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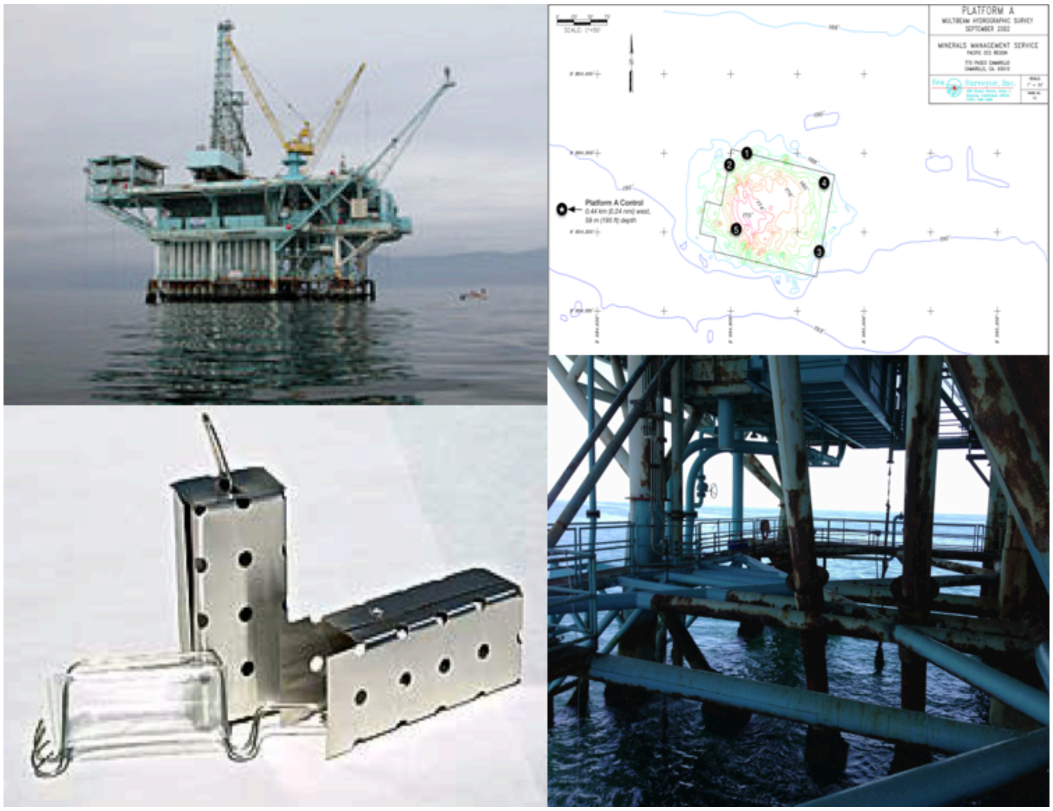
BOEM 2013-208

Determining the Potential Release of Contaminants into the Marine Environment from Pacific OCS Shell Mounds



US Department of the Interior
Bureau of Ocean Energy Management
Pacific OCS Region

BOEM
Bureau of Ocean Energy Management

Determining the Potential Release of Contaminants into the Marine Environment from Pacific OCS Shell Mounds

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DISCLAIMER

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Abbreviations, Acronyms, & Units

Abbreviations & Acronyms:

AMS	Applied Marine Sciences, Inc.
AXYS	Axys Analytical Services
BOEM	Bureau of Ocean Energy Management
BSEE	Bureau of Safety and Environmental Enforcement
EST	Environmental Sampling Technologies
GC	Gas chromatograph
K_{ow}	Octanol-Water Partition Coefficient
LMCL	Lower method calibration limit
OPR	Ongoing precision and recovery
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
POCS	Pacific Outer Continental Shelf
POCIS	Polar Organic Chemical Integrative Samplers
PQL	Practical quantification limit
PPM	Parts per million
PRC	Performance Reference Compound
RL	Reporting limit
SDL	Sample detection limit
SPMD	Semipermeable Membrane Device
SPME	Solid Phase Micro-Extraction

Units:

in.	inch
ft	feet
km	kilometer
m	meter
mi	mile
ng	nanogram
ng/L	nanogram/Liter
nm	nautical mile
pg	picograms
pg/L	picograms/Liter
ppt	part per trillion
ppm	parts per million
L	liter
yd	yard

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Executive Summary

Bureau of Ocean Energy Management (BOEM) and Bureau of Safety and Environmental Enforcement (BSEE) regulations require the complete removal of platform structures and associated debris following decommissioning of offshore oil and gas facilities in the Pacific Outer Continental Shelf (POCS). After decommissioning, platform owners may be required to remove shell mounds located beneath the platforms that formed during operations. Shell mounds consist of discharged drilling muds and cuttings interlayered with shells and marine organisms falling from the platform infrastructure and BOEM and BSEE are still considering whether some mounds may be left in place.

BOEM, BSEE, and the State of California have limited information about the types and concentrations of contaminants in shell mounds beneath oil and gas production platforms in the Santa Barbara Channel. The purpose of the current study was to assess whether chemical contaminants, most notably polynuclear aromatic hydrocarbons (PAHs), the toxic component of crude oil, contained within POCS shell mounds might be escaping into the marine environment to the extent of posing a risk to marine organisms. Information from this study would be useful for evaluating the effects on the marine environment of the potential abandonment or removal of shell mounds following decommissioning of offshore oil and gas facilities, and the development of measures to minimize any adverse effects.

Aquatic scientists have used various methods over the past several decades to assess the movement of contaminants from sediments and water into aquatic food webs. The most prevalent methods have been caged bivalves, fish or invertebrate muscle tissue, and passive samplers, which include semi-permeable membrane devices (SPMDs), solid phase micro-extraction (SPME) devices, and polar organic chemical integrative samplers (POCIS). This study used SPMDs deployed at two POCS platforms in the Santa Barbara Channel, Platform A and Platform B, and at one control site close to each of the platforms to assess the potential release of PAHs from platform shell mounds into surrounding waters.

PAHs are complex organic molecules consisting of various numbers of rings (predominantly benzene and sometimes pentene rings) formed from carbon atoms with other atoms attached to the ring carbons and extending outside the rings. PAHs comprised of fewer carbon rings are more water soluble than are those comprised of more carbon rings. Consequently, the preponderance of PAHs with different numbers of rings can provide clues about how fresh or weathered the source of the PAHs is, which in this case is crude oil. Moreover, within a class of PAH (e.g., naphthalene) are different forms (homologs) that are differentiated by the numbers of carbons attached to the ring(s), referred to as alkyl. Typically, PAH alkyl homologs are distinguished as C-0 through C-4 or more, depending on the number of extra-ring carbons. As the PAHs are partially combusted or degraded by microbes, the extra-ring carbons are removed, leaving behind only hydrogen atoms on the rings.

Study data provided insights into the chemical source of the detected PAHs and their weathering patterns, spatial patterns in their concentrations and compositions, and their potential harm to marine life.

The SPMDs that were deployed for up to 35 days detected very low concentrations of PAHs in the water column. The composition of the PAHs, especially the relative abundances of parent

compounds (i.e., bare ring) and different alkyl groups, were consistent with a crude oil source rather than a combusted hydrocarbon source.

The SPMD-derived PAH data from this study provides insight into the presence and potential physical or spatial sources of PAHs present at low concentrations in this portion of the Santa Barbara Channel. First, measured PAH water concentrations were in the parts per trillion or ppt, which is typically too low to be detected by most other sampling and analytical techniques. Observed PAHs were dominated by the following compound groups: naphthalenes, fluorenes, phenanthrenes/anthracenes, dibenzothiophenes, fluoranthenes/pyrenes, and chrysenes. Second, the composition of PAHs observed at all stations were consistent with relatively fresh sources of petroleum rather than older weathered hydrocarbons, as would be expected from the 30-40 year old drill cuttings buried in the shell mounds. Third, due to the background water concentrations of PAHs detected at control sites in this study, uncertainties were introduced about the physical sources of water-borne PAHs detected at the platforms. As a consequence, the shell mounds cannot be entirely ruled out as a source of some of the PAHs reported in this study.

Moreover, although the shell mounds can not be entirely ruled out as a source of some of the PAHs reported in this study, the fact that the SPMDs deployed over the thicker areas of each shell mound at Platforms A and B, where the highest concentration of hydrocarbon-containing drill cuttings have been reported, did not detect higher PAH concentrations than those deployed over the fringes of the mounds. This suggests that the shell mounds are not the primary source of detected PAHs. Rather the most likely source of the detected PAHs is natural oil seepage, which is prevalent throughout the Santa Barbara Channel (Wilkinson, 1972; Kraus and Estes, 1977; Fisher, 1978; Reed and Kaplan, 1979, Spies et al., 1980; Stuermer et al., 1982 and Quigley, 1997). This appears especially true near Platform A where seepage has been reported previously (Allen and Schlueter, 1969).

Although this study was able to accurately detect very low (part per trillion) concentrations of PAHs in the water adjacent to Platforms A and B, as well as at the two control sites, the proximity of natural hydrocarbon seeps to the study area and their contribution to detected PAH concentrations prevented this study from definitively differentiating the contribution, if any, made by the shell mounds to those PAH concentrations. Additionally, the composition of study PAHs is indicative of un-weathered crude, although some of the PAH compounds observed are found in both weathered and un-weathered crude oil. Based on observed PAH concentrations at the two control sites and the dominance of un-weathered crude oil PAHs in study results, the potential contribution of any shell mound PAHs, which are likely to be highly weathered, to measured PAHs can be assumed to be very low, if at all.

Finally, PAH concentrations observed in the water column, regardless of the source of the PAHs, were more than an order of magnitude lower than regulatory water quality objectives established by the State of California to protect marine biota and human health. Consequently, any potential contribution of PAHs from platform shell mounds to observed water concentrations of PAHs is likely very small and probably poses no appreciable risk to area marine biota.

1. Study Background

1.1 Study Purpose

Current Bureau of Ocean Energy Management (BOEM) and Bureau of Safety and Environmental Enforcement (BSEE) regulations require the complete removal of platform structures and associated debris following decommissioning of offshore oil and gas facilities in the Pacific Outer Continental Shelf (POCS). State of California regulations frequently require similar removal of part of or all infrastructure associated with offshore oil and gas production activities through the following:

1. Individual coastal consistency permits issued by the California Coastal Commission,
2. Clean Water Act compliance as mandated by the State of California Water Quality Control Board, or
3. Subtidal land lease conditions issued by the California State Lands Commission.

