USGS
science for a changing world

Prepared in cooperation with the Bureau of Ocean Energy Management

Comparison of Aliphatic Hydrocarbons, Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Polybrominated Diphenylethers, and Organochlorine Pesticides in Pacific sanddab (*Citharichthys sordidus*) from Offshore Oil Platforms and Natural Reefs along the California Coast

Open-File Report 2013–1046

U.S. Department of the Interior
U.S. Geological Survey

Comparison of Aliphatic Hydrocarbons, Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Polybrominated Diphenylethers, and Organochlorine Pesticides in Pacific sanddab (*Citharichthys sordidus*) from Offshore Oil Platforms and Natural Reefs along the California Coast

By Robert W. Gale, Michael J. Tanner, Milton S. Love, Mary M. Nishimoto, and Donna M. Schroeder

Prepared in cooperation with the Bureau of Ocean Energy Management

Open-File Report 2013–1046

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2013

Suggested citation:
Gale, R.W., Tanner, M.J., Love, M.S., Nishimoto, M.M., and Schroeder, D.M., 2013, Comparison of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polybrominated diphenylethers, and organochlorine pesticides in Pacific sanddab (*Citharichthys sordidus*) from offshore oil platforms and natural reefs along the California coast: U.S. Geological Survey Open-File Report 2013–1046, 31 p. and supplemental tables.

Contents

Figures

Tables

Supplemental Tables

Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
micrometer (µm)	0.00003937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Volume	
liter (L)	61.02	cubic inch (in^3)
milliliter (mL)	1 x 10^{-3} liter	
microliter (µL)	1 x 10^{-6} liter	
	Flow rate	
milliliter per minute (mL/min)	0.06102	cubic inches per minute (in^3/min)
	Mass	
metric ton (t)	1.102	ton, long (2,240 lb)
kilogram (kg)	2.205	pound avoirdupois (lb)
gram (g)	0.03527	ounce, avoirdupois (oz)
milligram (mg)	1 x 10^{-3} gram	
microgram (µg)	1 x 10^{-6} gram	
nanogram (ng)	1 x 10^{-9} gram	
	Concentration	
microgram per milliliter (µg/mL)	=	part per million (ppm; 10^6)
nanogram per milliliter (ng/mL)	=	part per billion (ppb; 10^9)
microgram per gram (µg/g)	=	part per million (ppm; 10^6)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Concentrations of chemical constituents in liquid solutions (reagent solution, calibration standards, or bile) are given in nanogram per milliliter (ng/mL), or micrograms per milliliter (µg/mL). Concentrations of chemical constituents in solid matrices are given in microgram per gram (µg/g) or nanogram per gram (ng/g).

Comparison of Aliphatic Hydrocarbons, Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Polybrominated Diphenylethers, and Organochlorine Pesticides in Pacific sanddab (*Citharichthys sordidus*) from Offshore Oil Platforms and Natural Reefs along the California Coast

Robert W. Gale[1], Michael J. Tanner[1], Milton S. Love[2], Mary M. Nishimoto[2], Donna M. Schroeder[3]

Abstract

Recently, the relative exposure of Pacific sanddab (*Citharichthys sordidus*) to polycyclic aromatic hydrocarbons (PAHs) at oil-production platforms was reported, indicating negligible exposure to PAHs and no discernible differences between exposures at platforms and nearby natural areas sites. In this report, the potential for chronic PAH exposure in fish is reported, by measurement of recalcitrant, higher molecular weight PAHs in tissues of fish previously investigated for PAH metabolites in bile. A total of 34 PAHs (20 PAHs, 11 alkylated PAHs, and 3 polycyclic aromatic thiophenes) were targeted. In addition, legacy contaminants—polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs),—and current contaminants, polybrominated diphenylethers (PBDEs) linked to endocrine disruption, were measured by gas chromatography with electron-capture or mass spectrometric detection, to form a more complete picture of the contaminant-related status of fishes at oil production platforms in the Southern California Bight. No hydrocarbon profiles or unresolved complex hydrocarbon background were found in fish from platforms and from natural areas, and concentrations of aliphatics were low less than 100 nanograms per gram (ng/g) per component]. Total-PAH concentrations in fish ranged from 15 to 37 ng/g at natural areas and from 8.7 to 22 ng/g at platforms. Profiles of PAHs were similar at all natural and platform sites, consisting mainly of naphthalene and methylnaphthalenes, phenanthrene, fluoranthene, and pyrene. Total-PCB concentrations (excluding non-ortho-chloro-substituted congeners) in fish were low, ranging from 7 to 22 ng/g at natural areas and from 10 to 35 ng/g at platforms. About 50 percent of the total-PCBs at all sites consisted of 11 congeners: 153 > 138/163/164 > 110 > 118 > 15 > 99 > 187 > 149 > 180. Most OCPs, except dichlorodiphenyltrichloroethane (DDT)-related compounds, were not detectable or were at concentrations of less than 1 ng/g in fish. *p,p′*-dichlorodiphenyltrichloroethane (*p,p′*-DDE) ranged from 5.6 to 33 ng/g at natural areas and from 17 to 76 ng/g at platforms, and comprised greater than 90 percent of the total-DDT concentrations at all sites. The only detectable PBDE congeners were PBDE-47 and PBDE-100, the total concentrations of which ranged from 0.4 to 1.8 ng/g at natural areas and from 0.5 to 3.0 ng/g at platforms. Total-PAH, -PCB, and -DDT concentrations were compared with other Southern California Bight studies involving shoreline mussel, (*Mytilus* Species, Kimbrough and others, 2008) and near shore sampling (Pacific sanddab, Schiff and Allen, 2000). At corresponding sites, only total-PCB concentrations agreed well with results from this study; total-DDT concentrations were generally much lower than concentrations documented in previous studies for samples collected nearer to shore by sewage treatment outfalls or 14 years earlier or closer in time to when DDT production was halted (1970). Natural areas and platforms in the Bight do not appear to be affected by harbor or urban pollution. Platforms were no more polluted than the nearby natural areas, with these locations exhibiting only low concentrations of PAHs, PCBs, DDTs, and other contaminants.

[1]U.S. Geological Survey.

[2]University of California, Santa Barbara, Marine Sciences Institute, Santa Barbara, California.

[3]Bureau of Ocean Energy Management (BOEM), Pacific Region, Camarillo, California.

Introduction

General Petroleum Exposure

Petroleum hydrocarbons exist as a naturally occurring highly complex mixture of aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, and polycyclic aromatic compounds found in oil-containing deposits and are released into the environment through naturally occurring seeps. Sediment contamination by petroleum hydrocarbons released during platform operation creates a longer-term source of exposure for biota than intermittent oil releases into the water column. The relative hydrocarbon contamination after emplacement of an exploratory oil platform was reportedly slight, discernible only at locations close to the rig (Lytle and Lytle, 1979). Aliphatic hydrocarbon fractions in sediments consisted predominately of normal and branched C_{17} to C_{25} olefins, with higher concentrations of odd carbon numbered normal, predominately C_{29}, alkanes; reflecting about 50 percent marine hydrocarbons loading into surficial sediments. A similar distribution of hydrocarbons has been further documented by Marcias-Zamora (1996) for a region south of the study area in the Southern California Bight . Aliphatic hydrocarbon concentrations ranged from 0.8 to 70.6 micrograms per gram (µg/g or parts per million) (average 15 µg/g); concentrations of the unresolved complex mixture ranged from less than the detection limit to 220 µg/g (average 37 µg/g); and total-polycyclic aromatic hydrocarbon (PAH) concentrations ranged from less than the detection limit to 1.9 µg/g (average 0.4 µg/g). In addition to the more aged hydrocarbon profiles in sediments, consisting of higher molecular weight compounds, some lower molecular weight components (odd carbon numbered alkanes: C_{15} and C_{17}) were found, possibly resulting from plankton and benthic algae or from bacterial activity. Though unable to eliminate contributions from natural seeps, Marcias-Zamora reported potential sources of hydrocarbon input from sewage treatment plants and large harbor facilities, and a general southward transport of materials in the Southern California Bight (Marcias-Zamora, 1996).

Bioaccumulation of aliphatic and aromatic hydrocarbons by marine fishes has often been studied as part of injury and risk assessments resulting from petroleum spills. Fish collected within the slick of the Ecofisk North Sea oil platform blowout of 1977 contained mostly pristane, aliphatic hydrocarbons, and low concentrations of aromatics, and were not substantially different from background aliphatic and aromatic hydrocarbon concentrations in fish (Law, 1978). In highly polluted areas off the Canary Islands associated with petroleum industry, hydrocarbon concentrations in fish ranged from 8,800 to 12,800 nanograms per gram (ng/g) concentrations from twenty to fifty-fold greater than those reported for fish from the Ecofisk blowout (Quintero and Diaz, 1994). Hydrocarbon patterns reflected biogenic components (pristane and hopanes) and preferential bioaccumulation of elevated concentrations of odd carbon numbered hydrocarbons. These patterns showed seasonal variations suggesting a relation with the reproductive cycles of the different species studied. Odd carbon numbered hydrocarbons typically result from biogenesis of algae, whereas even carbon numbered hydrocarbons and especially alkylated aromatics are signature compounds from petroleum related contamination. This differential accumulation of major odd and even carbon numbered hydrocarbons in limpets was used to differentiate pollution sources along the coasts of the Canary Islands (Pena-Mendez and others, 2001) and clearly indicated that sufficient amounts of aliphatic and aromatic hydrocarbons were bioaccumulated to discern polluted areas. Hydrocarbon concentrations ranged from 31 to 295,700 nanograms per gram dry-weight (ng/g dw) (average 28,400 ng/g dw) for the limpet *Patella ulyssiponensis*, and from not detectable to 744,000 ng/g dw (average 216,000 ng/g dw) for *Patella crenata*; concentrations of PAHs and alkyl-substituted PAHs ranged from not detectable to 61 ng/g dw (average 5.4 ng/g dw) and not detectable to 2,200 ng/g dw (average 210 ng/g dw) for *P. ulyssiponensis*, and from not detectable to 24,300 ng/g dw (average 5,900 ng/g dw) and not detectable to 22,900 ng/g dw (average 3,400 ng/g dw) for *P. crenata*. Gonzalez and others (1992) reported that hydrocarbons in fish from the Campeche Bank, Mexico, oil production area consisted of predominately C_{10} to C_{14} hydrocarbons ranging from 450 to 500 ng/g dw, and that C_{25} to C_{30} hydrocarbons predominated in shrimp and were about twenty-fold greater than those in fish. In the Gulf of Naples, another region of heavy petroleum industry, hydrocarbons in fish were determined to range from 770 to 33,200 ng/g dw (average 2,700 ng/g dw) (Amodio-Coccheri and Cirillo, 2003). Concentrations of aliphatics in fish collected from sewage-effected Buenos Aires coastal waters averaged about 70 µg/g dw and were determined to consist of predominately C_{12} to C_{25} hydrocarbons from bioaccumulation of fossil fuels from sewage particulates (Colombo and others, 2007).

Arias and others (2009) reported an average concentration of PAHs of 1,100 ng/g dw in whole fish from the Bahia Blanca estuary, Argentina, which was ranked as a moderate exposure risk in their assessment. Differences in bioavailability, diet composition and seasonal effects on diet composition, and biotransformation processes were proposed to explain large variations in PAH concentrations among biological species. Concentrations of higher molecular weight PAHs in fish muscle tissue were determined to decrease throughout a week-long period after uptake and to not bioconcentrate to any substantive extent. The half-life of benzo(*a*)pyrene (BaP) was reported longest in fat (12.4 days, d), with a whole-body half-life of 2.4 d; however, measurements after about 20 days indicated that BaP concentrations in tissue might be reaching steady-state, balancing bioaccumulation and degradation (Lemaire and others, 1990). Stein and others (1993) determined that though BaP residence times in fish were short, BaP-DNA adducts in liver were moderately persistent, maintaining steady-state concentration from 28 to 84 days. In long-term feeding trials that introduced low concentrations of 16 PAHs into diets, Nácher-Mestre and others (2010)

reported that the PAH concentrations in fish decreased from initial concentrations of 46.6 ng/g total-PAHs and 9.1 ng/g BaP equivalents (BaP-eq), which were accumulated from the previous maintenance diets. Naphthalene (about 200 ng/g) was completely lost and the other PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, and chrysene, approximately 0.6 to 6 ng/g each) decreased about ten-fold throughout the first 6 months. In the second 6 months, these latter PAHs increased again, from 2 ng/g to about 6 ng/g total-PAHs, though less than 0.01 ng/g BaP-eq was reported. The concentration lowering was proposed to result from growth dilution in addition to removal through detoxification pathways. No accumulation was noted for trace concentrations of 5- or 6-ring aromatic compounds. Using cardio-respiratory evaluation to determine fitness, Claireaux and Davoodi (2010) reported the following:

> "…oil exposure impaired function in fishes, with individuals unable to meet temperature-driven increases in tissue oxygen demand. Oil exposed fish were found to require their venous oxygen stores early, while non-exposed fish had no recourse to their stored supply [during the course of the study]."

Petroleum Exposure in the Southern California Bight

General colonization of natural areas near seeps and oil platform areas by fishes has been reported recently (Love and others, 2003). Some platforms were important to regional fish production, serving as marine refuges, and produced most or all of the adult fish found in the vicinity. Platforms acted as natural rocky outcrops, producing and attracting fishes, and fishes at platforms grew faster than at natural outcroppings and were at least as healthy. The macrofaunal benthic community condition in the Southern California Bight was assessed by Ranasinghe and others (2010). The overall condition was determined to be good and unchanging throughout the 9-year study; there was no evidence of disturbance near the Channel Islands and none on the mainland shelf. Bay and estuary communities were more frequently disturbed because of proximity to anthropogenic inputs (sewage treatment plant effluent and harbor areas).

Discharges from 23 oil platforms operating in the Southern California Bight in 1996 and 2000 were estimated from available data by Steinberger, and others (2004). Volumes of produced water (high salinity brine commingled with oil or gas in a well) were about 5 x 10^9 liters and relatively constant with time; amounts of associated solids decreased several-fold, from 12 metric tons in 1996 to 3 metric tons in 2000. These inputs into the Southern California Bight were considered minor compared to inputs from nearby coastal publicly owned treatment works. In contrast to platform events, releases of heavy crude from natural seeps offshore of Goleta, California, were estimated at 20 to 25 metric tons per day, and resulted in subsequent fallout of weathered oil to sediments with a period of 0.4 to 5 days (Farwell and others, 2009). Oil released from the seeps formed surface slicks and plumes of weathered oil in sediment. This weathered oil was depleted in all lower molecular weight components, which were dissipated by evaporation on the ocean surface (less than C_{16} components), and later by aerobic and anaerobic biodegradation. Dissolution was considered negligible, except for polar PAH components. Decreases in output of natural seeps of as much as 50 percent were reported in areas near oil-producing reservoirs with no net difference in total output (Quigley and others, 1999).

The effects of produced water on embryonic, larval, and juvenile Atlantic cod (*Gadus morhua*) were recently reported by Meier and others (2010). At 1 percent produced water, no effects on survival or hatching success were reported, but larvae had elevated concentrations of vitellogenin and cytochrome P450-1A biomarkers, failed to feed, and eventually starved. This was attributed to increased incidence of jaw deformities. Though alkylphenols (produced water additive) were bioconcentrated, juveniles efficiently metabolized the shorter chain congeners.

Triterpenoids were used to distinguish biogenic hydrocarbons (termed syngenetic biolipids) from petroleum hydrocarbons in the Southern California Bight by Simoneit and Kaplan (1980). The 17αH,21βH hopanes were demonstrated to be sensitive markers of petroleum pollution. The 17αH,21βH C_{27} to C_{35} hopanes comprised the major biogenic triterpenoids, whereas 17αH,18αH,21βH-28,30-bisnorhopane was the dominant triterpenoid in bight sediments and was proposed as a potential marker of Southern California petroleum. Extended C_{19} to C_{27} tricyclic diterpanes also were suggested as additional petroleum markers. Based on ratios of various biomarkers and PAHs, Simoneit and Kaplan concluded that sediments from the Southern California Bight contained petroleum from anthropogenic activity and seepage.

Environmental impacts of oil and gas drilling in the Southern California Bight were monitored from 1986 to 1990 (Steinhauer and others, 1994). Hydrocarbon concentrations were sometimes elevated, but because of natural seepage rather than drilling. The presence of seep-related particles in sediments was recognized as an important factor in characterizing ambient hydrocarbon concentrations. No hydrocarbon concentrations sufficient to affect biota were determined in this study. In surface sediments collected near drilling operations, concentrations of aliphatics ranged from 23 to 180 µg/g dw and total-PAH concentrations ranged from not detectable to 1.5 µg/g dw. The greatest contributions to sediment loadings were determined to be from drilling muds (hydrocarbons from 137 to 988 µg/g dw, and total-PAHs from 0.87 to 51 µg/g dw) and tarballs (total-alkanes from 77 to 133 µg/g dw, hydrocarbons from 2 to 5 percent, aromatics from 3 to 19 percent, and an unresolved complex mixture comprising about 96 percent of the material). Biochemical and physiological measures of exposure of California halibut (*Paralichthys californicus*) to sediments from the Coal Oil Point natural oil seep (not shown) failed to demonstrate dose-response relations, which prevented estimates of sediment thresholds for biomarker responses such

as P450 enzyme induction (Seruto and others, 2005). Seruto and others, also speculated that insensitivity for natural petroleum might be unique due to higher concentrations of lower molecular weight PAHs or other uncharacterized inhibitors as compared with sources of urbanized PAHs.

Peterson and others (1996) rationalized the typical failure to detect evidence of exposure or sublethal effects on fishes at drilling operations to a combination of two factors: resident fish populations are mobile over a much greater spatial range than the scale of environmental changes occurring at oil production platforms and natural seeps, and resident fish exposure to hydrocarbons and other contaminants is negligible. Effects on population sizes from exposure to hydrocarbons and PAHs near platforms have been observed at distances of about 1,000 meters (m) in shallow waters with depths of only a few meters (Armstrong and others, 1979); however, the distances for effects drop off sharply as water depth increases. Osenberg and others (1992) reported that decreased populations extended only 100 m from oil platforms in less shallow waters with depths of 10 to 12 meters.

