WHOLE-BODY CONCENTRATIONS OF ELEMENTS IN THREE FISH SPECIES FROM OFFSHORE OIL PLATFORMS AND NATURAL AREAS IN THE SOUTHERN CALIFORNIA BIGHT, USA

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ABSTRACT

There is concern that offshore oil platforms off Southern California may be contributing to environmental contaminants accumulated by marine fishes. To examine this possibility, 18 kelp bass (*Paralabrax clathratus* Girard, 1854), 80 kelp rockfish (*Sebastes atrovirens* Jordan and Gilbert, 1880), and 98 Pacific sanddab (*Citharichthys sordidus* Girard, 1854) were collected from five offshore oil platforms and 10 natural areas during 2005–2006 for whole-body analysis of 63 elements. Forty-two elements were excluded from statistical comparisons as they (1) consisted of major cations that were unlikely to accumulate to potentially toxic concentrations; (2) were not detected by the analytical procedures; or (3) were detected at concentrations too low to yield reliable quantitative measurements. The remaining 21 elements consisted of aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, gallium, iron, lead, lithium, manganese, mercury, nickel, rubidium, selenium, strontium, tin, titanium, vanadium, and zinc. Statistical comparisons of these elements indicated that none consistently exhibited higher concentrations at oil platforms than at natural areas. However, the concentrations of copper, selenium, titanium, and vanadium in Pacific sanddab were unusual because small individuals exhibited either no differences between oil platforms and natural areas or significantly lower concentrations at oil platforms than at natural areas, whereas large individuals exhibited significantly higher concentrations at oil platforms than at natural areas.

Twenty-seven active and seven decommissioned offshore oil-and-gas production platforms (henceforth referred to as "oil platforms") are located within the Southern California Bight between Point Arguello in the north and the US-Mexico border in the south. Over the next few decades, many active platforms are expected to undergo decommissioning as their economic profit margins decline. Decommissioned platforms in Southern California historically have undergone complete removal. However, recent ecological studies indicate that platforms provide artificial structure for marine life, including many fish species of recreational and commercial importance, and may contribute to rebuilding overfished stocks (Love et al. 2000, 2005, 2006). Platform decommissioning options range from leaving the entire intact structure in place to removal of part or all of the structure. Regardless of the option selected, resource managers are concerned that environmental contaminants associated with the drilling process (i.e., contaminated drilling mud and cuttings), the produced water, and other platform-related activities (e.g., sanitary and domestic wastes) could pose toxic risks to fishes and consumers of tainted fishes, including marine birds, mammals, and humans.

Drilling muds or fluids are specially formulated mixtures of fresh water or seawater with clays, minerals, chemicals, and other materials used for cleaning drill bits, transporting cuttings, reducing friction, and stabilizing the borehole (Raco 1993). Drill cuttings are particles of crushed sedimentary rock produced in the process of drilling. Barium sulfate is added to drill muds as a weighting agent, and the appearance of barium in cuttings is due to drilling mud adhering to the cuttings (Raco 1993). Chromium can originate from chrome or ferrochrome lignosulfonate, which are drilling mud additives (Phillips et al. 2006). Drill cuttings can contain elevated concentrations of lead and zinc, possibly as a result of using pipe-thread compound to lubricate the threads of drill pipes (Raco 1993, Phillips et al. 2006). These and other metals also originate from formation of solids and mud additives. Most produced water is a brine that may contain dissolved solids, metals, organic compounds, and sulfur at substantially higher concentrations than in seawater. Produced water can contain trace elements, and various petroleum hydrocarbons, including monoaromatic compounds, polycyclic aromatic hydrocarbons, and polar compounds [Gale et al. (2013) report on polycyclic aromatic hydrocarbons in fishes living around California oil platforms]. Nickel and vanadium are components of crude oil (Phillips et al. 2006). Sanitary and other domestic wastes are generated by platform personnel, and include sewage, garbage, and waste water, and any associated contaminants (Raco 1993).

Previous surveys of inorganic contaminants in liver, kidneys, gonads, and axial muscle of marine fishes from the Southern California Bight included measurements of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, copper, iron, manganese, mercury, molybdenum, nickel, lead, selenium, silver, thallium, tin, vanadium, and zinc (e.g., Stapleton 1968, McDermott et al. 1976, Pollock et al. 1991, SCCWRP 1994, Phillips et al. 1997, Allen et al. 2004, IEc 2007, Groce and Gartman 2008). However, these early studies generally focused on runoff from urban areas or discharge from nearshore sewage outfalls. Relatively little attention has been given to documenting elemental body burdens in fishes from oil platforms (Bascom et al. 1976, McDermott-Ehrlich and Alexander 1976).

The purpose of our study was to determine if offshore oil platforms in the Southern California Bight represent a major source of contamination by trace elements in fish species of economic (commercial and recreational) importance. Natural hard substrates (i.e., rocky outcrops or reefs) and soft substrates (i.e., mud and sand) located somewhat away from selected platforms were intended to serve as relatively uncontaminated reference sites. Specific objectives were to document body burdens of elements in representative midwater and bottom-dwelling fish species and to determine if elemental concentrations in fishes from platforms differed from those at natural areas.