Following decommissioning of oil and gas platforms operators may be required to remove discharged drilling muds and cuttings that are interlayered with shells and marine organisms falling from the platform infrastructure. BOEM, BSEE, and the State of California have limited information about the types and concentrations of contaminants in shell mounds beneath oil and gas production platforms in the Santa Barbara Channel. Chemical assessments of the POCS shell mounds underlying Platform Gina and Platforms A and B were conducted in 2006 and 2011, respectively (Weston Solutions 2007, DCOR 2011). Prior to these efforts in federal waters, the State of California and Chevron Corporation conducted an assessment of the shell mounds remaining after the removal of the Chevron 4-H platforms (Hazel, Hope, Hilda, and Heidi), located in State waters (Phillips et al 2006). This and other studies have indicated the presence of elevated concentrations of the metals barium and zinc and some polycyclic aromatic hydrocarbon (PAH) compounds (Weston Solutions and Science Applications 2007, DCOR 2011, Phillips et al. 2006) within shell mound sediments. Nevertheless, little is known about the potential movement of contaminants from these shell mounds into the water column and eventually into the marine food web, and questions persist about their effects.

The purpose of the current study was to assess whether chemical contaminants, most notably PAHS, contained within POCS shell mounds could be migrating into the marine environment to the extent of posing a risk to marine organisms. Information from this study will be helpful for evaluating the effects on the marine environment of the potential abandonment or removal of shell mounds following decommissioning of offshore oil and gas facilities, and the development of mitigation measures designed to minimize any adverse effects.

1.2 Shell Mounds

Offshore oil and gas production platforms have been present off the Southern California coast since 1958 (MEC 2003). At present, there are 23 offshore platforms located in Federal waters, installed between 1968 and 1989 and operating in water depths ranging between approximately 45 and 365 m (BOEM 2013).

The hard substrate provided by the platform structure is colonized by sessile (fixed) invertebrates, especially mussels, barnacles, and rock scallops that settle and grow on its surface, forming a biotic layer. This biotic layer can be up 0.5 m thick and extend from the intertidal to depths of 30 m.

Encrusting organisms are routinely removed from the platform structure as a result of predation, storms, and mechanical cleaning by the platform operators.

When removed or shed, the organisms, especially their hard parts, create a mound underneath each platform that combines with rock cuttings and muds from drilling operations and normal marine deposition of suspended sediments. The height and areal extent of these shell mounds are dependent on water depth and age of the platform (Schroeder and Love 2004, MEC 2003). Shell mounds may be as high as 8 m above the seafloor at platforms located in shallower waters (MEC 2003) and can cover more than 6 km^2 at platforms located in deeper waters of the POCS (Schroeder and Love 2004). Table 2.1 provides information on the shell mounds and platforms located in the POCS (MEC 2003, BOEM 2013).

1.3 Study Design Options & Approach

Various methods are available to assess the movement of contaminants into aquatic food webs including:

1. Analysis of tissues of caged bivalves and fish (i.e., biosentinel studies),
2. Deployment of passive samplers, such as SPMDs, SPME devices, or POCIS, and
3. Deployment of active samplers using *in situ* solid phase extraction.

SPMDs, SPMEs, and POCIS are recently developed sampling devices used to monitor trace concentrations of organic contaminants. When placed in an aquatic environment, SPMDs and SPMEs accumulate hydrophobic organic compounds, such as polychlorinated biphenyls (PCBs), PAHs, and organochlorine pesticides from the surrounding waters. POCIS, which were not used here, are effective samplers for compounds that are more water-soluble than hydrocarbons, such as some pesticides, prescription drugs, steroids, hormones and other endocrine-disrupting compounds.

SPMDs in particular are designed to simulate the passive uptake of highly lipid-soluble organic compounds, such as PAHs, across biological membranes. They integrate ambient concentrations of contaminants throughout the deployment period. SPMDs are constructed of a tubular polyethylene membrane filled with a thin film of triolein, a purified lipid. The SPMD acts like a biological membrane, such as a fish gill, in selectively absorbing lipid-soluble organic compounds from water.

An alternative approach for assessing contaminant uptake in biota is to analyze fish and mussel tissues from the locations of interest. Recent studies have collected fish from beneath POCS platforms (Gale et al. 2012, Love 2012, Love et al. 2009) and caged bivalves at abandoned platforms located in state waters (Phillips et al. 2006) and analyzed them chemically to assess the potential uptake of contaminants from oil and gas platforms and associated shell mounds. NOAA and EPA have employed resident and caged bivalves to monitor the status and trends of contaminants in the nation's coastal waters and Great Lakes since the early 1980's (Kimbrough et al. 2008, Salazar et al. 1995, EPA 2012). Following the deconstruction and removal of the 4-H platforms in 2001, an assessment of potential contaminant migration from associated shell mounds was conducted that included direct coring of the shell mounds and deploying caged bivalves (Phillips et al. 2006). However, the use of fish tissues and caged bivalves to monitor contaminant levels from specific sources have their limitations. Many fish species range over too large an area to be useful for assessing the location of their contaminant uptake. Likewise, bivalves have depth and seasonal limitations to deployment. Therefore, study authors decided not to use chemical analysis of marine

Table 2.1. Pacific Outer Continental Shelf (POCS) platform and associated shell mound information. Information on Platforms A and B are highlighted.

Area Production Unit	Platform Name	Date Installed	First Production	Water Depth m (ft)	Distance From Shore km (mi)	Shell Mound Volume m^3 (yd^3)	Shell Mound Height m (ft)	Estimated Shell Mound Size m (ft)	Bottom Slope %
San Pedro Unit	Edith	1/12/83	1/21/84	49 (161)	13.7 (8.5)				
	Elly	3/12/80		78 (256)	13.8 (8.6)				
	Ellen	1/15/80	1/13/81	81 (266)	13.8 (8.6)				
	Eureka	7/8/84	3/17/85	213 (699)	14.5 (9.0)				
Pt. Hueneme Unit	Gina	12/1/80	2/11/82	29 (96)	6.0 (3.7)	3,211 (4,200)	4 (13)	46 x 64 (150 x 210)	1.01
Santa Clara Unit	Gail	4/5/87	8/8/88	226 (740)	15.9 (9.9)	382 (500)	1 (3)	4 scattered small mounds	3.6
	Grace	7/30/79	7/25/80	97 (318)	16.9 (10.5)	4,205 (5,500)	4 (13)	61 x 119 (200 x 390)	0.38
	Gilda	1/6/81	12/19/81	63 (208)	14.2 (8.8)	5,635 (7,370)	5 (18)	67 x 87 (220 x 285)	1.10
Pitas Point Unit	Habitat	10/8/81	12/15/83	89 (293)	12.6 (7.8)	5,230 (6,840)	6 (19)	Diameter 76 (250)	0.40
Carpinteria Area	Hogan	9/1/67	6/10/68	46 (152)	6.0 (3.7)	9,557 (12,500)	8 (26)	Diameter 79 (260)	0.33
	Houchin	7/1/68	4/28/69	50 (163)	6.6 (4.1)	8,350 (10,922)	6 (21)	Diameter 85 (280)	0.38
	Henry	8/31/79	5/15/80	52 (172)	6.9 (4.3)	5,505 (7,200)	6 (19)	Diameter 76 (250)	0.67
	Hillhouse	11/26/69	7/21/70	58 (190)	8.9 (5.5)	5,199 (6,800)	7 (22)	55 x 82 (180 x 270)	0.88
	A	**9/14/68**	**3/3/69**	**58 (190)**	**9.3 (5.8)**	**5,551 (7,260)**	**6 (20)**	**43 x 79 (140 x 260)**	**1.02**
	B	**11/8/68**	**7/19/69**	**58 (190)**	**9.2 (5.7)**	**6,568 (8,590)**	**5 (18)**	**49 x 64 (160 x 210)**	**1.03**
	C	2/28/77	8/1/77	59 (193)	9.2 (5.7)	3,509 (4,590)	4 (13)	49 x 72 (160 x 235)	1.14
Santa Ynez Unit	Hondo	6/23/76	4/2/81	256 (840)	8.2 (5.1)	1,147 (1,500)	3 (9)	3 mounds: 12 x 52 (40 x 170), 18 x 40 (60 x 130), 15 x 30 (50 x 100)	5.6
	Harmony	6/21/89	12/30/93	365 (1,197)	10.3 (6.4)				
	Heritage	10/7/89	12/18/93	328 (1,076)	13.2 (8.2)				
	Hermosa	10/5/85	6/9/91	184 (604)	10.9 (6.8)	<382 (<500)	1 (2)	2 mounds: 9 x 18 (30 x 60), Diameter 6 (20)	5.0
	Harvest	6/12/85	6/3/91	206 (676)	10.8 (6.7)				
	Hildago	7/2/86	5/27/91	131 (430)	9.5 (5.9)	<382 (<500)	<1 (<2)	Small and scattered	4.3
Pt. Pedernales Unit	Irene	8/7/85	4/13/87	73 (240)	7.5 (4.7)	2,844 (3,720)	3 (9)	Diameter 65.5 (215)	0.71

Source: Weston Solutions and Science Applications, 2007 animal tissues for these reasons and settled on employing SPMD technology because of its advantages as stated below.

Although passive sampler technology is relatively new, the technology and its associated protocols are improving (EPA 2012). There are many advantages of using SPMDS instead of aquatic organisms:

1. They can be deployed in waters that are outside the habitable range of or otherwise toxic to organisms. Passive samplers also have no restrictions on the physical environments where they can be deployed.

2. SPMD data have greater precision than animals tissue sentinels (EOA 2012, Phillips et al. 2006). They are more easily standardized than aquatic organisms, especially in studies sampling in different environments or in different seasons,

3. Migration, mortality, and metabolism issues, which are common when dealing with living organisms, are avoided with SPMDs.

4. SPMDs can be deployed for long periods of time (days to months) to estimate the time-weighted mean concentrations of contaminants, integrating fluctuations in contaminant concentration levels that could be due to surface runoff events, water movements, chemical spills, etc.

5. An important property of SPMDs in some environments is that they predominantly sample contaminants in the dissolved phase and not those attached to particulate material (Gourlay-Francé et al. 2008). Most toxicity is mediated through exposure to dissolved contaminants.

The optimal approach to determining PAH flux out of the shell mounds would require placing flux chambers on the surface of the shell mounds located under the platforms. These chambers must be carefully pushed into the seafloor surface with minimal disturbance of sediment chemical profiles. Then small volumes of water would be removed from each flux chamber over several weeks on a regular schedule for PAH measurements. Sampling would typically be performed by divers in water depths that are shallower than POCS platforms are located. Regardless of diver depth and safety and operational constraints posed by diving under operating production platforms, it is uncertain if accurate measurements of PAH flux could be determined in the small volumes of water that would be periodically withdrawn from the chambers. Therefore, based on technological restraints, this methodology was not used.

An SPMD sampling program was judged the best approach for evaluating PAHs in water near the Platform shell mounds. By measuring PAHs in bottom waters under and at distance from Platforms A and B, useful information could be obtained to directly address the issue of whether PAH concentrations in the bottom waters at the study sites were high enough to be toxic to marine life. The data could also be analyzed to see if there were patterns consistent with local sources. Spatial patterns in PAHs were examined by placing the SPMDs at different locations under each platform encompassing various shell mound thicknesses in order to determine whether higher PAH concentrations were associated with thicker portions of the shell mounds. Consequently, results are organized to highlight the concentrations and source of PAHs and differences among sites based upon analysis of the concentrations and relative composition of PAHs accumulated by the SPMDs.