Rainbow seaperch (*Hypsurus caryi*) and rubberlip seaperch (*Rachochilus toxodes*) from a natural petroleum seep in the Santa Barbara Channel were investigated for a number of chemical markers, biomarkers, and sublethal effects by Spies and others (1996). PAHs and metabolites in bile, cytochrome 450-1A, immunohistochemistry and histopathology were measured. Bile metabolites of naphthalene and phenanthrene were elevated at the seeps compared with a reference site (111 and 137 µg/g as compared to 22 and 30 µg/g, respectively). Greater content of cytochrome P450-1A was documented in fish from the seep and total lesion scores were slightly higher for seep-dwelling fish, consistent with more limited movement and a greater degree of benthic feeding. Several biomarkers for xenobiotic chemicals that induce cytochrome P450-1A were proposed, including cartilage displaysia and abnormal branching of gill filaments and lamellae.

Semiquantitative measures of exposure to petroleum hydrocarbons in Southern California bays and harbors relative to nearby Channel Islands (not shown) using fluorescent aromatic compounds (FACs) in bile to estimate PAH exposure and a comet assay to assess DNA damage, were compared by Brown and Steinert (2003). From three to five-fold greater concentrations of FACs were measured in fish from harbors relative to islands. Concentrations of FACs in California halibut at harbors ranged from 1,200 to 4,100 ng BaP equivalents per milliliter (mL) bile (average 2,200 ng BaP-eq/mL). Pacific sanddab at Channel Island sites ranged from 200 to 840 ng BaP-eq /mL bile (average 400 ng BaP-eq/mL). A significant correlation between total-FAC concentrations (parent and substituted PACs) and DNA damage was documented at only two of eight harbor sites and was presumed due to contaminants other than PAHs. The FAC method integrates non-PAH and PAH fluorescence, producing elevated responses relative to PAH selective methods. In a recent study (Gale and others, 2012), PAH metabolites in Pacific sanddab (*Citharichthys sordidus*), kelp rockfish (*Sebastes atrovirens*), and kelp bass (*Paralabrax clathratus*), were measured by HPLC-fluorescence; the concentrations of the PAH-glucuronides and the corresponding hydroxy-PAHs (OH-PAHs) were compared, and the resulting values were much lower than FAC estimates of total-PAH concentrations.

Fish collected near natural tar seeps, at nearby natural reefs, and at locations that were more distant from natural seeps, have exhibited concentration gradients of PAH metabolites in bile, indicating exposure (Gonzalez and others, 1992; Spies and others, 1996; Roy and others, 2003). However, because of natural regional hydrocarbon sources in the Southern California Bight, aliphatic and aromatic petroleum hydrocarbon concentrations in fish from platform sites must be interpreted within the context of the fish living in this local background. In addition, the variability in overall PAH exposure at platforms and near natural seeps results from the distribution of exposures of individual fish of differing ages to parent PAH sources from localized water concentrations and individual prey items. Additional variability is introduced by movement of fishes to and from different populations (Straughan and others, 1982; Peterson and others, 1996; Seruto and others, 2005). All of these factors contribute to the overall potential for exposure of resident fish populations to petroleum and other contaminants which, in turn, affects the health of individual species and ultimately affects overall ecosystem health.

The variability in concentrations of PAH metabolites within resident populations of platform and natural seep fishes from the Southern California Bight was recently determined (Gale and others, 2012); this previous investigation into PAH exposure at platforms and nearby natural areas reported only low concentrations of 1-hydroxypyrene in kelp rockfish from only the Santa Barbara Point Reef natural site. 1-Hydroxypyrene, suggested by Vuorinen for use as a bioindicator of PAH exposure of fish (Vuorinen and others, 2003; 2006) was not detected at any of the platforms (Gale and others, 2012). 1-hydroxyfluorene was the most prevalent OH-PAH measured by Gale and others (2012); 1-hydroxfluorene was detected at only 2 of 7 platforms, and at low concentrations, less than 50 ng per mg protein. The highest concentrations of another isomer, 2-hydroxyfluorene were documented in fish from Platform Holly and were only about 3-fold above the concentrations documented in fish from Horseshoe Reef, East Anacapa Island, and Coche Point natural sites; the concentrations at these sites were low and the concentration differences among these sites were not substantial (Gale and others, 2012). The PAH metabolite concentration ranges reported were among the lowest reported in the recently reviewed literature (refer to the Section: Comparison to Other Studies) and are approaching those concentrations reported in fish from pristine ocean sampling (Goksøyr and others, 2009).

Nonpetroleum Exposure in the Southern California Bight

The fate and dynamics of nonpetroleum related organic contaminants in sediments along the Palos Verdes shelf has been studied in detail; for overviews see Schiff (2000) and Schiff and others (2000) and Venkatesan and others (2010). The predominant nonpetroleum related contaminants in sediments are 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (*p,p'*-DDT) and its degradation products resulting from historic discharges of DDT manufacturing waste; a second major contaminant class, polychlorinated biphenyls (PCBs) again resulted from historic discharges of manufacturing waste (Zeng and Venkatesan, 1999; Schiff, 2000; Schiff and others, 2000; Eganhouse and others, 2000; Eganhouse and Pontillo, 2000). Total-DDT related chemicals (DDT and its degradation products, or DDTs), originally from sediment stores close to outfalls, provided sources for widespread contamination of sediments in the Southern California Bight by resuspension, transport, and redeposition. The degradation of *p,p′*-DDT to 1,1- dichloro-2,2-di(4-chlorophenyl)ethene (*p,p′*-DDE) indicates hydrolytic dehydrochlorination at the sediment surface, whereas formation of 1,1-dichloro-2-di(4-chlorophenyl) ethylene (*p,p′*-DDMU) represents reductive dechlorination in subsediments. Most of the changes in concentrations of DDTs and degradates result from mobilization of sediments and subsequent resettling over greater areas of less contaminated sediment farther from the source. Long-term predictions suggest that the existing inventory of DDTs will remain buried and that surface concentrations will gradually decrease throughout the next several decades. In addition, erosion processes south of the outfalls will introduce some DDEs into the surface sediments and release some DDEs into the overlying water column by prevailing ocean currents (Sherwood and others, 2002). The percent of DDE degradates in DDTs is uniformly about 90 percent in sediments far from sources, but is much lower, about 10 percent, in sediments near sources (Eganhouse and others, 2000; Eganhouse and Pontillo, 2000). Compared with the profiles of DDTs, the profiles of PCB congeners were highly conserved over much greater distances down-plume from waste treatment plant outfalls, due to the lack of substantial metabolic activity.

The termination of the dominant source of DDT to the Los Angeles County Sanitation District's Joint Water Pollution Control Plant (JWPCP) submarine outfalls in 1970 decreased DDT input by thirty-fold. In 1973, the total-DDT concentration in outfall sediments was about 440 µg/g. In the several years that followed, total-DDT in some impacted marine fishes decreased from four to eight-fold from peak concentrations, though, no decrease was noted in the bottom-feeding Dover sole (*Microstomus pacificus*) (Smokler and others, 1979). Resident top-level carnivores such as the California sea lion (*Zalophus californianus*) and the harbor seal (*Phoca vitulina*) were reported to continue to exhibit elevated concentrations of contaminants, mainly DDTs and PCBs, compared with transient species such as the northern elephant seal (*Mirounga angustirostris*) (Blasius and Goodmanlowe, 2008). Farther south, below San Diego Harbor (not shown), monitoring has shown some areas of the shelf contaminated with PCBs (Parnell and others, 2008). Parnell and others (2008) have attributed most of the current PCB loading in fish to the ongoing practice of dumping contaminated sediments dredged from San Diego Bay.

To extend our previous work, which investigated potential acute exposure to PAHs by determining metabolites in bile of fishes at platform and nearby natural areas, in this study, we measure recalcitrant, higher molecular weight PAHs in fish tissues of Pacific sanddab to provide a measure of any potential chronic exposure to PAHs of fish resident at platforms and nearby natural areas, which was not readily detectable by PAH metabolite measurements. In addition, legacy contaminants, PCBs and organochlorine pesticides (OCPs), and the more recent contaminants, polybrominated diphenylethers (PBDEs), were measured to provide critical information about exposure in fish populations at platforms compared to natural seeps, and insight into the movement or recruitment of fish from nearby locations. Measurements of aliphatic hydrocarbons, PAHs, PCBs, PBDEs, and OCPs in fish populations from natural areas also were determined, providing a measure of the background exposure concentrations of petroleum hydrocarbons from natural petroleum seepage, and PAHs and other contaminants from waste treatment plant outfalls and harbor activities that are transported into the vicinities of platforms and natural areas.

Methods

Study Sites and Sample Collection

In earlier phases of this research, heavy metal burdens in fishes and PAH-metabolites in bile from fishes were characterized at platforms and nearby natural areas in the Southern California Bight (Love and others, 2009; Gale and others, 2012). Sites previously selected for the metals and bile metabolite studies were used during the present study to provide continuity. Pacific sanddab was selected as a model species, being a widespread, opportunistic-feeding bottom dweller that does not make widespread movements (Love and Goldeberg, 2009). The whole fish samples (less gall bladders), corresponding to the fish previously investigated for bile metabolites, were used in this study. The sampling effort was done by the Marine Science Institute at the University of California at Santa Barbara. Sampling corresponded to the previously selected 13 sites (7 platform sites and 6 adjacent, natural area reference sites) outlined in earlier work (fig. 1) (Gale and others, 2012). Pacific sanddab that were platform resident and others that were part of the regional background (the areas off Point Conception, within the Santa Barbara Channel, and within the San Pedro Basin, not shown) were collected (table 1).

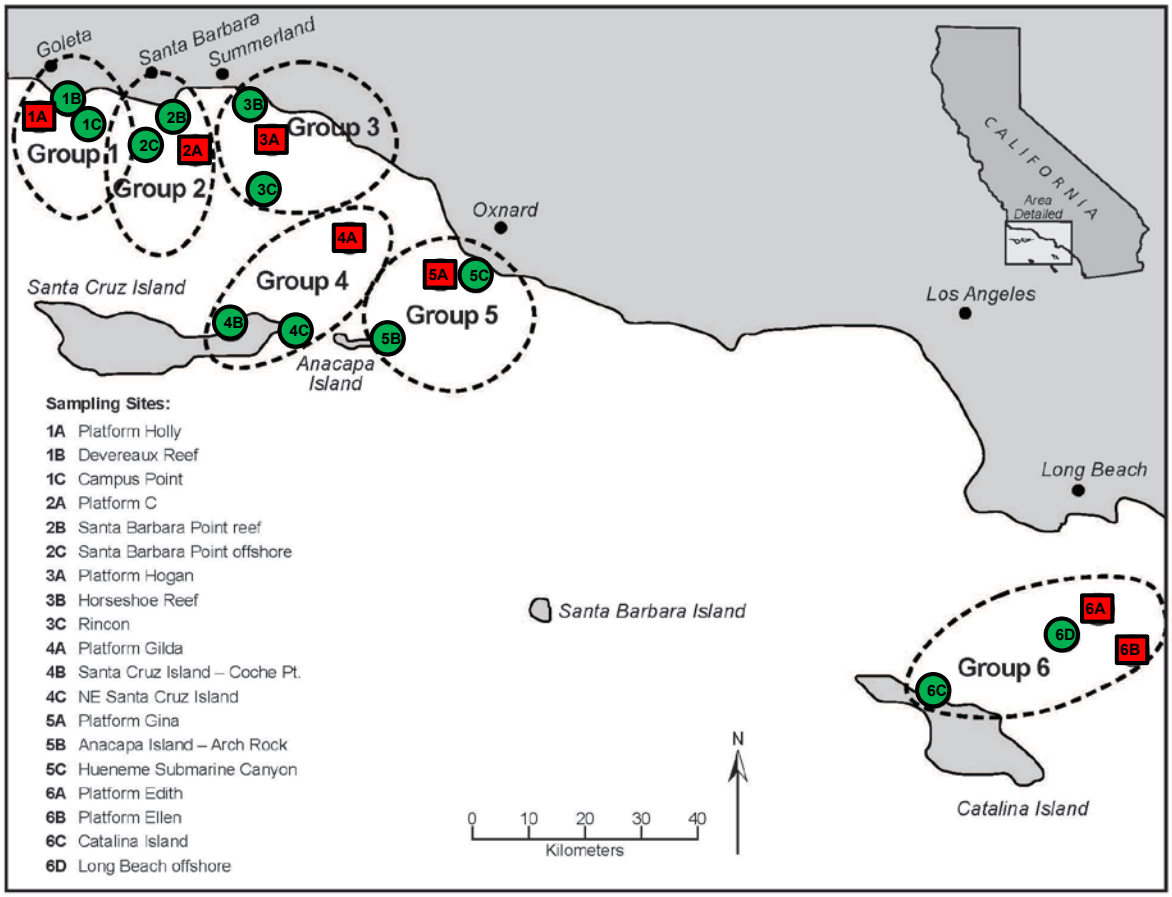

Figure 1. Site locations in the Southern California Bight. Platforms (red) and natural areas (green).

Table 1. Samples for whole-fish composites of Pacific sanddab from natural areas and platforms.

[g, grams; ±, plus or minus; cv, coefficient of variation (percent relative standard deviation)]

Sample	Latitude (degrees, minutes)	Longitude (degrees, minutes)	Composite		
			Range (g)	Number	Average (g) ± cv (percent)
Natural areas			10–242	32	54.9 ± 125
CAND (Campus Point)	34.22.365	-119.50.168	20–42	5	34.4 ± 25
RIND (Rincon)	34.15.300	-119.33.120	11–242	5	77.4 ± 123
HUEN (Hueneme)	34.07.097	-119.12.685	12–40	6	22.7 ± 50
NESC (NE Santa Cruz)	34.01.870	-119.30.380	86–231	5	171.6 ± 36
EDND (Platform Edith Natural Area)	33.35.050	-118.12.770	17–27	5	19.8 ± 21
SBPN (Santa Barbara Natural Area)	34.22.800	-119.41.670	10–29	6	17.3 ± 39
Platforms			11–82	36	32.1 ± 61
HOLL (Holly)	34.23.339	-119.54.436	24–33	5	28.8 ± 15
PLATC (Platform C)	34.19.987	-119.38.029	11–27	9	17.4 ± 30
HOGA (Hogan)	34.20.275	-119.32.539	13–56	5	31.2 ± 55
GINA (Gina)	34.07.050	-119.16.684	13–22	6	17.2 ± 24
GILD (Gilda)	34.10.896	-119.25.236	41–74	5	54.2 ± 25
EDIT (Edith)	33.35.670	-118.08.050	24*	1	24*
ELLE (Ellen)	33.35.000	-118.07.770	43–82	5	60.4 ± 27

*Platform EDIT—only one sample was available.

Adult Pacific sanddab of the same size class, were collected from the decommissioned oilrig platforms and the platform shell mounds, and from natural areas away from platforms. The fish were collected by spearfishing with SCUBA gear or other standard collection methods such as hook-and-line, traps, or trawls. Five fish were collected at each site; additional collection trips were necessary to collect some species at sparsely populated sites, and were completed within a few days of the initial collection trips. The fish samples were immediately placed on ice and were returned to the laboratory for gall bladder excision for measurement of PAH metabolites in bile (Gale and others, 2012). Following gall bladder removal, the whole fish (less gall bladders) were placed in an appropriately labeled storage container and transferred to either a -20 degrees Celsius (ºC) or a -80 ºC freezer. The frozen samples were labeled with the collection site identifier, wrapped in aluminum foil, placed in a ziplock bag, and packaged on dry ice for overnight transport to the U.S. Geological Survey (USGS), along with chain of custody forms and any additional, pertinent sample collection documentation. Following arrival, the samples were inventoried and stored in a -20 ºC freezer when not in use.

Compositing and Homogenization

Only Pacific sanddab, collected from near seven offshore oil-platforms and from six nearby natural sites, were targeted for contaminants analysis (table 1). The fish ranged in size from 10 to 242 g (n=68), with 76 percent of the samples being less than 50 g; though sample size differences confound detailed data interpretation, the small sizes of some individual fish and the cost of analyzing individual fish was prohibitive. The gallbladders (with a small part of the liver) were excised for PAH metabolite analyses, and the remaining fish (less gallbladder) used for PAH and organochlorine contaminant analyses. Individual whole fish (less gallbladder) were removed from the -20 ºC freezer and homogenized by a combination of band-sawing, slicing, and, finally, grinding. Composites were made by homogenizing 3-g portions of each previously homogenized individual fish sampled at each site; sufficient tissue was retained to allow analysis of individual fish should sufficient concentrations of any analyte be found in any composite sample. This method of compositing did not allow statistical testing for the effects of variable fish size; moreover, had size-related differences been present, small individuals were given the same weight as large individuals in the composited sample.

Materials

Dichloromethane, hexanes, acetone, methanol, methyl-*t*-butylether, and 2,2,4-trimethylpentane (all Optima Grade) were obtained from Fisher Scientific (Fair Lawn, New Jersey). All open-column fractionations were performed in 1-centimeter (cm) inner-diameter glass columns. The octadecyl silica/Silica Gel (C_{18}/SG) columns for PCB/PBDE/OCP fractionation were prepared by layering 1.00 g of octadecyl silica [C_{18} 40 micrometers (µm), 60 angstroms (Å) pore size, Varian, Palo Alto, California] on top of 5.00 g of silica gel 60 (70–230 mesh, activated at 130 °C, Merck, Darmstadt, Germany). The potassium-hydroxide impregnated silica gel (KS) was prepared by reacting a methanolic solution of 168 g of KOH (Fisher Scientific, Fair Lawn, New Jersey) with 300 g of silica gel 60, followed by rotary evaporation to remove methanol and activation of the KS at 130 °C; 5.00 g columns were used for cleanup of aliphatic hydrocarbon/PAH fractions after low-performance size-exclusion chromatography (LP-SEC). The deactivated SG was prepared by adding 3.00 mL of water (Millipore Synergy UV 18 megaohm per centimeter (mΩ/cm) water-purification system, Millipore, Billerica, Massachusetts) to 100 g of silica gel 60, previously activated at 130 °C; 5.00 g of the deactivated SG were used for aliphatic hydrocarbon/PAH fractionation.