Methods

Sampling Locations and Collections

The study area included five oil platforms that extend over a distance of 186 km from roughly southwest of Santa Barbara to south of Long Beach (Fig. 1). At the time of this survey, and for a number of years previous, all of these platforms were producing either oil or gas. To facilitate comparisons of elemental concentrations, each platform was grouped with two nearby natural areas (predominant bottom substrate characteristic given in parentheses) as follows: Platform Holly with Devereux Reef (hard) and Campus Point (soft);
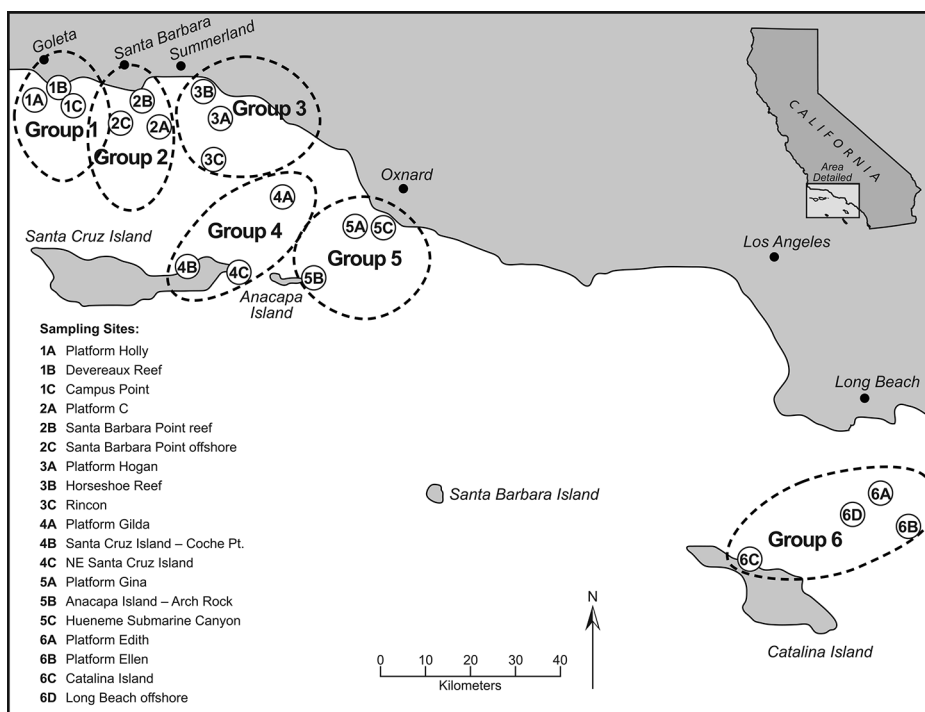
Figure 1. Map of the study area showing locations of five oil platforms and 10 natural areas. Each platform is grouped with two nearby natural areas.

Platform Hogan with Horseshoe Rock (hard) and Rincon (soft); Platform Gilda with Santa Cruz Island—Coche Point (hard) and Northeast Santa Cruz Island (soft); Platform Gina with Anacapa Island—Arch Rock (hard) and Hueneme Submarine Canyon (soft); and Platform Edith with Catalina Island—Blue Cavern (hard) and an unnamed locality off San Pedro (soft; Table 1). No natural site was <3.2 km from its associated platform and many sites were 8–16 km from its associated platform. With the exception of the well-known natural oil seeps in the Platform Holly-Devereux Reef-Campus Point area (Spies and Davis 1979), we know of no other natural or anthropogenic sources of petroleum that might have complicated our platform–natural site comparisons.

Three species of fish, the bottom-dwelling Pacific sanddab (*Citharichthys sordidus* Girard, 1854), along with midwater jacket-associated kelp bass (*Paralabrax clathratus* Girard, 1854) and kelp rockfish (*Sebastes atrovirens* Jordan and Gilbert, 1880), were sampled. All fishes were collected either by spearing or with hook and line during July–December 2005 and July–August 2006. Brief species accounts (Love 2011) are as follows: kelp bass grow as large as 72 cm. This species is substrate-oriented and inhabits kelp beds, rocky reefs, and such human-made structures as oil platforms. It is most often found at depths of 2.4–30 m and feeds on fishes, cephalopods, and benthic invertebrates (especially crustaceans). Kelp bass is an important recreational game fish. Kelp rockfish attain a maximum length of about 42 cm, and usually occur on or near substrata in kelp beds or rocky areas at depths of 3–30 m. This species feeds on organisms living on the substrate such as crabs, bottom-dwelling shrimps, fishes, and cephalopods. Kelp rockfish is an important recreational and minor commercial species. Pacific sanddab grow to at least 41 cm, and inhabit sandy and muddy bottoms at depths of 1–550 m. It is an opportunistic predator, feeding on a variety of crustaceans, as well as smaller fishes, squids, and octopuses. Sanddabs are a minor recreational

Table 1. Characteristics of the 15 sampling sites and sample sizes of kelp bass (KBA), kelp rockfish (KRO), and Pacific sanddab (PSD). Each of five oil platforms is grouped with two nearby natural areas (reference sites). Under Habitat type, the sea floor characterization is given in parentheses.

Group	Site	Habitat type	Geospatial coordinates	Distance to nearest shore (km)	Water depth (m)	Year installed	Fish sample size		
							KBA	KRO	PSD
1	Platform Holly	Platform	34°23.366′N, 19°54.406′W	3.1	64	1966	—	10	10
	Devereux Reef	Natural area (hard)	34°24.100′N, 19°51.560′W	0.8	15	—	—	10	—
	Campus Point	Natural area (soft)	34°22.365′N, 19°50.168′W	3.6	67	—	—	—	10
2	Platform Hogan	Platform	34°20.275′N, 19°32.539′W	6.1	46	1967	—	10	8
	Horseshoe Rock	Natural area (hard)	34°23.610′N, 19°33.629′W	1.7	9	—	—	10	—
	Rincon	Natural area (soft)	34°15.355′N, 19°33.230′W	15.1	87	—	—	—	10
3	Platform Gilda	Platform	34°10.932′N, 19°25.150′W	14.1	62	1981	—	10	10
	Santa Cruz Island—Coche Point	Natural area (hard)	34°02.233′N, 19°36.600′W	0.1	17	—	—	10	—
	NE Santa Cruz Island	Natural area (soft)	34°01.759′N, 19°30.362′W	1.5	55	—	—	—	10
4	Platform Gina	Platform	34°07.059′N, 19°16.625′W	6.3	28	1980	8	—	10
	Anacapa Island—Arch Rock	Natural area (hard)	34°00.980′N, 19°21.316′W	0.2	12	—	10	—	—
	Hueneme Submarine Canyon	Natural area (soft)	34°07.100′N, 19°12.730′W	3.0	23	—	—	—	10
5	Platform Edith	Platform	33°35.726′N, 18°08.501′W	15.5	49	1983	—	10	10
	Catalina Island—Blue Cavern	Natural area (hard)	33°26.693′N, 18°28.552′W	0.1	26	—	—	10	—
	Unnamed locality off San Pedro	Natural area (soft)	33°35.006′N, 18°12.770′W	14.1	60	—	—	—	10

and commercial species. All three species are abundant throughout Southern California and all appear to be somewhat sedentary (Love 2011).