1.4 Study Siting

Of the shell mounds studied previously at Platforms Gina, A and B, and the 4-H platforms, the shell mounds at Platforms A and B were determined to provide the best locations for this study. Figure 2.1 illustrates the location of Platforms A and B within the Santa Barbara Channel. The age of these platforms and their location in relatively shallow water compared to other POCS platforms have allowed the accumulation of larger shell mounds that rise more than 6 m from the surrounding seafloor. Most of the production well drilling at the two locations occurred concurrently in the early 1970's when current water quality regulations governing oil and gas platform discharges were less stringent. Given that both platforms were drilling into the Monterey Formation with wells of comparable depth and drilling was conducted concurrently, it was assumed that similar drilling programs were employed at both platforms. The thicker shell mounds at these two older sites were presumed to concentrate PAHs and therefore provide a larger potential source of contamination to the surrounding waters. Additionally, because core samples were collected recently from the shell mounds at Platforms A and B, there are some limited data on PAH concentrations (DCOR 2011). Finally, the entire Pitas Point Unit, which includes Platforms A and B, is located in close proximity to the former 4-H platform locations in state waters where previous assessments of shell mound contaminants and potential food web uptake of those contaminants had been conducted (Phillips et al. 2007).

2. Sampling & Analysis

2.1 SPMD Samplers

The study deployed SPMD samplers to measure PAH concentrations at the study locations. Environmental Sampling Technologies (EST) provided the SPMD devices. The aluminum and stainless steel SPMD carriers each measured approximately 9.5 cm long and 4.5 cm wide (Figure 2.2). Within each carrier were two flattened, low-density polyethylene tubing strips containing a thin film of pure lipid (triolein). The triolein strips each measured 15.24 cm in length. Three SPMD carriers deployed on an array at each station provided a total of 91.4 cm of flattened polyethylene tubing (i.e., 3 carriers × 2 strips × 15.24 cm) containing triolein. Prior to deployment of the SPMDs in the field, the strips were fortified with Performance Reference Compounds (PRCs) (fluoranthene-d10, anthracene-d10) to determine potential losses of PAHs during deployment. These PRCs are PAHs that have been labeled with stable isotopes (deuterium), which allow them to be distinguished during analysis from the normal fluoranthene and anthracene PAHs.

2.2 SPMD Deployment and Retrieval

AMS deployed SPMD samplers beneath Platforms A and B and at two control locations between June 19 and 21, 2013. Figures 2.3 and 2.4 illustrate the approximate locations of the SPMD arrays, relative to each platform and shell mound topography. Table 2.2 provides the latitude and longitude of the arrays.

At each platform, five arrays were deployed atop or on the flanks of the shell mounds by lowering them from the platform deck to the seafloor on a weighted hydro-line. The SPMDs were positioned to hang approximately 1-m above the mounds. One array (array 5) was deployed near the highest point of the shell mound and the other four were deployed around the margins, as allowed by access from the platform. The goal of this arrangement was to test whether the arrays placed where the shell mound was thickest would show the highest concentrations of PAHs, due to a potentially

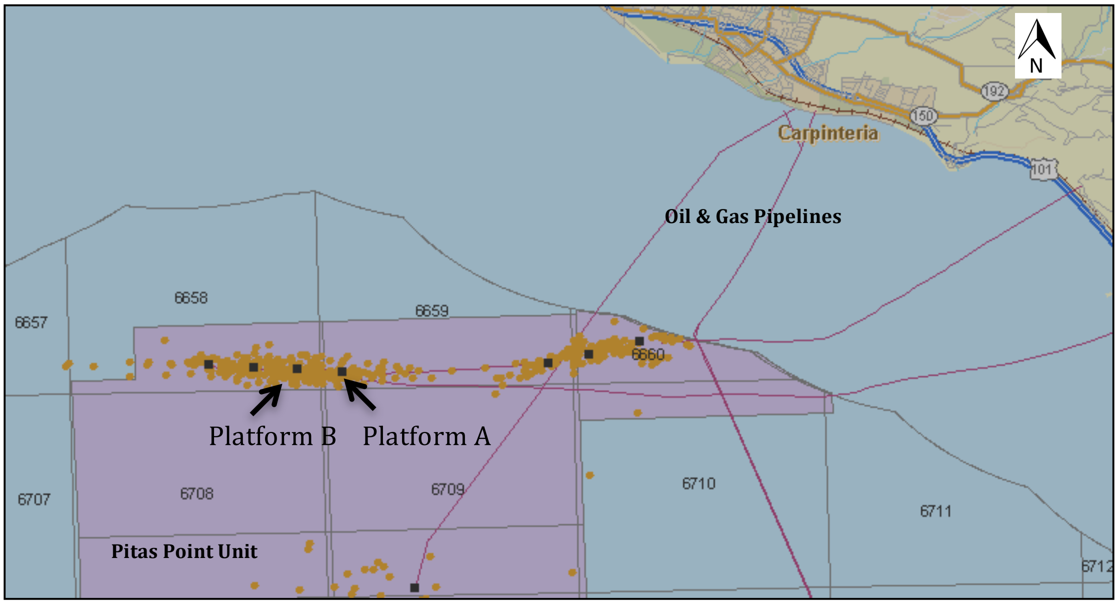

Figure 2.1. Study location in the Santa Barbara Channel.

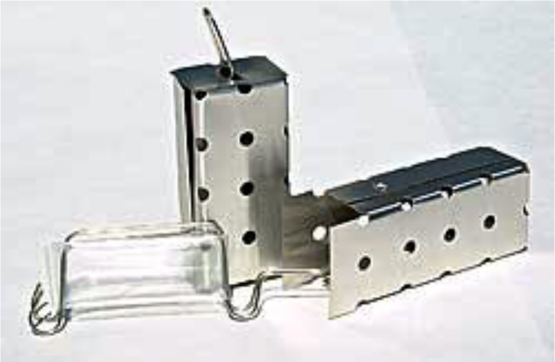

Figure 2.2. SPMD samplers.

greater local amount of drill cuttings containing PAHs. Sediment cores collected from shell mounds from the 4-H platforms after removal of the platform reported that the shell layer covering the shell mound is thickest along the flanks of the mounds and thinnest at the highpoint of the mounds where the accumulation of drill cuttings was greatest (deWit 2002). The SPMD arrays at each platform were considered to be replicate samples, so that the results could be compared statistically between Platform A and Platform B. Extreme care was taken to avoid fouling the lines on the platform substructure or other potential entanglements located under each platform.

For the control sites, which were meant to approximate ambient PAH concentrations near the platforms, an array approximately 0.2–0.4 km (0.2 nautical mi) was deployed west of each platform at the same water depth. These arrays were deployed from the M/V JAB using Sonardyne Type

7986 Lightweight Release Transponders. A Sonardyne Type 7967 OBC/LRT Deck Unit was used to trigger the releases during recovery.

SPMDs will accumulate or release PAHs while exposed to air, as well as to water. Consequently, to account for any air-borne PAHs, field-blank SPMDs were exposed to the air while sampling SPMDS were assembled and deployed in the field. Field blank SPMDs were exposed at Platform A (site 1), Platform B (site 4), and Control A. These same blanks were re-exposed during retrieval while the SPMD samplers were removed from the water and returned to their sealed storage cans. These field blanks were analyzed in the lab with the sampling SPMDs. Reported PAH mass loadings were then adjusted to account for PAHs reported in the field blanks, as was done for the laboratory blanks and the time zero blank.

Table 2.2. Deployment, retrieval and location information for each control SPMD array and Platforms A and B.

Location	Deployment Date	Latitude	Longitude	Retrieval Date	Days Deployed
Platform A (Center Point)	6/19/2013	34.331458° N	119.613011° W	7/24/2013	35 days
Platform B (Center Point)	6/21/2013	34.332620° N	119.622130° W	7/24/2013	33 days
Platform A Control	6/20/2013	34.332361° N	119.616465° W	7/25/2013	35 days
Platform B Control	6/20/2013	34.332365° N	119.654430° W	7/25/2013	35 days

SPMDs were retrieved between July 24–25, 2013, for a total deployment period of 33–35 days (Table 2.2). All five of the SPMD arrays deployed at Platform A were successfully recovered, as were the Control A and Control B arrays. At Platform B, three of the SPMD arrays were recovered, but two (numbers 2 and 3) (Figure 2.4) had become entangled on subsurface platform structures and could not be retrieved. For the Platform B-3 array, the line severed at a depth of about 30 ft and had to be left. The Platform B-2 array could not be pulled up, so based on the recommendation of the Platform B supervisor; field personnel attached weights to the surface end of the line and cast it away (eastward) from the platform.

2.3 SPMD Sample Handling

After the SPMD samplers were received from EST, they were stored at AMS in sealed storage cans at -20°C before leaving for and after returning from field efforts. During deployment and retrieval operations, the SPMDs (in the cans) were stored in coolers on double-bagged wet ice until deployed, and after retrieval. SPMD arrays were placed on clean aluminum foil laid down on the platform or boat deck to prevent contamination from surfaces. Field personnel handled the metal SPMD carriers with nitrile gloves and limited their exposure to air as much as possible.

