have changed appreciably over time. "Hot spot" areas persist near the outfall diffusers along the 60-m isobath. The outfall area (OA), defined as the general area within 1.5 km of the diffusers, contains roughly 47% of the total COC mass.
- For a significant number of primary-replicate pairs of sediment results for Total DDT Compounds and for Total PCBs (expanded list), the relative percent difference (RPD) values exceeded the project goal of 50%; this is likely an indication of the heterogeneity in the sediment bed.
- For water, the values of maximum COC concentrations at nearly every sample location were greatest at the deepest sample depth (i.e., closest to the sediment bed). Based on the results of high resolution grab water sampling, concentrations exceeded applicable IROD cleanup goals (both human health and ecological) at many locations, most notably at the diffusers and down-current (northwest) of the diffusers.
- For fish, the highest values for maximum COC concentrations and for average COC concentrations were reported in samples from specimens caught in the collection areas nearest the outfall diffusers. This trend was observed both for BSB and WC.
- For each fish collection area, the 95% upper confidence limit (UCL) was calculated for both fish species (BSB and WC). The resulting values are regarded as the exposure point concentrations (EPCs) for the collection area. For DDTs in WC, the EPC exceeded the IROD cleanup goal in the outfall diffusers collection area and in the two areas down-current of the diffusers. For PCBs in WC, the EPC exceeded the IROD cleanup goal in the collection area at the outfall diffusers and at the area immediately down-current. There are no IROD goals for BSB.

### *Time Trends*

Results for each medium were compared to results from previous investigations at PV Shelf.

- DDTs in Sediment. Results from EPA's previous sediment sampling event conducted in 2009 were compared to results from the 2013 event. For Total DDTs in the upper 8 cm of the sediment bed, the respective mean concentrations (average concentrations based on output from the geostatistical model) were 56 mg/kg OC and 77 mg/kg OC. The respective mass estimates of Total DDTs for the upper 8-cm interval were 1.7 metric tons (MT) and 3.6 MT. The respective estimates of mass of Total DDTs for the entire EA bed were 14 MT and 42 MT. The apparent increases in concentrations and total mass were attributed primarily to the heterogeneity of the sediment bed. However, the mass values for both events are significantly less than historical estimates from researchers in the 1990s.
- PCBs in Sediment. Results from EPA's previous event conducted in 2009 were compared to the 2013 event, using the short list of 29 congeners. For Total PCBs in the upper 8 cm of the sediment bed, the respective mean concentrations (average concentrations based on output from the geostatistical model) were 3 mg/kg OC and 5 mg/kg OC. The respective mass estimates of Total PCBs for the upper 8-cm interval were 0.11 MT and 0.28 MT. For the entire EA bed, the respective estimates were 1.0 MT and 2.9 MT. As with DDTs, the apparent increases in concentrations and total mass were attributed primarily to the heterogeneity of the sediment bed.
  - DDTs in Water. Results from a 1997 (high volume) study conducted at PV Shelf by the Southern California Coastal Water Research Project (SCCWRP) indicated that Total DDTs were about 5 nanograms per liter (ng/L) for samples collected along the 40-m and 60-m isobaths, near the ocean bottom, and at locations near the outfall diffusers. This MNR high resolution event showed results ranging from about 0.01 to 1 ng/L for these locations/depths. The corresponding PSD results (2010 and 2013) were higher, ranging from about 3 to 7 ng/L. Rigorous data comparisons and time trend analysis were not possible, due to variabilities in sample collection methods, analytical methods, ocean currents (mixing), and, for PSD events, uncertainties regarding equilibrium dynamics and COC partitioning between the sampling device and the water column, and temperature effects.
  - PCBs in Water. Results from the SCCWRP study indicated that Total PCBs were in the range of 0.4 ng/L for samples collected along the 40-m and 60-m isobaths, near the ocean bottom, at locations near the outfall diffusers. This MNR high resolution event showed results ranging from about 0.005 to 0.1 ng/L for these locations/depths. The corresponding PSD results (2010 and 2013) were higher, ranging from about 0.03 to 0.1 ng/L. Similar to DDTs, rigorous data comparisons and time trend analysis were not possible, due to variabilities in sample collection methods, analytical methods, ocean current (mixing), and, for PSD events, uncertainties regarding equilibrium dynamics, COC partitioning between the sampling device and the water column, and temperature effects.
  - DDTs in Barred Sand Bass. A 2002/2004 study jointly conducted by the National Atmospheric and Oceanic Administration (NOAA) and EPA (collections from August 2002 to June 2003), indicated that the average concentration of total DDTs in BSB caught in the area closest to the outfalls, was 880 micrograms per kilogram (ug/kg), and 300 ug/kg for fish

caught off Bluff Cove/Palos Verdes Point (about 10 km northwest of the outfalls). BSB results published by the Sanitation Districts in 2014 (collected from June to October 2012) were 130 ug/kg and 65 ug/kg for these areas, respectively, and 70 ug/kg for BSB caught off Long Point/Point Vicente (about 5 km northwest of the outfalls). Results from this MNR event (June 2014 to August 2016 collections) showed values of Total DDTs in BSB to be 290 ug/kg, 97 ug/kg, and 140 ug/kg for these areas, respectively. Rigorous data comparisons and time trend analysis for DDTs in BSB were not possible, due to variabilities in sample collection methods, analytical methods, and uncertainties regarding fish age, mobility, and foraging habits.

PCBs in Barred Sand Bass. The 2002/2004 NOAA/EPA study indicated that the average concentration of PCB congeners in BSB caught in the area closest to the outfalls was 98 ug/kg, and 40 ug/kg for fish caught off Bluff Cove/Palos Verdes Point. Based on the most recent available Sanitation Districts BSB data for total Aroclors published in 2014, results were lower than for NOAA and above the data from this MNR report, at 67 ug/kg and 17 ug/kg, from these respective areas, and at 31 ug/kg for BSB caught off Long Point/Point Vicente, about 5 km northwest of the outfalls. Results from this MNR event showed values of 35 ug/kg, 16 ug/kg, and 23 ug/kg for these areas. Rigorous data comparisons and time trend analysis were not possible, due to variabilities in sample collection methods, analytical methods, congeners versus Aroclor lists, and uncertainties regarding fish age, mobility, and foraging habits.

- DDTs in White Croaker. The 2002/2004 NOAA/EPA study (collections from September 2002 to June 2004) indicated that the average concentration of DDTs for WC caught in the area nearest the outfall was 1,400 ug/kg; and for WC caught off Long Point/Point Vicente, about 5 km northwest of the outfalls, the value was 990 ug/kg. Results from this MNR event (October 2014 to July 2016 collections) showed values of Total DDTs to be 770 ug/kg for both of these areas. Results published by the Sanitation Districts in 2016 (collected in November and December 2015) were 2,900 ug/kg and 1,600 ug/kg, respectively. Rigorous data comparisons and time trend analysis were not possible, due to variabilities in sample collection methods, analytical methods, and uncertainties regarding fish age, mobility, and foraging habits. However, the Sanitation Districts has published fish results since the late 1990s, and the data set indicates a dramatic reduction in DDT concentrations in WC since that time.
- PCBs in White Croaker. The 2002/2004 NOAA/EPA study indicated that the average concentration of PCBs for WC caught in the area closest to the outfalls was 350 ug/kg; for fish caught in the area off Long Point/Point Vicente, the value was 120 ug/kg. Results from this MNR event showed values of 82 ug/kg and 120 ug/kg for these same areas. Results published by the Sanitation Districts in 2016 were 270 ug/kg and 150 ug/kg, respectively. Rigorous data comparisons and time trend analysis were not possible, due to variabilities in sample collection methods, analytical methods, congener lists, and uncertainties regarding fish age, mobility, and foraging habits. However, the Sanitation Districts has published fish results since the late 1990s, and data indicate a drop in PCB concentrations in WC.

### *Compliance with IROD*

Results for each medium were compared to the cleanup criteria set forth in the IROD. As indicated in the table below, though cleanup objectives related to the isolation cap appear to have been met, IROD cleanup goals for sediment, water, and fish have not been met.

Overall, conditions at PV Shelf regarding COC contamination in sediment appear to be improving – concentrations in the 0-2-cm bed-depth interval continue to decline, and concentrations in the 0-8-cm bed-depth interval were lower than the performance objectives related to the interim cap described in the IROD, even without the cap. However, significant areas of sediment remain highly contaminated, and COC concentrations in samples of water and fish exceeded the associated IROD cleanup goals, both for DDTs and PCBs. EPA will continue the MNR sampling program to evaluate the effectiveness of MNR and to develop final remediation alternatives for PV Shelf cleanup.

#### **Summary of IROD Compliance**

<b>Medium/COC</b>	<b>Representative value</b>	<b>IROD post-capping objective</b>	<b>IROD interim cleanup level</b>
<b>Sediment (average concentrations)</b>			
<i>Total DDTs (mg/kg OC)</i>	77	78	46
<i>Total PCBs - short list (mg/kg OC)</i>	5	7	7
<i>Total PCBs (mg/kg OC)</i>	10	-	-
<b>Water (human health)</b>			
<i>p,p'-DDE (ng/L)</i>	1.1	-	0.22
<i>Total PCBs (ng/L)</i>	0.19	-	0.064
<b>Water (ecological)</b>			
<i>Total DDTs (ng/L)</i>	1.6	-	1
<i>Total PCBs (ng/L)</i>	0.19	-	30
<b>White Croaker - Outfall Collection Area</b>			
<i>Total DDTs (ug/kg)</i>	1,000	-	400
<i>Total PCBs (ug/kg)</i>	98	-	70

#### Abbreviations

- mg/kg OC - milligrams per kilogram normalized for organic carbon
- ug/kg - micrograms per kilogram (parts per billion)
- ng/L - nanograms per liter (parts per trillion)

#### Notes

1. For Total PCBs, all values are for the expanded congener list, unless otherwise noted.
2. For sediment, all values are for the 0-8-cm bed-depth interval (the bioactive zone at PV Shelf). The representative values are the mean (average) OC normalized concentrations as generated by the current output of the geostatistical model.
3. For water, the representative values are maximum concentrations from the current MNR data set. The representative values for p,p'-DDE and for Total DDTs are from the near-bottom sample for location 4C, and the representative value of Total PCBs is from the mid-column sample at location 7C.
4. For fish, the representative value is the exposure point concentration.



*Lessons Learned*

Difficulties were encountered in duplicating sampling program design and in analyzing time trends, due to inconsistent approaches in past sample collections, laboratory analyses, and data processing. In future MNR monitoring events, approaches to sample collection, laboratory analysis, and data processing should be identical or similar to those used for this MNR study, and the sampling/collection locations used for this study should be reoccupied to the extent practical. This approach will be important for a meaningful comparison of data (“apples to apples”) for examining time trends, assessing accurately the effectiveness of MNR, and determining whether COC concentrations have reached applicable cleanup levels.

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## ACRONYMS AND ABBREVIATIONS

°C	degrees Celsius
%	percent
2D	two-dimensional
3D	three-dimensional
ABSG	acid-base silica gel
ALS	ALS Life Sciences Division Environmental
AWQC	Ambient Water Quality Criteria
BD <sub>d</sub>	dry bulk density
BD <sub>w</sub>	wet bulk density
BSB	barred sand bass
C-13	carbon 13 isotope
CalEPA	California Environmental Protection Agency
CDFG	California Department of Fish and Game
CDFW	California Department of Fish and Wildlife
cm	centimeter(s)
COC	chemical of concern
CSM	conceptual site model
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethene
DDT	dichlorodiphenyltrichloroethane
DGPS	differential global positioning system
DPH	California Department of Health
DOC	dissolved organic carbon
DQOs	data quality objectives
EA	effluent-affected
EDL	estimated detection limit
eDMS	environmental data management system
ELAP	Environmental Laboratory Accreditation Program
EPA	United States Environmental Protection Agency
EPC	exposure point concentration
Eurofins CS	Eurofins Calscience Laboratories, Inc.
FS	Feasibility Study
FSP	Field Sampling Plan
FYR	5-year review
g	gram(s)
g/cm <sup>3</sup>	grams per cubic centimeter
GC	gas chromatography
GCS	Geographic Coordinate System
GC/MS	gas chromatography/mass spectrometry
Gilbane	Gilbane Federal
GIS	geographic information system
GMU	GMU Geotechnical, Inc.