Kelp bass and kelp rockfish were captured by spear, Pacific sanddab by hook and line. Immediately following capture, fishes were weighed and measured (total length), assigned a unique identification number, then wrapped and bagged in clean plastic and held on wet ice until returning to the laboratory. In the laboratory, fish samples were stored frozen (–10 °C) for roughly 1 wk to 6 mo until shipment to the US Geological Survey (USGS) Columbia Environmental Research Center (CERC), Columbia, Missouri, for further processing and analysis.

Sample Preparation

Frozen samples held in coolers with dry ice were transported by overnight air freight to CERC. At CERC, frozen fish weighing <100 g were minced with a titanium meat cleaver and placed in a chemically clean 118-ml jar equipped with a filter lid to enable lyophilization. Frozen samples >100 g but <300 g were initially cut into small cubes with a food-service band saw, then further processed in a meat grinder containing a titanium blade and extrusion plate. Samples >300 g were also cut into pieces with the band saw and homogenized with a Hobart meat grinder. All samples were processed through the meat grinder three times, collected in a plastic bag, then hand-kneaded to facilitate mixing and produce a homogenized mass. A portion of the resulting ground product was placed in a 118-ml cleaned glass jar and archived for future organic contaminant analysis. A second ground portion was placed in a 118-ml jar equipped with a filter lid for lyophilization. All filter-lid aliquots were lyophilized in a Virtis Genesis 35EL freeze dryer, with moisture content determined during the lyophilization process. After lyophilization, each dried fish sample was transferred to a plastic bag and further reduced with a Teflon® roller pin to a coarse powder. This final product was then transferred to a 40-ml glass vial that was sealed and stored in a desiccator until further processing. To prevent cross-contamination, all equipment used to process a fish sample was cleaned before processing the next fish sample.

Chemical Preparation

To prepare digestates from dried samples for semi-quantitative scans of multiple elements and quantitative determinations of total arsenic by inductively coupled plasma mass spectrometry (ICP-MS), an aliquant of each sample (approximately 0.25 g) was heated with 6 ml of nitric acid in a sealed low-pressure Teflon® vessel by using a microwave oven. The cooled digestate liquid was transferred into a 125-ml polyethylene bottle with ultrapure water (>10 megOhm cm^{-1}) to a final weight of 101.5 g (100 ml). Final acid matrix was 6% nitric acid.

For quantitative determination of total selenium, an additional tissue aliquant (approximately 0.5 g) of each dried sample was subjected to a magnesium nitrate–nitric acid dry ashing procedure, followed by hydrochloric acid reduction. The dry ashing procedure consisted of three steps: boiling with nitric acid for solubilization and partial oxidation, ashing at 500 °C with magnesium nitrate to complete the oxidation and decompose any remaining organic matter, and heating with hydrochloric acid to dissolve the ash and reduce all selenium to the selenite (Se^{+4}) oxidation state required for hydride generation. Following reduction, the digestates were diluted to approximately 100 ml with deionized water, yielding a final acid matrix of 10% hydrochloric acid. For quantitative determination of total mercury, there was no chemical preparation (digestion) because the dried sample was thermally decomposed during analysis (see below).

Instrumental Analysis

To perform a scan of elements (excluding mercury and selenium), samples were analyzed by ICP-MS using the semi-quantitative scan mode (TotalQuant®, Perkin-Elmer Sciex; Orazio et al. 2007). This scanning mode has a manufacturer's reported accuracy of ±30% to ±50%. All samples were diluted 10 times with a CETAC ASD-500 autodiluter as part of the analytical sequence. Internal standards were scandium (10 µg L^{-1}), rhodium (10 µg

L^{-1}), and thorium (10 µg L^{-1}), and the external standard consisted of a National Institute of Standards and Technology (NIST) traceable reference solution (Trace Metals in Drinking Water; High Purity Standards, Charleston, South Carolina) to which five elements (gold, praseodymium, tantalum, terbium, and thulium) were added for improved calibration in the rare earth region of the mass spectral range.

Quantitative arsenic determinations were conducted using a PE/SCIEX Elan 6000 inductively coupled plasma dynamic reaction cell mass spectrometer (ICP-DRC-MS), which was operated in "Standard Mode" and optimized according to the manufacturer's specifications (May et al. 2001). Samples were automatically delivered to the ICP-MS with a software-controlled CETAC ASD-500 autosampler/autodiluter system. All sample digestates were analyzed with 10 times predilution by autodiluter. The ICP-MS quantitative method was designed to determine the monoisotopic arsenic mass, ^{75}As. The internal standard was rhodium (10 µg L^{-1}), which was metered into the sample line via peristaltic pump. Calibration standards for arsenic were 1.5, 3.0, 6.0, 12, and 24 ng ml^{-1}. During the analysis, any digestate concentration exceeding the upper calibration standard was automatically diluted 10 times in serial fashion until its concentration was below this concentration.

Mercury was determined with a direct mercury analyzer in which a dried sample (50–60 mg) was combusted in a stream of oxygen. All mercury in the sample was volatilized and trapped by amalgamation on a gold substrate and was thermally desorbed and quantitated by atomic absorption spectrophotometry (USEPA 2007). The entire sequence was conducted with a Milestone DMA-80 analyzer equipped with an automated sample carousel.

The determination of selenium in dry-ashed samples was accomplished by flow injection hydride generation atomic absorption spectroscopy (May et al. 2008). In this procedure, the digestate is mixed with a hydrochloric acid carrier solution and then reduced by sodium tetrahydridoborate which has been stabilized with sodium hydroxide. The resulting volatile hydrogen selenide is transferred with argon carrier gas into a heated quartz cell mounted on an atomic absorption spectrophotometer for decomposition and measurement.

