RISK ASSESSMENT OF SEAFOOD FOLLOWING THE F/V ROYAL PACIFIC DIESEL SPILL IN VENTURA HARBOR, CALIFORNIA

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California Environmental Protection Agency Office of Environmental Health Hazard Assessment

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## LIST OF ABBREVIATIONS

BaPE	benzo[a]pyrene equivalent
CDFW	California Department of Fish and Wildlife
	(formerly California Department of Fish and Game, CDFG)
cPAH(s)	carcinogenic polycyclic aromatic hydrocarbon
F/V	fishing vessel
LOC	Level of Concern
MDL	method detection limit
NAS	National Academy of Sciences
OEHHA	Office of Environmental Health Hazard Assessment
OSPR	Office of Spill Prevention and Response
PAH(s)	polycyclic aromatic hydrocarbon
QA	quality assurance
ppb	parts per billion
WPCL	Water Pollution Control Laboratory

## PREFACE

The Office of Environmental Health Hazard Assessment (OEHHA), a department within the California Environmental Protection Agency, is responsible for evaluating potential public health risks associated with seafood consumption following marine oil spills in California. This task includes making recommendations on fisheries closure and reopening to the California Department of Fish and Wildlife. OEHHA's authorities to conduct these activities are based on a mandate in the:

- California Fish and Game Code
  - o Section 5654

This report presents a seafood risk assessment conducted by OEHHA to support these recommendations following the F/V Royal Pacific diesel spill.

## ACKNOWLEDGMENTS

OEHHA acknowledges the California Department of Fish and Wildlife (CDFW), Office of Spill Prevention and Response (OSPR), for their efforts and collaboration in the fisheries closure spill response and their assistance in the preparation and review of this document. Lori Chumney, Beckye Stanton, Jennifer Gold, and Mike Connell participated in fisheries closure sampling; Michael Anderson, Bruce Joab, and Regina Donohoe assisted with planning the sampling events, and Randy Imai, Julie Yamamoto, and David Crane assisted with various fisheries closure-related activities. Additionally, Gail Cho reviewed the analytical results and QA documentation, and contributed to the laboratory methods section of the report. OEHHA thanks individuals from U.S. Fish and Wildlife Service who assisted in fisheries closure sampling.

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## EXECUTIVE SUMMARY

On November 18, 2013, an allision<sup>1</sup> occurred between the F/V Royal Pacific and Golden Eagle commercial fishing vessels in Ventura Harbor, California. The allision resulted in a spill of approximately 200 gallons of diesel fuel into harbor waters. Much of the product was initially contained by the Ventura County Fire Department and Clean Seas, LLC within the southeast corner of the harbor. However, an unknown amount of product was unable to be contained and drifted throughout the harbor. Because fishing and mussel harvesting occur in the harbor and adequate information was not available to determine the potential threat to public health from the consumption of fish and shellfish from the area affected by the spill, the Office of Environmental Health Hazard Assessment (OEHHA) recommended to the California Department of Fish and Wildlife (CDFW) that fishing and shellfish harvesting be closed throughout the harbor and the adjacent Ventura Keys, pending an investigation.

After evaluating updated information from on-scene responders on the morning of November 20, OEHHA could not rule out a potential public health threat related to the consumption of seafood from the harbor. Thus, testing of seafood for oil spill-related contamination was needed. OEHHA recommended to CDFW that the fisheries closure be maintained. The northern boundary was revised to exclude the Ventura Keys area, which, upon further evaluation, had not been affected by the spill.

Sampling in response to the Royal Pacific diesel spill was planned to establish the degree and geographic extent of seafood contamination. Mussels were selected as the best indicator species to assess the risk of seafood consumption from the spill area. Samples were collected on November 20 and 21 (the first sampling event), and December 11, 2013 (the second sampling event). They were collected from multiple sites in the area impacted by the diesel spill, as well as from a reference site at the north end of the harbor (the Harbor Patrol pier) where sheen had not been seen.