LP-SEC used a primary 60 x 2.5 cm glass column containing 70 g of Biobeads S-X3 and a 30 x 2.5 cm glass guard column containing 10 g of S-X3 (Bio-Rad Laboratories, Richmond, California) with a dichloromethane mobile phase [flow rate 4.00 milliliters per minute (mL/min)]. High-performance size-exclusion chromatography (HP-SEC) used a Phenogel® guard column and a 30 x 2.12 cm Phenogel® (10 µm, 100 Å pore) analytical column (Phenomenex, Torrance, California) with a dichloromethane mobile phase (flow rate also 4.00 mL/min).

All analytical standards for aliphatic hydrocarbons, PAHs, OCPs, PCBs, and PBDEs were purchased from AccuStandard, New Haven, Connecticut. Deuterated and perdeuterated procedural and instrumental internal standards were purchased from Cambridge Isotope Laboratories, Andover, Massachusetts.

Sample Cleanup and Analysis

Two parallel analytical schemes were used to analyze the fish: the first, targeting aliphatic hydrocarbons and selected PAHs (consisting of a set of 20 parent PAHs, 11 alkyl-substituted PAHs, and 3 polycyclic aromatic thiophenes), and the second, targeting PCBs, OCPs, and PBDEs, as outlined in figure 2. The schemes allowed independent optimization of extraction and fractionation procedures for aliphatic hydrocarbons/PAHs and PCB/OCP/PBDEs, respectively.

Aliphatic Hydrocarbons, Polycyclic Aromatic Hydrocarbons, and Polyaromatic Compounds

Previous investigation of these samples for PAH-related bile metabolites indicated that acute exposure to PAHs was low; therefore, sample preparation for 34 PAHs (consisting of 20 parent PAHs, 11 alkyl-substituted PAHs, and 3 polycyclic aromatic thiophenes) was planned; and sensitivity increased by concentrating the final extracts to 200 microliters (µL).

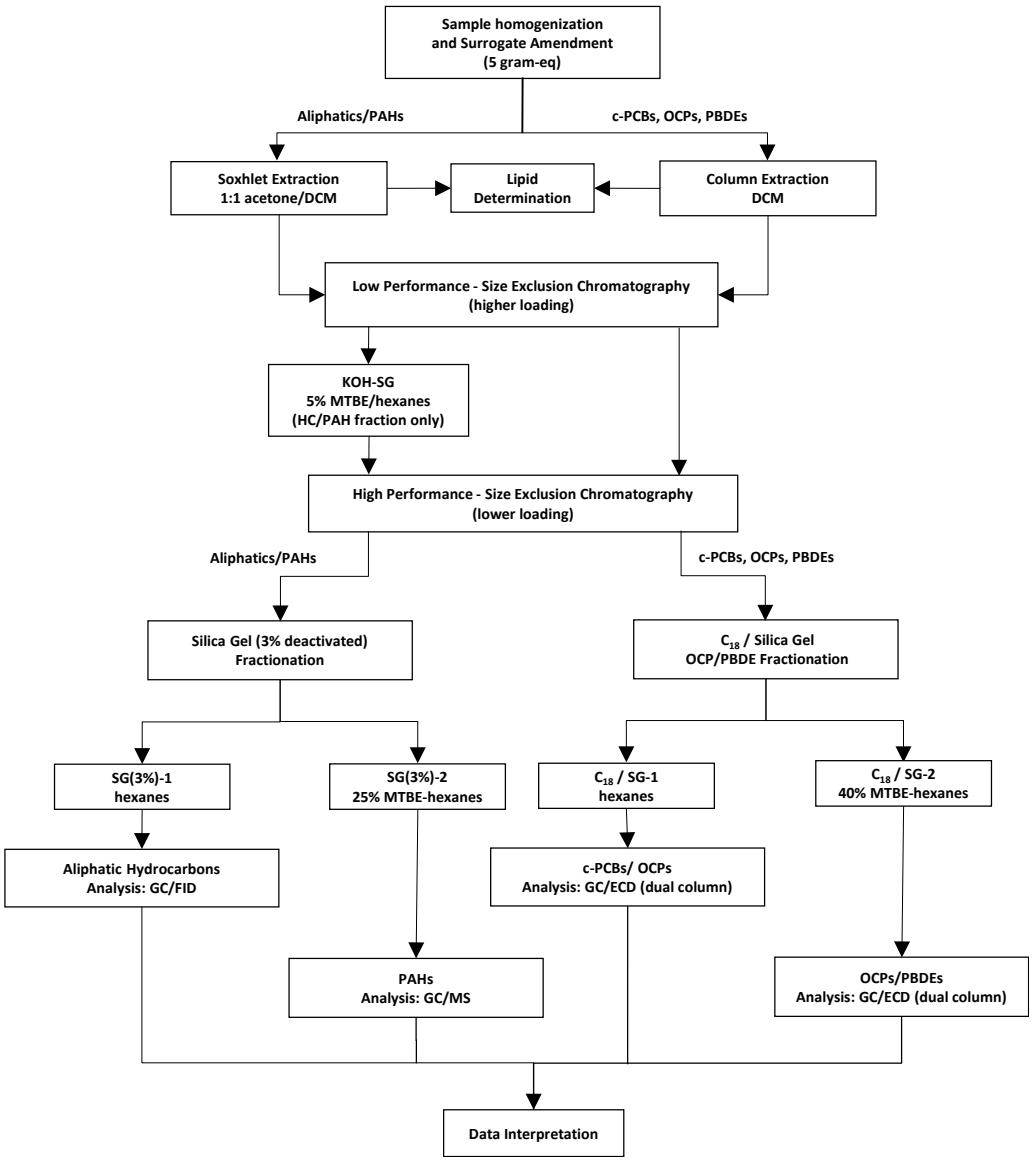

Figure 2. Analytical scheme for aliphatic hydrocarbons (HCs), polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic thiophenes (PACs) (left), and polychlorinated biphenyl congeners (c-PCBs), organochlorine pesticides (OCPs) and polybrominated diphenylethers (PBDEs) (right). Eq, equivalents; DCM, dichloromethane; SG, silica-gel; KOH-SG, potassium hydroxide impregnated SG; %, percent; MTBE, methyl-t-butyl ether; C_{18}, octadecylsilane; GC/FID, gas chromatography-flame ionization detection; GC/ECD, GC-electron capture detection; GC/MS, GC-mass spectrometry.

Accordingly, approximately 5-g portions of fish composite samples were removed for analysis, dehydrated by addition of anhydrous sodium sulfate (Na_2SO_4), and spiked with 250 ng of each of 16 perdeuterated PAHs (d-PAHs) as procedural internal standards (surrogates). Soxhlet extraction was used to recover potentially recalcitrant PAHs from fish tissues. Samples were soxhlet-extracted with 1:1 acetone:dichloromethane (volume:volume, v:v) for 18 hours, solvent-exchanged to dichloromethane and extractable lipids determined on a 2-percent aliquant.

The analytes were separated from residual higher molecular weight compounds in the extracts by sequential LP-SEC and HP-SEC. The LP-SEC step was capable of higher lipid loadings (750 milligrams, mg) but with a lower resolution separation of the analytes from higher molecular weight biogenic interferences. Therefore, a KS cleanup, eluting with 5 percent methyl-*t*-butylether in hexanes, was introduced after the LP-SEC fractionation step to remove additional biogenic compounds, before clean-up by the HP-SEC fractionation step. After removal of biogenic interferences, the aliphatic hydrocarbons and the PAHs were separated using 3 percent water-deactivated silica gel. Activated silica gel sorbents may strongly retain or degrade some aromatic sulfur heterocycles (dibenzothiophene, benzonaphthothiophene, and benzo[*b*]naphtho[2,1-*d*]thiophene); therefore, slight water-deactivation of silica gel was used to minimize degradation while fractionating most aliphatic hydrocarbons from the aromatics. The aliphatic hydrocarbons were eluted with hexanes, followed by elution of the PAHs with 25 percent methyl-*t*-butylether in hexanes.

The fractions for alkane analysis were concentrated to approximately 1.0 mL and 100 ng of *p*-terphenyl-d_{14} added as the instrumental internal standard. Aliphatic hydrocarbons were quantified by gas chromatography with flame-ionization detection (GC-FID) using cool on-column injection onto a retention gap (3 m x 530 µm inner diameter, methyl-deactivated) connected by a press-tight fitting to a 5-percent phenyl-methylsiloxane capillary column (60 m x 250 µm inner diameter, 0.25 µm film thickness). The hydrogen carrier gas was pressure-regulated at 25 pounds per square inch gauge (psig) and the FID was held at 330 °C. The GC temperature was held at 40 °C for 5 min, then ramped at 10 °C/min to 310 °C and held for 15 min. Aliphatic hydrocarbon standards (C_9–C_{40} n-alkanes, pristine, and phytane) at six concentrations ranging from 0.20 to 100 µg/mL were used for component identification and calibration.

For PAH screening, the final extracts were concentrated to approximately 1.0 mL and 100 ng of 2-methylnaphthalene-d_{10} and benzo[*e*]pyrene-d_{12} were added as instrumental internal standards. The PAH analytes were quantified by gas chromatography with quadrupole mass spectrometric detection, using cool on-column injection onto a retention gap (3 m x 530 µm inner diameter, methyl-deactivated), connected by a press-tight fitting to a 5-percent phenyl-methylsiloxane capillary column (30 m x 250 µm inner diameter, 0.25 µm film thickness). The helium carrier gas was pressure-regulated at 13 psig. The GC temperature was held at 50 °C for 2 min, ramped at 25 °C/min to 130 °C, held for 1 min, then increased at 6 °C/min to 310 °C and held for 5 min. The transfer-line, source, and quadrupole were held at 310, 230, and 120 °C, respectively. Standards of 34 PAHs at 6 concentrations ranging from 10 to 2,000 ng/mL were used for component identification and isotopic-dilution calibration. After screening for PAHs and other potential contaminants or interferences at 5 gram-equivalents/milliliter (g-eq/mL) in full-scan mode (35-600 atomic mass units (amu)) to avoid degraded chromatography from overloading the GC column with high amounts of matrix, the extracts were concentrated to 25 g-eq/mL (200 µL final volume) and PAHs were quantified by GC-MS using selected-ion monitoring.

Polychlorinated Biphenyls, Organochlorine Pesticides, and Polybrominated Diphenylethers

As was done for the aliphatic hydrocarbon and PAH analyses above, 5-g portions of fish composite samples were removed for analysis, dehydrated by addition of anhydrous Na_2SO_4, and spiked with 40 ng each of the procedural internal standards: 2,4,5-trichlorobiphenyl (PCB 029); 2,2′,4,4′,6,6′-hexachlorobiphenyl (PCB 155); 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (PCB 204); and octadeuterated 1,1- dichloro-2,2-di(4-chlorophenyl)ethane (*p,p′*-DDD-d_8). PCBs, OCPs, and PBDEs were column-extracted from tissues with dichloromethane. Activated silica gel fractionation was used to separate most PCB congeners and a few pesticides from most of the pesticides and PBDEs. Dichloromethane extractable lipids were determined on 2 percent aliquants of the extracts.

The analytes were separated from residual higher molecular weight compounds in the lipophilic extracts by sequential LP-SEC and HP-SEC. The KS cleanup between the LP-SEC and the HP-SEC steps was omitted, as KS removes some pesticides. After removal of biogenic interferences, the PCBs, OCPs, and PBDEs were fractionated using C_{18} layered SG. The first silica gel fraction (SG-1) was eluted with hexanes and comprised greater than 90 percent of the total-PCB concentration, along with six pesticides: aldrin, pentachlorobenzene, hexachlorobenzene, heptachlor, *p,p′*-DDE (partial recovery), and mirex. The second silica gel fraction (SG-2) was eluted with 40 percent methyl-*t*-butylether/hexanes and comprised less than 10 percent of the total-PCB concentrations (greater than 50 percent of 22 of the less-chlorinated congeners and greater than 10 percent of 18 additional less-chlorinated congeners), along with the remaining pesticides and PBDEs.

Final extracts from SG-1 and SG-2 were concentrated to 1.0 mL (5 g-eq/mL) and 40 ng of 2,4,6-trichlorobiphenyl (PCB 30) and 2,2′,3,3′,4,4′,5,6,6′-nonachlorobiphenyl (PCB 207) were added as instrumental internal standards. Individual congeners of PCBs and PBDEs, and organochlorine pesticides were quantified by dual-column gas chromatography with electron-capture detection (GC-ECD), using cool on-column injection onto retention gaps (3 m x 530 µm inner

diameter, methyl-deactivated), connected by press-tight fittings to a 100-percent methylsiloxane capillary column and to a 5-percent phenyl-methylsiloxane capillary column (each 60 m x 250 µm inner diameter, 0.25 µm film thickness) from Agilent, Inc., Santa Clara, California. The hydrogen carrier gas was pressure-regulated at 25 psig and the ECDs were held at 330 °C. The initial GC temperature was 60 °C and immediately ramped at 15 °C/min to 150 °C, then ramped at 1 °C/min to 240 °C, and finally ramped at 10 °C/min to 330 °C and held for 15 min. As many as nine concentrations of standards, ranging from 0.03–30 ng/mL (PCB congeners), 0.1–80 ng/mL (OCPs), and 2–200 ng/mL (PBDE congeners), were used for component identification and internal standard calibration. Potential analyte peaks were identified on one column and confirmed on the second column wherever possible (Schwartz and Stalling, 1991).

Principal Components Analysis

The PCA applications used in this study were part of the Soft Independent Modeling by Class Analogy software SIMCA-P 8.0 (UMetrics AB, Umeå, Sweden). Principal Components are bilinear projection models constructed by decomposing a class data matrix into score, loading, and residuals matrices (Schwartz and Stalling, 1991). The objective was to build models for each class of contaminant, projecting the n-dimensional pattern or profile of the contaminant dataset onto two or three dimensions for interpretation of the relations between samples. Concentration data were normalized before PCA, removing the strong correlation of the first PC with total concentration.

Quality Control

Exposure to light was avoided or minimized during all sample and standard handling steps to reduce losses from photodegradation of PAHs, and to a lesser extent, of PBDEs. Method performance was monitored using several quality control measures. The inclusion of procedural blanks was used to assess the laboratory background of analytes and the recoveries of procedural internal standards. Procedural spikes were used to assess the recoveries of all analytes through the procedure. Bluegill (*Lepomis macrochirus*) fish tissue (negative control) matrix blanks were used to assess the potential background interferences from tissue subjected to the cleanup and fractionation schemes, and negative control fish tissue samples spiked with low concentrations of analytes were used to determine method recoveries of the analytes. An "in-house" positive control material prepared from common carp (*Cyprinus carpio*) from Saginaw Bay, Michigan, with environmentally incorporated residues of many analytes, was used to monitor the long-term performance of the analytical methods for several years (Hinck and others, 2007). Replicated (actually pseudoreplicate) analyses of randomly selected field samples in triplicate were used to demonstrate the reproducibility of the methods for the study samples. The procedural internal standards were added to all samples at the beginning of the preparatory scheme, before the extraction step, to monitor and adjust recoveries for each sample (sample handling losses).

Method reporting limits (MRLs) for total-aliphatic hydrocarbon and –PCB concentrations were set at 3 times the average total amounts measured in the procedural blanks run with each set, or based on the lowest calibration standard run in the calibration curve (200 ng/mL per alkane and 0.1 ng/mL per PCB congener). The MRLs were set to 10 ng/mL for PAHs, 0.1 ng/mL for OCPs, and 2 ng/mL for PBDEs, based on procedural background amounts and the analysis of low-concentration calibration standards.

Aliphatic hydrocarbons were only screened, using external standards and quality control samples, and no procedural internal standards were used to monitor recoveries throughout the aliphatic hydrocarbon cleanup procedures. Recoveries of aliphatic hydrocarbons were estimated from recoveries of spiked negative control fish material (matrix spikes), and were within quality control guidelines of 50 to 125 percent, indicating acceptable performance of the screening method.

Results and Discussion

Quality Control Results

A brief summary of quality control related information associated with the various analytical measurements is presented below.

Recoveries of the deuterated PAH procedural internal standards (deactivated silica-gel, fraction 2) were within quality control guidelines of 50 to 125 percent. All sample recoveries were between 51 and 119 percent; recoveries of volatile components (naphthalene-d_8, acenaphthylene-d_{10}, acenaphthene-d_{10}) were lower, ranging from 51 to 78 percent. Recoveries of less volatile PAHs (fluorene-d_{10} through benzo[*g,h,i*] perylene-d_{12}) averaged 79 to 92 percent. Isotope-dilution quantification inherently corrects each target PAH analyte for the recovery of the corresponding labeled surrogate. The precision of replicate analyses (n=3) of Pacific sanddab from Platform C for those PAHs greater than the reporting limits of the method ranged from 5 to 19 percent.