2.4 Chemical Analysis

Fourteen SPMD samples were analyzed for PAH concentration by Axys Analytical Services, Ltd. (Axys) (Table 2.3). In addition to the SPMDs deployed in the field, an SPMD was analyzed that represented the initial concentration of PAHs when EST prepared all SPMDs ("EST Spike" sample). This sample was prepared like all SPMDs deployed in the field, but was stored at -20°C from the

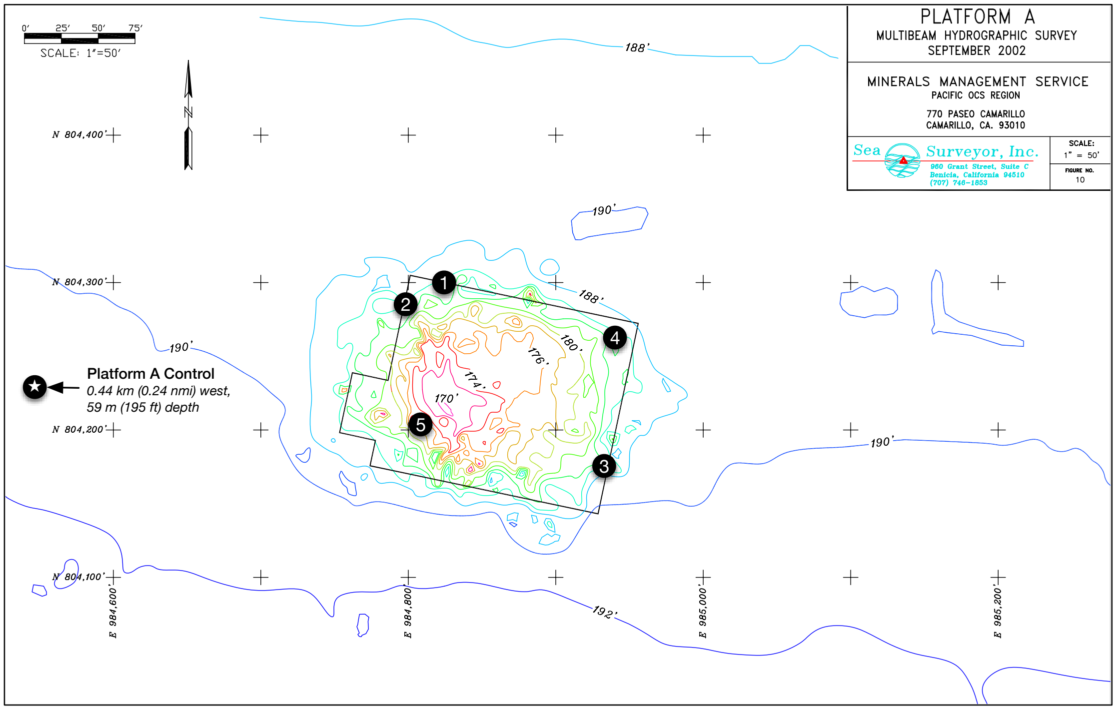

Figure 2.3. SPMD deployment locations at Platform A. (Base Map Source: MEC 2003).

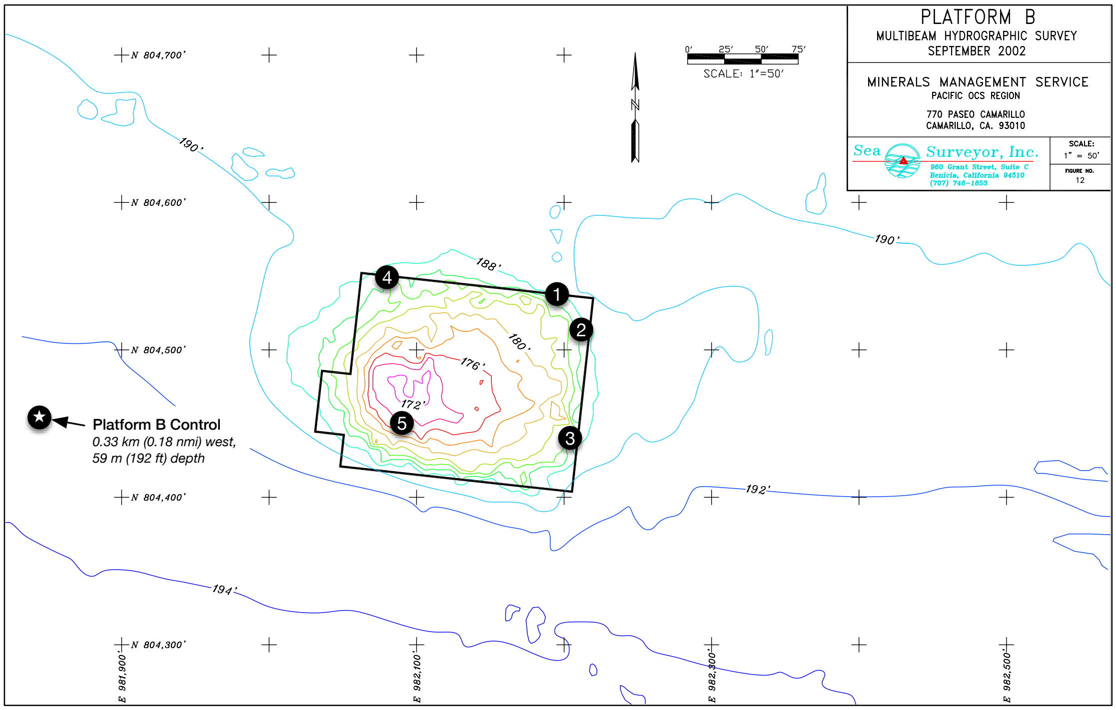

Figure 2.4. SPMD deployment locations at Platform B. (Base Map Source: MEC 2003).

time it was received from EST until it was sent for analysis. Differences in PAH concentration between this SPMD time zero sample and those deployed in the field represented uptake or loss of PAHs in the field.

Table 2.3. SPMD samples analyzed for PAH concentrations.

Study Location	SPMD Samples	Description
Platform A	5	Arrays deployed at Platform A (5 of 5 recovered)
Platform B	3	Arrays deployed at Platform B (3 of 5 recovered)
Control A	1	Array deployed at Control A
Control B	1	Array Deployed at Control B
Field Blank A	1	Field Blank exposed to air for Platform A sites
Field Blank B	1	Field Blank exposed to air for Platform B sites
Field Blank Control	1	Field Blank exposed to air for control sites
EST Spike	1	Archived sample representing initial PAH concentration in all SPMDs

2.4.1 Analytical Procedures

SPMDs were analyzed for determination of PAHs by low-resolution mass spectrometry (LRMS), using an RTX-5 capillary gas chromatograph (GC) column. The extraction and analysis process is described in detail in an analysis narrative report (Appendix A). Briefly, SPMD samples were extracted and analyzed in one batch with a procedural blank (Lab Blank) and an ongoing precision and recovery (OPR) reference sample. Analyte concentrations were determined by isotope dilution or internal standard quantification procedures, and recovery-corrected for possible losses during extraction and cleanup. The results were not blank-corrected.

PAH concentrations were reported for the SPMDs in units of ng/sample, where sample refers to the number of SPMD strips that were analyzed. Six SPMD strips were analyzed for each sample, with the exception of the following:

1. Array 5 at Platform A, for which four strips were analyzed, because two were not retrievable during field recovery, and
2. All Field Blanks (A, B, and Control), for which three SPMD strips were provided by EST.

The PAH concentrations in samples, with reporting limits (RLs) and data quality flags, are shown in Appendix B. Axys reports RLs using the sample detection limit (SDL), which accounts for any effects of sample matrix and recovery during the analytical process.

2.4.2 Data Quality Assurance / Quality Control (QA/QC)

The following data QA/QC issues were identified by Axys when analyzing the SPMD samples:

1. The sample from the Platform A-1 array had a small puncture in one of the SPMDs. The puncture was sealed to remediate it.
2. For the sample from the Platform A-4 array, half of the sample extract was inadvertently lost. Because the recovery values of the labeled standards were within the method control

limits and the isotope dilution quantification procedure automatically corrected for such losses, the data were considered to be unaffected.

3. Indeno(1,2,3-cd)pyrene was detected in the Lab Blank above the method control limits. This might indicate low-level impurities somewhere in the sampling and analysis stream. However, the reported concentration was below the lower method calibration limit (LMCL), and sufficiently low to not pose a problem in the analysis and the data were not considered to be significantly affected.

2.5 Data Analysis

The following sections describe how we corrected the raw PAH concentrations reported by the lab (ng/sample), calculated water concentrations (ng/L), and conducted statistical analyses to compare sites.

2.5.1 Data Corrections

The raw data for SPMDs reported by Axys were adjusted to account for the effects of laboratory processing (lab blank), initial PAH concentrations absorbed by the SPMDs during manufacture (time zero blank), and exposure to airborne PAHs during assembly, deployment and retrieval in the field (field blank), as follows:

1. PAH compounds with no reported results (i.e., non-detects, as identified by U flags; Appendix B) were recoded to a value of 1/2 of the listed RL for that compound to simplify further corrections.
2. The Lab Blank result was subtracted from all field sample results. The Lab Blank was an Axys procedural blank that represented the background for the entire processing and analysis of a single sample. Axys had not reported blank-corrected results.
3. Results were scaled to the equivalent of six analyzed SPMD strips, as needed. Because the number of SPMD strips analyzed was different for some arrays/sites, it was necessary to standardize the results in this way.
4. The value of the corrected EST Spike sample was subtracted from all field results. This effectively removed the starting (time zero) concentration of PAHs acquired by all SPMDs when initially prepared at EST.
5. The value of the corrected Field Blank sample associated with each array (Table 2.4) was subtracted from array results. For example, the Field Blank A results were subtracted from the results for arrays 1–5 at Platform A.

2.5.2 Water Concentration Calculations

Ambient water concentrations of PAHs were calculated from the SPMD mass data using a spreadsheet calculator that models water concentrations from the SPMD data (Alvarez 2013). This spreadsheet calculator is based on models previously developed by Huckins and others (2006). The average water concentrations of selected chemicals are estimated using PRC loss data, chemical sampling rates (when available), and the mass amounts of chemicals accumulated in the SPMD during deployment. The uptake of chemicals into passive samplers follows integrative (linear), curvilinear and equilibrium phases during the deployment/exposure period. Integrative uptake is the predominant phase for compounds with log K_{ow} (octanol-water partition coefficient) values ≥ 5.0 and exposure periods of as much as one month in SPMDs. During the integrative uptake phase the ambient chemical concentration (C_w) is determined by

$$C_w = N/R_S t$$

where

N is the amount of the chemical accumulated by the sampler (typically ng),

R_s is the sampling rate (L/d), and

t is the exposure time (d).

For SPMDs, regression models have been created which estimate a chemical's site specific R_s and its C_w based on the log K_{ow} of the chemical, the PRC's release rate constant and SPMD-water partition coefficient. A PRC's release rate is determined from the amount of PRC initially added to the SPMD and the amount remaining after deployment. (Alvarez 2013)

In this calculator, we used anthracene-d10 as the performance reference compound. Deuterated anthracene is typically used as the PRC standard as it was here. Since deuterated and normal anthracene have different retention times and mass charges the deuterated standard does not interfere with the analysis for anthracene in the sample using mass spectrometry. A second PRC was added by EST to the SPMDs during preparation (fluoranthene-d10) and could not be used in the calculator, because the initial spike concentration of that compound was less than the final. We converted the calculated water concentrations (pg/L) to units of ng/L (ppt) and recoded negative water concentrations (i.e., PAH losses) as zero (Appendix C).

2.5.3 Statistical Tests

For PAH concentrations and percent contribution to PAH total concentration, we tested for differences between the Platform A and B sites and their associated control sites by comparing mean values and 95% confidence intervals of recovered arrays. The Platform A group consisted of five observations and the Platform B group consisted of three observations (Table 2.4). The 95% confidence intervals were calculated using the R statistical programming language (R Core Team 2013)

3. Results

The chemical data from the SPMDs can be expressed two ways: (1) the total amount or measured mass for PAH analytes detected in the SPMD triolein, which would correspond to what would be present in an equivalent amount of lipid in a fish, and (2) the predicted concentrations of the PAH analytes in seawater that resulted in the measured mass in the SPMDs at the end of the deployment period. We chose to emphasize the second way of presenting the data, because water concentrations, rather than tissue concentrations of exposed organisms, are routinely used as the basis of water quality criteria and determining whether water quality is harmful to biota.