GPC	gel-permeation chromatography
GS	galvanized steel
H:V	horizontal-to-vertical
HRGC/HRMS	high resolution gas chromatography/high resolution mass spectrometry
ICs	Institutional Controls
ID	identification
IRIS	Integrated Risk Information System
IROD	Interim Record of Decision
IS	internal standard
ITSI	Innovative Technical Solutions, Inc.
ITSI Gilbane	ITSI Gilbane Company
JWPCP	Joint Water Pollution Control Plant
$K_f V_f$	SPME water partitioning coefficient
$K_{PEW}$	polyethylene water partitioning coefficient
kg	kilogram(s)
km	kilometer(s)
$km^2$	square kilometers
L	liter(s)
LCS	laboratory control sample(s)
m	meter(s)
$m^3$	cubic meter(s)
MC	moisture content
MDL	method detection limit
mg/kg	milligrams per kilogram (parts per million)
mgd	million gallons per day
MIV	mass inventory volume
mL	milliliter
mm	millimeter(s)
MNR	monitored natural recovery
Montrose	Montrose Chemical Corporation
msl	mean sea level
MT	metric ton(s)
MVS	Mining Visualization System
NAD 83	North American Datum of 1983
ng/L	nanograms per liter (parts per trillion)
NIST	National Institute of Technology and Standards
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
NRDA	National Resource Damage Assessment
OA	outfall area
OC	organic carbon
OCP	organo-chlorine pesticide
OEHHA	Office of Environmental Health Hazard Assessment
OU	Operable Unit
p,p'-DBH	bis(4-chlorophenyl)methanol
p,p'-DBP	bis(4-chlorophenyl)methanone



p,p'-DDA	2,2-bis(4-chlorophenyl)acetic acid
p,p'-DDM	1-chloro-4-[1-(4-chlorophenyl)methyl]benzene
p,p'-DDMS	1-chloro-4-[2-chloro-1-(4-chlorophenyl)ethyl]benzene
p,p'-DDMU	1,1-bis(4-chlorophenyl)-2-chloroethene
p,p'-DDNS	1-chloro-4-[1-(4-chlorophenyl)ethyl]benzene
p,p'-DDNU	1,1-bis(4-chlorophenyl)ethene
p,p'-DDOH	2,2-bis(4-chlorophenyl)ethanol
PBL	Portuguese Bend Landslide
PCBs	polychlorinated biphenyls
PE	performance evaluation
PED	polyethylene device
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
POLA	Port of Los Angeles
POP	persistent organochlorine pollutant
ppb	parts per billion
ppm	parts per million
PRC	performance reference compound
PSD	passive sampling device
psi	pounds per square inch
PV Shelf	Palos Verdes Shelf
PVSTIEG	Palos Verdes Shelf Technical Information Exchange Group
QAPP	quality assurance project plan
QATS	Quality Assurance Technical Services
QC	quality control
QCSR	Quality Control Summary Report
R <sup>2</sup>	coefficient of determination
RA	remedial action
RAC	Remedial Action Contract II
RAO	remedial action objective
RD	Remedial Design
RI	Remedial Investigation
RL	reporting limit
RO	reverse osmosis
ROD	Record of Decision
RPD	relative percent difference
RV	research vessel
SAIC	Science Applications International Corporation
Sanitation Districts	Sanitation Districts of Los Angeles County
SCCWRP	Southern California Coastal Water Research Project
SG	specific gravity
SGC	silica gel cleanup
SOP	standard operating procedure
SPME	solid-phase microextraction
SPI	sediment profile imaging
SRM	standard reference material

SWRCB	(California) State Water Resources Control Board
TN	total nitrogen
TO	Task Order
TOC	total organic carbon
Trustees	(state and federal) Natural Resource Trustees
UCL	upper confidence limit
ug/kg	micrograms per kilogram (parts per billion)
um	micron(s)
USGS	United States Geological Survey
Veridian	Veridian Environmental, Inc.
Vista	Vista Analytical Laboratory
Water Board	California Regional Water Quality Control Board
WC	white croaker
WHO	World Health Organization
WQL	Water Quality Laboratory

## **1.0 INTRODUCTION**

The United States Environmental Protection Agency (EPA), Region IX, conducted a sampling and analysis program of various environmental media at Palos Verdes Shelf (PV Shelf), Los Angeles County, California. PV Shelf is Operable Unit (OU) 5 of the Montrose Chemical Corporation (Montrose) Superfund Site, 20201 Normandie Avenue, Los Angeles, California.

Gilbane Federal (Gilbane; formerly ITSI Gilbane), Concord, California, was EPA's prime contractor for this program conducted under EPA Remedial Action Contract II (RAC) Number EP-S9-08-03, Task Order (TO) 0068. The main purpose of this program is to support monitored natural recovery (MNR) of PV Shelf. MNR is a component of the interim remedy for the site, as described in the Interim Record of Decision (IROD) for Montrose OU 5, signed by EPA in 2009.

To implement the MNR component, EPA gathers data periodically to characterize various environmental media at the site, including sediment, water, and fish; the data may also be used to support the possible remedial design (RD) of an interim isolation cap, a second component of the interim remedy. EPA will also use data from this program to develop the Final Record of Decision (ROD) for PV Shelf.

### **1.1 HISTORY OF MONTROSE OU 5**

Since 1937, the Joint Water Pollution Control Plant (JWPCP) in Carson, California, operated by the Sanitation Districts of Los Angeles County (Sanitation Districts), has sent treated wastewater (effluent) to ocean outfalls at White Point on the Palos Verdes Peninsula. From the 1950s to 1971, the Montrose plant on Normandie Avenue discharged process wastes from the manufacture of dichlorodiphenyltrichloroethane (DDT) into the local municipal sewer system, where the wastes entered the wastewater stream. The wastewater was treated at JWPCP and subsequently discharged to the Pacific Ocean by way of the Palos Verdes Hills tunnels and the White Point outfalls. Details on the White Point outfalls, their diffusers (emitters), and the history of JWPCP emissions are available in the Sanitation Districts' references cited herein (Sanitation Districts 2006, 2012, and 2016). Until polychlorinated biphenyls (PCBs) were banned in 1976, PCBs from various other local industries were also present in the waste stream treated at JWPCP. In 1971, annual mass emissions from JWPCP were estimated at 167,000

metric tons [MT] of effluent solids, containing 21 MT of DDT and 5.2 MT of PCBs (Science Applications International Corporation [SAIC], 2004). Montrose stopped discharging DDT wastes to the sewer system in 1971, but damage to the natural environment, notably the collapse of the California brown pelican population due to DDT-related egg-shell thinning, already had occurred.

Due to DDT contamination, the State of California issued an interim health advisory in 1985 discouraging human consumption of white croaker (WC) fish. Subsequently, in 1990, the California Department of Fish and Game (CDFG; now the California Department of Fish and Wildlife [CDFW]) closed the area at PV Shelf to commercial fishing for WC.

In 1994, five state and federal Natural Resource Trustees (Trustees), issued a Natural Resource Damage Assessment (NRDA) documenting the ecological impacts caused by DDT- and PCB-contaminated sediment in the PV Shelf area. Major conclusions of the NRDA are summarized below.

- The effluent-affected (EA) sediment formed a shallow deposit varying in thickness from 5 centimeters (cm) to 1 meter (m), and covering 44 square kilometers (km<sup>2</sup>).
- Concentrations of chemicals of concern (COCs; i.e., DDT compounds and PCBs) varied with depth in the deposit, with the highest concentrations buried under cleaner, but still contaminated, sediment.
- An estimated 110 MT of DDT compounds and 10 MT of PCBs were mixed within the EA sediment (Lee et al., 1994).

The NRDA findings were used as the basis for EPA's conceptual site model (CSM) for PV Shelf as presented in the Remedial Investigation (RI) report (EPA, 2007b) and in the IROD (EPA, 2009b).

Since the 1970s, loading rates of contaminated suspended solids emitted through the Sanitation Districts' White Point outfalls have diminished due to several factors, including: (1) industrial pre-treatment programs related to the Clean Water Act of 1972; (2) the closures of several local industrial facilities, including the 1982 closure of the Montrose Normandie Avenue plant (now the Montrose Superfund Site); and (3) the Sanitation Districts' secondary treatment of wastewater at JWPCP, which was initiated in November 1983 and fully on-line in November 2002. DDTs have not been detected in JWPCP effluent since 2002, and PCBs have not been

detected in JWPCP effluent since 1985 (Sanitation Districts, 2012). Sanitation Districts continues to operate JWPCP and the White Point outfalls, serving 2.5 million southern California residents and 2,300 industries, treating an average of 273 million gallons per day (mgd) of wastewater (Sanitation Districts, 2012).

Since 1994, organizations including the Sanitation Districts and the Southern California Coastal Water Research Project (SCCWRP), have contributed to EPA's understanding of PV Shelf through technical studies. EPA over the years has directly sponsored and funded field studies at PV Shelf, including assessing degradation of COCs, modeling sediment transport, and tracking fish movements. In 2009, as part of the MNR component of the interim remedy, EPA conducted a baseline sampling event of the sediment bed at PV Shelf (ITSI Gilbane, 2013b). The MNR study presented herein is a continuation of the MNR remedy component.

## **1.2 SITE DESCRIPTION**

PV Shelf encompasses a bed of contaminated solids (sediment) emitted from the wastewater outfall system that has settled on the seafloor in the Pacific Ocean at water depths varying from about 40 m to 200 m or greater. The bed of contaminated sediment is situated on the western edge of the North American continental shelf off the Palos Verdes Peninsula in southern California. The distance from the shoreline to the inshore edge of the sediment bed (approximate water depth = 40 m) is about 1.5 kilometers (km). Catalina Island, one of the Channel Islands, is the closest island to PV Shelf, at a distance of about 42 km.

The sediment bed varies in width from about 1.5 to 4 kilometers, and is about 25 km in length. The continental shelf in this area slopes in the seaward direction at about 1 to 4 degrees. A shelf break (i.e., the zone of transition from the relatively flat shelf to the steeper continental slope) occurs at water depths of 70 to 100 m. The seafloor then drops sharply at a slope of about 13 degrees to a water depth of 800 m (Lee, 1994). Figure 1-1 shows the PV Shelf Study Area with bathymetry (depth) isobaths. EA sediment deposits historically have been encountered outside the Study Area on the shelf break and even the shelf slope itself, in ocean water as deep as 500 m (Sanitation Districts, 1992).

Previous researchers have surmised that materials from the Portuguese Bend Landslide (PBL) and other landslides on the Palos Verdes Peninsula have settled on the ocean floor and mixed

with the contaminated solids discharged from the Sanitation Districts' outfalls, resulting in a general enlargement of the EA deposit (Kayen et al., 2002).

The EA bed at PV Shelf generally is distinguishable from the underlying native sediment bed due to differing physical and chemical properties, e.g., higher organic carbon (OC); higher moisture content (MC); lower mean grain size; lower dry bulk density ( $BD_d$ ); and higher COC concentrations (Lee et al., 2002). Previous investigators have described a three-layer characterization of the vertical sediment profile at PV Shelf, as follows (EPA, 2009b):

- Surficial sediment – Shallow sediment in the 0-20-cm bed-depth interval (though this interval can vary widely) has relatively low to moderate DDT concentrations. Characteristics of this layer conform to deposition of relatively less contaminated material and physical reworking by waves, currents, and benthic invertebrates.
- Heavily contaminated sediment – Below the shallow sediment, a layer with low values of  $BD_d$  and high DDT concentrations is encountered. The thickness of this layer varies along PV Shelf, but appears to be greatest near the diffuser sections of the Sanitation Districts' outfalls.
- Native sediment – Beneath the heavily contaminated sediment lies the native sediment bed; the bed generally is sandy and is coarser and less cohesive than the layers above. It also is further characterized by higher values of  $BD_d$  and lower concentrations of COCs and OC.

Investigations have shown that DDT at PV Shelf has undergone significant degradation through reductive dechlorination to form several breakdown products, including p,p'-DDE and 1,1-bis(4-chlorophenyl)-2-chloroethene (p,p'-DDMU), while PCBs have not exhibited biodegradation at PV Shelf (Eganhouse et al., 2008). Figure 1-2 illustrates potential microbial degradation pathways for DDT at PV Shelf, and indicates that p,p'-DDMU and 1,1-bis(4-chlorophenyl)ethene (p,p'-DDNU) have been detected historically in samples of PV Shelf sediment (Eganhouse et al., 2007).

In 2002, the following characteristics of the EA deposit were reported (Lee et al., 2002):

- The maximum thickness of the EA deposit was about 70 cm.
- The approximate volume of the EA bed was 10 million cubic meters ( $m^3$ ).
- About 70 percent (%) of the volume was present in water depths less than 100 m.
- The EA bed exhibited strong spatial continuity, notably in the alongshore direction.
- The dominant direction for transport of sediment was to the northwest.

Estimates of the mass of DDTs at PV Shelf by previous researchers have varied greatly, ranging from about 60 MT to 120 MT (Lee, H.J., 1994; Murray et al., 2002; see Section 4.1.2 of this report). The mean concentration of DDTs in surface sediment (non-OC normalized) at the shelf has been reported as 12 parts per million (ppm); the mean concentration of PCBs (non-OC normalized) has been reported as 0.69 ppm (EPA, 2009b).

More details on PV Shelf and the origin and fate and transport of COCs found at the site are available in several sources, including those listed below.