Quality Control

Calibration.—Runs of a laboratory control solution (Trace Metals in Drinking Water; High Purity, Charleston, South Carolina) after every 10 samples served to monitor calibration throughout each of seven semi-quantitative scans. Separate calibration solutions (Spex ClaritasPPT Standards) were also analyzed during each run and, except for potassium, exhibited recoveries ranging from 75% to 130%. Potassium exhibited recoveries ranging from 102% to 167% (average, 130%). A continuing calibration blank (CCB) and an independent calibration verification standard (ICVS) were analyzed every 10 samples to confirm the calibration status of the ICP-MS during quantitative instrumental analyses of sample digestates for arsenic. All CCB blanks were within ±3 times the instrument detection limit, and ICVS recoveries ranged from 92% to 101%. In addition, NIST SRM 1640 Trace Elements in Natural Water was analyzed for arsenic in each ICP-MS run; recoveries were 100%. Mercury calibration was checked during each instrumental run using two reference tissues: International Atomic Energy Agency (IAEA) SRM 407 whole-body fish and National Research Council Canada (NRCC) SRM DOLT-3 dogfish liver; measured concentrations deviated <8% from the certified mean for each material. For selenium, a calibration check solution was analyzed at the beginning and end of each analytical run, with measured concentrations deviating <10% from actual, except for one case of 11.1%.

Control Materials.—Two tissue control materials were analyzed with each group of semi-quantitative ICP-MS samples: NIST SRM 1566b oyster tissue and NRCC SRM DORM-2 dogfish muscle. Recoveries of aluminum, cadmium, calcium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, silver, sodium, vanadium, and zinc from NIST 1566b ($N = 6$) ranged from 71% to 128%, except for three measurements of iron (149%, 176%, and 224%); and one measurement each of aluminum (53%), nickel (146%), and potassium (166%). Recoveries of arsenic from four reference tissues—IAEA SRM 407

whole-body fish (N = 2); NRCC DORM-2 dogfish muscle (N = 3); NRCC SRM TORT-1 lobster hepatopancreas (N = 5); NIST 1566b oyster tissue (N = 5)—ranged from 100% to 109%. Recoveries of cadmium, calcium, copper, iron, lead, magnesium, manganese, molybdenum, potassium, rubidium, silver, sodium, strontium, and zinc from NRCC DORM-2 (N = 6) ranged from 77% to 132%, except for three measurements of iron (155%, 160%, and 184%). Accuracy of mercury measurements by thermal combustion amalgamation atomic absorption spectroscopy was determined with five reference tissues analyzed with the samples (NIST RM50 tuna fillet, N = 10; NRCC DORM-2, N = 9; NIST SRM 2976 mussel tissue, N = 10; IAEA SRM 407 whole-body fish, N = 9; and NRCC SRM DOLT-3 dogfish liver, N = 9); mercury recoveries ranged from 95% to 103%. Similarly, three reference tissues were analyzed for selenium along with the samples (IAEA SRM 407 whole-body fish, N = 8; CERC whole-body striped bass research material, N = 7; NRCC DORM-2 dogfish muscle, N = 1); selenium recoveries ranged from 94% to 105%.

Analytical and Method Precision.—Analytical precision for the semi-quantitative scan on digestates of whole-body fish samples was estimated by repeated runs of a reference solution, which exhibited percent relative standard deviation (%RSD) values of ≤11%, except for one measurement each of aluminum (21%) and strontium (14%). Internal standards (rhodium, scandium, and thorium) differed by ≤33% from the beginning to the end of the analytical runs. Instrumental precision for selenium, determined by repeated analysis of a standard throughout each run, was 3% RSD. Duplicate analysis of fish digestates (N = 30) for arsenic by quantitative ICP-MS produced relative percent differences (RPD) <3%. Method precision for whole-body fish tissues determined from triplicate digestion and analysis of fish samples (N = 13) by ICPMS semi-quantitative scan exhibited %RSDs <30% for most elements, but higher %RSDs were observed in some measurements of aluminum (44% and 47%), barium (36%), lead (33%), and strontium (39%). Replicate (N = 3) digestion and analysis of samples for arsenic (N = 6), mercury (N = 4), and selenium (N = 8) produced %RSDs <15%.

Spikes.—For samples analyzed for metals by semi-quantitative ICP-MS, spiking elements were selected that represented the entire mass spectral range (barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, terbium, thulium, vanadium, and zinc). Recoveries of low and high concentrations of these elements spiked into fish samples (N = 13) prepared for the semi-quantitative scan ranged from 84% to 121% (average, 104%), except for one instance of a higher recovery of barium (147%). The average recovery was 104%. Samples of fish spiked with arsenic (N = 26), mercury (N = 22), and selenium (N = 32) exhibited recoveries ranging from 89% to 120%, and averaged 104%. Recoveries of arsenic and selenium in analysis (post-digestion) spikes (N = 42) ranged from 91% to 109%, and averaged 101%.

Interference Checks.—As a check for potential interferences on arsenic in quantitative ICP-MS, dilution percent differences (DPDs) based on 5× dilutions of the fish digestates were determined (N = 30). The DPDs were <6% for this element in the whole-body fish matrix. A synthetic solution containing high concentrations of aluminum, calcium, carbon, iron, magnesium, molybdenum, phosphorus, potassium, sodium, sulfur, and titanium was analyzed to observe the effects of these potential interfering elements on the determination of arsenic concentrations in this matrix. Recoveries of arsenic in the matrix ranged from 110% to 130%; recoveries for two analytical runs exceeded the ±20% allowance by 8% and 10%, indicating a slightly positive potential interference on the element, at least when analyzed within this synthetic matrix. It is unlikely that this interference would translate to the whole-body fish matrix.