Recoveries of the procedural internal standards indicative of OCP and PCB analytes (PCB 029, 155 and 204) in the first silica-gel fraction, SG-1, were within quality control guidelines of 50 to 125 percent and ranged from 62 to 105 percent in all samples, with the lowest recoveries (62 to 93 percent) occurring for the most volatile procedural internal standard (PCB 029). Recoveries of total-PCB concentrations from the fortified negative control material were 103 percent, with individual congeners ranging from 60 to 117 percent. Again, lower recoveries were limited to only the three volatile monochloro-substituted PCB congeners (PCBs 1, 2, and 3). The recovery of total-PCB concentrations from the positive control material

was 120 percent of the historical average. The precision of replicate analyses (n=3) of Pacific sanddab from Platform C ranged from 2 to 74 percent for those PCB congeners greater than the reporting limits of the method. Most of the variability was introduced as a result of most congeners being near the method reporting limits; precision for those PCB congeners at concentrations greater than 10 times the reporting limits generally ranged from 2 to 20 percent. The precision for total-PCB concentrations (sum of PCB congener concentrations above the reporting limit) was artificially much improved by the weightings introduced from congeners with greater concentrations: sanddab from Platform C averaged 10 ng/g total PCBs, coefficient of variation 1.8 percent. The procedural blank analysis indicated a mass-based method background of about 12 ng of total-PCB amounts; this is equivalent to about 2.6 ng/g total-PCB concentrations in the 5-g field samples and is less than 20 percent of the lowest PCB concentrations measured in any field samples.

The recoveries of the procedural internal standard *p,p'*-DDD-d_8, indicative of the OCP analytes second silica-gel fraction (SG-2), were within quality-control guidelines (50 to 125 percent) with recoveries in most samples between 99 to 117 percent.

Recoveries of OCPs from the fortified negative control material (whole bluegill) ranged from 78 to 113 percent, though for most analytes recoveries were more precise, averaging about 92 percent. The exception was methoxychlor, recovered at 132 percent, the result of only partial chromatographic resolution from background interference. The recovery of OCPs from the positive control Saginaw Bay carp material ranged from 50 to 125 percent of the historical average for those pesticides with concentrations substantially above the reporting limits, with an average OCP recovery of 110 percent. The slightly higher values for coefficients of variation were related to slight on-column degradation of active contaminants (endrin, *p,p'*-DDT, and methoxychlor) and the precision of methoxychlor was less than most other OCPs because of PBDE and PCB interferences. Only 16 of the 29 targeted OCPs were quantified at concentrations above the MRL (0.1 ng/g) in the replicates, and 15 of these OCPs were less than 0.5 ng/g and had larger coefficients of variation (5 to 16 percent); the concentration of the remaining OCP (*p,p'*-DDE) averaged 11 ng/g and had a smaller coefficient of variation (1.2 percent). The procedural blank analyses indicated negligible background concentrations of OCPs. The long-term MRLs for OCPs are less than 0.1 ng/g.

The procedural blank analyses indicated normal laboratory background concentrations of individual PBDEs ranging from less than 0.01 to 0.03 ng/g (PBDE-099 and -100), which were considered when evaluating the lower PBDE concentration samples (Supporting Information, tables S5 and S6). The precision of replicate analyses (n=3) of Pacific sanddab from Platform C for PBDE-047 was 1.6 percent at a concentrations of 0.50 ng/g; the precision was undetermined for all PBDEs because concentrations of selected PBDE congeners were less than the method reporting limits of 0.4 ng/g for replicates of this sample.

This Study

The masses of the 68 Pacific sanddab from natural and platform locations ranged from 10 to 242 g, with fish from the natural areas averaging 55 g and fish from platform locations averaging 32 g, from table 1. This size range included immature and mature life stages of sanddab. On average, fish from natural areas were larger than fish from platforms. The effects on contaminant concentrations for each class of contaminant in fish are discussed later in this section. The fish masses from the natural areas were biased by all fish from northeast Santa Cruz, which were larger (86–231 g, average 172 g, n=5) than the averages of any other natural or platform location (averages 17–77 g). Only one of the five fish collected from the Rincon natural area was similar in size to those from the northeast Santa Cruz natural area (242 g). All other fish from natural and platform locations were smaller, and similar in size, ranging from 10 to 42 g and averaging 29 g (n=58). Only one Pacific sanddab sample (24 g) could be collected from Platform Edith. This sample was low in extractable lipid, about three-fold lower than most other platform samples, and the sample was relatively high in contaminants; this combination caused lipid-normalized values to be elevated relative to all other samples, as will be discussed.

Extractable lipid content of Pacific sanddab from natural and platform locations ranged from 0.57 to 2.27 percent and averaged 1.43 percent (n=13 composites of 5 fish each, table 2). Recoveries of procedural internal standards were within quality-control specifications, and generally ranged from 80 to 100 percent, which indicated complete extraction and recovery of the analytes. This indicated that extraction efficiencies for lipids (as total dichloromethane-extractable residues) were also excellent.

The percentage of extractable lipids averaged 1.63 percent (n=6 composites) for fish from the natural areas and was slightly less (1.35 percent, n=7 composites) for fish from the platform locations. Comparisons were made among composites that contained predominantly larger fish and those that contained mostly smaller fish; this grouped fish composites into platforms and natural areas (because of size differences). Note that fish composites from platforms Ellen and Edith had much lower percentages of extractable lipids. Overall, lipid normalization made only slight differences, again, mostly for those composites of small fish.

Thirteen composite samples of Pacific sanddab were prepared and analyzed for aliphatic hydrocarbons, PAHs, PCBs, OCPs, and PBDEs by USGS, and the results are presented below. All contaminant values in field samples were adjusted for recoveries of procedural internal standards (surrogates) and corrected for procedural blank background values (Detailed individual sample information may be found in the Supporting Information, tables S1–S8). Procedural blank values were adjusted for surrogate recoveries before being used to correct field results for background contaminant values.

Table 2. Lipid values for whole-fish composites of Pacific sanddab from natural areas and platforms.

[Lipids are expressed as a percent based on wet tissue weight, of dichloromethane column-extractable material; ±, plus or minus; cv, coefficient of variation (percent relative standard deviation); range, average, and coeffificent of variation summarize the composites from the natural areas and from the platforms]

Sample	Extractable lipids (percent)
Natural areas	Range: 1.30–2.27 Average ± cv: 1.63 ± 24
CAND (Campus Point)	2.08
RIND (Rincon)	2.27
HUEN (Hueneme)	1.31
NESC (NE Santa Cruz)	1.32
EDND (Platform Edith Natural Area)	1.52
SBPN (Santa Barbara Natural Area)	1.30
Platforms	Range: 0.57–1.72 Average ± cv: 1.35 ± 32
HOLL (Holly)	1.57
PLATC (Platform C)	1.68
HOGA (Hogan)	1.44
GINA (Gina)	1.72
GILD (Gilda)	1.54
EDIT (Edith)	0.57
ELLE (Ellen)	0.92

Aliphatic Hydrocarbons

As a supplemental part of the analysis of fish for polycyclic aromatic hydrocarbons, the first deactivated silica gel fractions, containing aliphatic hydrocarbons that were separated from PAHs, were retained and screened to assess the patterns and concentrations of nonaromatic hydrocarbons in fish collected from platforms and nearby natural areas. As stated for the extraction of lipids, recoveries of procedural internal standards ranged from 80 to 100 percent, thus, recoveries of about 90 percent were estimated for aliphatic hydrocarbons from C_9 to C_{40}. This indicated complete extraction and recovery of the analytes, including aliphatic hydrocarbons. Aliphatic hydrocarbons comprise a major fraction of petroleum and may be used to assess contamination by oil, from platforms and natural seeps, in the marine environment (Law, 1978; Lytle and Lytle, 1979; Simoneit and Kaplan, 1980; Gonzalez and others, 1992; Steinhauer and others, 1994; Quintero and Diaz, 1994; Marcias-Zamora, 1996; Peterson and others, 1996; Spies and others, 1996; Quigley and others, 1999; Pena-Mendez and others, 2001; Farwell and others, 2009.

Aliphatic hydrocarbon concentrations were uniformly low in all samples from the platforms and the natural locations and below the limits of detection of the screening method used. Method limits of detection were estimated at 20 ng/g based on tissue wet-weight (ww) per component or 200 ng/g ww for total-aliphatic hydrocarbons. Reporting limits were 200 ng/g ww for total-aliphatic hydrocarbons. Because of the lack of detectable components, calculated metrics such as total hydrocarbons, even-numbered carbon and odd-numbered carbon alkane concentrations, the carbon predominance index, and ratios between C_{17}/pristane, C_{18}/phytane, and pristane/phytane ratios could not be determined. Application of these metrics in situations of sufficient detectable concentrations may have been otherwise used to evaluate the petrogenic and pyrogenic contamination contributions at platform sites and the nearby natural areas.

Polycyclic Aromatic Hydrocarbons

Total-PAH concentrations (expressed are the sum of 20 parent PAHs, 11 alkyl-substituted PAHs, and three polycyclic aromatic thiophenes) in composite Pacific sanddab ranged from 15 to 37 ng/g ww in samples collected at natural areas and from 8.7 to 22 ng/g ww in samples collected at platforms (tables 3, S1, S2). Average total-PAH concentrations were low in fish from all locations, but concentrations in fish from natural areas were nearly twice concentrations in fish from platforms ($p=0.0045$); however, because of the small numbers of samples and the use of composite whole-fish samples (including gut-contents), any interpretation of this difference would require further investigation.

Seven of the 34 target PAHs (naphthalene, 2-methyl and 1-methylnaphthalenes, biphenyl, phenanthrenes, fluoranthene, and pyrene) were reported in Pacific sanddab from natural areas and platforms; additionally, 2-methylphenanthrene was reported in sanddab from four of the six natural areas, and chrysene and benzo(*k*)fluoranthene were reported only in sanddab from the Campus Point natural area. (fig. 3*A*). The numbers of positive samples are few for the parent PAHs (this study) and for the OH-PAH metabolites (Gale and others, 2012). The positive OH-PAH detections included only 2 Pacific sanddab individuals, all other OH-PAH positives were for other species, for which parent PAHs were not determined in this study. This paucity of data necessitated prudence in reaching conclusions or associations between positive PAH concentrations and positive OH-PAH concentrations.

Normalization of contaminant concentrations for extractable lipids in the composite samples was performed for PAHs and for the other targeted contaminants. Lipid normalization decreased the differences in contaminant concentrations between composites from platforms and natural areas but did not improve the comparability of samples within natural areas and within platforms, or between samples from natural areas and platforms (table 3 and fig. 3). Lipid-normalization was anticipated to decrease the variance of the sample set, if the fish were exposed to a relatively constant long-term background of contaminants, though no quantitative statistical comparisons were made. However, the low-lipid samples from Platforms Edith and Ellen had concentrations of contaminants

Table 3. Total-PAH concentrations for whole-fish composites of Pacific sanddab from natural areas and platforms.

[ng/g, nanograms per gram; lipid, dichloromethane extractable material; ±, plus or minus; cv, coefficient of variation (percent relative standard deviation)]

Sample	Total PAHs (ng/g wet weight)	Total PAHs (ng/g lipid)
Natural areas	Range: 15–37 Average ± cv: 27 ± 29	Range: 1,200–2,200 Average ± cv: 1,700 ± 24
CAND (Campus Point)	37	1,800
RIND (Rincon)	29	1,300
HUEN (Hueneme)	21	1,600
NESC (NE Santa Cruz)	29	2,200
EDND (Platform Edith Natural Area)	30	2,000
SBPN (Santa Barbara Natural Area)	15	1,200
Platforms	Range: 8.7–22 Average ± cv: 15 ± 30	Range: 950–2,300 Average ± cv: 1,200 ± 44
HOLL (Holly)	16	1,000
PLATC (Platform C)	22	1,300
HOGA (Hogan)	18	1,300
GINA (Gina)	14	1,300
GILD (Gilda)	11	700
EDIT (Edith)	13	2,300
ELLE (Ellen)	8.7	950

that were similar to samples with higher lipid content on a wet-weight basis; therefore, lipid normalization served to increase the difference between these two samples and the rest of the sample set.

Polychlorinated Biphenyls

Total-PCB concentrations were quantified in samples by summing concentrations of 90 individual congeners, 22 unresolved pairs of congeners, and 2 unresolved multiplets of congeners. Procedural blank concentrations of PCBs were low (13 ng total PCBs per sample), corresponding to 2.6 ng/g ww total-PCBs in a typical 5 g-eq/mL extract. These background concentrations were approximately five- to ten-fold less than the lowest concentration determined for a field sample. Congener concentrations were adjusted for recoveries of surrogates and corrected for procedural background concentrations of PCBs.

Tissue wet-weight concentrations and lipid-normalized total-PCB concentrations in composite Pacific sanddab samples are presented in tables 4, S3, and S4. Total-PCB concentrations were low in all composite samples from platforms and natural areas. It was estimated that about 50 percent of the total-PCB concentration in all samples comprised nine congeners: PCBs 153, 138/163/164, 110, 118, 15, 99, 187, 149, 180, ranked in decreasing order of overall contribution to the total-PCB concentration in most samples. About one-half of these congeners (PCBs 118, 138, 153, 180, 187) were reported as among the 12 congeners (of 27 target PCBs) comprising most of the total-PCB concentration in Pacific sanddab from the Southern California Bight by Schiff and Allen, 2000, collected in areas overlapping some sampling locations in this study. Using all 12 PCB congeners suggested by Schiff and Allen accounted for 41 to 50 percent of the total-PCB concentrations, whereas using just the six congeners in common with Schiff and Allen and this study accounted for 29 to 40 percent of the total-PCB concentrations. Some of the apparent difference results from the smaller subset of 27 congeners selected for analysis, 7 of which were not detected in any sample, by Schiff and Allen (2000). The broader target list used here allowed a greater number of potentially bioaccumulated congeners to be investigated, several of which (PCBs 110, 15, 99, and 149) were determined to be major components of the total PCB loading of the Pacific sanddab at these locations.

Tissue-weight based total-PCB concentrations ranged from 7 to 22 ng/g ww in samples collected at natural areas and from 10 to 35 ng/g ww in samples collected at platforms. Samples in table 4 and in figure 4 are grouped by natural or platform location for comparison. Within the natural areas and platform groups, samples have concentrations that range no more than two-fold that of the average concentrations reported for each group. Average total-PCB concentrations were low at all locations, but were nearly twice as great at platforms compared to natural areas, The PCB concentrations do not indicate clear separation between these two groups of locations, suggesting that PCBs were not associated with the platforms, but may be associated with other, more widely ranging sources. Normalization of PCB concentrations for the percentages of extractable lipids in the composite samples does not affect the variation in concentrations for natural areas, but approximately doubles the variation in concentrations for platforms. Most of the increase after lipid-normalization for platform sample concentrations resulted from the two low-lipid composites from Platform Edith (only one fish collected) and, to a lesser extent, from Platform Ellen. Lipid-normalization provided a marked difference in contaminant concentrations for these samples compared with the remaining samples in either the platform or natural area groups. As noted for PAHs, lipid-normalization of PCB concentrations did not increase the comparability within natural areas, within platforms, or between natural areas and platforms.

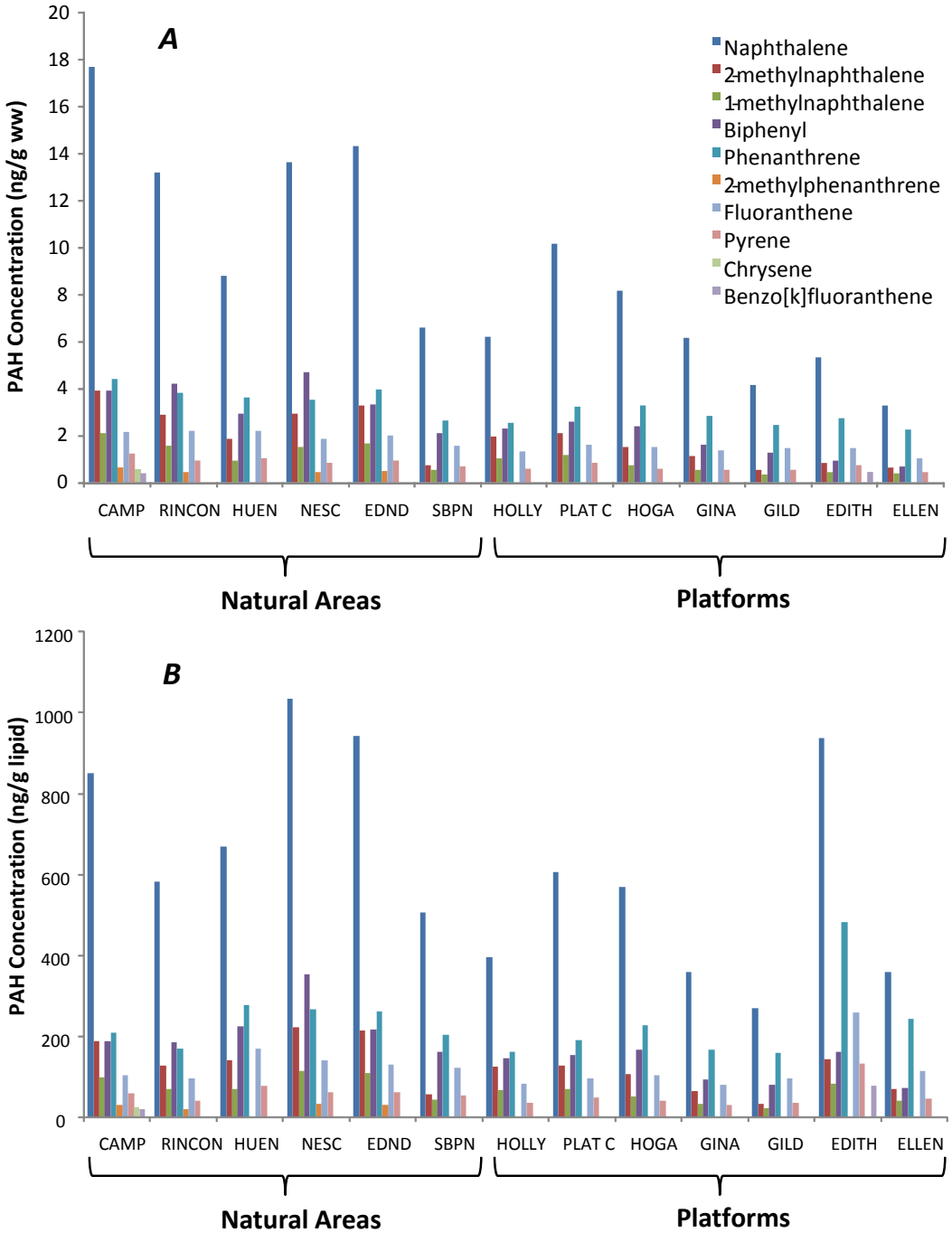

Figure 3. Concentrations of polycyclic aromatic hydrocarbons in Pacific sanddab tissues from natural areas and platforms. *A*, Tissue concentration in nanograms per gram (ng/g ww) based on wet weight; *B*, Tissue concentrations normalized to extractable lipid weight.