- *The Distribution and Character of Contaminated Effluent-Affected Sediment, Palos Verdes Margin, Southern California, Expert Report* (Lee, H.J., 1994)
- *Final Palos Verdes Shelf Superfund Site Remedial Investigation Report* (CH2M Hill, 2007) <https://www3.epa.gov/region9/superfund/pvshelf/pdf/pvs-remediation-inv.pdf>
- *Feasibility Study (FS), May 2009, Palos Verdes Shelf, Operable Unit 5 of the Montrose Chemical Corp. Superfund Site* (EPA, 2009a) <https://www3.epa.gov/region9/superfund/pvshelf/pdf/final-feas-study-may09.pdf>
- *Interim Record of Decision, Palos Verdes Shelf, Operable Unit 5 of the Montrose Chemical Corporation Superfund Site, Los Angeles County, California* (EPA, 2009b) <https://www3.epa.gov/region9/superfund/pvshelf/pdf/PvsIrodFinal.pdf>

### 1.3 DESCRIPTION OF INTERIM REMEDY

The interim remedy as described in the IROD has the following components (EPA, 2009b):

- Continue the existing Institutional Controls (ICs) program.
- Monitor natural recovery to achieve specific remedial action objectives (RAOs).
- Place an in-situ isolation cap (layer of clean sand) over the most contaminated and erosive area of sediment. Features of successful cap implementation are described below.
  - The cap would reduce immediately the mean DDTs concentration in shelf surface sediment to 78 milligrams per kilogram (mg/kg) OC.
  - Natural recovery would reduce the mean DDT concentration in surface sediment to an interim cleanup level of 46 mg/kg OC (double the cleanup level of 23 mg/kg OC) by the first post-cap 5-year review (FYR).
  - The cap would reduce immediately the mean PCB concentrations in surface sediment across the shelf to the interim cleanup level of 7 mg/kg OC.

Specific RAOs promulgated in the IROD include the following (EPA, 2009b):

- Reduce to acceptable levels the risks to human health from ingestion of fish contaminated with DDTs and PCBs.

- Achieve the goal of 400 micrograms per kilogram (ug/kg) DDTs and 70 ug/kg PCBs in WC.
- Maintain the ICs program that aims to prevent contaminated fish from reaching markets and educates anglers on safe fish consumption practices.
- Achieve the interim goal of mean DDT concentrations in surface sediment of 46 mg/kg OC Total DDTs in surface sediment (double the cleanup level of 23 mg/kg OC) and PCBs of 7 mg/kg OC by the first FYR.
- Reduce to acceptable levels the risks from DDTs and PCBs to the ecological community (i.e., benthic invertebrates and fish) at PV Shelf.
  - Support the Trustees' strategies to sustain wildlife recovery.
- Reduce DDTs and PCBs in water to meet EPA's Ambient Water Quality Criteria (AWQC) as cited in the IROD:
  - Achieve the human health AWQC for DDT (p,p'-DDE = 0.22 nanograms per liter [ng/L]) within 30 years of remedial action (RA).<sup>1</sup>
  - Collect and assess PCB data to determine the schedule to meet human health AWQC for PCBs (i.e., 0.064 ng/L) by the first FYR.
- Minimize impacts to sensitive habitats and biota during cap placement by the following:
  - Develop a monitoring program to protect kelp beds.
  - Use low-impact techniques, measure the speed of ocean currents and COCs in the water column, and monitor sediment resuspension. Stop work if site-specific standards are exceeded.

#### 1.4 OBJECTIVES OF THE SEDIMENT SAMPLING PROGRAM

The area studied during the 2013 sediment sampling program focused on the portion of the PV Shelf Study Area from Palos Verdes Point on the northwest to Point Fermin on the southeast, i.e., the main part of the EA sediment unit. The *Final Sampling and Analysis Plan for Sediment Sampling, Part I- Quality Assurance Project Plan* (QAPP; ITSI Gilbane, 2014) provides a detailed description of the project objectives. These are summarized below.

- Determine whether the values for the mass of COCs in the sediment bed are continuing to decrease; i.e., is the trend of recovery indicated by the 2009 sediment results evident?

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<sup>1</sup> The AWQC (ecological) for "DDT and its metabolites" was published in 1980 using guidelines for establishing water quality criteria under Section 304 of the Clean Water Act of 1977. The AWQC (human health) for p,p'-DDE was published in 2002 using methodology for establishing AWQCs for protection of human health (referred to as the "2000 Methodology" [EPA, 2000a]), which incorporated scientific advances in cancer and non-cancer risk assessments, exposure assessments, and bioaccumulation factors in fish.



- Determine whether installation of the isolation cap will be necessary to attain the cap-related cleanup goals stipulated in the IROD.

The desired data include the following:

- Physical parameters pertinent to evaluating (modeling) sediment transport and possibly designing the interim isolation cap. Parameters include grain size (particle size); wet sediment bulk density (BD<sub>w</sub>); specific gravity (SG); and MC. Values of BD<sub>w</sub> and MC are also used in calculating concentrations of COCs and contaminant mass.
- Chemical parameters pertinent to evaluating the progress of MNR and selecting areas where an isolation cap will be placed. Parameters include concentrations of the prevalent DDT forms encountered at PV Shelf; individual PCB isomers; and total organic carbon (TOC).
- The list of DDTs and their breakdown products include the o,p'- and p,p'- isomers of DDT; dichlorodiphenyldichloroethene (DDE); and dichlorodiphenyldichloroethane (DDD)<sup>2</sup>. These chemicals have been recognized by toxicity databases, including EPA's Integrated Risk Information System (IRIS).
- Additional chemicals of interest for PV Shelf include p,p'-DDMU and p,p'-DDNU, as these have been recognized as DDT breakdown products in sediment at PV Shelf (Eganhouse et al., 2008).
- The PCB congeners of interest for PV Shelf include 46 individual congeners (see Section 2.1.6.2).

## 1.5 OBJECTIVES OF THE WATER SAMPLING PROGRAM

### 1.5.1 High Resolution Sampling Program

The *Final Quality Assurance Project Plan – Water Sampling Program* (QAPP; Gilbane Federal, 2014) presents details for the goals and objectives of the project. The objectives of the sampling program conducted in 2015 are summarized below.

- Assess water column concentrations of DDTs and PCBs at very low concentrations for the purpose of evaluating the extents of dissolved-phase contamination.
- Determine whether water column concentrations of DDTs and PCBs exceed the AWQC values presented in the IROD.

The desired data are described below.

- The IROD for PV Shelf states that AWQC for DDTs and PCBs are being considered in assessments of the progress of site cleanup (EPA, 2009). Because these criteria are less than 1 ng/L, EPA determined that high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) methods would be used for testing water column

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<sup>2</sup> The o,p'- and p,p'- isomers are also referred to as 2,4'- and 4,4'- isomers.

samples at PV Shelf. This sampling event would be the first time that high resolution analytical techniques were used to analyze samples of the PV Shelf water column.

- The analyte lists for DDT isomers and PCB congeners will be the same as for the current sediment program.
- The water sampling locations were to be established at sediment coring locations, and depth profiles would be based on recent deployment depths of passive sampling devices (PSDs).
- The high-resolution data would be compared to water column data acquired by previous PSD sampling programs and other programs that used filtered, high-volume pumped samples.

### **1.5.2 PSD Program**

The *Final Quality Assurance Project Plan for Passive Sampling for Persistent Organochlorine Pollutants (POPs) in the Water Column of the Palos Verdes Shelf (2013)* (Fluen Point Environmental, 2013) presents details for the goals and objectives of the project. The objectives of the sampling program conducted in 2013 are to:

- Assess whether using performance reference compounds (PRCs) addresses the problem of offset in the 2010 results from polyethylene devices (PEDs) and devices with solid-phase microextraction fibers (SPMEs);
- Measure the dissolved concentrations of DDTs and PCBs in different horizons of the water column and along a spatial gradient away from the highly contaminated zone and at stations up-current of the most highly contaminated sediment; and
- Compare dissolved DDT and PCB concentrations to those measured using the same (i.e. PED), and similar (i.e. SPME) methods in 2010.

The desired data are described below.

- Analyte mass in the passive samplers, temperature, dissolved organic carbon (DOC) and salinity will enable the calculation of dissolved concentrations in the water column.
- Contaminants to be measured include congeners of DDT and their breakdown products (including p,p'-DDMU and p,p'-DDNU), and forty-four PCB congeners.

## **1.6 OBJECTIVES OF THE FISH SAMPLING PROGRAM**

The *Final Quality Assurance Project Plan – Fish Sampling Program* (QAPP; Gilbane, 2016a) presents objectives and informational inputs for the project. The goals of the sampling program conducted from 2014 through 2016 are summarized below.

- Determine fish tissue concentrations of DDTs and PCBs at very low concentrations to assess contaminant trends over time.

- Determine whether installation of the isolation cap will be necessary to attain the cap-related fish cleanup goals recommended in the IROD.
- Determine whether concentrations of DDTs and PCBs in fish exceed IROD fish cleanup goals.

The proposed data inputs would include the following:

- The IROD for PV Shelf presents cleanup goals to reduce the risk to human health from the consumption of WC caught in the vicinity of PV Shelf; the values are 400 ug/kg for DDTs and 70 ug/kg for PCBs (EPA, 2009). Based on previous fish testing for the EPA ICs program at PV Shelf, the desired reporting limits (RLs) for fish testing were established at less than 1 ug/kg; this would require HRGC/HRMS methods.
- The IROD identifies monitoring for DDTs and PCBs in WC as a key element of MNR at PV Shelf. The QAPP developed for fish (Gilbane, 2016a) describes how the seven EPA fish collection areas and numbers of samples were derived by consensus during the Palos Verdes Shelf Technical Information Exchange Group (PVSTIEG) scoping meeting held in January 2014. Barred sand bass (BSB) was also added as an indicator species for this study because high concentrations of DDTs and PCBs had been found in this species during previous studies (National Oceanic and Atmospheric Administration [NOAA]/EPA, 2007). Historically there has been a high catch frequency for BSB reported by boat-based anglers near PV Shelf, and, during EPA's fish tracking study previously conducted at PV Shelf, BSB demonstrated site fidelity to PV Shelf (Lowe, 2013).
- The fish tissue data set will be compared to the IROD cleanup goals and used to calculate parameters for each fish collection area. These parameters include minimum and maximum concentrations, average concentrations, and exposure point concentrations (EPCs) of DDTs and PCBs.

## **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<sup>2</sup>.

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  $\pm 1.5$  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 (°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  $\mu\text{m}$ . 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):  $^{13}\text{C}$ -4,4'-DDT,  $^{13}\text{C}$ -4,4'-DDE,  $^{13}\text{C}$ -4,4'-DDD,  $^{13}\text{C}$ -PCB28,  $^{13}\text{C}$ -PCB52,  $^{13}\text{C}$ -PCB118, and  $^{13}\text{C}$ -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:  $^{13}\text{C}$ -4,4'-DDE, PCB 50,  $^{13}\text{C}$ -PCB 52, PCB 98,  $^{13}\text{C}$ -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  $-20^{\circ}\text{C}$  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° 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.

## **3.0 RESULTS**

This section presents the results of the MNR sampling program, including collection of sediment cores, generation of sediment samples, collection of water samples, collection of fish, and results of laboratory tests on samples of sediment, water, and fish tissue.

### **3.1 SEDIMENT**

#### **3.1.1 Core Retrieval**

Daily cruises for core collection were conducted on October 15-17, 21-23, and 28-29, 2013. Appendix E includes cruise notes and video recordings of the coring drops. Primary and replicate cores were collected as planned (Sections 2.1.1 and 2.1.2). Horizontal accuracy was  $\pm 3$  m, and the actual sediment core locations were within 30 m of target locations. The coring crew experienced one bad weather day (heavy winds, high seas) on October 28, 2013; otherwise, core retrieval operations went as planned.

Core retrieval was difficult at location BA10C on the 70-m isobath, where three drops of the coring device resulted in lack of recovery (likely due to rocky substrate); one drop of the coring device resulted in the liner coming off; and a satisfactory core 25 cm in length was retrieved on the fifth drop. At BA2B on the 150-m isobath and BA2DC on the 40-m isobath, two drops were required to obtain a satisfactory core. At BA3DC on the 30-m isobath, three drops were made to obtain a satisfactory core. At OA24 on the 70-m isobath, five drops were made to obtain a usable core. At several locations, damage to the coring device or the liners in the coring device occurred during the operation, requiring additional drops. For the eight days of core collection, the daily coring success rates (defined as the number of usable retrieved cores divided by the number of drops) were 86, 94, 63, 48, 47, 73, 100, and 75%. Tables 3-1 and 3-2 present coordinates of the cores collected for the shelf-wide area and OA, respectively.

Table 3-3 presents the lengths of the sediment cores collected. The maximum core length was 86 cm at location BA4DC (offshore of Portuguese Bend). Other cores with lengths of 80 cm or more were retrieved at location BA5DC (also offshore of Portuguese Bend), and at locations OA05, OA08, and OA11 (near the Sanitation Districts' outfall diffusers). The overall average length of successfully retrieved cores was approximately 53 cm. Average core lengths along individual isobaths were as follows: 56 cm for the 40-m isobath; 70 cm for the 60-m isobath; 32

cm for the 100-m isobath; and 50 cm for the 150-m isobath. For the 10 locations where replicates were collected, ratios of primary core lengths to replicate core lengths varied from 1.5:1 (BA2B) to 1:0.8 (OA16).

### **3.1.2 Generation of Sediment Samples**

Cores were cut into slices at JWPCP during two separate events, one event occurring from November 18-22, 2013, and another event conducted from December 9-11, 2013. Core cutting was conducted by Sanitation Districts' staff at the WQL at JWPCP. Each slice had an approximate thickness of 2 cm. Cuts were made until the bottom remaining material was less than 2 cm in thickness, and any remainder was discarded. A total of 2,084 sediment slices was generated from the sediment cores collected during the 2013 sampling event.