Blank Equivalent Concentrations.—Blank equivalent concentrations (BECs) were computed for digestion blanks analyzed with each set of fish samples. For most elements determined by the ICP-MS semiquantitative scan, BECs were generally below reporting limits

of the semi-quantitative scan [Note: the reporting limits for semi-quantitative "scan" data were set at 0.04 μg g^{-1} dry weight for most elements, based on a solution level of 0.1 ng ml^{-1}, a dry weight of 0.25 g, and a final digestate volume of 100 ml; exceptions were barium, copper, nickel, strontium, titanium, and zinc (0.4 μg g^{-1} dry weight), iron (4 μg g^{-1} dry weight), and calcium, magnesium, potassium, and sodium (40 μg g^{-1} dry weight)].

The BEC concentrations above reporting limits were most often observed for aluminum and iron. Mean BECs for arsenic, mercury, and selenium were at or below their respective method detection limits (MDLs) except for one measurement of selenium (BEC of 0.06 μg g^{-1} dry weight, MDL of 0.008 μg g^{-1} dry weight).

Instrument Detection, Method Detection, and Method Quantitation Limits.—The instrument detection limit (IDL) for arsenic by quantitative ICP-MS was 0.006 ng ml^{-1}, the IDLs for mercury by thermal combustion/amalgamation atomic absorption spectroscopy were 0.001 and 0.003 ng, and the IDL for selenium determined by flow injection hydride generation atomic absorption spectroscopy was 0.020 ng ml^{-1}. The MDLs were computed as 3*(SDb 2 + SDs 2)1/2, where SDb = standard deviation of a blank (N = 3) and SDs = standard deviation of a low-concentration sample or spiked sample (N = 3). The MDLs were established for each analytical run and ranged as follows: arsenic, 0.008 to 0.047 μg g^{-1} dry weight; mercury, 0.015 to 0.047 μg/g dry weight; and selenium, 0.004 to 0.022 μg g^{-1} dry weight. Method Quantitation limits (MQLs) were computed as 3.3*MDLs. The MQLs established for each analytical run ranged as follows: arsenic, 0.026 to 0.16 μg g^{-1} dry weight; mercury, 0.050 to 0.16 μg g^{-1} dry weight; and selenium, 0.013 to 0.071 μg g^{-1} dry weight.

Overall, the quality control results were acceptable based on specifications by CERC.

Data Analysis

Computerized databases were created as Excel spreadsheets. Raw data were analyzed by using SAS/STAT® and SAS/GRAPH® (SAS Institute, Inc., Cary, North Carolina). Characteristics of fish samples were assessed by conducting one-way analysis of variance (ANOVA) to compare mean values for length, weight, and moisture content among oil platforms and natural areas. To facilitate statistical comparisons of elemental concentrations that fell below reporting limits for semi-quantitative elemental scans by ICP-MS or that fell below detection limits for quantitative determinations of arsenic, mercury, and selenium, we substituted values that were one-half the reporting limit or detection limit. However, statistical comparisons based on substituted values in these "left censored data sets" are likely to yield biased estimates of the mean and standard deviation (Newman 1995). Thus, interpretations based on censored data should be viewed with caution.

When comparing elemental concentrations in various fish species from the two habitat types (oil platforms and natural areas), we assumed that fish size might account for some variation in elemental concentrations. This assumption is based on general observations by several investigators that concentrations of at least some elements can occasionally vary with fish age (or length and weight, which are proxies of age; e.g., Phillips and Russo 1978, Mance 1987). Additionally, we assumed that elemental concentrations could vary locally among each grouping of oil platform and two nearby natural areas (see Table 1 for Group designations). We used analysis of covariance (ANCOVA) with mixed effects, with the type of habitat and length (the continuous covariate) as fixed effects, and Group and Group*Length interaction as random effects (Littell et al. 1996). We estimated all effects using restricted maximum likelihood as the fitting algorithm, which yields unbiased estimates of covariance and variance, and we tested these effects using F-tests based on Satterthwaite's formula for degrees of freedom (Littell et al. 1996). Although we assumed that any of these effects or interactions could be present, the occurrence of a length effect complicated our interpretations of elemental concentrations at oil platforms and natural areas. Thus, we retained the length effect only if it was significant at the 0.05 level. We first determined if the interaction term was significant, and removed it from the ANCOVA model if significance was not achieved. If the interaction term was removed, we then tested

the length effect for significance, and removed it if not significant (at which point, the ANCOVA simplifies to an ANOVA with random effects). Least squares means and 95% confidence intervals were also computed for each habitat type regardless of whether a statistically significant difference was detected.

We interpreted results from the linear mixed models analysis of elemental concentrations for each fish species as follows: a significant Habitat Type*Length interaction indicated that the effect of habitat type on elemental concentration varied with fish length and, conversely, the effect of fish length varied between oil platforms and natural areas. If Habitat Type*Length interaction was significant, we calculated separate mean concentrations of the element at each habitat type for small fish and large fish (the selected lengths representing small and large fish were chosen from the ranges of minimum lengths and maximum lengths common to both habitat types). If Habitat Type*Length interaction was not significant but length was significant, we calculated the mean concentration of the element within each habitat type for fish of average length. If both Habitat Type*Length interaction and length effects were not significant, we omitted both effects, thus reducing the model to an ANOVA that estimated only the habitat type effect. In this instance, the mean concentration of an element at each habitat type applied to all fish regardless of length.

Additional statistical comparisons were made by computing Pearson product-moment correlation coefficients between moisture content and fish length or weight. Moreover, to ensure normality, raw data were routinely subjected to standard transformations (e.g., angular transformation for moisture percentage; logarithmic transformation for length, weight, and concentrations of various elements).

Results

In total, 196 whole-body fish samples (18 kelp bass, 80 kelp rockfish, and 98 Pacific sanddab) were analyzed for 63 elements during this study. Geometric mean lengths and weights of fishes were as follows (95% confidence limits in parentheses): kelp bass, 34.3 cm (32.9–35.8 cm), 533 g (466–610 g); kelp rockfish, 25.1 cm (24.2–26.1 cm), 264 g (234–299 g); and Pacific sanddab, 19.4 cm (18.6–20.2 cm), 82 g (72–94 g) (Table 2). Although mean lengths and weights did not vary over sampling sites for kelp bass, they varied significantly for kelp rockfish and Pacific sanddab (Table 3).