Table 4. Total-polychlorinated biphenyl concentrations for whole-fish composites of Pacific sanddab from natural areas and platforms.

[ng/g, nanograms per gram; lipid, dichloromethane extractable material; ±, plus or minus; cv, coefficient of variation (percent relative standard deviation)]

Sample	Total PCBs (ng/g wet weight)	Total PCBs (ng/g lipid)
Natural areas	Range: 7.5–22 Average ± cv: 13 ± 37	Range: 570–1,400 Average ± cv: 820 ± 38
CAND (Campus Point)	12	590
RIND (Rincon)	16	690
HUEN (Hueneme)`	11	860
NESC (NE Santa Cruz)	11	800
EDND (Platform Edith Natural Area)	22	1,400
SBPN (Santa Barbara Natural Area)	7.5	570
Platforms	Range: 10–35 Average ± cv: 23 ± 41	Range: 600–5,900 Average ± cv: 2,100 ± 85
HOLL (Holly)	35	2,200
PLATC (Platform C)	10	600
HOGA (Hogan)	21	610
GINA (Gina)	17	1,500
GILD (Gilda)	24	1,000
EDIT (Edith)	34	5,900
ELLE (Ellen)	16	1,700

The principal components analysis (PCA) of the PCB congener concentrations in fish from natural area and platform locations indicated separation of Platforms Edith and Holly from the other locations and from each other (refer to fig. 5). Compared in Aroclor®1242/1248/1254/1260-space, the cluster containing most of the natural area and platform locations compared more closely with Aroclor® 1254, whereas Platforms Edith and Holly, though still more closely associated with Aroclor® 1254, tended to exhibit some Aroclor® 1260-like character (fig. 5*A*); this difference may be the result of source composition, weathering, biomagnification (foodweb differences), and metabolism. Examination of the loadings for the dataset (not shown) indicated that the separations were based on the few major congeners summarized above. The dataset was normalized to total-PCB concentrations before principal components analysis; however, the separation between samples continued to follow the relative proportion of these few major congeners. Other natural area and platform locations were grouped more closely together, which is emphasized in figure 5*A*, in which the four Aroclors® are included in the score-plot. Removing the four Aroclors® from the score-plot emphasized the distribution of samples, which followed a trajectory away from projections for Platforms Edith and Holly, with the Santa Barbara natural area being furthest-removed from the major cluster of natural areas and platforms. Trajectories, such as this, which follow a smooth path in PCA scores plot, were determined to be typical of a series of samples with similar concentration profiles and that have proportionally decreasing component concentrations, which produce sequential losses of those components decreasing below the detection limits (R.W. Gale, unpub. data, 2012).

Closer inspection of the PCB profiles confirmed the inference made above—that as the concentrations of the several major congeners tended to decrease, their relative concentrations among sites remained similar, and that the minor contributing congeners tended to increase, relatively, forming a general low-concentration PCB background profile common to all samples.

Organochlorine Pesticides

Thirty-one pesticides were targeted in the samples; including 4 benzene hexachloride (BHC) (or hexachlorocyclohexane, HCH) isomers (α-HCH, β-HCH, γ-HCH, δ-HCH), 7 chlordane components (*cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, heptachlor, heptachlor epoxide), 6 DDT series components (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE), 3 endosulfan components (endosulfan I, endosulfan II, endosulfan sulfate), and 5 chlorinated isodrin components (aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone). Concentrations were adjusted for recoveries of surrogates and corrected for procedural background concentrations of OCPs.

Procedural blank concentrations of most pesticides were below the reporting limit (less than 0.1 ng absolute, less than 0.02 ng/g ww), though background concentrations of pesticides, or interferences, were slightly above the detection limit for six pesticides: hexachlorobenzene, pentachloroanisole, dacthal, and *trans*-chlordane (0.05 ng), methoxychlor (0.15 ng), and *p,p'*-DDE (0.6 ng). Some pesticides were not detectable in any sample (pentachlorobenzene, δ-BHC, heptachlor, endosulfan sulfate, aldrin, and dacthal), and additional pesticides (pentachloroanisole, γ-BHC, endosulfan I and II, total endrin, and mirex) were not detectable in most samples. Recoveries of OCPs from fortified negative control fish matrix ranged from 78–113 percent (average cv 90 ± 11 percent). The exception was methoxychlor, with a slightly biased recovery of 132 percent, resulting from incomplete resolution from an interference.

Tissue weight-based concentrations of OCPs detected in Pacific sanddab composites from natural areas and from platforms are presented in tables 5 and S5 and lipid-normalized concentrations in tables 6 and S6. Samples are grouped into natural areas and platforms for comparison. As previously

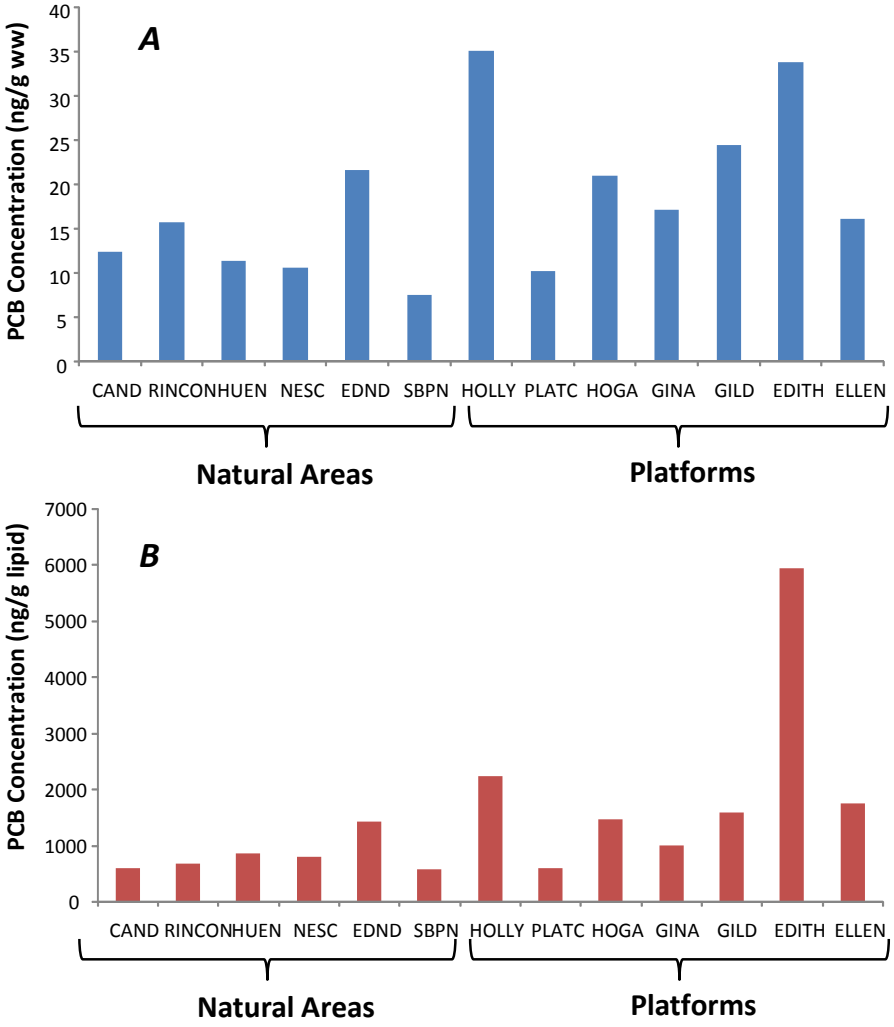

Figure 4. Total-polychlorinated biphenyl concentrations in Pacific sanddab tissues from natural areas and platforms. *A*, Tissue concentration in nanograms per gram (ng/g ww) based on wet weight; *B*, Tissue concentrations normalized to extractable lipid weight.

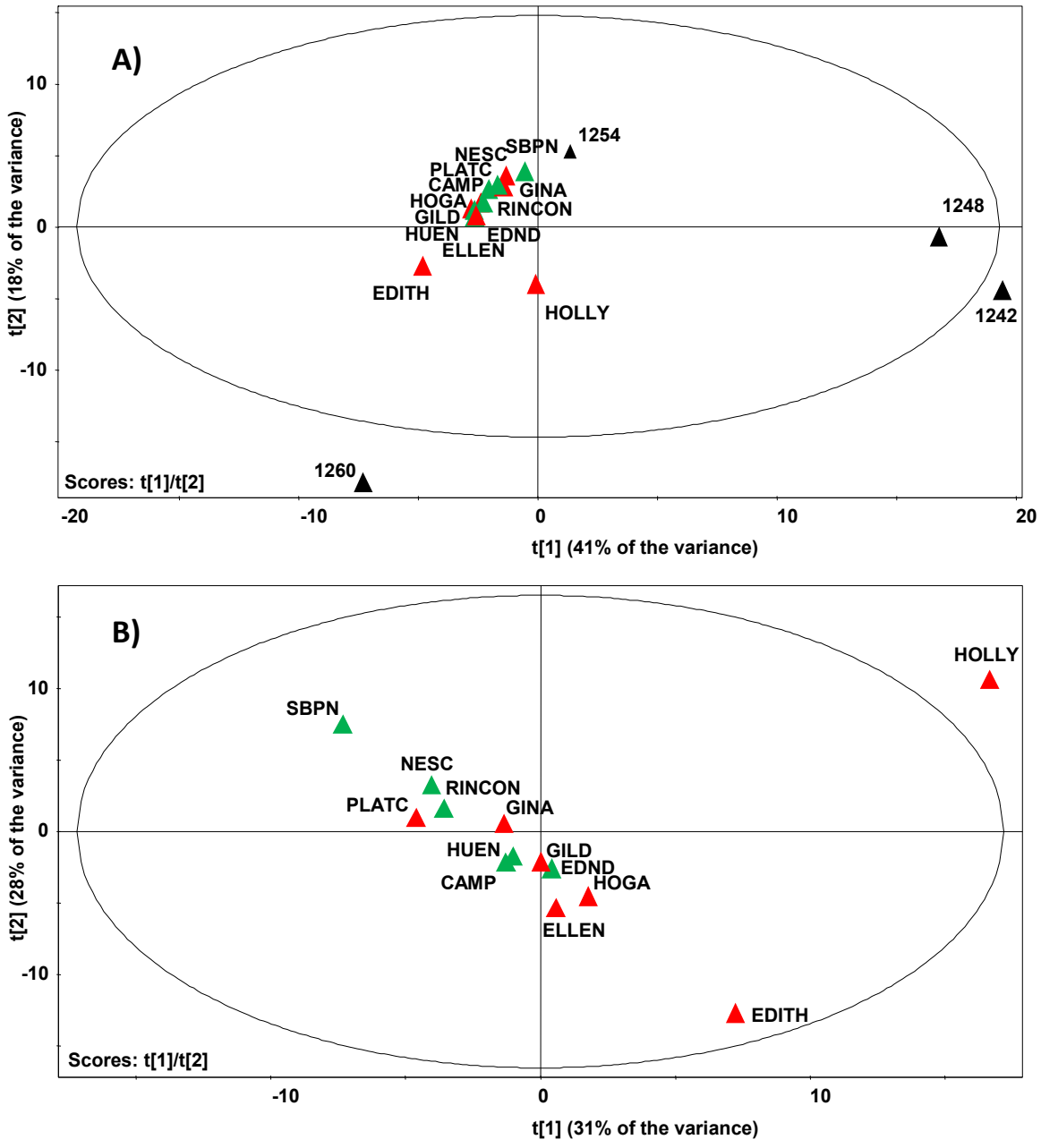

Figure 5. Principal components analysis of polychlorinated biphenyl congeners in Pacific sanddab tissues from natural areas (green) and platforms (red). A, Score-Plot with Aroclors® included; B, Score-Plot with Aroclors® omitted. The percent of the total variance that is explained by each plotted principal component (x and y axes) is reported in the axis label.

Table 5. Ranges of organochlorine pesticide concentrations in composite samples of Pacific sanddab from natural areas and platform locations (wet-weight basis).

[ng/g, nanograms per gram based on wet-weight; cv, coefficient of variation (percent relative standard deviation); n, number of samples in which the analyte was detected (Natural Areas n=7; Platform Locations n=6); ±, plus or minus; <, less than; total endrin, the sum of endrin, endrin aldehyde, and endrin ketone]

Pesticide	Natural areas				Platform locations			
	Range ng/g wet-weight	Average ng/g wet-weight	cv	(n)	Range ng/g wet-weight	Average ng/g wet-weight	cv	(n)
Pentachlorobenzene	< 0.03			0	< 0.03			0
Hexachlorobenzene	0.06 – 0.2	0.1	± 34	6	0.05 – 0.2	0.1	± 39	6
Pentachloroanisole	< 0.03 – 0.04	0.03	± 34	1	< 0.03			0
alpha-BHC (α-HCH)	< 0.03 – 0.05	0.03	± 23	4	0.05	0.05	± 1.0	3
beta-BHC (β-HCH)	0.04 – 0.08	0.06	± 22	6	< 0.03 – 0.09	0.06	± 41	6
Lindane (γ-HCH)	< 0.03 – 0.04	0.03	± 26	1	0.04	0.04		1
delta-BHC (δ-HCH)	< 0.03			0	< 0.03			0
Heptachlor	< 0.03			0	< 0.03			0
Heptachlor epoxide	< 0.03 – 0.04	0.03	± 12	2	0.04 – 0.08	0.06	± 59	4
Methoxychlor	0.09 – 0.6	0.3	± 57	5	0.04 – 0.5	0.3	± 64	6
cis-Chlordane	0.05 – 0.2	0.1	± 53	6	0.04 – 0.2	0.1	± 62	6
trans-Chlordane	< 0.03 – 0.07	0.05	± 37	4	0.05 – 0.08	0.06	± 26	4
Oxychlordane	< 0.03 – 0.07	0.04	± 23	6	0.06 – 0.1	0.1	± 63	5
cis-Nonachlor	0.1 – 0.3	0.2	± 32	6	0.1 – 0.4	0.2	± 50	6
trans-Nonachlor	0.1 – 0.7	0.3	± 49	6	0.2 – 1.0	0.5	± 84	6
o,p'-DDE	0.04 – 0.05	0.05	± 11	4	0.06	0.06	± 6.9	2
o,p'-DDD	< 0.03 – 0.1	0.07	± 60	4	0.04 – 0.1	0.07	± 65	5
o,p'-DDT	0.04 – 0.2	0.08	± 59	6	< 0.03 – 0.09	0.06	± 38	5
p,p'-DDE	5.6 – 33	17	± 48	6	17 – 76	34	± 110	6
p,p'-DDD	0.3 – 0.6	0.5	± 27	6	0.3 – 0.7	0.5	± 37	6
p,p'-DDT	0.4	0.2	± 56	6	0.1 – 0.5	0.3	± 78	6
Endosulfan I	0.03	0.03		1	< 0.03			0
Endosulfan II	0.03	0.03		1	< 0.03			0
Endosulfan sulfate	< 0.03			0	< 0.03			0
Aldrin	< 0.03			0	< 0.03			0
Total endrin	< 0.03 – 0.04	0.03	± 19	2	0.04	0.04		1
Dieldrin	0.04 – 0.10	0.07	± 24	6	0.03 – 0.2	0.09	± 74	6
Mirex	0.03 – 0.05	0.04	± 42	1	0.03 – 0.04	0.03	± 11	4
Dacthal	< 0.03			0	< 0.03			0

Table 6. Ranges of organochlorine pesticide concentrations in composite samples of Pacific sanddab from natural areas and platform locations (lipid-weight basis).

[ng/g, nanograms per gram based on extractable lipid amount; lipid, dichloromethane extractable material; cv, coefficient of variation (percent relative standard deviation); n, number of samples in which the analyte was detected (Natural Areas n=7; Platform Locations n=6); ±, plus or minus; ; <, less than; total endrin, the sum of endrin, endrin aldehyde, and endrin ketone; the reporting limit for lipid-normalized concentrations is given as the maximum wet-weight limit adjusted for the minimum percent extractable lipid].