OEHHA has established a protocol for assessing the risk associated with consuming seafood following an oil spill. The contaminants of concern in seafood following an oil spill are specific polycyclic aromatic hydrocarbons (PAHs) that are considered to have the potential to cause cancer (cPAHs). The concentrations of cPAHs measured in seafood are compared to a Level of Concern (LOC), i.e., a concentration that is considered to pose an unacceptable health risk if consumed at the stated rate and for the predicted duration. The LOC for the most sensitive population, based on sensitivities related to age (which affects sensitivity to cancer) and seafood consumption rate, is 27 parts per billion (ppb) (wet weight) cPAH, expressed as total benzo[a]pyrene equivalents ( $\Sigma$ BaPE).

 $\Sigma$ BaPE concentrations in mussels collected within the closure boundary during both sampling events were below 27 ppb. OEHHA determined that consumption of mussels

<sup>&</sup>lt;sup>1</sup> When one vessel strikes a stationary object or vessel

posed no ongoing significant oil-related health risk. Following a recommendation from OEHHA, CDFW lifted the existing closure area on January 3, 2014.

### INTRODUCTION

On Monday, November 18, 2013, at 1339 hours, the California Office of Emergency Services reported an allision<sup>2</sup> between the Royal Pacific and Golden Eagle commercial fishing vessels in Ventura Harbor, California. The allision resulted in a ruptured fuel tank on the Royal Pacific, with a subsequent spill of approximately 200 gallons of diesel fuel into harbor waters. The California Department of Fish and Wildlife (CDFW), Office of Spill Prevention and Response (OSPR) informed the Office of Environmental Health Hazard Assessment (OEHHA) about the spill at 1502 hours, as required by state law (Fish and Game Code §5654).

Much of the product was initially contained by the Ventura County Fire Department and Clean Seas, LLC within the southeast corner of the harbor. However, an unknown amount of product was unable to be contained and drifted throughout the harbor. Additionally, fishing and mussel harvesting was reported to occur in the harbor. Because adequate information was not available to determine the potential threat to public health from the consumption of fish and shellfish from the spill-impacted area, OEHHA recommended to CDFW that fishing and shellfish harvesting be closed throughout the harbor and the adjacent Ventura Keys, pending an investigation. OEHHA also advised that fishers avoid fishing in areas where there was a visible sheen on the water. After receiving this recommendation from OEHHA, CDFW declared an immediate fisheries closure for this area (see map, Figure 1).

Fish and Game Code §5654 requires that, if a closure is in effect for more than 48 hours after notification of the spill, expedited testing of seafood is required before fisheries can be re-opened. On November 20, OEHHA considered the likely environmental fate of the spilled product in the harbor and determined that a potential public health threat related to the consumption of seafood from the harbor could not be ruled out without testing. Thus, OEHHA recommended to CDFW that the fisheries closure be maintained; the northern boundary was revised to exclude the Ventura Keys area after a bird survey crew reported seeing no sheen in the area. CDFW issued an amended fishery closure declaration on November 20 (see map, Figure 2). Fishery closure signs were posted around the harbor on November 19 and 20. The public was further notified with a Notice to Mariners, which was broadcast by the U.S. Coast Guard on the first day of the closure. The Notice to Mariners included the boundaries of the area closed to all fishing activity.

<sup>&</sup>lt;sup>2</sup> When one vessel strikes a stationary object or vessel

# CONTAMINANTS AND SPECIES OF CONCERN RELATING TO SEAFOOD CONSUMPTION FOLLOWING OIL SPILLS

#### **Contaminants of Concern**

Oil, as defined under California Government Code §8670.3, is "any kind of petroleum, liquid hydrocarbons, or petroleum products or any fraction or residues there from, including, but not limited to, crude oil, bunker fuel, gasoline, diesel fuel, aviation fuel, oil sludge, oil refuse, oil mixed with waste, and liquid distillates from unprocessed natural gas." The contaminants of concern in seafood following an oil spill are specific polycyclic aromatic hydrocarbons (PAHs) that are considered to have the potential to cause cancer (cPAHs). Cancer is the effect of greatest concern related to human consumption of oiled seafood (see Klasing and Brodberg, 2013, for discussion).