PAHs are complex organic molecules consisting of various number of carbon rings (predominantly benzene and sometimes pentene rings) formed from carbon atoms with other atoms attached to the ring carbons and extending outside the rings. PAHs comprised of fewer carbon rings are more water soluble than are those comprised of more carbon rings. Consequently, the preponderance of PAHs with different numbers of rings can provide clues about how fresh or weathered the PAHs mixtures are. Moreover, within a class of PAH (e.g., naphthalene) are different forms (homologs) that are differentiated by the numbers of carbons attached to the ring(s), referred to as alkyl. Typically, PAH alkyl homologs are distinguished as C-0 through C-4 or more, depending on the number of extra-ring carbons. As the PAHs are partially combusted or degraded by microbes, the extra-ring carbons are removed, leaving behind only hydrogen atoms and eventually leave only the C-0, or parent compounds.

We condensed the data set to six dominant compound groups consisting of 2–4 ringed PAHs, which constituted more than 94% of the total resolved PAHs (Appendix D) and would, therefore, probably be representative of site differences for total PAHs:

1. Naphthalenes
2. Fluorenes
3. Phenanthrenes/Anthracenes
4. Dibenzothiophenes
5. Fluoranthenes/Pyrenes
6. Chrysenes.

The SPMD samples contained parent (bare ring or C0) compounds and alkylated homologs of these PAH compounds (i.e., chains of additional carbons attached to the aromatic ring or C1, C2, C3, etc.) (Table 3.1). We calculated water concentrations for these six PAH groups by summing the parent and alkyl homologs for each. For example, concentrations for the naphthalenes class are the sum of the parent compound (C0-naphthalene) plus homologs of that compound with 1–4 added carbons (C1-, C2-, C3-, and C4-naphthalene). Measurable water concentrations of these PAH compounds were found in all of the SPMDs deployed in this study. We also calculated the percent contribution of those PAHs to the total water concentration for those compounds to interpret compositional differences of the PAH compound groups between sites.

Table 3.1. Six dominant PAH groups in recovered SPMDs and the alkyl homologs present across all sites.

PAH Class	Rings	Alkyl Homologs Present			
		C-1	C-2	C-3	C-4
Naphthalenes	2	x	x	x	x
Fluorenes	3	x	x	x	
Phenanthrenes/Anthracenes	3	x	x	x	x
Dibenzothiophenes	3	x	x	x	x
Fluoranthenes/Pyrenes	4	x	x	x	
Chrysenes	4	x	x		

3.1 The Source of PAHs

The PAH composition of mixtures provides clues to their original chemical source. In this case, the pattern of ring alkylation is informative. In Figure 3.1 we plot the concentrations of C0–C4 homologs for the six PAHs in a typical sample from this study. One can see a recurring pattern of ring alkylation in most of the PAH groups, whereby the concentrations are lowest in the parent (C0) compound, are higher in C1 homologs, and peak in the C2 or C3 homologs. This pattern is typical of crude oils (Youngblood and Blumer 1975). Decreasing concentrations in the chrysene homolog series are the exception in these samples (Figure 3.1).

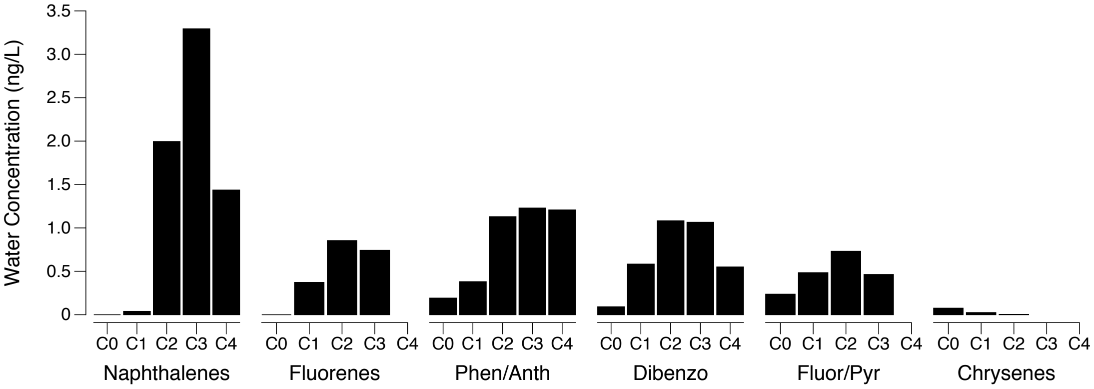

Figure 3.1. Water concentrations of the alkyl homolog series of 2–4 ring PAHs for the Platform A-3 Sample.

3.2 Site Differences in PAH Water Concentrations and Composition

We first compare the water concentrations of PAHs at the sites and then discuss compositional differences between sites.

3.2.1 PAH Water Concentrations

There were several patterns in the SPMD-derived water PAH concentration data. First, the concentrations of nearly all PAH groups were higher at the platforms than at the controls sites, especially at Platform A (Table 3.2). The one exception to this pattern at Platform A was naphthalenes, which for some unknown reason were highest at the control A site. Second, at the Platform B control site, only dibenzothiophenes and fluoranthenes/pyrenes were detected at concentrations below (outside) the 95% confidence intervals of the reported concentrations for the same PAH compounds in Platform B samples. The 95% confidence intervals are a standard statistical measure for reporting the spread of the data and are used to estimate the range within which the true mean of a set of data is expected to occur with a probability of 0.95. Finally, Platform A had significantly higher concentrations of PAHs than Platform B across all the major PAH groups (Table 3.3; Figure 3.2).

Table 3.2. Water concentrations (ng/L) of six dominant PAH groups (including all alkyl homologs) calculated for SPMDs deployed at each array site.

	Naph		Fl		Phen/Anth		Dibenzo		Fluo/Pyr		Chry		Total PAHs	
Array Site	**A[1]**	**B[1]**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
1	3.77	0.74	1.59	0.73	3.09	0.41	2.18	0.39	1.39	0.80	0.09	0.04	12.11	3.11
2	4.29	ND	1.26	ND	2.22	ND	1.75	ND	1.05	ND	0.09	ND	10.66	ND
3	6.76	ND	1.97	ND	4.14	ND	3.37	ND	1.91	ND	0.1	ND	18.25	ND
4	4.62	1.04	1.61	0.57	3.43	1.23	2.76	0.49	1.71	0.81	0.13	0.05	14.26	4.19
5	5.36	0.76	1.92	0.39	3.33	0.90	2.15	0.42	1.53	0.87	0.10	0.05	14.39	3.39
Control	4.14	0.47	0.47	0.21	0.92	0.69	1.07	0.24	0.88	0.72	0.05	0.03	7.53	2.36

[1] = Platforms A and B

ND = No data. Arrays 2 and 3 at Platform B were not recovered.

Table 3.3. Mean water concentrations (ng/L) of PAH groups (with 95% confidence intervals).

PAH Group	A Sites		B Sites	
	Platform A (n = 5)	Platform A Control (n = 1)	Platform B (n = 3)	Platform B Control (n = 1)
Naphthalenes[1]	4.96 (3.52–6.40)	4.14	0.85 (0.43–1.26)	0.47
Fluorenes[1]	1.67 (1.31–2.03)	0.47[2]	0.56 (0.14–0.99)	0.21
Phen/Anth[1]	3.24 (2.38–4.10)	0.92[2]	0.85 (-0.18–1.87)	0.69
Dibenzo[1]	2.44 (1.66–3.23)	1.07[2]	0.43 (0.31–0.56)	0.24[2]
Fluo/Pyr[1]	1.52 (1.11–1.92)	0.88[2]	0.83 (0.73–0.92)	0.72[2]
Chrysenes[1]	0.10 (0.08–0.12)	0.05[2]	0.05 (0.03–0.06)	0.03
Total PAHs[1]	13.93 (10.37–17.50)	7.53[2]	3.56 (2.17–4.96)	2.36

[1] = Platform A and Platform B 95% confidence intervals do not overlap.

[2] = Control concentration occur either lower or higher (outside) the estimated 95% confidence interval range for PAH concentrations reported at each platform.

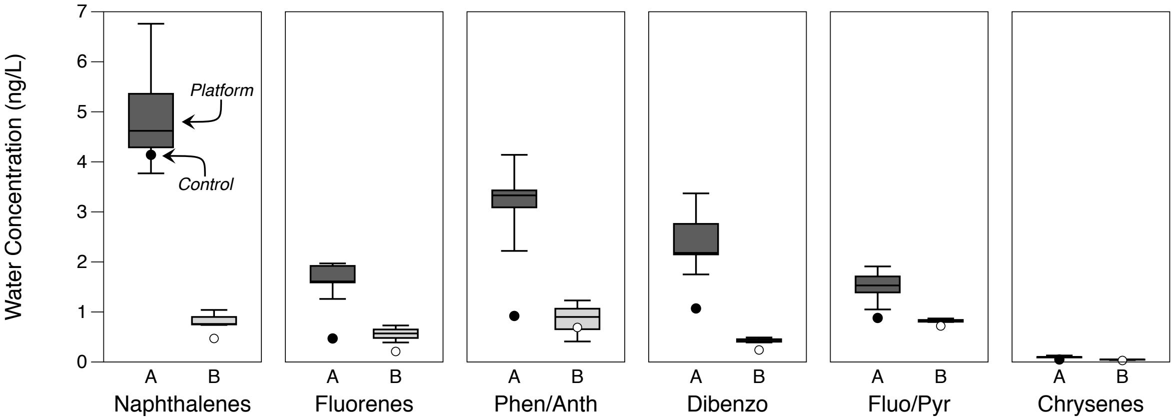

Figure 3.2. Water concentrations of PAH groups at Platform A and B sites. Each box plot shows the spread in the data with the range (lines above and below boxes), median (lines through boxes) and the 25% and 75% quartiles (the lower and upper boundaries of the boxes) of these data. Associated controls are shown as points.

3.2.2 PAH Composition

The samples from within each platform were relatively consistent in the composition of PAHs, but the two platforms differed significantly in the contribution of certain PAH groups to total PAHs. Platforms A and B differed primarily in the percentage contributions of naphthalenes, dibenzothiophenes and fluoranthenes/pyrenes (Table 3.5 and Figure 3.2). The naphthalenes and dibenzothiophenes have larger contributions to PAH totals at Platform A, than at Platform B. The converse is true for fluoranthenes/pyrenes. This suggests that PAHs collected at Platform A and Platform B have different hydrocarbon sources. For unknown reasons, the single array at Control A had a much higher contribution of naphthalenes to total PAHs than did the other three sites (Platform A, Platform B and Control B

Table 3.4. Percentage contribution of six dominant PAH groups (Including all alkyl homologs) to the total PAH concentrations of SPMDs at each array site.