Pesticide	Natural areas				Platform locations			
	Range ng/g wet-weight	Average ng/g wet-weight	cv	(n)	Range ng/g wet-weight	Average ng/g wet-weight	cv	(n)
Pentachlorobenzene	< 2			0	< 5			0
Hexachlorobenzene	4.7 – 9.5	7.1	± 22	6	6.6 – 10	8.4	± 18	6
Pentachloroanisole	1.7 – 2.6	2.1	± 31	1	< 5			0
alpha-BHC (α-HCH)	1.4 – 2.4	2.0	± 14	4	3.1 – 3.4	3.3	± 9.9	3
beta-BHC (β-HCH)	3.1 – 4.5	3.9	± 13	6	3.5 – 5.6	4.4	± 18	6
Lindane (γ-HCH)	2.0 – 2.5	2.3	± 14	1	2.6	2.6		1
delta-BHC (δ-HCH)	< 2			0	< 5			0
Heptachlor	< 2			0	< 5			0
Heptachlor epoxide	1.5 – 1.8	1.6	± 4.0	2	2.1 – 5.4	3.9	± 70	4
Methoxychlor	6.6 – 33	19	± 46	5	3.9 – 30	19	± 55	6
cis-Chlordane	4.0 – 13	7.4	± 37	6	5.7 – 15	9.1	± 42	6
trans-Chlordane	1.7 – 4.4	2.9	± 30	4	3.2 – 5.1	4.0	± 30	4
Oxychlordane	1.8 – 3.3	2.5	± 12	6	5.0 – 9.3	7.4	± 52	5
cis-Nonachlor	8.4 – 19	11	± 25	6	11 – 28	20	± 47	6
trans-Nonachlor	9.7 – 44	18	± 42	6	23 – 64	42	± 60	6
o,p'-DDE	2.3 – 3.7	3.1	± 16	4	3.5 3.8	3.7	± 7.2	2
o,p'-DDD	2.0 – 5.9	3.8	± 34	4	2.3 – 24	8.5	± 200	5
o,p'-DDT	2.9 – 11	4.8	± 51	6	2.8 – 13	6.3	± 93	5
p,p'-DDE	430 – 2,200	1,000	± 33	6	1,000 – 13,000	4,100	± 260	6
p,p'-DDD	22 – 38	28	± 16	6	35 – 58	43	± 29	6
p,p'-DDT	3.3 18	10	± 30	6	11 – 82	30	± 180	6
Endosulfan I	1.8	1.8		1	< 5			0
Endosulfan II	1.3	1.3		1	< 5			0
Endosulfan sulfate	< 2			0	< 5			0
Aldrin	< 2			0	< 5			0
Total endrin	1.4 – 1.7	1.6	± 11	2	2.6	2.6		1
Dieldrin	3.3 – 5.5	4.3	± 16	6	4.1 – 11	6.6	± 54	6
Mirex	1.4 – 3.3	2.3	± 44	1	2.2 – 6.2	3.6	± 58	4
Dacthal	< 2			0	< 5			0

mentioned, six pesticides (pentachlorobenzene, δ-BHC, heptachlor, endosulfan sulfate, aldrin, and dacthal) were not detected in any sample (< 0.02 ng/g ww). Most other pesticides were detected at concentrations of < 1 ng/g ww in all composite samples from natural areas and platforms.

The exceptions were the DDTs: *p,p′*-DDE ranged from 5.6 to 33 ng/g ww at natural areas and from 17 to 76 ng/g ww at platforms. In addition to *p,p′*-DDE, there were detectable concentrations of the DDT-series of chemicals in most samples, ranging from not detectable to about 1 ng/g ww; typically, the *p,p′*-isomers predominated, with the DDT-series decreasing in the order: *p,p′*-DDE >> *p,p′*-DDD > *p,p′*-DDT >> *o,p′*-DDT ≈ *o,p′*-DDD > *o,p′*-DDE. The concentrations of *p,p′*-DDE were similar in Pacific sanddab from platforms and from natural areas when compared on a wet weight or a lipid normalized basis (fig. 6). The exception is the single Pacific sanddab sampled from Platform Edith. This is the only sanddab that could be sampled at this site and had an extractable lipid content about three-fold less than all other samples; this suggests that this species—and particularly this sample—may not be resident at this platform or representative of contaminant loadings at this site, or that the health and nutrition of this individual may have been compromised.

Concentrations of chlordane-related compounds were low with concentrations ranging from 0.1 to 1.0 ng/g ww and displayed similar profiles at natural areas and platforms (tables 5 and 6, and Supporting Information tables S5 and S6). Generally, chlordane-related compounds followed the order: *trans*-nonachlor > methoxychlor > *cis*-nonachlor ≈ *trans*-chlordane ≈ *cis*-chlordane ≈ oxychlordane ≈ heptachlor epoxide; heptachlor was not detected in any composite sample.

Overall, the coefficients of variation for pesticide concentrations were not reduced by lipid-normalization; the decreases were inconsistent and increases were seen for some chlordane components as for other analytes. This generally did not provide better comparisons among the natural areas or among the platforms. The low concentrations of extractable lipids in Pacific sanddab from Platforms Edith and Ellen tended to weight more greatly the lipid-normalized concentrations from these two sites and did not produce any insight into the distributions of contaminants between natural areas and platform locations.

The principal components analysis of the normalized Pacific sanddab OCP concentrations did not indicate clear or partial groups by natural areas or platform locations (fig. 7). OCP concentrations in Pacific sanddab composites were grouped closely for the replicated samples (PLATC), indicating the adequate reproducibility of the analytical method. The loadings plot for the separation of the first two principal components of the OCPs indicates that the DDT-series components most greatly structured the data, followed by analytes detected only occasionally and at low concentrations in some composite samples.

Lipid-normalization of OCP concentrations did not increase the principal components analysis class separation of the samples into better-defined groups (data not shown). The low lipid content samples from Platforms Ellen, and especially Edith, were separated from the rest of the natural areas and platform locations, again, suggesting that these samples were more different from the rest of the samples because of lipid concentrations rather than because of contaminant concentrations. The major components separating the samples were DDT-related, though concentration differences were small and variable. Generally, lipid-normalization demonstrated that differences in extractable lipid content between fish from the natural areas and the platform locations provided the major determinant for separating the samples, and that differences in lipid content were much more important that the much smaller differences in pesticide concentrations between samples. Many of the values for lipid-normalized concentrations of OCPs are low, and only appear to be substantial because of the magnification caused by the lipid-normalization process. The lipid-normalized values less than about 1 ng/g lipid are suspect and should be discounted or carefully reviewed before forming conclusions about the relations between contaminant concentration and differences between Pacific sanddab from natural areas and platform locations.

Selected Polybrominated Diphenylethers

Total-PBDE concentrations were quantified in samples as the sum of nine congeners representing major PBDE components in commercial formulations. Congener concentrations were adjusted for recoveries of surrogates and corrected for procedural background concentrations of PBDEs.

The amount of total-PBDEs in the procedural blank was low, approximately 0.2 ng. This background was contributed by PBDE-100 (0.05 ng absolute) and PBDE-99 (0.15 ng absolute). Total-PBDE concentrations in these samples were comprised of only two congeners: PBDE-47, the predominant congener in composite samples at all locations, comprising from 70 to 100 percent of the total; the remaining 30 percent (or less) was comprised of PBDE-100. PBDE-99 was not quantified in any composite sample at concentrations above the reporting limit of 0.4 ng/g ww (2–5 ng/g lipid). Total-PBDE concentrations were documented at less than 3 ng/g ww (or less than ten-fold above the reporting limit for quantification). Recoveries of PBDEs fortified in negative control fish tissue ranged from 90 to 94 percent.

Tissue weight-based concentrations and lipid-normalized total-PBDE concentrations in Pacific sanddab composite samples are presented in tables 7, S7, and S8. All composite sample concentrations were low with respect to the reporting limits of this study, ranging from 0.4 to 3.0 ng/g ww. The tissue- weight-based and lipid-normalized total-PBDE concentrations are shown in figure 8, with the results grouped by natural area and platform location. The PBDE concentrations do not indicate clear separation between natural areas and platforms. There were no samples with substantial PBDE concentrations and the relative concentrations between natural areas and platforms are not consistent. Lipid-normalization did not enhance the comparability between the two groups of samples.

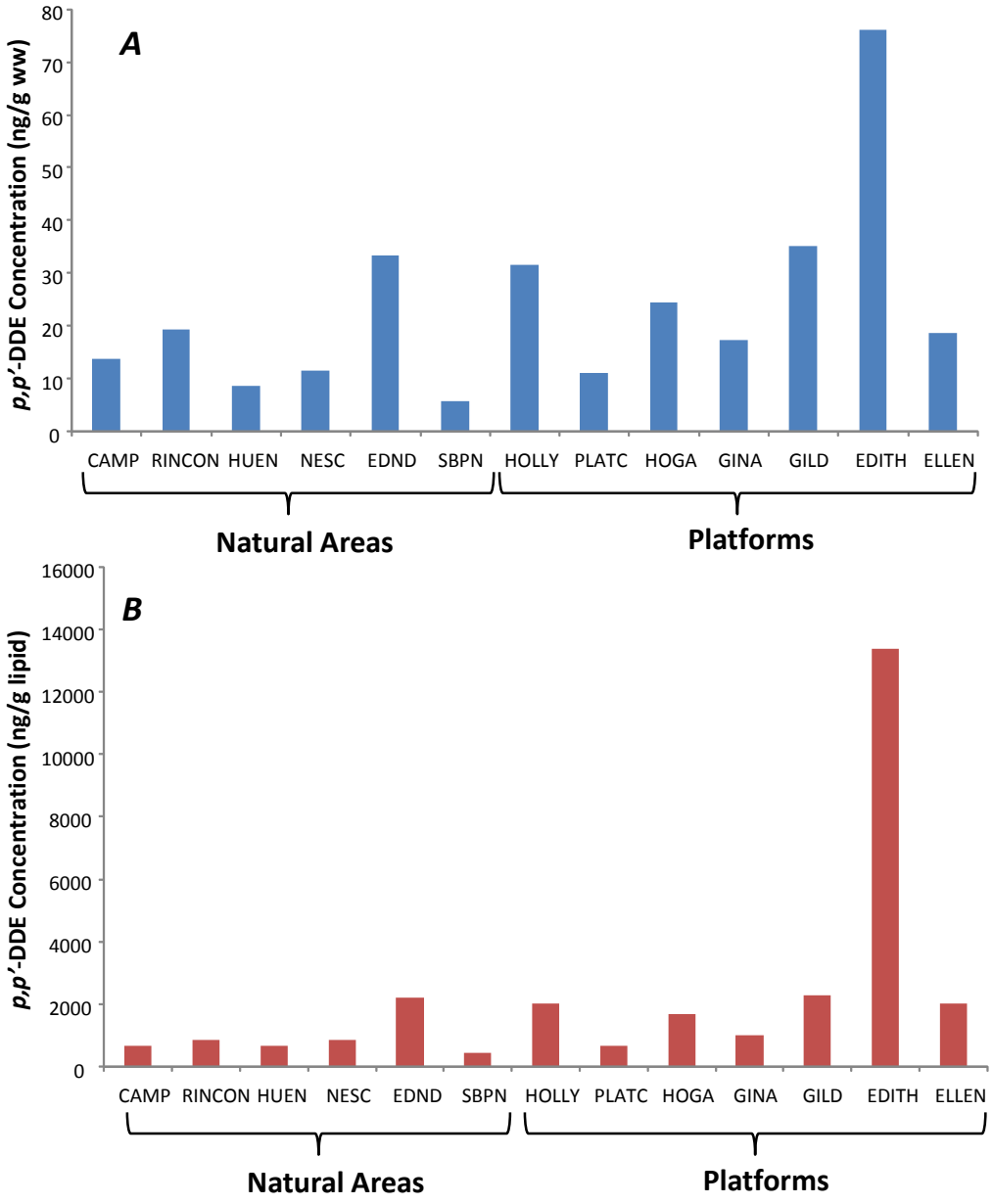

Figure 6. Concentrations of p,p′-dichlorodiphenyldichloroethylene (p,p′-DDE) in Pacific sanddab tissues from natural areas and platforms. *A*, Tissue concentration in nanograms per gram (ng/g ww) based on wet weight; *B*, Tissue concentrations normalized to extractable lipid weight.

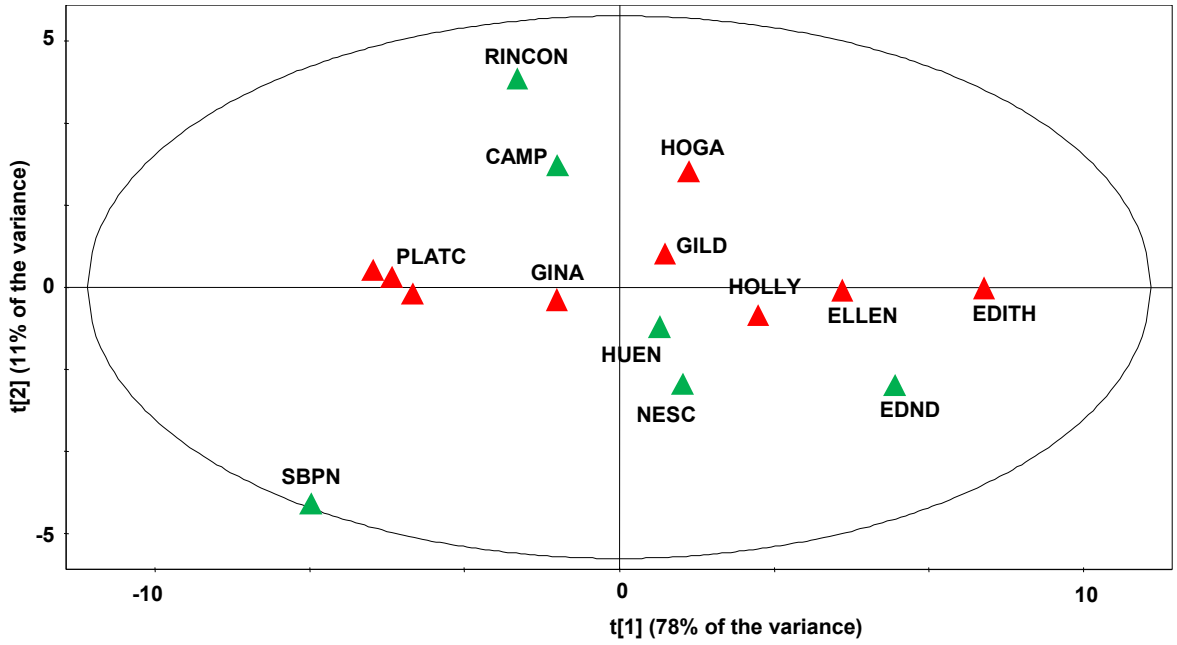

Figure 7. Principal components analysis (Score-Plot) of organochlorine pesticides in Pacific sanddab tissues from natural areas (green) and platforms (red). The percent of the total variance that is explained by each plotted principal component (x and y axes) is reported in the axis label.

Table 7. Total-polybrominated diphenylether concentrations for whole-fish composites of Pacific sanddab from natural areas and platforms.

[ng/g, nanograms per gram; lipid, dichloromethane extractable material; cv, coefficient of variation (percent relative standard deviation); ±, plus or minus; <, less than; The reporting limit for lipid-normalized concentrations is given as the maximum wet-weight limit adjusted for the minimum percent extractable lipid]

Sample	Total PBDE (ng/g wet weight)	Total PBDEs (ng/g lipid)
Natural areas	Range: < 0.4–1.8 Average ± cv: 0.8 ± 80	Range: < 30–120 Average ± cv: 47 ± 84
CAND (Campus Point)	0.5	25
RIND (Rincon)	1.0	46
HUEN (Hueneme)	0.6	43
NESC (NE Santa Cruz)	0.6	49
EDND (Platform Edith Natural Area)	1.8	120
SBPN (Santa Barbara Natural Area)	< 0.4	< 30
Platforms	Range: 0.5–3.0 Average ± cv: 1.4 ± 65	Range: 30–190 Average ± cv: 120 ± 49
HOLL (Holly)	3.0	190
PLATC (Platform C)	0.5	30
HOGA (Hogan)	2.1	150
GINA (Gina)	1.1	67
GILD (Gilda)	2.6	170
EDIT (Edith)	0.8	140
ELLE (Ellen)	1.5	170

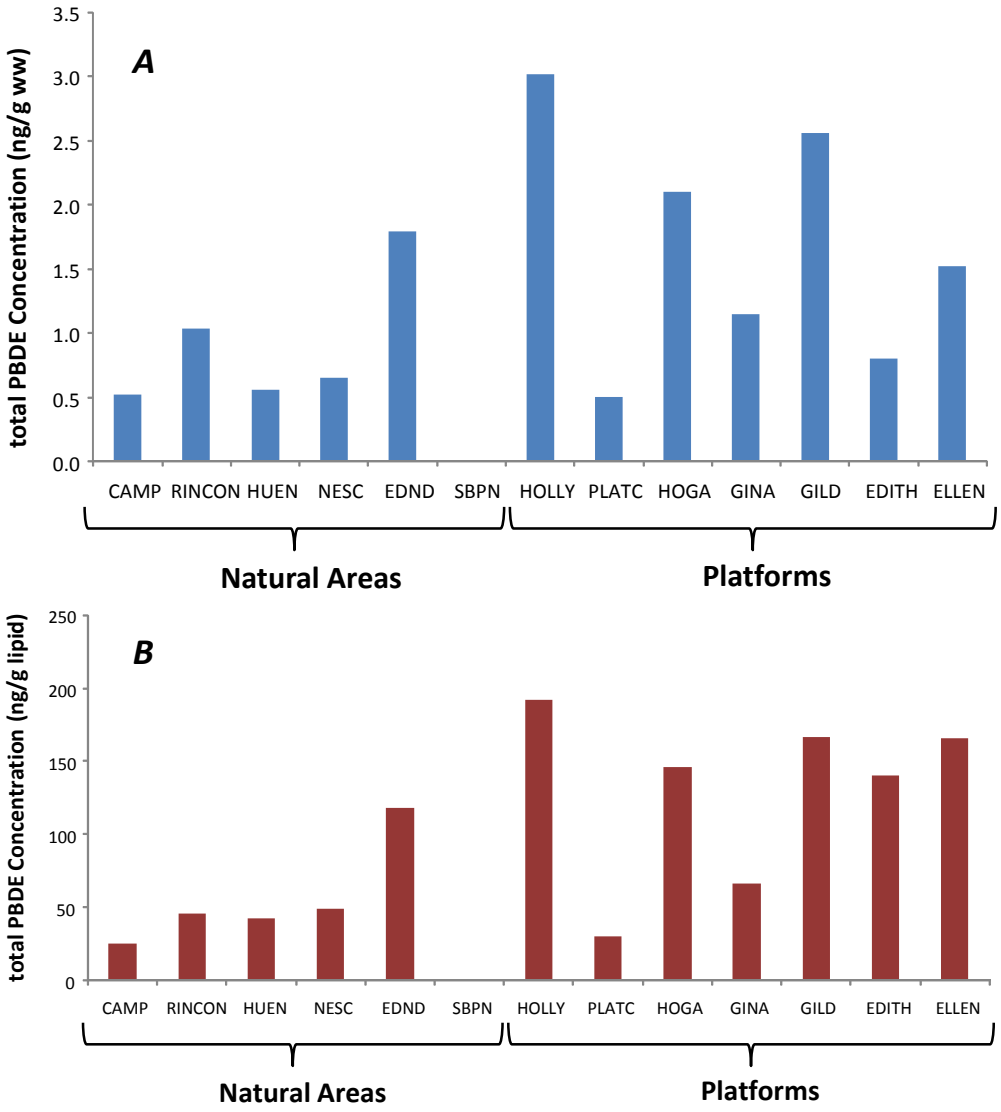

Figure 8. Total-polybrominated diphenylether concentrations in Pacific sanddab tissues from natural areas and platforms. *A*, Tissue concentration in nanograms per gram (ng/g ww) based on wet weight; *B*, Tissue concentrations normalized to extractable lipid weight.