### **3.1.3 Results of Physical Tests – Sediment**

As described previously, GMU composited sediment samples before conducting physical tests. A total of 1,215 samples was generated. Sample counts were as follows: 516 samples were generated for the shelf-wide cores; 44 samples were generated for the shelf-wide replicate cores; 540 samples were generated for the OA cores; and 111 samples were generated for the OA replicate cores.

#### *3.1.3.1 Grain Size*

Values of percent retained and cumulative percent retained were reported for standard sieve and hydrometer tests, along with corresponding phi scale values based on the Wentworth Classification System. The phi scale is a base-two logarithmic scale with the negative exponent of the grain size in millimeters (mm). Table 3-4 presents grain-size data for cores along the 60-m isobath, where the highest COC concentrations typically are centered (Lee, H.J., 1994). Cores collected northwest of the outfalls had lower average sand content and higher average clay content than cores collected southeast of the outfalls. Summary tables of grain size test results for shelf-wide and OA samples are provided in Appendices F and G, respectively.

#### *3.1.3.2 Bulk Density, Moisture Content, and Specific Gravity*

Appendices H and I present tables showing values of  $BD_w$  and SG (as reported from the geotechnical laboratory) and MC values (as reported from the chemistry laboratory) for the shelf-wide and OA samples, respectively. The SG value is the ratio of the density of the dry-

solids fraction of the sample to the density of water. The tables also report computed values of  $BD_d$ , calculated as follows:

$$BD_d = \frac{BD_w}{1+W}$$

where:

- $BD_d$  = dry bulk density of the sediment in grams per cubic centimeter ( $g/cm^3$ )
- $BD_w$  = wet bulk density of the sediment in  $g/cm^3$
- $W$  = fractional moisture content (non-dimensional)

Ranges of values in single samples were as follows:

- MC values ranged from about 16% in core BA6B (located on the 150-m isobath, in the 44-48-cm bed-depth interval), to about 78% in core BA4B (on the 150-m isobath, in the 8-12-cm interval).
- $BD_d$  values ranged from 0.62  $g/cm^3$  in core BA8C (located on the 70-m isobath near the Sanitation Districts' outfall diffusers, in the 16-20-cm bed-depth interval), to 1.6  $g/cm^3$  in core BA6B (on the 150-m isobath, in the 44-48-cm bed-depth interval).
- SG values ranged from 2.05 in core BA8C (located on the 60-m isobath, in the 20-24-cm bed-depth interval), to 2.86 in core OA18 (on the 90-m isobath, in the 2-4-cm bed-depth interval).

For the 0-8-cm interval, average values over all cores were 39% for MC, 1.06  $g/cm^3$  for  $BD_d$ , and 2.68 for SG. For the core intervals below 8 cm, the average values were 37% for MC, 1.14  $g/cm^3$  for  $BD_d$ , and 2.66 for SG. MC testing was not possible for BA10C for the 0-2-cm interval due to insufficient sample volume; thus, the  $BD_d$  value was not calculated for this sample.

### **3.1.4 Results of Chemistry Tests – Sediment**

Appendices J and K present test results for TOC and DDT analyses of samples derived from the shelf-wide and OA cores, respectively. Appendices L and M present the results for PCB tests for the shelf-wide and OA samples, respectively. Appendix N includes the complete reports from the analytical laboratory.

#### **3.1.4.1 Total Organic Carbon**

Reported values of TOC for single samples ranged from 0.54% in core BA10C (located on the 60-m isobath southeast of the Sanitation Districts' diffusers, in the 16-20-cm bed depth interval), to 19% in core BA8C (on the 60-m isobath, in the 16-20-cm interval). Table 3-4 lists the TOC



values for cores collected along the 60-m isobath. Values generally were higher for cores northwest of the Sanitation Districts' outfalls than for cores southeast of the outfalls.

Coefficients of determination ( $R^2$ ) were calculated using Microsoft Excel for TOC concentrations versus concentrations of Total DDT Compounds, and TOC concentrations versus Total PCBs (expanded list). The results showed good (albeit non-linear) correlations with concentrations of Total DDT Compounds ( $R^2 = 0.73$ ) and with Total PCBs ( $R^2 = 0.79$ ). (An  $R^2$  value of 1.00 indicates a strong correlation; a value of 0 indicates no correlation.) Appendix O includes graphic representations of these correlations.

#### *3.1.4.2 DDTs in Sediment*

Results of individual DDT analytes were organized into the two DDT groupings (summations) listed below (see Appendices J and K).

- Total DDTs is the summation of the o,p'- and p,p'- isomers of DDD, DDE, and DDT.
- Total DDT Compounds is the summation of Total DDTs plus p,p'-DDMU and p,p'-DDNU.

One DDT form was detected in at least one sample from every core, and at least one DDT form was detected in every sample from 36 out of 37 shelf-wide cores and in all 35 OA cores. Values of Total DDT Compounds for a single sample ranged from 1.1 ug/kg in core BA5BR (located on the 150-m isobath, in the 56-60-cm bed-depth interval) to 350,000 ug/kg in core BA8C (on the 60-m isobath, in the 16-20 cm interval). The most prevalent DDT compounds – both in terms of the number of detections and the magnitude of concentrations – were p,p'-DDE and p,p'-DDMU. For the entire sediment data set, concentrations of p,p'-DDE showed moderate correlation with concentrations of p,p'-DDMU ( $R^2 = 0.65$ ; see Appendix O). The parent compound DDT was reported only at low relative concentrations. Table 3-5 shows average concentrations of the DDT groupings in the 0-8-cm bed-depth interval of each core. Figure 3-1 is an interpretive rendering of these average concentrations of Total DDTs in the 0-8-cm bed-depth interval. Figure 3-2 shows an exaggerated vertical profile of interpretive DDTs along the 60-m isobath, where the diffuser portions of the 90-inch and 120-inch outfalls (the outfalls that Sanitation Districts typically operates) are located, and where contaminant concentrations in sediment are highest.

### 3.1.4.3 PCBs in Sediment

Results for individual PCB congeners were summarized into two groups: Total PCBs – short list (the congener list previously used for the 2009 sediment data set), and Total PCBs – expanded list (see Appendices L and M). At least one PCB congener was detected in at least one sample from every core collected. Reported detections of Total PCBs in single samples ranged from 0.14 ug/kg in core BA5B (located on the 150-m isobath, in the 52-56-cm bed-depth interval) to 17,000 ug/kg in core BA8C (on the 60-m isobath, in the 32-36-cm interval). PCBs were not detected at the deepest intervals in the 23 cores with at least one sample interval with no detections; for the other 44 cores, PCBs were detected in samples generated from every bed-depth interval in the core. Table 3-6 shows average concentrations of Total PCBs in the 0-8-cm bed-depth interval of each core. Figure 3-3 shows interpretive concentration contours of the average concentrations of Total PCBs (short list) for the 0-8-cm interval without OC-normalization. The bottom half of Figure 3-4 shows a cross section of the sediment bed showing Total PCBs (short list) along the 60-m isobaths for the 2013 data set, again without OC normalization. Figures 3-5 and 3-6 are corresponding figures using the expanded list of Total PCBs.

### 3.1.5 OC Normalization of DDTs and PCBs

EPA's interim remedy in the IROD is based on contaminant concentrations in sediment after normalization for OC (EPA, 2009b). Researchers have reported that the toxicity of nonionic organic chemicals (such as DDTs and PCBs) in sediment appears to correlate well with concentrations of contaminants in the sediment OC fraction, but does not correlate well with the overall dry weight concentrations of the chemicals, i.e., the bioavailability of contaminants is related to the OC fraction (DiToro et al., 1991; Michelsen, T.C., 1992). For these reasons, similar to the 2009 sediment data processing, calculations were performed on the 2013 sediment laboratory data to provide normalization for OC, as follows:

$$\mu\text{g} / \text{kg OC} = \frac{\mu\text{g} / \text{kg dry weight}}{\text{kg TOC} / \text{kg dry weight}}$$

where:

$$\begin{aligned} \mu\text{g}/\text{kg OC} &= \text{micrograms of the chemical per kilogram of organic carbon} \\ \mu\text{g}/\text{kg dry weight} &= \text{micrograms of the chemical per kilogram of dry weight sample} \\ \text{kg TOC}/\text{kg dry weight} &= \text{percent TOC in dry weight sample expressed as a decimal,} \end{aligned}$$

e.g., 1% TOC = 0.01

For example:

$$\frac{650 \mu\text{g Total DDTs} / \text{kg dry weight}}{0.01 \text{ kg TOC} / \text{kg dry weight}}$$
$$= 65,000 \mu\text{g Total DDTs} / \text{kg OC}$$

Table 3-5 shows the OC normalized average concentrations of the DDT groupings in the 0-8-cm bed-depth interval of each core. Table 3-6 shows normalized concentration of PCBs.

### 3.1.6 Results of Geostatistical Modeling – Sediment Data

All chemical results were entered into ARC-GIS and MVS software. The software packages were used to generate concentration contour plots and to calculate characteristics of the EA sediment bed, including mass of COCs. The computational approach used by the MVS model is described below.

- In the model input, the value for the horizontal-to-vertical (H:V) anisotropy was set to 20,000.
- The 2013 sediment data set was used to extrapolate values of  $BD_d$  and COC concentrations at each of the 2.3 million individual cells. The MVS model used a computational approach called cell averaging.
- The model calculated a mass inventory volume (MIV) for each cell by multiplying the  $BD_d$  value by the COC concentration. Eight DDT analytes were calculated individually; the PCB congeners were grouped into a summation (Total PCBs) and then multiplied by the  $BD_d$ .
- The model extrapolated these MIV values to generate an MIV for each cell node.
- The nodal MIVs were summed.
- The respective summations were divided by the number of nodes to attain average MIV values.
- The average MIV values were then multiplied by the modeled volume to produce the total mass.

Table 3-7 lists the average values of contaminants across the EA bed, and includes estimates in the 0-8-cm bed-depth interval. Table 3-8 lists the estimates of contaminant mass. As previously mentioned, a report with full details of the MVS modeling effort and output is included in Appendix C.

## 3.2 WATER RESULTS

### 3.2.1 Grab Sampling Events

Grab samples of the water column were collected during three field deployments in 2015. In developing an optimal approach for collecting water samples at depth, a pilot test was conducted in March 2015 by staff from Kinnetic Laboratories, Inc., Carlsbad, California, and the Sanitation Districts' *Ocean Sentinel*. The pilot test assessed the feasibility of collecting a water sample directly into a 2.5-L sample bottle. Several samples were successfully collected during this cruise. A second sampling cruise was conducted from September 15 through September 25, 2015. A third cruise on November 30, 2015, was conducted using Kinnetic's 10-m RV *D.W. Hood*. This cruise was successful in re-collecting sample BA6DC-WO20-1115-1 (the original sample bottle had been broken during transport).

Sixty-nine primary water samples were collected from three depths at 23 sampling locations, and 68 water samples were also collected from four depths at 17 sampling locations where PSD samples had been collected previously. A total of 137 primary samples, 11 field replicates, and three equipment rinsate samples was collected and submitted to ALS for high resolution analyses.

During each sampler deployment, the boat propellers were stopped for variable amounts of time depending on the location and position of the wire cable and sampler trip rope, to avoid tangling the sampling gear. Without propulsion, the boats may have drifted, leading to possible positioning variances estimated to be as much as two boat lengths (i.e., 40 m for the Sanitation Districts' *Ocean Sentinel*, and 20 m for Kinnetic's *D.W. Hood*). Table 3-9 summarizes the grab sample collection data. Appendix P contains cruise notes and field notes. Videos of the sample collection are also included.

### 3.2.2 DDTs in the Water Column

Appendix Q presents tables of DDT test results organized by grid transect. Detected results for DDT analytes in water were reported by the testing laboratory in ng/L using three significant figures. As was done for sediment data, results for individual DDT analytes were organized into summations of Total DDTs and Total DDT Compounds. Non-detects were assigned values of zero in calculating the summations. The summations are included in Appendix Q.

Figures 3-6 and 3-7 present concentrations of p,p'-DDE for the water column at each sample location for the western and eastern sectors of the sampling area, respectively. Contaminant concentrations are shown in relation to vertical distance in the water column above the ocean bottom for each sample. Figures 3-8 and 3-9 show concentrations of Total DDTs in the same manner. Tables 3-10, 3-11, and 3-12 show results for Total DDT Compounds (all DDT forms combined) along the 150-m, 60-m, and 40-m isobaths, respectively; sample locations were grouped by distance relative to the Sanitation Districts' outfall diffusers.

A DDT isomer was detected in at least one sample collected at each location. All eight DDT isomers were reported in one sample (BA5DC-WO38-0915-1, a mid-column sample down-current of the outfall diffusers). The DDT compound most frequently detected was p,p'-DDE, and in the clear majority of samples, this compound and p,p'-DDMU were detected at concentrations far exceeding all other DDT forms. The water data set showed fairly strong correlation between concentrations of p,p'-DDE and p,p'-DDMU ( $R^2 = 0.82$ ; see Appendix O).