	Naph		Fl		Phen/Anth		Dibenzo		Fluo/Pyr		Chry		Total PAHs	
Array Site	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
1	30.7	23.0	12.9	22.7	25.1	12.8	17.7	12.3	11.3	25.0	0.7	1.2	98.4	97.0
2	39.5	ND	11.6	ND	20.4	ND	16.1	ND	9.7	ND	0.9	ND	98.1	ND
3	36.7	ND	10.7	ND	22.4	ND	18.3	ND	10.4	ND	0.6	ND	99.1	ND
4	31.5	23.8	11.0	13.0	23.4	28.1	18.9	11.3	11.7	18.5	0.9	1.2	97.4	95.8
5	36.6	21.6	13.1	11.1	22.8	25.4	14.7	11.9	10.5	24.6	0.7	1.5	98.3	96.1
Control	53.1	18.6	6.0	8.5	11.8	27.6	13.7	9.4	11.3	28.6	0.7	1.2	96.7	94.0

ND = No data. Arrays 2 and 3 at Platform B were not recovered.

The data in Figures 3.2 and 3.3, and Tables 3.2 and 3.4 more clearly illustrate some subtleties in the data not yet discussed. The PAH concentration and composition for most PAH groups tend to cluster by platform group—A sites (Platform A arrays and Control A array) versus B sites (Platform B arrays and Control B array). However, there is generally a larger separation between the platform and control site arrays at Platform A than at Platform B, especially for naphthalenes and fluorenes and phenanthrene/anthracenes. This pattern suggests greater spatial variation surrounding Platform A than at Platform B, perhaps due to a source of PAHs in the vicinity of Platform A. Moreover the SPMD arrays deployed at the topographic high point of the shell mound at each platform did not exhibit higher concentrations of PAHs (Array 5; Figure 2.3, Figure 2.4 Table 3.2, Figure 3.4). Therefore, it appears that proximity of an array to thicker regions of the shell mounds did not result in noticeably higher PAH concentrations.

Table 3.5. Mean percentage contribution of PAH groups (with 95% Confidence Interval Ranges).

PAH Group	**A Sites**		**B Sites**	
	Platform A (n = 5)	**Control A (n = 1)**	**Platform B (n = 3)**	**Control B (n = 1)**
Naphthalenes	35.0 (30.3–39.6)	53.1	22.8 (20.1–25.5)	18.6
Fluorenes	11.9 (10.5–13.2)	6.0	15.6 (11.1–31.1)	8.5
Phen/Anth	22.8 (20.7–24.9)	11.8	22.1 (1.8–42.4)	27.6
Dibenzothiophene	17.1 (15.0–19.3)	13.7	11.8 (10.5–13.1)	9.4
Fluo/Pyr	10.7 (9.7–11.7)	11.3	22.7 (13.6–31.8)	28.6
Chrysenes	0.7 (0.6–0.9)	0.7	1.3 (0.9–1.7)	1.2
Total PAHs	98.3 (97.5–99.0)	96.7	96.3 (94.8–97.9)	94.0

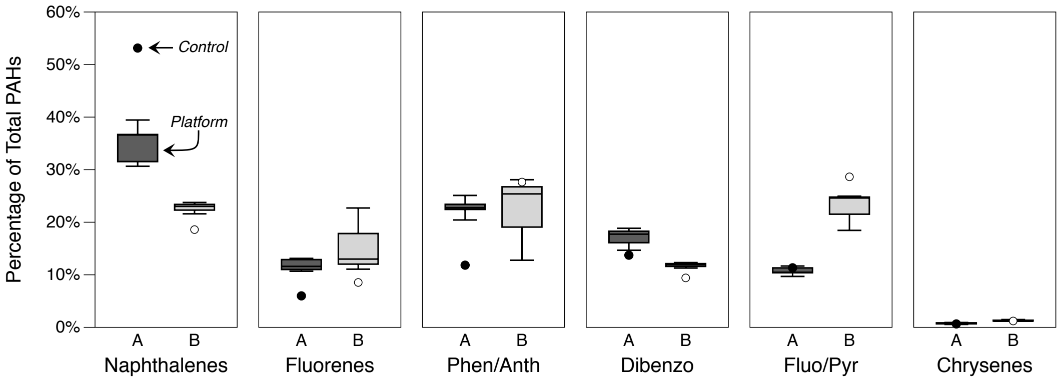

Figure 3.3. Percentage contributions of PAH compound groups to total PAHs at Platforms A and B sites. Each box plot shows the spread in the data with the range (lines above and below boxes), median (lines through boxes) and the 25% and 75% quartiles (the lower and upper boundaries of the boxes) of these data. Associated controls are shown as points.

3.1 Potential Field Sources of PAH Contamination

During deployment and retrieval of the SPMDs, field personnel observed two field sources of hydrocarbons that could have potentially influenced the PAH results from the SPMDs—boat engine exhaust and surface oil slicks.

1. While deploying the SPMDs at the control sites on June 20, 2013, the assembled array was towed behind the boat in the engine wash (wet exhaust from a ducted jet boat engine) while the boat repositioned near the target coordinates. The exposure period before the arrays were allowed to drop to the bottom was about 17 minutes at the Control A site and seven minutes at the Control B site.

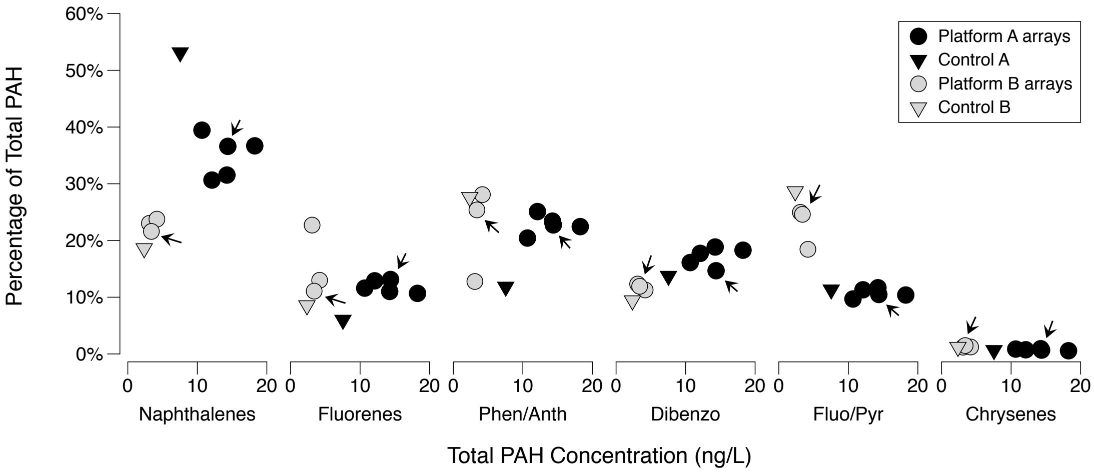

Figure 3.4. Plots by compound class of percentage of total PAHs versus water concentrations. (Arrows indicate samplers placed at the topographic high (i.e., thickest) point on the shell mound).

2. While retrieving the SPMDs on July 24, 2013, field personnel observed patches of oily sheen on the water surface near Platforms A and B. At Platform A, these patches appeared to bloom near the northwest corner of the platform structure and move eastward. At Platform B, patches appeared to the northwest and north, but were farther away. The source of the surface oil sheens was not apparent but assumed to originate from natural seepage at the seafloor, and they were not visible in the water directly above where the SPMD arrays were being retrieved, however droplets of seepage will move with the prevailing currents as they ascend towards the sea surface.

As discussed previously, the performance characteristics of passive samplers such as SPMDs make them particularly well suited for longer-term, integrated sampling. The chemical sampling rates for the SPMDs, as calculated by the water concentration calculator spreadsheet, range from 0.3–0.7 L/day across all reported homologs of the six PAH compound groups (Appendix C). Therefore, it is unlikely that exposing the SPMD samplers for several minutes to engine wash during deployment and surface oil sheen during retrieval would have a significant influence on the integrated uptake over a deployment period of over 30 days. Regardless of this understanding of how SPMDs work, every effort was made by the field teams to avoid any floating oil sheen while retrieving SPMD arrays. Upon retrieval, SPMDs were placed on ice and then frozen, stopping the absorbance reaction.

SPMDs from both control sites had low PAH concentrations compared to platform sites, so the potential exposure during towing did not appear to affect the conclusions of this study.

4. Discussion

There are three general conclusions that can be drawn from the SPMD PAH data gathered at Platforms A and B and their respective control locations:

1. The relative abundances of parent PAHs to their C-1, C-2, C-3 and C-4 homologs[1] in all of the samples are consistent with a crude oil source. Most crude oil has higher abundances of alkylated homologs (C-1 to C-4) than the parent compound (i.e., no side chains on the aromatic rings, C-0) (Youngblood and Blumer 1976). Although pyrogenic sources of PAHs (e.g., wildfires and incompletely combusted hydrocarbons in exhaust of internal combustion engines; dominated by bare-ring [i.e., non-alkylated, or C-0] compounds) could contribute to total PAHs. In our samples, alkylated PAHs were abundant and dominant (Figure 3.1). Therefore, we conclude that the sources of PAHs in water sampled for this study were crude oil that had not been refined or combusted.

2. There are generally higher PAH concentrations in the waters in the immediate vicinity of the platforms than at the control sites. The relatively elevated PAHs near the platforms suggest localized low concentration sources of hydrocarbons that are closer to the platforms than to the controls.

3. There are differences in concentrations of several PAHs between Platform A sites and the Control A site and Platform B and Control B sites that are consistent with a relatively fresh

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[1] Aromatic hydrocarbon rings forming the PAH that have no extra carbons or side-chains attached are called parent compounds and have the designation of C-0. In petroleum, most of the PAHs have side-chains or additional carbons attached and are typically more abundant than the parent compound and have the designations of C-1, C-2, C-3, C-4, etc.

source of petroleum oil near Platform A. The concentrations of total resolved PAHs and many of the compound groups, including the 2–4 ringed PAH groups, are higher at Platform A than at the Platform B and the two control sites (Tables 3.2 and 3.3 and Figure 3.2). Conversely, the higher molecular weight PAHs (e.g., fluoranthene/pyrene and chrysene) are proportionally depleted at Platform A. Because weathering of crude oil differentially depletes lower molecular weight compounds such as naphthalenes, these patterns suggest a source of relatively fresh PAHs that is either located closer to Platform A or that is less diluted there than the sources of PAHs captured at the Platform B and Control B locations.