### Species of Concern Relating to Seafood Consumption

Following the Ventura Harbor spill, a CDFW Wildlife Officer indicated that fishing activity, including mussel harvesting, takes place in the area of the harbor. Mussels were deemed a priority for sampling because of their tendency to bioaccumulate PAHs and their relative abundance in Ventura Harbor.

The determination of species and locations to sample following an oil spill is dependent on knowledge of the environmental fate of oil and its constituents and the specific spill scenario (e.g., volume, product, location, shoreline type, trajectory, and weather). Fish and shellfish accumulate PAHs to varying degrees, depending on seafood species and chemical structure. Finfish, in particular, can often swim away from a spill, depending on the extent of the spill relative to the home range and the availability of suitable habitat. Bivalve mollusks such as mussels, on the other hand, are not mobile and do not metabolize PAHs as rapidly as do finfish and some other shellfish (Meador et al., 1995; NAS, 2003; Yender et al., 2002). Finfish tend to accumulate lower molecular weight PAHs that are less toxic to humans, whereas mussels accumulate higher molecular weight PAHs that are more likely to be carcinogens. Crustaceans, such as crabs, have an intermediate ability to metabolize PAHs and generally accumulate lower molecular weight PAHs (Eisler, 2000; Meador et al., 1995; Topping et al., 1997). Thus, mussels may be used as an indicator species when assessing the risk of seafood consumption following an oil spill. A finding of non-significant levels of PAHs in mussels would be indicative of non-significant levels in finfish, as well. For these reasons, mussels were the only species evaluated following the spill.

## IDENTIFYING CONTAMINANT LEVELS IN SHELLFISH FOLLOWING THE ROYAL PACIFIC DIESEL SPILL

Sampling in response to the Royal Pacific diesel spill was planned to establish the degree and geographic extent of seafood contamination. Sampling was conducted following procedures outlined in the CDFW-OSPR Fisheries Closure Sampling and Analysis Plan. A summary of samples used for fisheries closure purposes, including

sites, dates, species, individuals per composite, sample identification numbers, and sample location coordinates, is shown in Table 1. A map of the sampling locations is presented in Figure 3.

#### Sampling Methods, Documentation, and Custody

For all sampling activities, collection was documented with GPS, photographs, and a photo and sample log form. Samplers wore two pairs of nitrile gloves to collect samples and changed gloves between each sample. Mussels were collected by hand and double wrapped in foil, dull side to the sample, before being placed in a heavy duty sealed plastic bag. The sample I.D., date and time of collection, site name, sampler, latitude/longitude of the sampling location, and way point number were written in indelible ink on an adhesive label, which was placed on the sealed plastic bag. This sealed bag was then placed in a second heavy duty plastic bag before being sealed and placed on ice in a cooler. Samples were held on ice in the sampler's possession until shipping via FedEx to TDI-Brooks International<sup>3</sup>. Just prior to shipping, samples were placed between two layers of fresh bagged ice and the cooler was sealed with shipping tape.

Standard CDFW chain-of-custody procedures were followed. Chain of custody forms were filled out at the end of each sampling event and enclosed inside the cooler in a sealed plastic bag prior to shipping.

### **Sampling Activities**

Mussel samples were collected from multiple sites in the area impacted by the diesel spill, as well as from a reference site at the north end of the harbor (the Harbor Patrol pier) where sheen had not been documented in the water. The target sample size was 15 mussels per composite sample of similar-sized mussels to the extent possible. The first sampling event was conducted by representatives from OSPR and U.S. Fish and Wildlife Service (USFWS). Eleven composite mussel (*Mytilus*) samples, comprised of approximately 15 individual mussels per composite, were collected on November 20 and November 21, and shipped to TDI-Brooks International on November 22. Of these, five composite samples, collected at increasing distances from the source, were selected for PAH analyses in order to conduct a seafood risk assessment. The remaining samples were archived in case further analyses were warranted.

Final results of the first sampling event were received by OEHHA on December 5. After conducting ∑BaPE calculations (see following section), OEHHA determined that mussels collected from two sites at two- and three-days post-spill were close to, but did not exceed, the Level of Concern (LOC, see discussion below). There was a clear trend for decreasing total PAH (data not shown) and ∑BaPE levels with increasing distance from the spill site.