The highest concentrations were found in BA4C-WO58-0915-1 (a near-bottom sample down-current [northwest] from the outfall diffusers), with maximum p,p'-DDE and p,p'-DDMU concentrations reported at 1.14 ng/L and 1.48 ng/L, respectively; the corresponding values for Total DDTs and Total DDT Compounds were 1.59 ng/L and 3.26 ng/L. The forms o,p'- and p,p'-DDT were rarely detected in any sample. For the T11 reference location (up-current [southeast] of the outfall diffusers), p,p'-DDE was reported at 0.0308 ng/L in sample T11-WO30-0915-1 (collection depth at 30 m); no other DDT forms were detected in any samples collected at T11.

### **3.2.3 PCBs in the Water Column**

Appendix R presents tables of PCB test results organized by the shore-normal transects. Detected results for PCBs in water were reported by the testing laboratory in picograms per liter (pg/L) using three significant figures. Results for individual PCB congeners were added into summations of Total PCBs, with non-detects assigned a value of zero. The summations are shown in Appendix R.

Figures 3-10 and 3-11 present concentrations of Total PCBs for the water column at each sample location for the western and eastern sectors of the sampling area, respectively. Contaminant

concentrations are shown in relation to vertical distance in the water column from the ocean floor for each sample. Tables 3-13, 3-14, and 3-15 show results for Total PCBs along the 150-m, 60-m, and 40-m isobaths, respectively; the nodes were grouped by distance relative to the Sanitation Districts' outfall diffusers.

At least two PCB congeners were detected in every water sample, and all 46 congeners were detected at least once. The maximum value of Total PCBs was 190 pg/L in sample BA7C-WO30-0315-1 (a mid-column sample in the vicinity of the outfall diffusers). Another relatively high result for Total PCBs (170 pg/L) was detected in sample BA4C-WO58 (a near-bottom sample down-current of the outfall diffusers). The minimum value for Total PCBs was 0.33 pg/L in mid-column sample BA10B-WO75-0915-1, collected at a depth of 75 m; the 5-m sample at the same location (BA10B-WO5-0915-1) had a Total PCBs result of 0.35 pg/L. Location BA10 is up-current of the outfall diffusers.

The maximum concentration for a PCB target analyte was 26.2 pg/L for PCB 8. The twelve dioxin-like PCB congeners were detected infrequently. Of these twelve congeners, PCB 126 was detected in three samples, all from location BA7C, in the vicinity of the outfall diffusers. The highest concentration of PCB 126 (1.16 pg/L) was detected in near-bottom sample BA7C-WO55-0315-1. The result for PCB 209 (5.23 pg/L), reported in the mid-column sample collected at reference location T11, is an anomalously high result; it was exceeded only by the result for a near-bottom sample collected at location BA7C at 91 m (5.36 pg/L). The few other low-level detections of PCB congeners in samples collected at T11 appear representative of background ocean water conditions.

### **3.3 FISH RESULTS**

#### **3.3.1 Collections and Laboratory Analysis**

Fish collections took place between June 2014 and August 2016. Fish were caught by Sanitation Districts' staff from their RV *Ocean Sentinel*, and by Seaventures Inc., staff on their vessel *Early Bird II*. Collection methods included hook and line, spear fishing, traps, and trawls. Coordinates for each fish caught, with catch date and time, are presented in Table 3-16. Appendix T includes cruise reports and records of fish collections. Fish weight, standard fish length, and total fish length are also indicated.

Fish specimens were transported under chain-of-custody protocol to Vista for testing of chemistry parameters. Vista stored all fish specimens in a freezer at -20° C prior to sample processing. Vista prepared 301 primary fish tissue samples (skin-off filets) and 16 replicate samples. These were analyzed for COCs using HRGC/HRMS methods, and for lipids using the Bligh-Dyer method.

### **3.3.2 DDTs in Fish Tissue**

Appendix U presents tables of DDT test results organized by fish collection area. Detected results for DDT analytes in fish tissue were reported by the testing laboratory in picograms per gram (pg/g) using three significant figures. Results of individual DDT analytes were organized into summations of Total DDTs and Total DDT Compounds. Non-detects were assigned values of the sample-specific estimated detection limit (EDL) in calculating the summations. This approach is consistent with EPA's ICs program at PV Shelf.

Tables 3-17 and 3-18 show the calculated values for Total DDTs and Total DDT Compounds, respectively, in fish samples, in units of ug/kg (parts per billion [ppb]). Values are given by collection area and for each fish species. Figure 3-12 shows maxima, minima, and average values of Total DDTs by collection area.

#### **3.3.2.1 DDTs in Barred Sand Bass**

All eight DDT forms were detected in BSB fish tissue, but o,p'-DDT (11 of 143 samples) and o,p'-DDD (three of 143 samples) were rarely detected (Appendix U). Total DDT results (Table 3-17) show that both the maximum value for a single BSB (701,000 pg/g in sample Z1BSB-2014-28) and the highest average (mean) value for any collection area were reported for samples of fish caught at Zone 1 (near the Sanitation Districts' outfall diffusers). For the BSB data set, p,p'-DDE, o,p'-DDE, and p,p'-DDMU were detected in all samples, and the highest results were for p,p'-DDE and p,p'-DDMU. The BSB data set also showed strong correlation between detected pair concentrations of p,p'-DDE and p,p'-DDMU ( $R^2 = 0.84$ ; see Appendix O). The minimum value of Total DDTs in a BSB sample was 8,770 pg/g in sample RFBSB-2016-09 from Redondo Flats. When examining Total DDTs and Total DDT Compounds in BSB by collection area (Table 3-17 and Table 3-18, respectively), Zone 1 had the highest maximum and average values.

### 3.3.2.2 *DDTs in White Croaker*

All eight DDT forms were detected in WC fish tissue, but o,p'-DDT was rarely detected (4 of 158 samples; Appendix U). The DDT isomers p,p'-DDE, o,p'-DDE, and p,p'-DDD were detected in all samples from all collection areas including Ventura Flats, the reference area for WC. The isomer p,p'-DDT was detected in at least one fish from each collection area. All concentrations of individual DDT forms above 1,000,000 pg/g were for p,p'-DDE (maxima of 2,010,000 pg/g in sample Z1WC-2014-19 [from Zone 1] and 1,860,000 pg/g in sample Z2WC-2014-15 [from Zone 2]). For the WC data set, p,p'-DDE and o,p'-DDE were detected in all samples; p,p'-DDMU was detected in all samples except for 10 fish from the Ventura Flats reference area; and the highest results were for p,p'-DDE and p,p'-DDMU. Similar to that of BSB, the WC data set showed strong correlation between p,p'-DDE and p,p'-DDMU ( $R^2 = 0.84$ ; see Appendix O). The maximum value of Total DDTs in a WC sample was 2,360,000 pg/g in sample Z1WC-2014-19 from Zone 1. The minimum Total DDTs result was 4,490 pg/g in sample VFWC-2015-19 from Ventura Flats. When examining Total DDTs by collection area (Table 3-17), Zone 1 and Zone 2 were nearly identical for maximum and average concentrations. When examining Total DDT Compounds (Table 3-18), Zone 1 had the greatest maximum value for a single sample; Zone 1 and Zone 2 had nearly identical average values.

### 3.3.3 **PCBs in Fish Tissue**

Appendix V presents tables of PCB test results organized by fish collection area. Detected results for PCB congeners in fish tissue were reported by the testing laboratory in pg/g using three significant figures. Results of individual PCB congeners were added into summations of Total PCBs, and consistent with EPA's ICs program, non-detects were assigned values of the sample-specific EDL. Table 3-19 shows the calculated values for Total PCBs in fish samples, expressed in units of ug/kg, for ease of comparison to IROD cleanup goals. Values are given by collection area and for each fish species. Figure 3-12 shows maxima, minima, and average values of Total PCBs by collection area.

#### 3.3.3.1 *PCBs in Barred Sand Bass*

All 46 target PCB congeners were detected in at least one fish sample from each collection area, including the BSB reference area at Huntington Flats. Maximum calculated values for Total PCBs (Table 3-19) were 171,000 pg/g in sample HFBSB-2016-13, and 164,000 pg/g in sample



HFBSB-2016-19, both from the Huntington Flats collection area. The minimum value for Total PCBs in any single sample was 3,770 pg/g in BSB sample Z2BSB-2014-12 from Zone 2. The twelve dioxin-like PCB congeners were consistently detected, albeit at low concentrations; of these twelve congeners, PCB 126 was detected at a maximum concentration of 58.1 pg/g in a sample from Huntington Flats (HFBSB-2016-13; Appendix V). When examining Total PCBs in BSB by collection area (Table 3-19), Huntington Flats had the highest maximum and average values (see discussion in Section 4.3.2).

#### *3.3.3.2 PCBs in White Croaker*

All 46 target PCB congeners were detected in at least one fish sample from each collection area, except for PCB 169, which was not reported in samples from the WC reference area at Ventura Flats. The maximum concentration for a PCB target congener was 35,300 pg/g for PCB 153 in sample Z2WC-2014-18, but care must be taken when assessing the maximum individual PCB data, due to the potential addition of non-target PCB co-elutes. The twelve dioxin-like PCB congeners were consistently detected at low concentrations. Maximum values for Total PCBs were 256,000 pg/g in sample Z2WC-2014-18 and 225,000 pg/g in sample Z2WC-2014-15, both from Zone 2. Like the DDT results for WC, the maximum Total PCBs concentrations occurred in Zones 1 and 2. The minimum value for Total PCBs was 1,340 pg/g in sample VFWC-2015-03 from Ventura Flats. When examining Total PCBs in WC by collection area (Table 3-19), Zone 2 had the greatest maximum and average values.

#### **3.3.4 Total Lipids in Fish Tissue**

Reported values of total lipids ranged from 0.539% to 4.52% in BSB, and from 0.931% to 6.06% in WC. These low levels of lipids in skin-off filets were expected and are consistent with previous lipids data from the Sanitation Districts. Lipid normalization was not performed on this contaminant data set, and no further lipids data evaluation was made. The percent-lipids results for each fish are presented in the DDT results tables in Appendix U. Appendix W includes the complete reports from the analytical laboratory.

## **4.0 DISCUSSION**

This section discusses the results for each of the environmental media, i.e., sediment, water, and fish. Topics include chemical data quality; patterns of COC contamination; temporal trends of contamination; comparisons to cleanup criteria; and uncertainty in the sampling and testing.

### **4.1 SEDIMENT**

Various efforts were made to validate the quality of chemical data gathered during this sampling event. These efforts are described below.

#### **4.1.1 Data Quality Assessment**

As previously discussed, analytical data were reviewed and validated following procedures specified in the sediment QAPP (ITSI Gilbane, 2013a). The Gilbane project chemist conducted an overall QC review after receiving data validation reports, and developed two Quality Control Summary Reports (QCSRs) to address the data for shelf-wide samples and the data for the OA samples. The QCSRs indicate that project data quality objectives (DQOs) were met. The qualified data are of acceptable quality, and should be considered usable to help determine whether the mass of contaminants is continuing to decrease. The rejected results, while not useable for their intended purposes, represent less than 0.1% of the total dataset. QCSRs for the shelf-wide and OA data sets are included in Appendix N.

Of the more than 29,000 primary sample results for the shelf-wide cores, five results (less than 0.1%) were rejected due to laboratory anomalies, rendering an analytical completeness factor of 99.9%, well exceeding the QAPP goal of 90%. Four shelf-wide samples were found to have insufficient volume for testing for various parameters; however, the field completeness was 99.6%, exceeding the QAPP goal of 90%.

Of the nearly 30,000 primary sample results for the OA cores, seventeen results (less than 0.1%) were rejected due to laboratory anomalies, rendering an analytical completeness factor of 99.9%, again exceeding the QAPP goal of 90%. Three samples were found to have insufficient volume for testing for various parameters (six tests in total); therefore, the field completeness was 99.8%, exceeding the QAPP goal of 90%.

#### *4.1.1.1 Performance Evaluation Sample – Sediment Testing*

EPA, with cooperation from the EPA Quality Assurance Technical Services (QATS) program, provided Eurofins CS with a sediment PE sample in May of 2014 to be analyzed and evaluated prior to analysis of project samples. For this sample, Eurofins CS performed the secondary cleanup step described in Section 2.1.6.2 for the analysis of DDTs. This comparison demonstrated that analytical results reported by Eurofins CS for all DDTs, PCBs, and TOC were acceptable, based on the confidence intervals developed for the sample. Results of the PE study are included in Appendix B.

#### **4.1.2 Distribution of COCs**

Figures 3-1 and 3-2 are current interpretations of the geometry of the DDT deposit in sediment at PV Shelf. This geometry is consistent with geometries previously reported or postulated by other investigators: the pattern of DDT contamination displays a center of mass near the Sanitation Districts' outfall diffusers, and the DDT concentrations generally diminish with distance from the diffusers. A significant deposit (hot spot) of Total DDTs appears in the 0-8-cm bed-depth interval along the 60-m isobath near the eastern diffuser of the 90-inch outfall. The bottom half of Figure 3-2 shows a cross section illustrating conditions of the sediment bed along the 60-m isobath, based on the 2013 data set. This image illustrates the difference between the 0-8-cm bed-depth interval (the bioactive zone at PV Shelf) and the bed below 8 cm: in the lower portion of the bed, the hot spot extends northwest of the outfalls. (It should be noted that the vertical images on Figures 3-2, 3-4, and 3-6 have a vertical scale factor of about 5,000, and in that regard, are exaggerations of conditions at PV Shelf.)