Moisture content averaged 68% (95% confidence interval) in kelp bass, 74% (95% confidence interval) in kelp rockfish, and 80% (95% confidence interval) in Pacific sanddab (Table 2). Although moisture content did not vary among sampling sites for kelp bass, significant differences were detected for kelp rockfish and Pacific sanddab (Table 3). With one exception, moisture content was not significantly correlated with length or weight in all three species (data not shown). Moisture content in kelp bass was exceptional because a significant inverse relation was detected with fish weight ($r = -0.53$, $P = 0.0244$). Due to variable moisture content of the sampled fishes, elemental concentrations were routinely expressed in terms of dry weight unless indicated otherwise. [Note: elemental concentrations reported as dry weight can be converted to wet weight by using the following equation: wet weight = dry weight × (100-moisture content) / 100), where wet weight concentration and dry weight concentration are μg g^{-1} and moisture content is %].

The elements measured during our study included calcium, magnesium, potassium, and sodium, which are major cations that must be present in fish tissues at required concentrations for proper functioning of cellular membranes and organ tissues, and for nerve conduction, muscle contraction, and other biochemical and

Table 2. Summary of fish total length and weight, and moisture content and total concentrations of 21 elements measured in whole-body samples of kelp bass, kelp rockfish, and Pacific sanddab. Except for moisture content, values are geometric means (ranges in parentheses). For moisture content, values are back-transformed angular means (ranges in parentheses). With three exceptions, all measurements of elements are semi-quantitative estimates made by ICP-MS. The exceptions are arsenic, mercury, and selenium, which were measured with quantitative techniques.

Variable	Kelp bass, $N = 18$	Kelp rockfish, $N = 80$	Pacific sanddab, $N = 98$
Total length (cm)[a]	34.3 (27.9–40.2)	25.1 (18.0–34.6)	19.4 (11.9–28.5)
Weight (g)	533 (288–874)	264 (86–790)	82 (14–289)
Moisture (%)	67.9 (62.9–71.5)	74.2 (66.8–87.9)	80.1 (70.9–84.2)
Elements (μg g^{-1} dry weight)			
Aluminum (Al)	2.80 (0.50–30.00)	7.90 (0.70–100.00)	16.00 (2.00–700.00)
Arsenic (As)	5.57 (3.40–13.1)	5.43 (2.38–36.40)	7.73 (3.94–23.50)
Barium (Ba)	0.85 (0.40–4.00)	0.72 (<0.40–2.00)	5.00 (0.50–1,000.00)
Cadmium (Cd)	0.35 (0.20–0.90)	0.28 (0.07–0.80)	1.20 (0.30–5.00)
Chromium (Cr)	0.55 (0.30–0.80)	0.86 (0.30–4.00)	1.20 (<0.04–8.00)
Cobalt (Co)	<0.04 (<0.04–0.04)	0.04 (<0.04–0.60)	0.05 (<0.04–0.30)
Copper (Cu)	1.00 (0.80–2.00)	1.90 (1.00–4.00)	2.70 (2.00–7.00)
Gallium (Ga)	<0.04 (<0.04–0.10)	<0.04 (<0.04–0.10)	0.15 (<0.04–0.50)
Iron (Fe)	120.00 (20.00–300.00)	140.00 (8.00–300.00)	120.00 (30.00–1,000.00)
Lead (Pb)	0.07 (<0.04–0.20)	0.10 (<0.04–2.00)	0.23 (0.06–2.00)
Lithium (Li)	0.28 (0.20–0.40)	0.50 (0.20–1.00)	0.88 (0.20–30.00)
Manganese (Mn)	1.80 (1.00–3.00)	1.80 (0.90–4.00)	5.70 (2.00–10.00)
Mercury (Hg)	0.38 (0.15–0.90)	0.20 (0.05–1.10)	0.28 (0.07–1.10)
Nickel (Ni)	0.46 (<0.40–3.00)	0.80 (<0.40–2.00)	0.65 (<0.40–3.00)
Rubidium (Rb)	2.00 (2.00–2.00)	2.00 (1.00–3.00)	3.10 (2.00–5.00)
Selenium (Se)	1.26 (0.91–1.80)	1.60 (1.01–2.30)	1.68 (1.15–4.70)
Strontium (Sr)	88.00 (60.00–100.00)	150.00 (60.00–400.00)	110.00 (50.00–300.00)
Tin (Sn)	2.70 (1.00–5.00)	1.00 (<0.04–20.00)	<0.04 (<0.04–4.00)
Titanium (Ti)	32.00 (20.00–50.00)	57.00 (10.00–200.00)	41.00 (10.00–400.00)
Vanadium (V)	0.11 (0.06–0.20)	0.50 (0.04–9.00)	0.45 (0.10–40.00)
Zinc (Zn)	43.00 (30.00–60.00)	60.00 (40.00–80.00)	53.00 (40.00–80.00)

[a]Total length (TL) can be converted to standard length (SL) by the following equations: for kelp bass, $Log_{10}SL = -0.11813 + 1.01623*Log_{10}TL$, $r^2 = 0.9953$; for kelp rockfish, $Log_{10}SL = -0.11657 + 1.01570*Log_{10}TL$, $r^2 = 0.9948$; and for Pacific sanddab, $Log_{10}SL = -0.10058 + 1.02399*Log_{10}TL$, $r^2 = 0.9970$.

physiological processes. In our study, mean concentrations of these cations varied as follows: for calcium, 22–43 mg g^{-1}; for magnesium, 1–1.9 mg g^{-1}; for potassium, 13–19 mg g^{-1}; and for sodium, 4–13 mg g^{-1}. However, healthy unstressed marine fish held in natural seawater are generally efficient at regulating internal concentrations of major cations so these elements are rarely monitored as part of routine contaminant surveys. For this reason, other than to report the measured concentrations, no further assessments of major cations were attempted.