<sup>&</sup>lt;sup>3</sup> TDI-Brooks International is a certified analytical laboratory, located in College Station, Texas, with experience in PAH analyses.

Limited research has provided insight into the bioaccumulation and depuration rates of PAH compounds in mussels. Pruell et al. (1986), for example, measured levels of several PAH compounds in mussels exposed to contaminated sediment in the laboratory at 3, 10, 20, and 40 days during a 40-day exposure period. Of those time periods, most five- and six-ring PAHs were found at the highest concentration in mussels following 20 days of laboratory exposure and had begun to depurate by 40 days. PAH concentrations of greatest human health concern are thus expected to peak in mussels somewhere between 10 and 40 days during an exposure period. In an earlier study, Fossato and Canzonier (1976) found that recoverable hydrocarbon fraction levels in mussels exposed to diesel fuel in a continuous-flow system for up to 41 days did not equilibrate with ambient concentrations until approximately 15 days into the exposure period. Because the Royal Pacific diesel spill occurred in a largely enclosed harbor, natural dispersion and evaporation of PAHs would be expected to be slower than in an open ocean environment. Thus, OEHHA determined that PAH levels could still be increasing in mussels as a result of the spill at the time the first samples were collected and additional sampling was necessary before the fishery could be re-opened. OEHHA notified OSPR of this finding on December 5.

The second sampling event was planned for 23 days post-spill. Sampling was conducted on December 11 by representatives from OSPR and OEHHA. Three sites with the highest  $\Sigma$ BaPE concentrations from the first sampling event were selected for re-sampling. Of those three, 30 mussels were collected from the site with the lowest  $\Sigma$ BaPE levels, with 15 of those used for quality control/quality assurance purposes. Composites of 15 mussels each were collected from the other two sites.

#### **Laboratory Methods**

TDI-Brooks International prepared and analyzed the tissue samples. Samples were maintained in a controlled-access freezer at <-16° C prior to preparation and analysis. Mussels were dissected, homogenized, and composited according to instructions provided by CDFW. Mussel tissues were extracted by pressurized fluid extraction, followed by gel permeation clean-up, and then analyzed for PAHs/alkylated homologs and hopane biomarkers by GC/MS-SIM (SW846 EPA Method 8270 Mod). Results for 51 PAH compounds were reported. Of those, eight are considered to be carcinogens (cPAHs) by the state of California: chrysene, benz[a]anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene<sup>4</sup>, dibenzo[a,h]anthracene, indeno[1,2,3,-cd]pyrene, naphthalene, and benzo[a]pyrene. The method detection limit (MDL) for all cPAHs was <1 part per billion (ppb) with the exception of naphthalene compounds. The MDL for naphthalene and the alkylated homologues of naphthalene was <4 ppb.

TDI-Brooks International provided results and associated Quality Assurance (QA) documentation for all samples, including controls, demonstrating that sample

<sup>&</sup>lt;sup>4</sup> Benzo(k)fluoranthene was reported as benzo(k,j)fluoranthene and assumed to be 100% benzo(k)fluoranthene

processing was reproducible, accurate, and free from cross-contamination. A certified reference material from the National Institute of Standards and Technology (NIST) for organics in mussels (SRM 1974c) was included in sample processing to provide an additional measure of analytical comparability. CDFW Water Pollution Control Laboratory (WPCL) staff reviewed the results and QA documentation. Reference materials and analytical quality controls were within acceptable ranges. All results passed QA review.