Previous investigations at the 4-H platforms in nearby state waters reported total PAH concentrations (Ocean Plan listing) in the shell mound sediments ranging from 0.064 to 0.081 ppm with a corresponding concentration in bagged *Mytilus* mussel tissue of 0.162 ppm (Phillips et al. 2006). Recent coring of the shell mounds at both Platforms A and B by the platform operator during installation of new pipelines reported PAH concentrations only above the practical quantification limits ((PQL) for naphthalene and 2-methylnapthalene at Platform B (EPA Method 8270). All other measured PAHs were below the PQL. Concentrations of 0.79 mg/kg (ppm) and 0.92 mg/kg (ppm), respectively, were reported in sediments for these two compounds (DCOR 2011). Directly comparing sediment PAH concentrations from past studies and in-water concentrations from this study is extremely difficult since with the background concentrations of PAH contributed from locally observed seeps there is no reliable way to determine how much, if any, of the analytes detected in the sediment have been released to the water column. Often the contaminant of concern is chemically bound to the sediment itself, is not water-soluble or bioavailable and becomes weathered over time. Additionally, there may be multiple distinct and indistinguishable hydrocarbon sources contributing to PAH concentrations in the water, such as from regional natural seepage.

Interpretation of the data leaves open the question of the source of crude oil at or near Platform A, and to a lesser degree Platform B. The most probable sources of observed PAHs are:

1. Natural oil seepage at or near the platform,
2. A leaking well head or pipeline near the platform, or
3. The shell mound.

Although leaking oil from subsea pipelines and other infrastructure is one possible source of the detected PAHs, this source is not considered a likely candidate because of in-place procedures and equipment to detect and stem the flow of any leaking oil. If any of the platform infrastructure was leaking, much higher water concentrations of PAHs would be expected. The most likely source of the PAHs is natural oil and gas seepage. The Santa Barbara Channel and the Monterey formation, in particular, the primary source of most POCS oil and gas production, has abundant petroleum seepage originating from geological sources that flows through naturally occurring fissures and fractures in overlying sediments into the water column (Wilkinson, 1972; Kraus and Estes, 1977; Fisher, 1978; Reed and Kaplan 1979, Spies et al., 1980; Stuermer et al., 1982 and Quigley, 1997). Work by Allen and Schlueter, (1969) at Platform A reported seepage around Platform A estimated at up to 10 bbls per day. At present, the volume of seepage near the platform may be substantially lower than this estimate, which was made months after the 1969 Platform A blowout but after some control measures were taken to stop leakage.

What contributions the PAHs within the shell mounds might be making, if anything, to water column PAHs is unfortunately unclear from the study results. As indicated above, the patterns of PAHs collected by individual SPMDs over the shell mounds themselves do not appear to indicate migration of hydrocarbons from the mounds (Table 3.2). The reported PAH signals detected by each SPMD did not correspond with the thickness of the shell mounds (Figures 2.3 and 2.4), as found by previous studies, in which the greatest concentration of hydrocarbons were located in the highest and thickest parts of the mounds (deWit 2002, MEC 2003). The differences among individual arrays, especially at Platform A, are more indicative of a point source of PAHs, such as from a natural seep that is located in close proximity to the platform and upcurrent from the control site. As indicated in the discussion above, study data are consistent with a crude oil source of relatively new and un-weathered oil located near Platform A and again near Platform B.

Even with a very extensive list of PAH analytes, assignment of samples to particular physical sources is difficult. For example, two recent reports, which primarily used aliphatic biomarker compounds in their analysis to distinguish sources of more than 400 oil samples using a much larger list of petroleum compounds than measured in the present study, found it difficult to distinguish oil samples between seeped and produced sources (Lorenson et al, 2009; Lorenson et al, 2011). Unfortunately sediment concentration data collected previously from the Platform A and B shell mounds (DCOR 2011) did not provide the level and detail of PAH analysis needed to compare to results from this study.

One source of data that possibly provides some additional insight to the source of PAHs at or near Platform A are those collected concurrently to the present study by the Southern California Coastal Research Project (SCCWRP) using SPMEs recovered from Platform A, Control A and Control B locations. The SPMEs measured PAHs in the waters just above the shell mounds and near the water surface. Unquantified differences in sampling efficiencies and uptake kinetics between the SPMEs and SPMDs make direct comparison between the two data sets problematic. However, in the SPME measurements, all PAHs, with the exception of 2,3,5-trimethylnaphthalene and 2-methylphenanthrene, were below method detection limits (Maruya 2013). While these compounds do occur in seawater in contact with crude oil, the detection of only two PAH analytes is insufficient to allow accurate assignment to the exact source of the oil but confirms that the concentration of PAHs at the study sites is very low. Additionally, the presence of alkylated benzenes in SCCWRP's SPMEs is consistent with a crude oil source as was concluded here.

Regardless of the source of the oil sampled by the SPMDs, the PAH concentrations measured do not suggest risks to wildlife or humans. The California Ocean Plan (Ocean Plan; State Water Resources Control Board, 2009) has established water quality objectives for the concentrations of PAHs below which human health is protected if aquatic life is consumed. Water quality objectives in the Ocean plan are established based upon laboratory toxicity and modeling results using estimated rates of bioaccumulation in marine life and consumption rates by humans with inclusion of appropriate safety factors. The water quality objective for PAHs has been set as cumulative concentrations (whole water samples) of a subset of the PAHs measured in the current study. Because we measured many more PAH compounds than are regulated by the Ocean Plan, a comparison between the current results and the Ocean Plan water quality objectives must be made using only those PAHs included in the Ocean Plan (Table 4.1 and Figure 4.1). When the PAHs included in the Ocean Plan water quality objective are compared to the concentrations of the same PAHs in the present study, the maximum concentrations measured in any of the current samples are less than 10% of the water quality objective (Table 4.1).

Table 4.1. Total PAH concentrations (ng/L) for the SPMD arrays with the highest concentrations, calculated using the PAH list for the Ocean Plan Water Quality Objective.

Platform A Sites		Platform B Sites		Ocean Plan Water Quality Objective
Platform A-4	Control A	Platform B-4	Control B	
0.6	0.5	0.7	0.3	8.8

The scientific literature and other regulatory documents also indicate the maximum concentrations measured near Platform A and Platform B are substantially below those likely to cause organism toxicity or human health concerns (Table 4.2). Kalf et al (1997) calculated Maximum Permissible Concentrations (MPC) of 10 PAHs and established Negligible Concentrations at 1% of the MPC, which took into account possible effects of combined toxicity due to the presence of other substances. The concentrations measured in the present study ranged from 2% to 42% of the Negligible Concentrations. While the California Toxics Rule (EPA, 2000) does not set maximum concentrations for PAHs in salt water, the freshwater concentrations established to protect humans who consume aquatic life are more than 5,400 times greater than the concentrations measured in the present study. Very recent studies designed to measure subtle, non-lethal effects of PAHs on marine organisms showed that *in vitro* exposure to PAHs from the Deepwater Horizon spill adversely affected the function of tuna cardiomyocytes (Brette et al, 2014). Nevertheless, the exposure concentrations of 22 μg/L and 61 μg/L were several orders of magnitude greater than ambient concentrations measured in the current study. Moreover, a direct connection between *in vitro* effects measured on tissues in the laboratory and *in vivo* effects on whole organisms in the wild has not been established. Consequently, while a number of studies have documented the incorporation of carbon from spilled or seeped PAHs into organisms in marine food webs (Spies et al, 1989; Mearns et al 2013), the ocean concentrations measured in the present study are well below both regulatory objectives and published toxic concentrations.

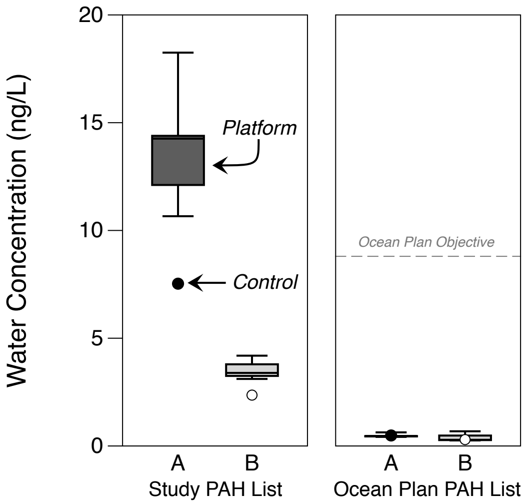

Figure 4.1. Total PAH water concentrations (ng/L), calculated using the PAH list in this study versus the list for the Ocean Plan Water Quality Objective.

Table 4.2. Water concentrations of PAH compounds measured in this study compared with published and regulatory maximum concentrations for the protection of aquatic life and human health.

Compound	Source		
	Kalf et al, 1997	California Toxics Rule	This Study
	Negligible Concentration[1] ng/L	CTR Freshwater fish consumption[2] ng/L	Maximum, ng/L
anthracene	0.7	$110x10^6$	0.3
phenanthrene	3	N/A	0.19
fluoranthene	3	$370x10^3$	0.18
benzo[*a*]anthracene	0.1	49	0.02
chrysene	3.4	49	0.11
benzo[*k*]fluoranthene	0.4	49	0.009
benzo[*a*]pyrene	0.5	49	0.013
benzo[*ghi*]perylene,	0.3	N/A	0.015
indeno[*1,2,3-cd*]pyrene	0.4	49	0.073

[1] = Negligible Concentration = Maximum Permissible Concentration/100, which takes into account possible effects of combination toxicity due to the presence of other substances.

[2] = Maximum freshwater concentration for the consumption of organisms by humans.

5. Study Conclusions

The current study was developed to assess whether PAHs in POCS shell mounds were migrating into the marine environment and posing a risk to marine organisms. The approach utilized multiple PAH-absorbing SPMDs deployed over the shell mounds of two nearshore POCS platforms and at one control/background location sited near each platform. The individual SPMDs at each platform were placed over both the thin margins and the thickest section of the shell mound where the lowest and highest concentrations of PAHs were expected to be located, respectively. Based on study results and analyses, the following study conclusions can be made.

1) The SPMDs at both the platform sites and control sites detected very low concentrations of PAHs in the water column.
2) The abundances of C-1, C-2, C-3 and C-4 homologs of 2–4 ringed PAHs relative to their C-0 parent compounds (naphthalenes, fluorenes. phenanthrenes/anthracenes, dibenzothiophenes, fluoranthenes/pyrenes, and chrysenes) in the SPMD samples are chemically consistent with a crude oil source rather than a combusted hydrocarbon source.
3) Detected PAHs at all stations are consistent with relatively fresh sources of petroleum rather than an older weathered hydrocarbon source, as would be expected from the 30-40 year old drill cuttings buried in the shell mounds.
4) Although the shell mounds can not be entirely ruled out as a source of some of the PAHs reported in this study, the fact that the SPMDs deployed over the thicker areas of each shell mound at Platforms A and B, where the highest concentration of hydrocarbon-containing drill cuttings have been reported, did not detect higher PAH concentrations than those deployed over the fringes of the mounds suggests that the shell mounds are not the primary source of detected PAHs.
5) Although this study was able to accurately detect very low (part per trillion) concentrations of PAHs in the water adjacent to Platforms A and B, as well as at the two control sites, the

proximity of natural hydrocarbon seeps to the study area and their contribution to detected PAH concentrations prevented this study from definitively differentiating the contribution, if any, made by the shell mounds to those PAH concentrations.