Eighteen trace elements exhibited concentrations in all samples that were below the ICP-MS reporting limit of 0.04 μg g^{-1}. Undetected elements were beryllium, bismuth, germanium, gold, hafnium, holmium, indium, iridium, lutetium, osmium, palladium, platinum, rhenium, ruthenium, tantalum, terbium, thulium, and ytterbium. Another 12 elements yielded concentrations equal to or greater than the reporting limit in one or more samples, but mean concentrations within fish species and site were <0.04 μg g^{-1}. These included dysprosium, erbium, europium, gadolinium, niobium, praseodymium, samarium, silver, tellurium, thallium, tungsten, and

Table 3. Variation in total length, weight, and moisture of kelp bass (KBA), kelp rockfish (KRO), and Pacific sanddab (PSD) sampled from various sampling sites.[a]

Site[b] or	Total length (cm)			Weight (g)			Moisture (%)		
F-statistic	KBA	KRO	PSD	KBA	KRO	PSD	KBA	KRO	PSD
PL1	—	22.9 C	17.8 AB	—	206 BC	59 AB	—	71.1 B	81.2 A
NA1	—	26.3 ABC	17.0 AB	—	284 BC	53 AB	—	72.1 B	80.5 A
PL2	—	28.0 AB	17.9 AB	—	376 AB	70 AB	—	70.7 B	80.4 A
NA2	—	23.3 BC	19.7 AB	—	200 C	83 AB	—	72.5 B	79.9 AB
PL3	—	22.4 C	21.7 A	—	214 BC	119 A	—	69.8 B	81.8 A
NA3	—	25.1 ABC	20.4 AB	—	234 BC	92 AB	—	72.5 B	80.0 AB
PL4	34.8 A	—	21.9 A	585 A	—	110 AB	67.3 A	—	79.9 AB
NA4	33.9 A	—	16.0 B	495 A	—	47 B	68.3 A	—	79.7 AB
PL5	—	30.2 A	21.7 A	—	546 A	124 A	—	82.3 A	79.6 AB
NA5	—	23.8 BC	20.7 AB	—	199 C	106 AB	—	81.5 A	77.8 B
$F_{(df1,df2)}$ [c,d]	0.39	5.39****	4.04***	1.76	6.63****	3.43 **	1.12	65.65****	4.77****

[a]Within a column, geometric means (total length or weight) or angular-transformed means (moisture) followed by the same capital letter are not significantly different ($P > 0.05$) according to Tukey's studentized range test.

[b]Names and locations of sampling sites are given in Table 1.

[c]For KBA, df1 = 1, df2 = 16; for KRO, df1 = 7, df2 = 72; for PSD, df1 = 9, df2 = 88.

[d]Codes: *, $P \leq 0.05$; **, $P \leq 0.01$; ***, $P \leq 0.001$; ****, $P \leq 0.0001$

zirconium. Still another eight elements—antimony, cerium, cesium, lanthanum, molybdenum, neodymium, uranium, and yttrium—contained mean concentrations in one or more fish species and sites that exceeded 0.04 µg g^{-1} (data not shown), but none of the means exceeded 0.12 µg g^{-1} or 3 times higher than their reporting limit (a computation procedure that we roughly equated to method quantitation limits of elements determined by quantitative procedures). Although these eight elements were detected in fish samples, we judged their concentrations to be too low for statistical comparisons.

Twenty-one trace elements were deemed suitable for statistical comparisons (Table 2). Results from mixed models ANCOVA or ANOVA indicated that none of the 21 quantitative elements deemed suitable for statistical comparison consistently exhibited higher concentrations in fish from oil platforms than from natural areas. Out of 63 possible comparisons (21 elements measured in three fish species), 44 did not differ between oil platforms and natural areas whereas 11 comparisons indicated that elemental concentrations were significantly higher at natural areas than at platforms (Fig. 2). The remaining eight comparisons exhibited significant Habitat Type*Length interactions, indicating that intraspecific differences in fish lengths between the two sites were responsible for differences in elemental concentrations. Although interactions were detected for rubidium, selenium, and tin in kelp rockfish, the concentrations of these elements did not differ significantly between oil platforms and natural areas over the length range of sampled fish. For selenium, titanium, and vanadium in Pacific sanddab, small individuals exhibited significantly lower concentrations at oil platforms than at natural areas, whereas large individuals exhibited higher concentrations at oil platforms than at natural areas. On the other hand, for copper and tin in Pacific sanddab, small individuals did not exhibit measurable differences between oil platforms and natural areas, whereas large individuals exhibited either significantly higher concentrations at oil platforms than at natural areas (copper) or significantly lower concentrations at oil platforms than at natural areas (tin). This
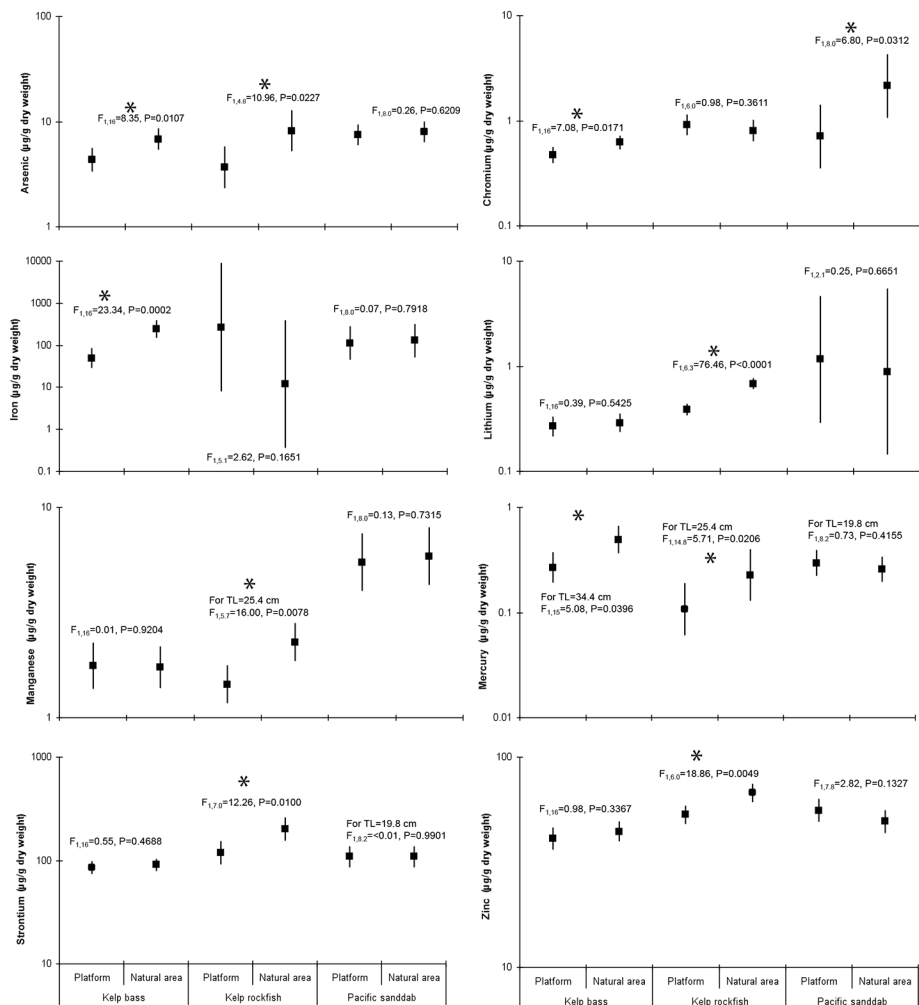
Figure 2. Comparison of arsenic, chromium, iron, lithium, manganese, mercury, strontium, and zinc concentrations (least-squares means and 95% confidence intervals) in whole-fish samples of kelp bass, kelp rockfish, and Pacific sanddab from Southern California oil platforms and natural areas, with F statistics and significance levels. Asterisks denote statistically significant differences.