# CONTAMINANT LEVELS IN FISH AND SHELLFISH TISSUE THAT POSE NO SIGNIFICANT RISK

OEHHA has established a protocol for assessing the risk associated with consuming seafood following an oil spill (Klasing and Brodberg, 2013). Concentrations of cPAHs in seafood are compared to an LOC, i.e., a concentration that is considered to pose an unacceptable health risk if consumed at the stated rate and for the predicted duration. LOCs were developed for three sensitive populations, defined by sensitivities related to age (which affects sensitivity to cancer) and seafood consumption rates. Of these three, the most health protective LOC was 27 nanograms per gram (ng/g) or ppb (wet weight) cPAH, expressed as total benzo[a]pyrene equivalents ( $\Sigma$ BaPE) (see Klasing and Brodberg, 2013, for details):

LOC (cancer) = 27 ng/g or ppb (wet weight) for  $\sum BaPE$ 

## **RESULTS AND CONCLUSIONS**

 $\Sigma$ BaPE concentrations in composite mussel samples are presented in Table 2. Individual cPAH concentrations from which  $\Sigma$ BaPE concentrations were calculated are presented in Appendix 1. The first sampling event was conducted two and three-days post-spill. Data from the five composite mussel samples showed that  $\Sigma$ BaPE concentrations were highest at the two sites closest to the source of the spill (20.2 and 19.2 ppb) and decreased with increasing distance from the source (7.6 and 3.2 ppb, respectively) until reaching apparent ambient  $\Sigma$ BaPE concentrations at the reference site near the Harbor Patrol Pier (3.8 ppb; see Figure 3 for sample locations). All individual cPAHs showed a similar pattern. Although  $\Sigma$ BaPE concentrations did not exceed the LOC at any site, as noted above, PAH concentrations can continue to accumulate in mussel tissues for days or longer following exposure to contaminated sediment or water. It was thus determined that additional sampling should be conducted before the fishery was re-opened.

OEHHA received the results from the second sampling event on January 3, 2014.  $\Sigma$ BaPE concentrations in composite mussel samples collected from the two areas closest to the spill site were nearly identical to those collected from the same sites during the first sampling event (20.5 and 18.5 ppb, respectively). However, the  $\Sigma$ BaPE concentration in mussels collected from the third sampling site – in the south central harbor area between the spill site and the prior reference site– had approximately doubled from 7.6 to 14.7 ppb. Because no samples exceeded the LOC and additional time had passed for depuration to occur (nearly seven weeks post-spill), OEHHA determined that consuming fish and shellfish from the harbor no longer posed a potential public health threat as a result of the spill. Therefore, OEHHA recommended to CDFW that the fishery be re-opened. CDFW issued a re-opening declaration on January 3, 2014.

In conclusion, based on a recommendation by OEHHA following the Royal Pacific diesel spill in Ventura Harbor, CDFW declared a fisheries closure on November 19, 2013, for the entire harbor and the adjacent Ventura Keys. When more complete oiling data became available, the closure area was reduced to exclude the Ventura Keys, which was not affected by the spill. OEHHA and CDFW began sampling activities for fisheries closure purposes on November 20, 2013. Results were compared to the LOC and, although ∑BaPE did not exceed the LOC, it was determined that additional sampling should be conducted prior to re-opening the fishery. The second sampling event was conducted on December 11, 2013. Results were made available to OEHHA on January 3, 2014, whereupon OEHHA recommended to CDFW that consumption of seafood from the area posed no significant ongoing oil spill-related health risk.

## Table 1. Summary of Sampling Activities

Sample location*	Date	Number of individuals/composite	Sample I.D.	GPS Coordinates (DD)**
		First Sampling Event		
Ventura Harbor (closest sample location to spill site, inside boom)	11/21/13	~15	VNDS004RI1112113MU1 CFG0123	34.240586 -119.261889
Ventura Harbor (close to spill site, outside boom)	11/20/13	~15	VNDS004RI1112013MU5 CFG0122	34.240839 -119.261608
Ventura Harbor (south-central harbor)	11/20/13	15	VNDS004RI1112013MU2 CFG0125	34.242861 -119.264739
Ventura Harbor (south-central harbor)	11/20/13	15	VNDS001ARI1112013MU1 CFG0124	34.245947 -119.265722
Ventura Harbor Harbor Patrol Pier area (reference site)	11/21/13	>15	VNDS004RI2112113MU1 CFG0126	34.252381 -119.266581
	S	Second Sampling Event***		
Ventura Harbor (closest sample location to spill site)	12/11/13	15	VNDS004RI1121113MU3 CFG0134	34.24051 -119.26184
Ventura Harbor (close to spill site)	12/11/13	15	VNDS004RI1121113MU2 CFG0134	34.24083 -119.26170
Ventura Harbor (south-central harbor)	12/11/13	30	VNDS004RI1121113MU1 CFG0133	34.24330 -119.26482