6) Based on observed PAH concentrations at the two control sites and the dominance of un-weathered crude oil PAHs in study results, the potential contribution of any shell mound PAHs to observed PAHs can be assumed to be very low.
7) The most likely source of PAHs is natural oil seepage, which is prevalent throughout the Santa Barbara Channel (Wilkinson, 1972; Kraus and Estes, 1977; Fisher, 1978; Reed and Kaplan, 1979, Spies et al., 1980; Sturmer et al., 1982 and Quigley, 1997). This appears especially true at near Platform A where seepage has been previously reported (Allen and Schlueter 1969).
8) Finally, PAH concentrations observed in the water column, regardless of the source of the PAHs, were more than an order of magnitude lower than regulatory water quality objectives established by the State of California to protect marine biota and human health. Consequently, any potential contribution of PAHs from platform shell mounds to observed water concentrations of PAHs is likely very small and probably poses no appreciable risk to area marine biota.

6. References

Allen, A.A. and R. S. Schlueter. 1969. Estimates of Surface Pollution Resulting from submarine Oil Seeps at Platform A and Coal Oil Point. Prepared by General Research Corporation for Santa Barbara County. 41 pgs.

Alvarez, D.A., 2010, Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies: U.S. Geological Survey, Techniques and Methods 1–D4, 28 p.

Alvarez, D.A. 2013. *Estimated Water Concentration Calculator from SPMD Data Using Multiple PRCs: Version 5.1*. Microsoft Excel spreadsheet. http://www.cerc.usgs.gov/Branches.aspx?BranchId=8. Accessed November 2013.

BOEM. 2013. Bureau of Ocean Energy Management Pacific Region Platform Operators and Platform Facts. http://www.boem.gov/BOEM-Newsroom/Offshore-Stats-and-Facts/Pacific-Region/Pacific-Platform-Operators.aspx. Accessed November 14, 2013.

California State Water Resources Control Board. 2009. California Ocean Plan. State Water Resources Control Board.*1001 I Street Sacramento, CA 95814 (916) 341-5250 Homepage: http://www.waterboards.ca.gov*

DCOR. 2011. Dos Cuadras Pipeline Replacement Project Riser Installation, OCS-P-0241 Platform A and Platform B. December 2011.

deWit, L. A. 2002. Shell Mounds Environmental Review. Final Technical Report. Prepared for California State Lands Commission and California Coastal Commission, Vol. 1.

Environmental Protection Agency (EPA). 2002. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California. 40 CFR Part 131. Vol. 65, No. 97/Thursday, May 18, 2000/Rules and Regulations

Environmental Protection Agency (EPA). 2012. *Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sites, Sediment Assessment and Monitoring Sheet (SAMS)*

#3. Prepared by the EPA Office of Superfund Remediation and Technology Innovation and the Office of Research and Development. OSWER Directive 900.1-110FS. December 2012.

Fisher, P.J.1978. Oil and tar seeps, Santa Barbara basin, California. California Offshore Gas, Oil and Tar Seeps, pp. 1-62. California State Lands Commission, Sacramento, California

Gale, R.W., M. J. Tanner, M.S. Love, M.M. Nishimoto, and D. M. Schroeder, 2012. *Comparison of concentrations and profiles of polycyclic aromatic hydrocarbon metabolites in bile of fishes from offshore oil platforms and natural reefs along the California coast: U.S. Geological Survey Open-File Report 2012–1248, 27 p. and supplemental tables. Weston Solutions, Inc. 2007. Physical and Chemical Characteristics of the Platform Gina Shell Mound, Final Report*. Prepared for the Mineral Management Service by Weston Solutions Inc. and SAIC. March 2007.

Gourlay-Francé C, C. Lorgeoux, and C. Tusseau-Vuillemin, M.H. 2008. *Polycyclic aromatic hydrocarbon sampling in wastewaters using semipermeable membrane devices: Accuracy of time-weighted average concentration estimations of truly dissolved compounds*. Chemosphere 73(8): 1194–1200.

Huckins, J.N., J.D. Petty, and K. Booij, 2006, Monitors of organic chemicals in the environment - semipermeable membrane devices: Springer, New York.

Kalf, , D.F., T. Crommentuijin, and E.J. van de Plassche..1997. *Environmental Quality Objectives for 10 Polycyclic Aromatic Hydrocarbons (PAHs).* Ecotoxicology and Environmental Safety, 36:1, pp 89–97. February 1997.

Kimbrough, K. L., W. E. Johnson, G. G. Lauenstein, J. D. Christensen, and D. A. Apeti. 2008. An Assessment of Two Decades of Contaminant Monitoring in the Nation's Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 74. 105 pp

Kraus, S.P., and J.E. Estes. 1977. Oil seep survey over Coal Oil Point and Santa Barbara Channel, California, October 1976. California Offshore Gas, Oil, and Tar Seeps, Staff Report, pp. 323-346. California State Lands Commission. Sacramento, CA.

Lorenson, T.D, F.D. Hostettler, R.J. Rosenbauer, K.E. Peters, K.A. Kvenvolden, J.A. Dougherty, C.E. Gutmacher, F.L. Wong, and W.R. Normark. 2009. Natural offshore seepage and related tarball accumulation on the California coastline; Santa Barbara Channel and the southern Santa Maria Basin; source identification and inventory. U.S. Geological Survey Open-File Report 2009-1225 and MMS report 2009-030, 116 p. [http://pubs.usgs.gov/of/2009/1225/].

Lorenson, T.D., I. Leifer, F.L. Wong, R.J. Rosenbauer,, P.L. Campbell, A. Lam, F.D. Hostettler, J. Greinert, D.P. Finlayson, E.S. Bradley, and B.P. Luyendyk. 2011. Biomarker chemistry and flux quantification methods for natural petroleum seeps and produced oils, offshore southern California. U.S. Geological Survey Scientific Investigations Report 2011-5210, 45 p. and OCS Study BOEM 2011–016.

Love, M., S., M. Nishimoto, and M. Saiki. 2009. *Reproductive Ecology and Body Burden of Resident Fish Prior to Decommissioning. MMS OCS Study 2009-019*. Marine Science Institute, University of California, Santa Barbara, California. MMS Cooperative Agreement Number 1435-01-05-CA-39315

Love, M.L., K.L. Kimbrough, W. E. Johnson, G. G. Lauenstein, J. D. Christensen, and D. A. Apeti. 2008. *An Assessment of Two Decades of Contaminant Monitoring in the Nation's Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 74*. 105 pp.

Love, ML., M. K. Saki, T.W. May, and J. L. Yee. 2012. *Whole-Body Concentrations of Elements in Three Fish Species from Offshore Oil Platforms and Natural Areas in the Southern California Bight, USA.* Bulletin of Marine Science 89(3): 717-734

Maruya, K. 2013. Southern California Coastal Water Research Project SCCWRP). Personal communication.

Mearns, A.J., D.J Reish, P.S. Oshida, T. Ginn, M.A. Rempel-Hester, C. Arthur, and N. Rutherford. 2013. *Effects of Pollution on Marine Organisms*. Water Environmental Research 85 (10): 1828–1933.

MEC. 2003. *An Assessment and Physical Characterization of Shell Mounds associated with Outer Continental Shelf Platforms Located in the Santa Barbara Channel and Santa Maria Basin, California. MMS. Contract No. 1435-01-02-CT-85136.* MEC Analytical Systems, Inc. and Sea Surveyor, Inc. February 2003.

Phillips, C.R., M. H. Salazar, S.M. Salazar, and B.J. Snyder. 2006. *Contaminant exposures at the 4H shell mounds in the Santa Barbara Channel*. Marine Pollution Bulletin 52:1668–1681.

Quigley, D. 1997. Quantitative Spatial and Temporal Variations in the Distribution of Natural Marine Hydrocarbon Seeps in the Santa Barbara Channel, California. M.S. thesis, Univ. of Calif., Santa Barbara.

R Core Team. 2013. *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org/.

Reed, W.E. and I.R. Kaplan. 1979. *The chemistry of marine petroleum seeps*. J. Geochem. Explor. 7: 255-293.

Salazar M.H. and S. M. Salazaar. 1995. Measuring bioaccumulation and bioeffects in transplanted bivalves as a pollution monitoring tool in Puget Sound. Puget Sound Research '95. pp 391-397. Puget sound Water Quality Authority.

Schroeder, D.M. and M. S. Love. 2004. *Ecological and political issues surrounding decommissioning of offshore oil facilities in the Southern California Bight.* Ocean and Coastal Management 47:21-48.

Spies, R.B. P.H. Davis, and D. Stuermer. 1980. *Ecology of a petroleum seep off the California coast. In* Marine Environmental Pollution (R. Geyer, Ed.). Elsevier, Amsterdam, pp. 229-263.

Spies, R.B., J.E. Bauer, and D.D. Hardin. 1989. A stable isotope study of sedimentary carbon utilization by *Capitella* spp.: effects of two carbon sources and geochemical conditions during their diagenesis *Marine Biology* **101**:68–74.

Stuermer, D.H., R.B. Spies, P.H. Davis, D.J. Ng, C.J. Morris, and S. Neal.1982. *The hydrocarbons in the Isla Vista marine seep environment*. Mar. Chem. 11: 413-426.

Weston Solutions, Inc. and Science Applications,. 2007. *Physical and Chemical Characteristics of the Platform Gina Shell Mound, Final Report*. Prepared for the Mineral Management Service by Weston Solutions Inc. and SAIC. March 2007.

Wilkinson, E.R. 1972. California Offshore Oil and Gas Seeps. Publ. TR08, 11 pp., Calif. Div. of Oil and Gas, Sacramento

Youngblood, W.W. and M. Blumer. 1975. Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and recent marine sediments. Geochimica Cosmochimica Acta. 39: 1303-1314.

7. Appendices

7.1 Appendix A: Laboratory Analysis Narrative Report

7.2 Appendix B: PAH Concentration Data

7.3 Appendix C: Calculated PAH Concentrations in Water

7.4 Appendix D: PAH Concentrations Combined into Dominant Compound Groups

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under US administration.

The Bureau of Ocean Energy Management

As a bureau of the Department of the Interior, the Bureau of Ocean Energy (BOEM) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS) in an environmentally sound and safe manner.

The BOEM Environmental Studies Program

The mission of the Environmental Studies Program (ESP) is to provide the information needed to predict, assess, and manage impacts from offshore energy and marine mineral exploration, development, and production activities on human, marine, and coastal environments.