Figures 3-3 through 3-6 are current interpretations of the geometry of PCBs in sediment at PV Shelf. The pattern of PCBs in the 0-8-cm bed-depth interval shows areas of elevated concentrations in an elongated area that extends seaward (cross-shelf direction) from water depths shallower than 60 m to the PV Shelf break. The vertical profiles illustrate the difference between the 0-8-cm bed-depth interval and the bed below 8 cm, where PCBs appear in elevated concentrations along the 60-m isobath in areas northwest of the Sanitation Districts' outfalls, similar to the pattern of DDTs.

#### *4.1.2.1 Dimensions of the EA Sediment Bed*

Based on Figures 3-1 and 3-2, the EA sediment bed covers an area that extends in the along-shelf direction from approximately 3,000 m southeast of the 120-inch (southernmost) outfall to approximately 7,500 m northwest of the northernmost outfall, and in the cross-shelf direction from about the 40-m isobath to past the shelf break.

Appendix X presents a comparison of the 2009 and 2013 shelf-wide cores and OA cores, showing depth in the core versus values of  $BD_d$  and the three COC groupings (Total DDTs, Total DDT Compounds, and Total PCBs). The profiles for most cores appear to corroborate the three-layer model described previously (Section 1.2), in that distinct differences in the  $BD_d$  values and COC concentrations can be noticed with depth. The 2009 and 2013 profiles display similar patterns in many cores, including 4C, 6C, and 8C, where the highest contaminant concentrations in the two data sets were at nearly identical bed depths in the core.

As was done for the 2009 data set, the EA bed thickness was assumed to be equal to the core length. Using this approach for the 2013 data set, the MVS geostatistical model created a shape of the EA bed with an estimated volume of 15 million  $m^3$ , equivalent to the volume modeled in 2009.

#### *4.1.2.2 Temporal Changes in the EA Deposit*

##### Changes in Spatial Distribution of Contaminants

The general shape of the EA deposit does not appear to have changed appreciably since previous sediment sampling events. Location BA8C near the Sanitation Districts' diffusers appears to represent the most contaminated area on PV Shelf: for the 2013 data set, maximum concentrations of both Total DDT Compounds and Total PCBs were found in core BA8C.

Figure 4-1 illustrates the differences in DDT concentrations in the top 2 cm of the sediment bed between 2002/2004, 2009, and 2013. Figure 4-2 shows the comparison of DDTs in the 0-8-cm bed layer (the bioactive layer) between 2009 and 2013. Figures 4-3 and 4-4 present the corresponding data for PCBs.

For the top 2 cm of the sediment bed, concentrations of both DDTs and PCBs appear to have decreased significantly since 2002/2004, notably near the Sanitation Districts' outfall diffusers.

(It is acknowledged that different sampling methods were used for the 2002/2004 event than those used in 2009 and 2013). For the 0-8-cm bed-depth interval, concentrations of DDTs and PCBs show overall increases between 2009 and 2013 for a major portion of the sampled area. Possible contributing factors for the increases include: (1) lower RLs achieved by Eurofins CS for the 2013 event for DDT and PCBs as compared to RLs previously used; and (2) uncertainties in the chemical analysis and modeling (Sections 4.4.1.3 and 4.4.1.4); and (3) heterogeneity of the deposit, as indicated by the high variability seen in the field replicate evaluation (Appendix Y).

#### Average Concentrations and Mass of Contaminants

As previously noted, Table 3-7 presents estimates for the average concentrations of COC groupings for the entire data set and the OA data set, and Table 3-8 presents estimates of the mass of COCs for the entire data set and the OA data set. Results for both the 2009 and 2013 data sets are shown. The results indicate that significant amount of DDTs and PCBs remain in sediment at PV Shelf. Though average and mass values for 2013 were greater than corresponding values for 2009, overall, mass of COCs has decreased over time, when compared to previous mass calculations (prior to the IROD).

Regarding estimates of COC mass, previous researchers have focused on p,p'-DDE, as this isomer was regarded as the most prevalent DDT form on the shelf, and hence representative of contaminants in the sediment bed (Lee, 1994). Table 4-1 summarizes estimates of the masses of p,p'-DDE and PCBs by various researchers and indicates the wide differences between studies. The 30 MT value for p,p'-DDE calculated by the MVS model based on the 2013 data set is greater than the 9.7 MT and 13.8 MT values for p,p'-DDE calculated by the two separate MVS models based on the 2009 data set. However, as mentioned above, the mass values derived from the 2009 and 2013 sediment data sets were significantly lower than those for previous mass estimates. These differences may be associated with:

- Different data sets (previous data sets were generated as much as 30 years ago)
- Ongoing MNR processes (see Section 5.0)
- The reduced area evaluated by the MVS model relative to the areas previously examined
- Differences between the computational approaches used in the MVS model and those used in previous approaches

Both for 2013 and 2009, the OA cores as depicted in Figure 2-2 (and in the MVS model) were within 1.5 km of any outfall diffuser section. For the 0-8-cm bed-depth interval, based on the 2013 data set, the OA contains approximately 47% of the entire mass of each COC grouping (i.e., Total DDTs, Total DDT Compounds, and Total PCBs). For the same bed-depth interval, based on the 2009 data set, the OA contained about 53% of the COC mass.

#### **4.1.3 Comparison of Sediment Data to Cleanup Goals**

As previously described, the IROD established the following objectives of the interim isolation cap:

- The mean DDT concentration in surface sediment on the shelf will be reduced from 150 mg/kg OC to 78 mg/kg OC (in combination with MNR, the interim cleanup level of 46 mg/kg OC in surface sediment would be reached within 5 years of cap placement).
- Mean PCB concentrations in shelf surface sediment will be reduced to the cleanup level of 7 mg/kg OC.

As previously described, the 2013 sediment data set was input into the MVS geostatistical model; the model output included the average (mean) concentrations of COCs in the sediment bed (Table 3-7). For the 2013 data set, the mean value of Total DDTs OC in the 0-8-cm bed-depth interval was 77 mg/kg OC (77,000 ug/kg OC). This value is just under the cap placement objective of 78 mg/kg OC. For PCBs (short list), the model output mean value of 5 mg/kg OC (5,000 ug/kg OC), also is under the interim sediment cleanup level of 7 mg/kg OC.

#### **4.1.4 Sediment Uncertainties and Possible Sources of Error**

##### *4.1.4.1 Coring Procedure*

There are limitations inherent in collecting cores of a layered low-density (soft bottom) seabed at the ocean depths seen in this study. Some researchers have postulated that gravity corers provide incomplete samples of the surface of the sediment column (Lee, H.J., 1994; Lee et al., 2002). During the 2013 coring event, a camera mounted on the coring device, as described in Section 2.1.4, recorded the progress of the drop through the water column and into the sediment bed. Review of the videos (Appendix E) show that, though blowoff of fine sediment away from (external to) the coring device is evident at the moment of impact of the device into the seafloor, there is no evidence of advance blowoff (movement of sediment ahead of impact), and there is no evidence of sediment escaping from the coring device at impact. There is no evidence of incomplete cores, provided that the entry angle is plumb to the sediment bed surface.

Vertical profiles (Appendix X) indicate that the bottom of the EA bed may not have been reached in several cores, based on elevated COC concentrations reported for samples generated for the core bottom. However, this limitation is balanced by the fact that all cores were collected using the same methodology, for both the 2009 and 2013 events.

#### *4.1.4.2 Spatial Uncertainty*

The coring frequency of the shelf-wide sampling was 34 cores over a modeled area of 30 km<sup>2</sup>, correlating to one core per 0.9 km<sup>2</sup>. At the OA, the coring frequency (including the shelf-wide cores from Sanitation Districts Transects 6 through 9) was 51 cores over a modeled area of 11 km<sup>2</sup>, correlating to one core per 0.2 km<sup>2</sup>. The OA coring frequency was improved from the coverage of 0.3 km<sup>2</sup> achieved in the 2009 sampling event.

#### *4.1.4.3 Laboratory Uncertainty*

Aliquots of select samples from cores BA5B, BA6BC, BA9C, OA10, and OA11 for the 2009 and 2013 sediment collections were retrieved from the Sanitation Districts' deep-freeze archive. The aliquots were extracted and analyzed in a single analytical batch by a single extraction technician and a single analyst at Eurofins CS in March 2017 (this approach was intended to minimize laboratory contribution to the uncertainty). Results of the analyses are presented in Table 4-2. The heterogeneity of the sample matrix is illustrated by R<sup>2</sup> values of 0.657 for p,p'-DDE and 0.627 for Total PCBs (short list) calculated for the 2009 versus the 2013 data sets (Appendix O). These R<sup>2</sup> values do not indicate a strong correlation for the two data sets. Another indication of the heterogeneity of the sample matrix is found in Appendix Z, which presents a graphical comparison of average p,p'-DDE concentrations for the 0-8-cm sediment layer between the 2009 and 2013 data sets.

#### *4.1.4.4 Uncertainty in the Geostatistical Model*

As described previously, Appendix C provides a detailed discussion of the MVS geostatistical modeling effort used on the sediment data set. The model output included values of mean (average) COC concentrations (OC normalized) and values of mass of COCs. The model also calculated values of "uncertainty" and "confidence" for the COC summations at each modeled node; the mean value of confidence for the entire sediment data set was reported as greater than 65%. The modeling report concludes that the site is well characterized for COCs.

To further bolster confidence in the sediment model, EPA sponsored a secondary geostatistical modeling effort independent of the primary effort, but using the identical sediment data set. The modeling was conducted by Sundance, Albuquerque, New Mexico. Sundance, in its model output, also produced values for average COCs OC normalized, and total COC mass, both for the entire sediment bed and for the 0-8-cm bed-depth interval. Appendix AA is a report that describes the modeling effort and the model output.

Table 4-3 summarizes model outputs from the primary and secondary geostatistical models, along with values of relative percent difference (RPD). As indicated, the secondary effort produced values of average concentrations that were generally about 20-to-30% lower than the primary model. Values of total COC mass in the entire (shelf-wide) bed were also lower in the output of the secondary model. The mass values for the 0-8-cm bed-depth interval varied slightly higher for Total DDTs and Total DDT Compounds, and slightly lower for Total PCBs. The RPD values for the model comparison are considered acceptable; as such, the secondary modeling effort validates the findings and output of the primary effort.

## **4.2 WATER COLUMN**

### **4.2.1 Data Quality Assessment – Water Column (High Resolution)**

Water sampling analytical data were reviewed and validated by an independent third-party validator following procedures specified in the water QAPP (Gilbane, 2014). Of the 6,850 primary sample results for the water sampling program, 13 results (less than 0.2%) in two samples, were rejected due to laboratory QC anomalies, for a data completeness of 99.8%, well above the QAPP goal of 90%.

The Gilbane project chemist conducted an overall QC review after receiving the data validation reports, and developed a QCSR to summarize the data quality anomalies for the water sampling program. The QCSR indicate that project DQOs were met and that all non-rejected data were usable for assessing vertical ocean water column concentrations. Laboratory reports and the QCSR for the high resolution water data set are presented in Appendix S.

### **4.2.2 Data Quality Assessment – Water Column (PSDs)**

The PSD results were reviewed against the field QC requirements for PSD sampling presented in the PSD QAPP (Fluen Point Environmental, 2013) by the Gilbane project chemists. A total of



14 PED and four SPME field blanks were collected and analyzed. All were non-detected for both DDTs and PCBs. A minimum of three field replicates was required by the sampling design; each sample was deployed in triplicate. The results were reported as averages; therefore an evaluation of RPDs was not applicable.

The planned PSD sample collection total was 153 primary PEDs and 54 SPMEs. Several PEDs were lost during deployment: one surface sampler was missing from station 7C, all three surface samplers were missing from stations 8C and 9C, and one near-bottom sampler was missing from station W3. Also, an entire mooring line from station W5 was not recovered. All SPME samplers were recovered; however, two failed before they could be analyzed (one of three from near-bottom at station 4C and one of three from near-bottom at station 7C). Overall, this represents a combined PSD field sampling completeness of 90.8%.

#### **4.2.3 Distribution of COCs in the Water Column**

Figures 3-6 and 3-7 present concentrations of p,p'-DDE for the water column at each sampling location; Figures 3-8 and 3-9 show concentrations of Total DDTs for the same locations. The patterns of contamination were very similar; this similarity is expected, because the contribution of p,p'-DDE made up more than 70% of the concentrations of Total DDTs in most samples (Appendix Q). In general, the bottom and near-bottom samples had higher concentrations than mid-column samples, with some exceptions at locations BA3C, BA3DC, BA4B, and BA7C, where elevated mid-column concentrations were measured. All near-surface samples have low p,p'-DDE and Total DDTs concentrations.