The principal components analysis of the PBDE congener concentrations in Pacific sanddab composites (fig. 9) did not indicate any partial groupings for natural areas and platform locations. Because only two PBDE congeners (PBDE-47 and 100) were quantifiable in these samples, the only separation possible is that based on the percentage of PBDE-100 in the samples. This is indicated by the linear separation of those samples with increasing percentages of PBDE-100 from most of the samples comprised of only PBDE-47 (cluster of sites in the left center of figure 9); for reference, the Pacific sanddab composite sample from Platform Edith natural area was comprised of 36 percent PBDE-100. The Santa Barbara natural area sample (SBPN) is separated from the rest of the samples because it had no quantifiable PBDEs.

Comparison to Other Studies

The concentrations of PAHs, PCBs, OCPs, and PBDEs were low and similar in composites of Pacific sanddab from natural areas and platform locations. No large differences in the concentrations or profiles of contaminants were observed between samples from natural areas and platforms.

Previous measurements of the bile of these Pacific sanddab for hydroxylated PAHs, and PAH-glucuronides or -sulfates did not indicate acute PAH exposure. The purpose of this report was to investigate the potential chronic exposure of Pacific sanddab to PAHs by determining tissue concentrations of the more persistent and bioaccumulative higher molecular weight PAHs. No evidence was found to indicate elevated PAH exposure of sanddab from any of the natural areas or platform locations and no greater exposure of sanddab at platform locations as compared with natural areas was observed.

The concentrations of PAHs, PCBs, DDTs, and isodrins in fish from platforms and nearby natural areas measured here were compared with previously reported concentrations (refer to table 8). Most reports of DDTs and PCBs in fish in the Southern California Bight were from studies done near shore to investigate contamination from industrial, harbor, and wastewater treatment outfalls. Few historic data exist for contaminant burdens in fishes at any of the platform locations or the natural areas near seeps studied in this report.

From 1980–1982, the total PCB input near the JWPCP outfall at Palos Verdes (not shown), was estimated at 281 kilograms per year (kg/year), and was similar to the estimated total PCB input from the Hyperion outfall at Santa Monica Bay (not shown); however, the input of total DDTs was estimated to be ten-fold greater (396 kg/year) from the JWPCP than from Hyperion (Brown and others, 1986). Concentrations of DDTs and PCBs in Pacific sanddab collected from sites near the Palos Verdes and Hyperion outfalls were reported by Brown and others (1986). Total-DDT concentrations ranged from 42 to 610 µg/g ww in liver and 0.33 to 15 µg/g ww in gonad, total-PCB concentrations from 4.8 to 16 µg/g ww in liver and 0.018 to 0.88 µg/g ww in gonad. The concentrations of total-PCBs at study sites reportedly remained constant from 1977 to 1987; however, concentrations of total-DDTs

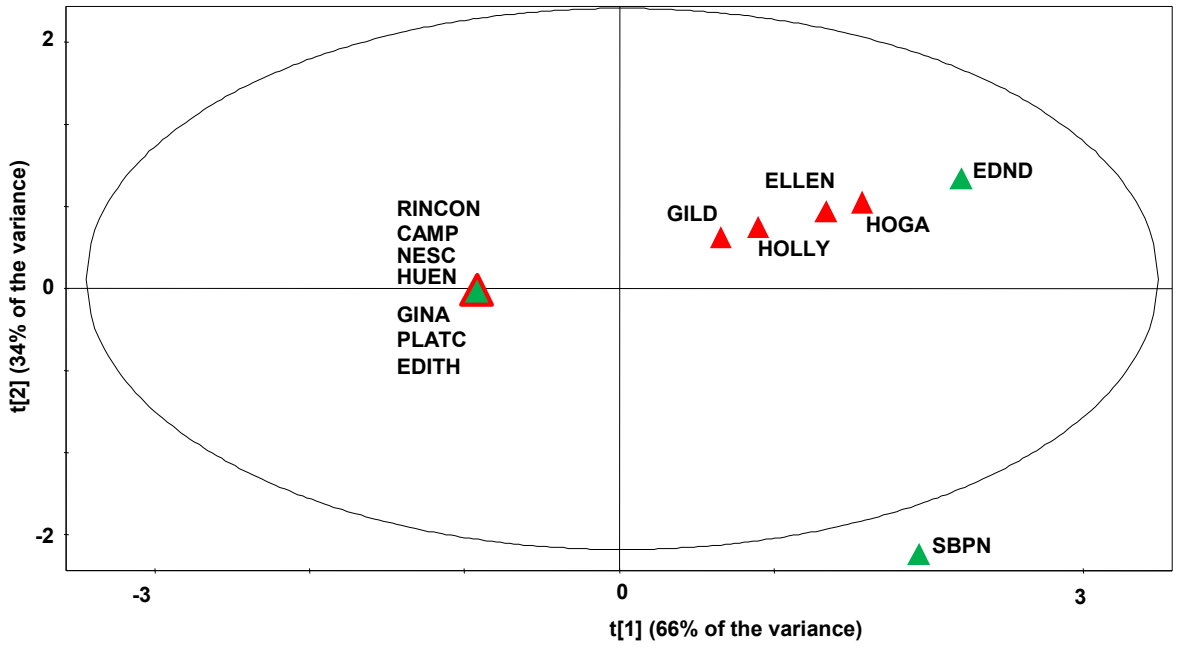

Figure 9. Principal components analysis (Score-Plot) of selected polybrominated diphenylether congeners in Pacific sanddab tissues from natural areas (green) and platforms (red). Only two congeners (major component, PBDE-47, minor component, PBDE-100) were detected in any sample; Santa Barbara natural area (SBPN) is isolated in this plot because there were no detectable polybrominated diphenylethers in the sample. The percent of the total variance that is explained by each plotted principal component (x and y axes) is reported in the axis label.

Table 8. Concentrations of contaminants determined in Pacific sanddab (this study) and reported in Pacific sanddab (Schiff and Allen, 2000) and in mussels (Kimbrough and others, 2008).

[ng/g, nanograms per gram wet-weight; USGS, U.S. Geological Survey; NOAA, National Oceanic and Atmospheric Agency; PAHs, total concentration of polycyclic aromatic hydrocarbons; isodrins, total concentration of aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone; chlordanes, total concentration of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, heptachlor, heptachlor epoxide; DDTs, total concentrations of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE; PCBs, total concentration of polychlorinated biphenyls; --, not reported; mi, miles]

This study						Selected from points closest to USGS locations	Schiff and Allen, 2000		Distance from closest USGS locations	Kimbrough and others, 2008					
Pacific sanddab (ng/g whole fish)							Pacific sanddab (ng/g liver)			Mussels (ng/g tissue)					
USGS locations	PAHs	Isodrins	Chlordanes	DDTs	PCBs		DDTs	PCBs		NOAA locations	PAHs	Isodrins	Chlordanes	DDTs	PCBs
	--	--	--	--	--		--	--	50 mi NW	SLSL	348	6.8	7.5	101	72
	--	--	--	--	--		100 – 1,000	10 – 50	30 mi N	PCPC	247	1.5	3.3	26	17
HOLL	16	0.09	1.5	33	35		0.05 – 1,000	0.05 – 10							
CAND	37	0.10	1	15	12		0.05 – 1,000	< 0.05							
SBPN	15	0.05	0.66	6.1	7.5		100 – 1,000	< 0.05		SBSB NW	112	2.7	7.9	18	18
PLATC	22	0.08	1.4	12	10		100 – 1,000	10 – 50							
HOGA	18	0.13	1.7	25	21		100 – 1,000	50 – 500							
RIND	29	0.13	1.7	21	16		100 – 1,000	10 – 50							
	--	--	--	--	--		--	--	20 mi SW (Offshore)	SCFP	121	3.4	6.2	12	15
NESC	29	0.06	0.43	12	11		100 – 1,000	10 – 50							
GILD	11	0.18	2.4	36	24		100 – 1,000	50 – 500							
GINA	14	0.10	1.4	18	17		100 – 1,000	50 – 500							
HUEN	21	0.04	0.35	9.0	11		100 – 1,000	50 – 500							
	--	--	--	--	--		--	--	Between HUEN (north) and EDIT (south)	PDPD	69	1.9	4.7	57	20
	--	--	--	--	--		1,000 – 10,000	50 – 500		TBSM	347	5.6	15	77	35
	--	--	--	--	--		1,000 – 10,000	500 – 2,000		MDSJ	2,093	12	37	96	75
	--	--	--	--	--		1,000 – 10,000	50 – 500		RBMJ	278	6.6	15	152	58
	--	--	--	--	--		10,000 – 43,300	500 – 2,000	10 mi NW	PVRP	90	1.9	5.9	462	44
EDND	30	0.06	0.95	34	22		100 – 1,000	10 – 50	Palos Verdes	SPBP	4,434	1.8	5.5	452	94
EDIT	13	0.03	0.46	77	34		100 – 1,000	10 – 50		LBBW	222	14	25	286	104
ELLE	8.7	0.04	0.62	19	16		100 – 1,000	10 – 50		ABWJ	522	2.5	17	175	107
	--	--	--	--	--		--	--	25 mi SW (Offshore)	SCBR	63	0.23	0.85	8.9	16
	--	--	--	--	--		100 – 1,000	10 – 50	15 mi SE	NBWJ	96	3.6	8.2	61	31
	--	--	--	--	--		100 – 1,000	10 – 50	60 mi SE	OSBJ	195	22	25	177	129

increased. Schiff (2000) suggested that historical sediments deposited near outfalls with high concentrations of DDTs might have resurfaced and been transported into the bight.

Elevated total-DDT concentrations and total-PCB concentrations in sediments were reported by Schiff (2000) for near shore locations in the general area of the northern USGS study sites (HOLL, CAMP, SBPN, PLATC, HOGA, RINC, GILD, and GINA). Concentrations of DDTs reported by Schiff (2000) were greater near some platform sites, ranging from 10 to 50 ng/g dw at Platforms Hogan, Rincon, Gilda, and Gina; and lower at other platform sites and natural areas, less than 20 ng/g dw at Platform Holly and Platform C and at Campus Point and Santa Barbara natural areas. Inputs were identified as mainly from the waste treatment plant outfall points and river and creek entries. Southern USGS study sites (Platforms Edith and Ellen, and Platform Edith natural area) were offshore too far for comparison.

Schiff and others (2000) reported that 89 percent of near-shore sediments in the Southern California Bight were contaminated with total-DDT concentrations and that almost 100 percent of Pacific sanddab collected at these near-shore locations in that study also were contaminated with total-DDTs and total-PCBs, having detectable liver concentrations of typically greater than 1 ng/g. Schiff and Allen (2000) reported that Pacific sanddab livers analyzed averaged about 15.9 percent lipid and total-DDT and -PCB concentrations averaged 654 ng/g and 74 ng/g, respectively.

Total-DDTs and total-PCBs in livers of Pacific sanddab were greatest in samples collected on the Palos Verdes Shelf at the sewage treatment outfall, near White Point, 42,000 ng/g and 1,100 ng/g, respectively (Schiff and Allen, 2000). This site was 20 kilometers north of three of the four most southern USGS sites in this study (Platforms Edith and Ellen, and the Platform Edith natural area). Schiff and Allen (2000) reported that total-DDT concentrations remained uniformly lower in areas much to the south of the outfall near White Point; however, total-PCB concentrations were higher at Orange County and the City of San Diego wastewater outfalls to the south of White Point (locations not shown). Though large reservoirs of contaminants existed at these outfalls, the current release concentrations were extremely low or undetectable. Yet, these reservoirs were considered an ongoing route of exposure for bottom-feeding species. Total-PCB concentrations were about ten-fold higher in livers of Pacific sanddab at these outfalls than in sanddab distant from the outfalls (2,000 ng/g as compared to 200 ng/g). Schiff and Allen (2000) also reported that the previous trend in increasing tissue concentrations with northward progress (following prevailing currents) has decreased and that substantial decreases have occurred during the past 10 to 20 years, with contaminant concentrations in Pacific sanddab collected at the same locations decreasing by one to two orders of magnitude (Tran and Zeng, 1998).

The concentration of *p,p′*-DDE in fish livers was determined to co-vary with the sediment concentration and normalizing concentrations to percent lipid and percent organic carbon increased these correlations. For PCBs, the covariance of tissue and sediment concentrations was determined to differ by PCB congener. Contamination was reported to be widespread but limited to DDE and PCBs by Schiff and Allen (2000). Pacific sanddab were contaminated throughout most of their range in the Southern California Bight. Although DDTs and PCBs often were measurable, PAHs were rarely detected, largely due to metabolism of PAHs (Schiff and Allen, 2000; Mearns and others, 1991).

Concentrations of DDTs near outfalls have not declined rapidly or continuously since the termination of DDT into the Palos Verdes outfall in 1970. From 2 to 5 years after termination, total-DDT concentrations in muscle ranged from 100 to 87,000 ng/g in the discharge zone, from 100 to 43,000 ng/g at the boundary of the discharge zone, and from 10 to 670 ng/g in the farther removed, control zone, with more DDT in the southern areas studied (Smokler and others, 1979). Twenty-four years after termination, total-DDTs in liver remained high in the discharge zone, ranging from 1,000 to 43,000 ng/g (Schiff and Allen, 2000). This study did not investigate fish close to the discharge or boundary zones, where exposure to DDT- and PCB-affected sediments remains high. This comparison of platform locations with nearby natural areas has indicated that exposure to urban pollution sources is negligible, and that any additional exposure to pollutants from platform discharges is indistinguishable, at this level of discrimination, from the background exposure defined by nearby natural areas.

The National Oceanic and Atmospheric Administration (NOAA) has reported monitoring data as part of the Mussel Watch Program in the Southern California Bight that overlap some of the USGS study areas (Kimbrough and others, 2008). PAHs, which bioaccumulate in mussels (*Mylitus* species), were found at all NOAA shoreline locations along the Southern California Bight, ranging from 63 to 4,400 ng/g. Conversely, PAHs are typically at much lower concentrations in water and sediments (and presumably in the food web) at locations further offshore, and are not substantially accumulated by fish. Bile metabolites of PAHs were not found in fishes collected at platform locations or at nearby natural areas in this study, nor were parent PAHs or aliphatic hydrocarbons found in tissues of Pacific sanddab at these locations.

Generally, lower concentrations of persistent organochlorine compounds were reported in the northern part of USGS study area (above Palos Verdes), at offshore locations (Kimbrough and others, 2008); higher concentrations were reported for Palos Verdes, and sites immediately south of Palos Verdes, and at other treatment plant outfalls. Within the USGS study area, concentrations of organochlorine contaminants in mussel tissue reported by Kimbrough and others (2008) ranged from 0.23 to 22 ng/g for total isodrins, from 0.85 to 37 ng/g for total-chlordanes, from 15 to 129 ng/g for total-PCBs, and from 8.9 to 462 ng/g for total-DDTs.

Comparisons of total isodrins in Pacific sanddab (this study) and mussel (Kimbrough and others, 2008) did not indicate any similarity in trends with locations. Total isodrins in Pacific sanddab were consistently low at all locations in each

of these studies, however, concentrations were about thirty- to fifty-fold lower in this study than reported by NOAA for mussels from the most closely corresponding near shore sites. Bioaccumulation of contaminant classes is highly dependent upon species-specific metabolism and comparisons between fish and bivalves are only suitable for investigating general trends. No correlations were observed for total-chlordanes among USGS Pacific sanddab samples and NOAA mussel samples from nearby sites. Again, total-chlordane concentrations in Pacific sanddab were from 10 to 50-fold lower in this study than concentrations in mussels reported by NOAA (Kimbrough and others, 2008). Total-PCB concentrations agreed somewhat among this study, and those of Kimbrough and others, (Kimbrough 2008), and Schiff and Allen (2000). The total-PAH, -DDT, -PCB, and isodrin concentrations are presented in table 8. At those sites most nearly corresponding sites reported by Kimbrough and others (2008), total-PCBs ranged from 7.5 to 34 ng/g (USGS), from 15 to 107 ng/g (Kimbrough and others, 2008), and from 10 to 50 ng/g (same range for all sites (Schiff and Allen, 2000). Total-DDT concentrations did not compare as well as total-PCB concentrations among studies, total-DDTs ranged from 6.1 to 77 ng/g (USGS), from 12 to 452 ng/g (Kimbrough and others, 2008), and from 100 to 1,000 ng/g (same range for all sites, Schiff and Allen, 2000). Unfortunately, several circumstances limit the comparability of the Kimbrough and Schiff datasets to this study. The data from Kimbrough and others (2008) though closer in time (2004–2005), report contaminant concentrations for a different target organism (mussel) with collection being limited to sites close to the coastline. The Schiff and Allen (2000), report contaminant concentrations in Pacific sanddab livers at collection sites much closer to the USGS study sites, but separated by about 14 years (July–August 1994).