\*Sampling locations are listed geographically, from south to north, within a sampling event \*\*GPS waypoints (latitude, longitude) reported in decimal degrees (DD) in WGS 84 \*\*\*Booms had been removed prior to the second sampling event

## Table 2. ∑BaPE Concentration in Mussels following the Royal Pacific Diesel Spill

Sample location*	Date	Number of individuals/composite	Sample I.D.	∑BaPE ng/g or ppb (wet weight)
		First Sampling Event		
Ventura Harbor (closest sample location to spill site, inside boom)	11/21/13	~15	VNDS004RI1112113MU1 CFG0123	20.2
Ventura Harbor (close to spill site, outside boom)	11/20/13	~15	VNDS004RI1112013MU5 CFG0122	19.2
Ventura Harbor (south-central harbor)	11/20/13	15	VNDS004RI1112013MU2 CFG0125	7.6
Ventura Harbor (south-central harbor)	11/20/13	15	VNDS001ARI1112013MU1 CFG0124	3.2
Ventura Harbor Harbor Patrol Pier area (reference site)	11/21/13	>15	VNDS004RI2112113MU1 CFG0126	3.8
		Second Sampling Event**		
Ventura Harbor (closest sample location to spill site)	12/11/13	15	VNDS004RI1121113MU3 CFG-135	20.5
Ventura Harbor (close to spill site)	12/11/13	15	VNDS004RI1121113MU2 CFG0134	18.5
Ventura Harbor (south-central harbor)	12/11/13	30	VNDS004RI1121113MU1 CFG0133	14.7

\*Sampling locations are listed geographically, from south to north, within a sampling event \*\*Booms had been removed prior to the second sampling event

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## Figure 1. Initial Closure Area