Tables 3-10, 3-11, and 3-12 show results for Total DDT Compounds along the 150-m, 60-m, and 40-m isobaths, respectively; the sample locations were grouped by water depth, and by distance relative to the Sanitation Districts' outfall diffusers. In examining vertical trends, concentrations generally were highest either in the near-bottom or mid-column samples along all isobaths. Average concentrations were all greatest in the near-bottom locations, lower in mid-column samples (except in the vicinity of the outfall diffusers along the 60-m isobath), and always lowest for the near-surface samples.

For along-shelf trends, concentrations generally were highest down-current of the outfalls, with elevated Total DDT Compounds concentrations from transects BA7 through BA3, while up-

current concentrations (transects BA9 and BA10) were relatively low. For cross-shelf trends between the 150-m, 60-m, and 40-m isobaths, the down-current concentration maxima and averages were similar at each sample depth, but in the vicinity of the outfall diffusers, the near-bottom concentrations along the 40-m isobath and the mid-column sample results along the 60-m isobath were greater.

Table 4-4 compares values for dissolved-phase DDTs from: (1) a SCCWRP event from 1999 (Zeng et al., 1999); (2) an EPA PSD sampling event from 2012 (Fernandez, 2012); (3) an EPA PSD sampling event from a draft data summary (Fernandez, 2015; see Appendix D); and (4) EPA's 2015 high resolution event described herein. In general, higher concentrations were measured in samples collected near the bottom of the water column (i.e., close to the sediment bed surface) during all sampling events. It also appears that the SCCWRP results are comparable to those from the PSD events. However, these results exceed by roughly an order of magnitude the results from the high resolution sampling event, for bottom and near-bottom samples.

Concentrations of dissolved-phase DDTs at PV Shelf would be expected to decline over time due to dispersion and mixing in the open ocean, and a net reduction of contaminated sediment exposed to the water column due to deposition of cleaner surface sediment. In that regard, the PSD results could be biased high. The high resolution grab sample results were significantly lower than the PSD results, but the general trend is similar in that elevated DDTs were detected in bottom or near-bottom samples at locations BA4C, BA5C, BA5DC, BA6DC, and BA7DC.

Figures 3-10 and 3-11 present high resolution concentrations of Total PCBs in water. In a pattern similar to that of p,p'-DDE, relatively high PCBs concentrations were reported for each transect from BA9 down-current through BA3. In general, the bottom and near-bottom samples had higher PCBs concentrations than mid-column samples, with some exceptions at locations BA3DC, BA4B, BA7C, BA8DC, and BA9DC, where elevated mid-column concentrations were measured. All near-surface samples have relatively low PCBs concentrations.

Tables 3-13, 3-14, and 3-15 show results for Total PCBs along the 150-m, 60-m, and 40-m isobaths, respectively, with the sample locations grouped by distance relative to the outfall diffusers. The vertical trends were similar to those for Total DDT Compounds, where

concentrations generally were highest in the near-bottom or mid-column samples along all isobaths. Average concentrations were greatest in the near-bottom samples, lower for samples collected at mid-column depths (except in the vicinity of the outfall diffusers along the 60-m isobath and up-current of the diffusers along the 40-m isobath), and always lowest for the near-surface samples.

The along-shelf PCBs concentrations generally were highest down-current of the outfall diffusers, with elevated concentrations from transects BA9 through BA2; concentrations were relatively low for up-current transect BA10. For cross-shelf trends between the 150-m, 60-m, and 40-m isobaths, the down-current concentration maxima and averages were similar at each sample depth (similar to the Total DDT Compounds concentrations); but in the vicinity of the outfall diffusers, the near-bottom sample concentrations along the 40-m isobath and the mid-column results along the 60-m isobath are greater.

Table 4-5 compares dissolved-phase PCBs results from the various PV Shelf sampling events previously described for DDTs. Similar to the DDTs comparison, the concentrations of Total PCBs in the near-bottom and bottom samples were higher than those in mid-column and near-surface samples (with an exception for the near-surface sample at BA7C).

SCCWRP's dissolved-phase results were higher than results for most other samples from similar depths, followed by results from near-bottom PEDs in 2013. The PED data from 2010 and shallower PED data from 2013 are generally comparable to the grab sample results from 2015. Dissolved-phase concentrations of PCBs, like those of DDTs, would be expected to decrease over time. SCCWRP's bottom-sample concentrations were greater than the concentrations in the 2010 and 2013 PEDs, and a downward trend continues in the 2015 grab samples, showing an overall decreasing trend for PCBs. The high resolution sample results from 2015 generally were lower than those for the other sampling events, but still show elevated PCBs in many bottom or near-bottom samples, and in mid-column samples from locations BA6C, BA7C, BA8DC, and BA9DC. One near-surface grab sample at BA7C was also anomalously high.

Figure 4-5 shows near-bottom concentrations of Total DDTs in the water column along the 150-m, 60-m, and 40-m isobaths, in relation to concentrations in sediment in the 0-2-cm bed-depth interval. Elevated concentrations of DDTs in water samples extend from transect BA7,

northwest (down-current) of the outfall diffusers, to beyond transect BA3 and the isobath boundaries, in a similar pattern to the elevated DDTs in the 0-2-cm sediment bed-depth interval.

Figure 4-6 is the equivalent figure for Total PCBs, and shows a widespread pattern of elevated concentrations, both in the near-bottom water column and in the 0-2-cm sediment bed-depth interval. The area of elevated PCBs extends from near location BA9B, down-current beyond location BA2B, and to the boundary of the sample coverage area.

#### **4.2.4 Comparison of High Resolution Water Data to Cleanup Goals**

For assessing possible risks to human and ecological health resulting from exposure to COCs in the water column, sample results (concentrations) were listed and compared to applicable cleanup goals on a point-by-point basis, as described below.

##### **4.2.4.1 DDTs**

The 2009 IROD established cleanup goals for DDTs in water, citing EPA's AWQC in effect at that time. The IROD AWQC as they apply to DDTs at PV Shelf are as follows:

- The human health AWQC is 0.22 ng/L for p,p'-DDE.<sup>3</sup>
- The ecological (saltwater aquatic life) AWQC is 1 ng/L for Total DDTs.

The high resolution results indicated that concentrations of p,p'-DDE exceeded the human health AWQC in 41 primary or replicate samples, and concentrations of Total DDTs exceeded the ecological AWQC in seven samples (Appendix Q). Locations of p,p'-DDE exceedances are shown on Figures 3-6 and 3-7. Locations of exceedances for Total DDTs are shown on Figures 3-8 and 3-9. The patterns of p,p'-DDE and Total DDTs concentrations are similar since p,p'-DDE constitutes more than 70% of the Total DDTs result in most samples. Except for transect BA2, multiple AWQC (human health) exceedances of p,p'-DDE concentrations extend from transect BA8 down-current through BA1 (Figures 3-6 and 3-7). AWQC (ecological) exceedances for Total DDTs are limited to transects BA4 and BA7 (Figures 3-8 and 3-9).

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<sup>3</sup> For assessing possible human health impacts related to DDTs in the water column, the EPA used the AWQC for p,p'-DDE (0.22 ng/L). Use of this criterion is justified because, in terms of frequency and magnitude of detections, p,p'-DDE is the most prevalent DDT form in the water column (and in other media) at PV Shelf, and its AWQC value is more conservative than that for p,p'-DDD (0.31 ng/L) and equally conservative to that for p,p'-DDT (0.22 ng/L).

#### 4.2.4.2 PCBs

The IROD established cleanup goals for PCBs in water, again citing EPA's AWQC. The IROD AWQC as they apply to PCBs at PV Shelf are as follows:

- The human health AWQC is 0.064 ng/L for Total PCBs.
- The ecological (saltwater aquatic life) AWQC is 30 ng/L for Total PCBs.

No other cleanup goals for PCBs in water were established in the IROD.

Concentrations of Total PCBs exceeded the AWQC for human health in 38 of 146 water samples. Appendix R presents all exceedances of the IROD AWQC for Total PCBs in shaded cells. Figures 3-10 and 3-11 present concentrations of Total PCBs in the water column. Similar to p,p'-DDE, Total PCBs at concentrations above the human health AWQC extend from transect BA9 down-current through BA3.

#### 4.2.5 Water Column Uncertainties

##### 4.2.5.1 Sampling Procedures

There are difficulties inherent in collecting ocean grab water samples at the depths and pressures attempted in this study. Samples were collected at sea directly into sample bottles; this approach was efficient in that it required no transfer of samples between bottles, and time-consuming decontamination procedures and associated handling of wastes were minimized.

Previous sampling events may have had the following sampling limitations: pumped samples required 1,100 to 2,300 L to be pumped through a filter and Teflon XAD-II resin column over several days for each sample (Zeng, 1999); and PSD samples required precise infusion of isotope-labelled compounds into each sampling device prior to each event, 30-day deployments for sampler equilibration allowing for sampler losses, and calculations for sampler concentrations based on variable water-polyethylene partitioning coefficients and temperature corrections (Fernandez, 2012, 2015).

The approach of grab sampling combined with high resolution analyses, by contrast, takes less labor and time; attains lower detection limits; and is representative of actual depth-specific water column conditions at the time of collection. For these reasons, this approach is recommended for future sampling at PV Shelf.

The two main sampling events for this MNR report were performed in March and September 2015, and this may lead to some temporal variability. The locations collected in March were BA8C, BA9DC, and W4. A review of the DDT and PCB results at these locations does not show any apparent anomalies or temporal bias between adjacent sampling locations. In Zeng's study, water column samples for DDTs and PCBs were collected in winter and summer 1997, but temporal trends were inconsistent and seasonal variability was not apparent (Zeng, 1999). Other possible variables that may affect COC concentrations in water include ocean currents, tidal influences, temperature and salinity cycles, and sedimentation patterns.

#### *4.2.5.2 Laboratory Uncertainty*

The high-resolution grab samples were filtered at the laboratory through glass fiber filters of nominal pore size of 0.7  $\mu\text{m}$ ; this size was identical to the filters used by Zeng in the field (1999). Unlike Zeng, however, the filters were not analyzed to determine COC concentrations in the particulates retained on the filter. Colloids smaller than 0.7  $\mu\text{m}$  may be adsorbed (lost from the filtrate) to the surfaces of laboratory glassware. The filtrates were subjected to GPC and silica gel cleanup (SGC) to remove potential biological and hydrocarbon interferences, and this approach may also remove some colloids from the sample. These factors may affect the final reported concentrations of dissolved contaminants.

The values of target PCB congeners reported with co-elutions have a degree of uncertainty. For this water study, 14 target congeners had co-elutions (Table 2-3), and the reported values for these 14 congeners may have been biased high. For example, the PCB 70/74 results report the co-eluted target congeners, but also report non-target congeners PCB 61 and PCB 76.

#### *4.2.5.3 Spatial Uncertainty*

Horizontal accuracy using DGPS navigation was estimated to be within 3 m. However, during each sampler deployment, the propellers were stopped for variable amounts of time, leading to tidal drift and an estimated location error up to  $\pm 40$  m. For each sampler deployment, the sample depth error is estimated as  $\pm 1.5$  m, due to ocean swells and drift away from the vertical of the sampling device on the wire cable.

Horizontal and vertical location errors lead to changes in the exact grab sample location for consecutive sampler deployments for adjacent near-bottom and bottom samples, and for field

replicates. Despite the temporal and spatial variability, the depth comparability of the DDTs and PCBs data sets were internally consistent at each location, the field replicate precision was good, and the results appear representative of the ocean water conditions at the time of sample collection.

### **4.3 FISH**

The IROD established interim cleanup levels for environmental media. This section discusses the MNR results with respect to the cleanup levels.

#### **4.3.1 Data Quality Assessment – Fish**

The fish tissue analytical data were reviewed and validated by an independent third-party validator following procedures specified in the fish QAPP (Gilbane, 2016a). A total of 6,850 primary sample results was generated for the fish sampling program, and no data points were rejected; thus, the analytical completeness was 100%. The planned fish collection total was 340, and the actual number of fish caught over a 27-month period (from June 2014 through August 2016) was 301, for a field sampling completeness of 89%.

The Gilbane project chemist conducted an overall QC review after receiving the data validation reports, and developed a QCSR to summarize the data quality anomalies for the fish sampling program. The QCSR indicated that project DQOs were met and that all data were usable for assessing fish tissue concentrations. The QCSR for the fish data set is presented in Appendix W.

The laboratory RLs were evaluated by the project team prior to sample collection to confirm that the laboratory was able to attain the required sensitivity for the project. For the tests for pesticides and PCBs, the reporting approach was to report each DDT isomer and PCB congener to a sample-specific EDL. The level of sensitivity achieved by HRGC/HRMS analysis for DDTs and PCBs is the lowest technically achievable, and met project objectives. All fish data are useable, as qualified, for comparison to the IROD target fish tissue concentration goals.

#### **4.3.2 Distribution of COCs in Fish**

As previously mentioned, Figure 3-12 shows COC results for BSB and WC for each collection area, including minimum, average, and maximum concentrations of Total DDTs and Total PCBs.