The distribution and sources of PBDEs in sediments from the Southern California Bight has recently been reported by Dodder and others (2012). Using a probabilistic approach, sediments from coastal embayments and to the lower slope of the outer continental shelf were investigated. Thirteen PBDEs were detected in 92 of 121 sites sampled, with a reported geometric mean total-PBDE concentration of 4.7 ng/g dry weight and a maximum concentration of 560 ng/g. The highest concentrations of PBDEs were determined to be predominately composed of PBDE-209, which is enriched in sediments and is mainly related to the production levels of the commercial PBDE technical mixtures. Highest total PBDE concentrations were determined to be associated with mouths of urban rivers along coastal embayments and were reportedly the result of urban runoff rather than wastewater treatment plants. Offshore sediments, near sites associated with this study had a reported geometric mean total-PBDE concentration of 2 ng/g dry weight, and ranged from 1.6 to 2.5 ng/g. Pacific sanddab from this study ranged in total-PBDE concentrations from <0.3 to about 3 ng/g ww, with only one congener, PBDE-047, being detected.

References Cited

Amodio-Coccheri, R., and Cirillo, T., 2003, Aliphatic hydrocarbons in biota from the Gulf of Naples (Italy): Marine Pollution Bulletin, v. 46, p. 374–377.

Arias, A.H., Spetter, C.V., Freije, R.H., and Marcovecchio, J.E., 2009, Polycyclic aromatic hydrocarbons in water, mussels (*Brachidontes* sp.*, Tagelus* sp.) and fish (*Odontesthes* sp.) from Bahia Blanca Estuary, Argentina: Estuarine, Coastal and Shelf Science, v. 85, p. 67–81.

Armstrong, H.W., Fucik, K., Anderson, J.W., and Neff, J.M., 1979, Effects of oilfield brine effluent on benthic organisms in Trinity Bay, Texas: Marine Environmental Research, v. 2, p. 55–69.

Blasius, M.E., and Goodmanlowe, G.D., 2008, Contaminants still high in top-level carnivores in the Southern California Bight—Levels of DDT and PCBs in resident and transient pinnipeds: Marine Pollution Bulletin, v. 56, p. 1,973–1,982.

Brown, D.A., Gossett, R.W., Hershelman, G.P., Ward, C.F., Westcott, A.A., and Cross, J.N., 1986, Municipal wastewater contamination in the Southern California Bight—Part I–Metal and organic contaminants in sediments and organisms: Marine Environmental Research, v. 18, p. 291–310.

Brown, J.S., and Steinert, S.A., 2003, DNA damage and biliary PAH metabolites in flatfish from southern California bays and harbors, and the Channel Islands: Ecological Indicators, v. 3, p. 263–274.

Claireaux, G., and Davoodi, F., 2010, Effect of exposure to petroleum hydrocarbons upon cardio-respiratory function in the common sole (*Solea solea*): Aquatic Toxicology, v. 98, p. 113–119.

Colombo, J.C., Cappelletti, N., Migoya, M.C., and Speranza, E., 2007, Bioaccumulation of anthropogenic contaminants by detrivorous fish in the Rio de la Plata estuary—1-Aliphatic hydrocarbons: Chemosphere, v. 68, p. 2,128–2,135.

Dodder, N.G., Maruya, K.A., Lauenstein, G.G., Ramirez, J., Ritter, K.J., and Schiff, K.C., 2012, Distribution and sources of polybrominated diphenyl ethers in the Southern California Bight: Environmental Toxicology and Chemistry, v. 21, p. 239–2,245.

Eganhouse, R.P., Pontolillo, J., and Leiker, T.J., 2000, Diagenetic fate of organic contaminants on the Palos Verde Shelf, California: Marine Chemistry, v. 70, p. 289–315.

Eganhouse, R.P., and Pontolillo, J., 2000, Depositional history of organic contaminants on the Palos Verde Shelf, California: Marine Chemistry, v. 70, p. 317–338.

Farwell, C., Reddy, C.M., Peacock, E., Nelson, R.K., Washburn, L., and Valentine, D.L., 2009, Weathering and the fallout plume of heavy oil from strong petroleum seeps near Coal Point, CA: Environmental Science and Technology, v. 43, p. 542–548.

Gale, R.W., Tanner, M.J., Love, M.S., Nishimoto, M.M., and Schroeder, D.M., 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, 38 p.

Goksøyr, A., Tollefsen, K.E., Grung, M., Loken, K., Lie, E., Zenker, A., Fent, K., Schlabach, M., and Huber, S., 2009, Balsa raft crossing the Pacific finds low contaminant levels: Environmental Science and Technology, v. 43, p. 783–790.

Gonzalez, C., Botello, A.V., and Diaz, G., 1992, Presence of aliphatic hydrocarbons in sediments and organisms from Campeche Bank, Mexico: Marine Pollution Bulletin, v. 24, p. 267–270.

Hinck, J.E., Blazer, V.S., Denslow, N.D., Echols, K.R., Gale, R.W., May, T.W., Claunch, R., Wieser, C., Anderson, P.J., Coyle, J.J., Gross, T.S., and Tillitt, D.E., 2007, Biomonitoring of Environmental Status and Trends (BEST) Program—Environmental contaminants, health indicators, and reproductive biomarkers in fish from the Mobile, Apalachicola-Chattahoochee-Flint, Savannah, and Pee Dee River Basins: U.S. Geological Survey Scientific Investigations Report 2007–5176, 114 p.

Kimbrough, K.L., Johnson, W.E., Lauenstein, G.G., Christensen, J.D., and Apeti, D.A., 2008, An assessment of two decades of contaminant monitoring in the Nation's coastal zone: Silver Spring, Maryland, NOAA Technical Memorandum NOS NCCOS 74, 105 p.

Law, R.J., 1978, Determination of petroleum hydrocarbons in water, fish and sediments following the EkoFisk blow-out: Marine Pollution Bulletin, v. 9, p. 321–324.

Lemaire, P., Mathieu, A., Carriere, S., Drai, P., Giudicelli, J., and Lafaurie, M., 1990, The uptake metabolism and biological half-life of benzo[*a*]pyrene in different tissues of sea bass, *Dicentrarchus labrax*: Ecotoxicology and Environmental Safety, v. 20, p. 223–233.

Love, M.S., Schroeder, D.M., and Nishimoto, M.M., 2003, The ecological role of oil and gas production platforms and natural outcrops on fishes in southern California and central California—A synthesis of information: U.S. Department of the Interior, U.S. Geological Survey, Biological Resources Division, Seattle, Washington, 98104, OCS Study MMS 2003–032, 66 p.

Love, M.S., Nishimoto, M., and Saiki, M., 2009, Reproductive ecology and body burden of resident fish prior to decommissioning: Santa Barbara, California, Marine Science Institute, University of California, Minerals Management Service OCS Study 2009–019, Minerals Management Service Cooperative Agreement Number 1435–01–05–CA–39315, 93 p.

Love, M.S., and Goldberg, S.R., 2009, A histological examination of the ovaries of Pacific Sanddab (*Citharichthys sordidus*), captures at two oil platforms and two natural sites in the Southern California Bight: Bulletin of the Southern California Academy of Sciences, v. 108, p. 45–51.

Lytle, T.F., and Lytle, J.S., 1979, Sediment hydrocarbons near an oil rig: Estuarine and Coastal Marine Science, v. 9, p. 319–330.

Marcias-Zamora, J.V., 1996, Distribution of hydrocarbons in recent marine sediments off the coast of Baja California: Environmental Pollution, v. 92, p. 45–53.

Mearns, A., Matta, M., Shigenaka, G., MacDonald, D., Buchman, M., Harris, H., Golas, J., and Lauenstein, G., 1991, Contaminant trends in the Southern California Bight: Seattle, Washington, Technical Memorandum, National Oceanic and Atmospheric Association, NOS ORCA 62, 441 p.

Meier, S., Morton, H.C., Nyhammer, G., Grøsvik, B.E., Makhotin, V., Geffen, A., Boitov, S., Kvestad, K.A., Bohne-Kjersem, A., Goksøyr, A., Folkvord, A., Klungsøyr, J., and Svarldal, A., 2010, Development of Atlantic cod (*Gadus morhua*) exposed to produced water during early life stages—Effects on embryos, larvae, and juvenile fish: Marine Environmental Research, v. 70, p. 383–394.

Nácher-Mestre, J., Serrano, R., Benedito-Palos, L., Navarro, J.C., Lopez, F.J., Kaushik, S., and Perez-Sanchez, J., 2010, Bioaccumulation and polycyclic aromatic hydrocarbons in gilthead sea bream (*Sparus aurata L.*) exposed to long term feeding trials with different experimental diets: Archives of Environmental Contamination and Toxicology, v. 59, p. 137–146.

Osenberg, C.W., Schmitt, R.J., Holbrook, S.J., and Canestro, D., 1992, Spatial scale of ecological effects associated with an open coast discharge of produced water: *in* Ray, J.P., and Engelhardt, F.R., eds., Produced water: Technological/Environmental Issues and Solutions, New York, New York, Plenum Press, p. 387–402.

Parnell, P.E., Groce, A.K., Stebbins, T.D., and Dayton, P.K., 2008, Discriminating sources of PCB contamination in fish on the coastal shelf off San Diego, California (USA): Marine Pollution Bulletin, v. 56, p. 1,992–2,002.

Pena-Mendez, E.M., Astorga-Espana, M.S., and Garcia-Montelongo, F.J., 2001, Chemical fingerprinting applied to the evaluation of marine oil pollution in the coasts of Canary Islands (Spain): Environmental Pollution, v. 111, p. 177–187.

Peterson, C.H., Kennicutt II, M.C., Green, R.H., Montagna, P., Harper Jr., D.E., Powell, E.N., and Roscigno, P.F., 1996, Ecological consequences of environmental perturbations associated with offshore hydrocarbon production—A perspective on long-term exposures in the Gulf of Mexico: Canadian Journal of Fisheries and Aquatic Science, v. 53, p. 2,637–2,654.

Quigley, D.C., Hornafius, J.S., Luyendyk, B.P., Francis, R.D., Clark, J., and Washburn, L., 1999, Decrease in natural marine hydrocarbon seepage near Coal Oil Point, California, associated with offshore oil production: Geology, v. 27, p. 1,047–1,050.

Quintero, S., and Diaz, C., 1994, Aliphatic hydrocarbons in fish from the Canary Islands: Marine Pollution Bulletin, v. 28, p. 44–49.

Ranasinghe, J.A., Schiff, K.C., Montagne, D.E., Mikel, T.K., Cadien, D.B., Velarde, R.G., and Brantlet, C.A., 2010, Benthic macrofaunal community condition in the Southern California Bight, 1944–2003: Marine Pollution Bulletin, v. 60, p. 827–833.

Roy, L.A., Steinert, S., Bay, S.M., Greenstein, D., Sapozhnikova, Y., Bawardi, O., Leifer, I., and Schlenk, D., 2003, Biochemical effects of petroleum exposure in hornyhead turbot (*Pleuronichthys verticalis*) exposed to a gradient of sediments collected from a natural petroleum seep in CA, USA: Aquatic Toxicology, v. 65, p. 159–169.

Schiff, K.C., 2000, Sediment chemistry on the Mainland Shelf of the Southern California Bight: Marine Pollution Bulletin, v. 40, p. 268–276.

Schiff, K.C., Allen, M.J., Zeng, E.Y., and Bay, S.M., 2000, Southern California: Marine Pollution Bulletin, v. 41, p. 76–93.

Schiff, K.C., and Allen, M.J., 2000, Chlorinated hydrocarbons in flatfishes from the Southern California, USA, Bight: Environmental Toxicology and Chemistry, v. 19, p. 1,559–1,565.

Schwartz, T.R., and Stalling. D.L., 1991, Chemometric comparison of polychlorinated biphenyl residues and toxicologically active polychlorinated biphenyl congeners in the eggs of Forster's terns *Sterna fosteri*: Archives of Environmental Contamination and Toxicology, v. 20, p. 183–199.

Seruto, C., Sapozhnikova, Y., and Schlenk, D., 2005, Evaluation of the relationship between biochemical endpoints of PAH exposure and physiological endpoints of reproduction in male California halibut (*Paralichthys californicus*) exposed to sediments from a natural oil seep: Marine Environmental Research, v. 60, p. 454–465.

Sherwood, C.R., Drake, D.E., Wiberg, P.L., and Wheatcroft, R.A., 2002, Prediction of the fate of *p,p'*-DDE in sediment on the Palos Verdes Shelf, California, USA: Contental Shelf Research, v. 22, p. 1,025–1,058.

Simoneit, B.R.T., and Kaplan, I.R., 1980, Triterpenoids as molecular indicators of paleoseepage in recent sediments of the Sourthern California Bight: Marine Environmental Research, v. 3, p. 113–128.

Smokler, P.E., Young, D.D., and Gard, K.L., 1979, DDTs in marine fishes following termination of dominant California input—1970–1977: Marine Pollution Bulletin, v. 10, p. 331–334.

Spies, R.B., Stegeman, J.J., Hinton, D.E., Woodin, B., Smoloxitz, R., Okihiro, M., and Shea, D., 1996, Biomarkers of hydrocarbon exposure and sublethal effects in embiotocid fishes from a natural petroleum seep in the Santa Barbara Channel: Aquatic Toxicology, v. 34, p. 195–219.

Stein, J.E., Reichert, W.L., French, B., and Varanasi, U., 1993, ^{32}P-Postlabeling analysis of DNA adduct formation and persistence in English sole (*Pleuronectes vetulus*) exposed to benzo[*a*]pyrene and 7H-dibenzo[*c*,*g*]carbazole: Chemico-Biological Interactions, v. 88, p. 55–60.

Steinberger, A., Stein, E.D., and Raco-Rands, V., 2004, Offshore oil platform discharges to the Pacific Outer Continental Shelf along the coast of Southern California in 1996 and 2000: Costa Mesa, California, Southern California Coastal Water Research Project, A Southern California Coastal Water Research Project Biennial Report, 2003–2004, p. 16–30.

Steinhauer, M., Crecelius, E., and Steinhauer, W., 1994, Temporal and spatial changes in the concentrations of hydrocarbons and trace metals in the vicinity of an offshore oil-production platform: Marine Environmental Research, v. 37, p. 129–163.

Straughan, D., Dalby, D.H., Crisp, D.J., Baker, J.M., Southward, A.J., McIntyre, A.D., and Vandermeulen, J.H., 1982, Observations of the effects of natural seeps in the Coal Point area: Philosophical Transactions Of the Royal Society of London, Series *B*, Biological Sciences, v. 297, p. 269–283.

Tran K., and Zeng E., 1998, Use of equilibrium partitioning theory to determine route(s) of chlorinated hydrocarbon uptake in hornyhead turbot, *in* Allen, M., Francisco, C., and Hallock, D., eds., Westminster, California, Southern California Coastal Water Research Project, A Southern California Coastal Water Research Project Annual Report 1997–98: p. 32–42.

Venkatesan, M.I., Merino, O., Baek, J., Northrup, T., Sheng, Y., and Shisko, J., 2010, Trace organic contaminants and their sources in surface sediments of Santa Monica Bay, California, USA: Marine Pollution Bulletin, v. 69, p. 350–362.

Vuorinen, P. J., Keinänen, M. and Vuontisjärvi, H., 2003, Bile PAH-metabolite concentrations in perch (*Perca fluviatilis*) exposed to crude oil and sampled in the Gulf of Finland near an oil refinery and in Baltic salmon (*Salmo salar*): Barcelona, Spain, Biological Effects of Environmental Pollution in marine coastal ecosystems (BEEP) workshop, December 4–6, 2003 (Extended Abstract).

Vuorinen, P., Keinanen, M., Vuontisjarvi, H., Barsiene, J., Broeg, K., Forlin, L., Gercken, J., Kopecka, J., Kohler, A., Parkkonen, J., Pempkowiak, J., and Schiedek, D., 2006, Use of biliary PAH metabolites as a biomarker of pollution in fish from the Baltic Sea: Marine Pollution Bulletin, v. 53, p. 479–487.

Zeng, E.Y., and Venkatesan, M.I., 1999, Dispersion of sediment DDTs in the coastal ocean off Southern California: The Science of the Total Environment, v. 229, p. 195–208.

Supplemental Tables

The Excel file containing all tables of supporting information may be downloaded from *http://pubs.usgs.gov/of/2013/1046/downloads/supplemental_tables.xlsx*

Table S1. Concentrations of selected polycyclic aromatic hydrocarbons (PAHs) and total PAHs in tissues (ng/g) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S2. Lipid-normalized concentrations of selected polycyclic aromatic hydrocarbons (PAHs) and total PAHs in tissues (ng/g lipid) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S3. Concentrations of selected congeners of polychlorinated biphenyls (PCBs) and total PCBs in tissues (ng/g) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S4. Lipid-normalized concentrations of selected congeners of polychlorinated biphenyls (PCBs) and total PCBs in tissues (ng/g lipid) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S5. Concentrations of selected organochlorine pesticides and total isodrins, chlordanes, and dichlorodiphenyldichloroethylenes in tissues (ng/g) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S6. Lipid-normalized concentrations of selected organochlorine pesticides and total isodrins, chlordanes, and dichlorodiphenyldichloroethylenes in tissues (ng/g lipid) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S7. Concentrations of selected polybrominated diphenylethers (PBDEs) and total PBDEs in tissues (ng/g) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Table S8. Lipid-normalized concentrations of selected polybrominated diphenylethers (PBDEs) and total PBDEs in tissues (ng/g lipid) of Pacific sanddab (*Citharichthys sordidus*) at platforms and nearby natural sites.

Publishing support provided by:
Rolla Publishing Service Center

For more information concerning this publication, contact:
Director, USGS Columbia Environmental Research Center
4200 New Haven Road
Columbia, MO 65201
(573) 875–5399

Or visit the Columbia Environmental Research Center Web site at:
http://www.cerc.usgs.gov/