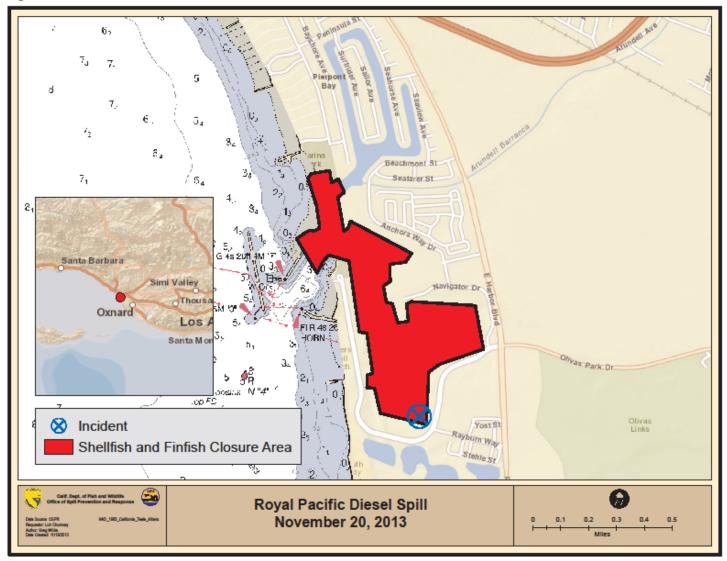


Figure 2. Revised Closure Area

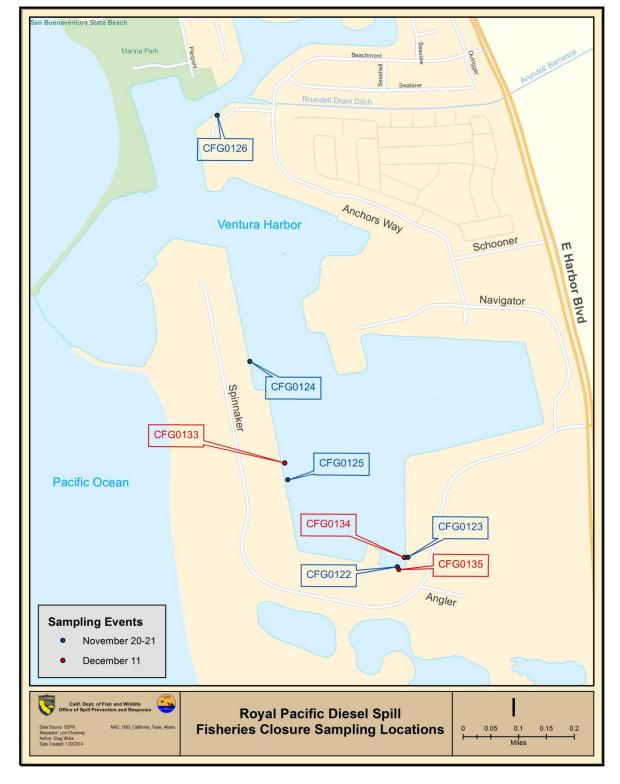


Figure 3. Sampling Locations, 2013

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		mpling Eve b (wet weig			
	Sample I.D.				
Target Compound	CFG0123	CFG0122	CFG0125	CFG0124	CFG0126
Naphthalene	1.84	2.49	1.78	1.47	1.88
C1-Naphthalenes	9.09	5.67	2.15	0.781	0.560
C2-Naphthalenes	33.8	15.9	8.43	1.78	0.844
C3-Naphthalenes	44.4	27.3	15.3	1.99	1.13
C4-Naphthalenes	41.2	25.7	15.6	2.43	<4
Benz(a)anthracene	5.20	5.51	1.64	0.628	0.620
Chrysene/Triphenylene	9.31	10.2	4.25	1.64	2.12
C1-Chrysenes	4.09	4.48	1.79	0.945	1.80
C2-Chrysenes	3.70	3.43	0.849	0.984	1.61
C3-Chrysenes	2.16	1.68	0.574	0.350	0.479
C4-Chrysenes	0.836	<0.2	<0.2	<0.2	<0.2
Benzo(b)fluoranthene	5.71	5.70	2.06	1.06	1.39
Benzo(k,j)fluoranthene	2.15	2.08	0.658	0.350	0.390
Benzo(a)pyrene	2.90	5.55	1.61	0.980	1.26
Indeno(1,2,3-c,d)pyrene	0.394	0.350	0.156	0.152	0.214
Dibenzo(a,h)anthracene	0.205	0.218	0.085	0.081	0.080
∑BaPE	20.2	19.2	7.6	3.2	3.8

Appendix 1. cPAH Concentrations in Mussels Collected in the First and Second Sampling Events Following the Royal Pacific Diesel Spill

\*Reported ∑BaPE concentrations may differ slightly from those calculated from cPAHs in this table because of rounding.

	cPAH, ppb (wet weight)* Sample I.D.			
Target Compound	CFG0135	CFG0134	CFG0133	
Naphthalene	1.44	1.48	0.792	
C1-Naphthalenes	0.658	0.43	0.478	
C2-Naphthalenes	2.64	1.58	1.38	
C3-Naphthalenes	9.88	4.37	3.89	
C4-Naphthalenes	29.6	13.2	7.41	
Benz(a)anthracene	4.31	4.35	2.87	
Chrysene/Triphenylene	8.97	9.57	7.74	
C1-Chrysenes	6.61	5.06	3.13	
C2-Chrysenes	6.29	4.75	1.87	
C3-Chrysenes	3.45	2.08	1.47	
C4-Chrysenes	0.761	0.802	<0.2	
Benzo(b)fluoranthene	5.58	5.57	3.43	
Benzo(k,j)fluoranthene	2.08	2.02	1.13	
Benzo(a)pyrene	8.44	8.77	8.40	
Indeno(1,2,3-c,d)pyrene	0.333	0.323	0.251	
Dibenzo(a,h)anthracene	0.150	0.161	0.133	
∑BaPE	20.5	18.5	14.7	

\*Reported ∑BaPE concentrations may differ slightly from those calculated from cPAHs this table because of rounding.