#### 4.3.2.1 DDTs

For BSB, there is an overall pattern of higher DDTs concentrations in samples of fish caught in EPA Zones 1 and 2 (near the Sanitation Districts' outfall diffusers). Samples of fish caught in the reference BSB collection area at Huntington Flats had elevated average and maximum concentrations of Total DDTs. The high maximum concentrations at the Huntington Flats reference area for DDTs in BSB may be indicative of individual fish having a significant contaminant load during summer spawning migration from PV Shelf or the ports of Los Angeles and Long Beach (ITSI Gilbane, 2013b), and do not appear to represent the local potential exposure of BSB to sediment conditions at Huntington Flats.

For WC, Figure 3-12 shows that the average and maximum Total DDTs values from Zones 1, 2, and 3 being higher than the corresponding values for the other collection areas. Significant concentrations of Total DDTs are also noted in the Breakwater Zone and Redondo Flats. The reference WC collection area at Ventura Flats has very low concentrations for DDTs. The widespread area of elevated DDTs concentrations in WC may be indicative of the fishes' wide range and mobility, and provide evidence of their apparent low site fidelity to the vicinity of the Sanitation Districts' outfalls area (Lowe, 2013).

#### 4.3.2.2 PCBs

An overall pattern of higher PCBs concentrations in BSB from Zones 1 and 2 is apparent. BSB caught at reference collection area Huntington Flats also had elevated average and maximum concentrations of Total PCBs, comparable to Zone 2, but less than Zone 1. A small number of BSB from Huntington Flats (and to a lesser extent Redondo Flats and the Breakwater Zone) had high concentrations of PCBs, resulting in elevated maximum and average Total PCBs concentrations. The elevated concentrations of PCBs at Huntington Flats, like those of DDTs, may indicate that individual fish migrated from PV Shelf or the shipping harbors, and that these concentrations are not necessarily representative of sediment conditions at Huntington Flats.

For PCBs in WC, Zones 1, 2, and 3 all had maximum concentrations exceeding 150,000 pg/g. The collection area with the highest average value for PCBs was Zone 1 at the outfall diffusers. Redondo Flats (northwest of the diffusers) and the Breakwater Zone (east of the diffusers) both showed significant levels of PCBs when compared to the Ventura Flats reference area. It appears that elevated PCB concentrations in WC are more widespread than for BSB. This



phenomenon may be related to the wide range and mobility of WC, as noted in previous studies (Lowe, 2013).

#### *4.3.2.3 Time Trends*

At this time, a meaningful analysis of time trends for fish at PV Shelf is difficult due to many factors, including fish mobility; differences in fish collection locations and depths by different researchers; differences in analyte lists; and differences in analytical procedures. Tables 4-6 and 4-7 show summaries of DDT and PCB data, respectively, generated from: NOAA's 2002/2004 study (NOAA/EPA, 2007); recent EPA studies from shallower pier fishing locations related to the ICs program (WC only; Gilbane, 2016b, 2017); the Sanitation Districts' 2012 (BSB) and 2015 (WC) data (Sanitation Districts, 2014, 2016); and this MNR study. An attempt was made to align locations of fish collections from these various efforts to examine time trends. There are more data available for WC than for BSB, as WC have been collected more consistently.

For DDTs, when comparing the NOAA 2002/2004 data set with the current MNR data set, the maximum and average DDTs results have decreased in both BSB and WC from 2002 to 2016 at all collection areas except the Breakwater Area. For WC at Zones 1, 2, and 3, where Sanitation Districts' data are available (collections in November and December 2015) and where comparisons can be made, the composited results for WC are notably higher than the averages from both the NOAA 2002/2004 study (Zones 1 and 2 only; collected from September 2002 to June 2004) and the 2014/2016 MNR study (October 2014 to July 2016 collections). For BSB at Zones 1, 2, and 3, the Sanitation Districts' results for DDTs for composited samples (collected from June to October 2012) are notably lower than the averages from the NOAA 2002/2004 study (Zones 1 and 3 only; collections from August 2002 to June 2003), and the 2014/2016 MNR study (Zones 1, 2, and 3; June 2014 to August 2016 collections). There are inadequate data to make more detailed observations.

For PCBs (collected concurrently with the DDTs), when comparing the NOAA 2002/2004 data set with the current MNR data set, the maximum and average PCBs results have decreased at all collection areas except Redondo Flats. For WC, decreases in average values were noted at Zones 1 and 2. For BSB at Zones 1, 2, and 3, the Sanitation Districts' results for total detectable Aroclors (total PCB congeners are not available) in composited samples, are consistent with the

decreasing average concentrations trend from the higher NOAA 2002/2004 study (Zones 1 and 3 only), to the lower 2014/2016 MNR study. Due to incomplete and inconsistent data sets, there are no other discernable time trends that can be made at present.

The Sanitation Districts has generated data on DDTs and PCBs in WC routinely since the late 1990s. For the collection areas closest to the outfalls, the data set shows dramatic decreases for DDTs in WC samples. Concentrations of PCBs in WC have remained consistent, but at low concentrations relative to DDTs (EPA, 2009b; Sanitation Districts, 2016).

#### **4.3.3 Comparison of Fish Data to Cleanup Goals**

The IROD established the following cleanup goals for protection of human health from ingestion of WC (the IROD did not establish cleanup goals for ingestion of BSB):

- For DDTs, 400 ug/kg
- For PCBs, 70 ug/kg

For PV Shelf, the adopted approach is to derive a representative EPC specific to each EPA fish collection area. For this data set, for each collection area, ProUCL software (EPA, 2015) was used to calculate the 95% upper confidence limit (UCL) on the mean concentration; this value is regarded as the area-specific EPC. The use of the 95% UCL on the mean is widely recognized as a conservative estimate for representing an EPC. This approach is recommended when conducting quantitative exposure assessments of contaminants in environmental media including fish tissue (EPA, 1989), and has been applied for the ICs program at PV Shelf (Gilbane, 2016b, 2017).

Figure 3-12 shows that for Total DDTs, the EPCs exceeded the cleanup goal in fish collection areas EPA Zone 1, EPA Zone 2, and EPA Zone 3. For Total PCBs, the EPCs exceeded the cleanup goal in collection areas EPA Zone 1, EPA Zone 2, and Redondo Flats. The EPC for DDTs in EPA Zone 3 and the EPC for PCBs at Redondo Flats exceed the IROD cleanup goals. EPA Zone 3 and Redondo Flats are outside the CDFW commercial WC catch ban area.

#### **4.3.4 Fish Uncertainties**

##### *4.3.4.1 Collection Procedures*

The fish sampling design has an inherent and unknown degree of uncertainty, since it is not intended to ascertain the environments to which each fish collected during this task has been exposed in its life cycle. It is impossible to know where a fish has travelled, what its feeding habits are, and where it has received its contaminant body burden. Further, it is not possible to determine the degree to which direct sediment contaminant exposure has occurred for each fish.

A wide variety of fish lengths and weights were measured in each species; however, no evaluation of potential age biases to fish contaminant exposure uncertainties was made. Fish tend to absorb contaminants throughout their lifetimes. For future events, the age of each fish and/or body burden based on weights and measures, should be assessed.

Fish samples were prepared as skin-off filets, and estimated concentrations in whole fish were not generated. Also, while lipid results were generated for each sample (Appendix U), lipid normalization was not performed for this study, but could be calculated in future assessments. There is typically a linear relationship between fat content and organo-chlorine content in fish; lipid normalizing is an approach to assess whether changes (over time) in contaminant concentration indicate an actual trend or are attributable to changes in fat content in the fish (EPA, 2000b).

##### *4.3.4.2 Spatial Uncertainty*

Due to the limited availability of fish, the actual collection locations for several BSB at Breakwater Zone and Redondo Flats, for several WC at Redondo Flats, and for most fish at EPA Zone 1, EPA Zone 2, and EPA Zone 3, were outside the designated boundaries of the planned 5-km by 1-km collection areas indicated on Figures 2-5 and 3-12. All fish collection locations were recorded and are included in Appendix T.

## **5.0 CONCLUSIONS**

This section presents the conclusions for the first MNR report. Table 5-1 is a summary of compliance with IROD criteria, organized by medium.

### **5.1 SEDIMENT**

Sediment cores were retrieved successfully from 34 locations for the shelf-wide program, and from 35 OA locations (near the Sanitation Districts' outfall diffusers). A significant amount of data was generated by testing more than 1,000 samples of recovered core material for both geotechnical and chemical parameters. The sample design and the methods of core collection, core cutting, and sample testing used during this study rendered high-quality data.

For the shelf-wide sampling program, the approach used for this study provided a sufficient data set with a level of confidence that allows for meaningful comparison to the 2009 data set as well as to any future data sets established to assess the progress of cleanup of DDT and PCBs.

The output from the geostatistical models indicated a widespread pattern of DDT contamination similar to EPA's 2009 data set and to patterns reported by previous investigators, including the Sanitation Districts and USGS. The model output also indicated a pattern of PCB contamination similar to EPA's 2009 data set. The pattern is similar to that of DDTs, with areas of higher concentrations at the Sanitation Districts' outfalls, but also with elevated concentrations extending seaward into deep water, and in areas both northwest and southeast of the outfalls.

Although interpretive patterns of COCs in the EA deposit have not changed appreciably over time, detected contaminant concentrations in surface sediment (0-2-cm bed-depth interval) have dropped significantly since 2002/2004. It is plausible that this is caused by deposition of clean material, and several factors of MNR, including: dechlorination; sediment erosion; and sediment resuspension with associated desorption of COCs from sediment into seawater (EPA, 2005).

Model output indicated an increase in COC mass between 2009 and 2013, though the mass values remain well below historical estimates. The apparent increase between 2009 and 2013 may be a function of the uncertainties in the sampling and analysis techniques, differences in MVS model assumptions, and in the demonstrated heterogeneity of the sediment deposit itself.

Model output also indicated mean (average) COC concentrations for the 0-8-cm bed-depth interval derived from the 2013 data set to be 77 mg/kg OC for Total DDTs and 5 mg/kg OC for Total PCBs (short list). These values were below the short-term objectives identified for the interim isolation cap (78 mg/kg OC DDTs; 7 mg/kg OC PCBs), as they were in 2009.

It is acknowledged that the selected remedy in the IROD, in particular the isolation cap component, was based heavily on interpretations of COC concentrations detected in samples of sediment collected from the 0-2-cm bed-depth interval; these samples were obtained using a different collection method from that used in the 2009 and 2013 coring programs. Because the results of EPA's coring programs present a picture of environmental conditions at PV Shelf significantly different than what was historically understood, and it is important to obtain a better understanding of actual site conditions, future sampling programs should be conducted using techniques similar to those used for the 2009 and 2013 programs.

## 5.2 WATER

Spatial distributions of DDTs and PCBs in the water column at PV Shelf were evaluated using two different methods:

- Water samples using a depth-discrete grab sampling method and then analyzing filtered samples using HRGC/HRMS for eight individual DDT forms and for 46 PCB congeners.
- PSDs were first prepared by impregnating with PRCs, then deployed at sea for approximately 30 days. The PSDs were then retrieved and lab-analyzed for DDTs and PCBs.

For both methods, summations of Total DDTs, Total DDT Compounds, and Total PCBs were calculated. The areal distributions of DDTs and PCBs in water appear similar to those found in shallow sediment, and the vertical concentration profiles of DDTs and PCBs at most water sampling locations decreased with increasing distance from the sea floor. The comparison of current high resolution water sampling results to previous water column data shows a general overall trend toward lower concentrations over time. These findings appear to confirm that contaminated sediments are a slowly decreasing source of DDT and PCB inputs to the water column at PV Shelf. However, concentrations of dissolved-phase p,p'-DDE and for PCBs exceed the corresponding IROD cleanup goals for human exposure in several locations and at several depth intervals. Exceedances of the IROD cleanup goal for dissolved-phase Total DDTs (ecological exposure) are less frequent.

### **5.3 FISH**

Specimens of two fish species (BSB and WC) were caught during 2014 to 2016 from seven collection areas in the vicinity of PV Shelf. Concentrations of DDTs and PCBs in samples of fish tissue (skin-off filets) were measured using HRGC/HRMS techniques. The distribution patterns of DDTs and PCBs in each fish collection area were similar to those found in the sediment, and the average concentrations of DDTs and PCBs in fish from most collection areas decreased with increasing distance from the Sanitation Districts' outfalls (with the noted exception of BSB from Huntington Flats). The comparison of these results to previous fish sampling data indicates that maximum and average DDTs and PCBs concentrations have decreased since 2002 for both BSB and WC. However, EPC concentrations in WC remain higher than the IROD cleanup goal at several fish collection areas, most notably at the areas closest to the outfall diffusers, on PV Shelf. These findings suggest that contaminated sediment continues to be a source for DDT and PCB inputs to fish at PV Shelf, but that the likely input rate is decreasing.

### **5.4 SUMMARY**

Conditions at PV Shelf regarding COC contamination appear to be improving – concentrations in the sediment 0-2-cm bed-depth interval continue to improve, and concentrations in the 0-8-cm bed-depth interval met the concentration performance objectives related to the interim cap described in the IROD, even without the cap. However, significant areas of sediment remain highly contaminated, and COC concentrations in samples of water and fish exceeded the associated IROD cleanup goals, both for DDTs and PCBs. EPA will continue the MNR sampling program to evaluate the effectiveness of MNR and to develop final remediation alternatives for PV Shelf cleanup.

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