study was not designed to investigate specific differences in elemental concentration by fish size, but such patterns could be the result of ontogenetic diet change.

Discussion

Our study measured trace elements in whole-fish samples even though many elements are known to selectively concentrate in liver and kidneys (Crawford and Luoma 1993, Goldstein and DeWeese 1999). Notable exceptions include mercury, which tends to concentrate in muscle (Goldstein et al. 1996, Philips et al. 1997, Weiner et al. 2003), and lead, which accumulates in scales, bone, and other active calcification areas (Eisler 1988b, Sorenson 1991). Nevertheless, for several trace elements,

concentrations measured in liver and muscle were correlated with concentrations measured in the whole body (Goldstein and DeWeese 1999). Thus, although selection of a specific tissue for analysis should depend upon the objective of the study, for general surveys of trace element occurrence and distribution, analysis of whole fish has the advantage of maximizing the amount of information returned with a limited number of analyses (Goldstein and DeWeese 1999).

Only one previous study compared levels of trace elements found in fishes living around Southern California oil platforms and the results were reported both in Bascom et al. (1976) and McDermott-Ehrlich and Alexander (1976). This previous research examined the concentrations of 11 elements (cadmium, chromium, copper, iron, molybdenum, nickel, lead, silicon, silver, vanadium, and zinc) in two benthic fish species (i.e., brown rockfish, *Sebastes auriculatus* Girard, 1854, and copper rockfish, *Sebastes caurinus* Richardson, 1844) at two platforms and one natural reef in the Santa Barbara Channel, California. With the exception of vanadium, which was significantly more elevated in platform fishes, no significant differences in elemental compositions were noted between platform and reef fishes.

Concentrations of copper and zinc in whole-fish samples from our study were well below literature-based toxicity thresholds for fishes, wildlife consumers of fish, or both (Hinck et al. 2009). By comparison, arsenic, cadmium, chromium, lead, mercury, and selenium in whole-fish samples equaled or exceeded the toxicity thresholds, raising the possibility of adverse effects. Arsenic concentrations (measured as total arsenic) in 4 kelp bass from a natural area (NA4, 4 of 10 fish), 14 kelp rockfish from three natural areas (NA1, 1 of 10 fish; NA2, 4 of 10 fish; and NA3, 9 of 10 fish), and 7 Pacific sanddab from an oil platform (PL2, 1 of 8 fish) and a natural area (NA3, 6 of 10 fish) equaled or exceeded the toxic threshold of 2.2–11.6 μg As g^{-1} wet weight (Hinck et al. 2009). Although arsenic concentrations as high as 10.2 μg g^{-1} wet weight were recorded during our study (i.e., a sample of kelp rockfish from NA3), the likelihood of toxicity was probably negligible because <10% of total arsenic generally occurs in the highly toxic inorganic form (Attar et al. 1992, USEPA 2000). A recent study by Peshut et al. (2008) determined that inorganic arsenic in marine fish from American Samoa typically constituted <0.5% of total arsenic. Eisler (1988a) reported that inorganic forms of arsenic are generally much more toxic than organic forms. In addition to being very toxic to aquatic biota, including fishes, inorganic arsenic can cause poor growth, food avoidance, and metabolic failure (Eisler 1988a). In mammals, arsenic is a teratogen and carcinogen that can traverse placental barriers and produce fetal death and malformations (Eisler 1988a).

Cadmium concentrations approached or equaled the toxic threshold of 0.23–15.6 μg g^{-1} wet weight (Hinck et al. 2009) in 1 of 18 kelp bass, 2 of 80 kelp rockfish, and 30 of 98 Pacific sanddab. The kelp bass was collected from an oil platform (PL4, 1 of 8 fish), as were the two kelp rockfish (PL2, 2 of 10 fish). Although 17 Pacific sanddab containing high concentrations of cadmium came from oil platforms (PL2, 3 of 8 fish; PL3, 7 of 10 fish; PL4, 3 of 10 fish; and PL5, 4 of 10 fish), 22 highly contaminated sanddabs also came from natural areas (NA1, 2 of 10 fish; NA2, 5 of 10 fish; NA3, 7 of 10 fish; NA4, 1 of 10 fish; and NA5, 7 of 10 fish). Toxic responses from excessive exposure to cadmium in fishes may include decreased growth, respiratory disruption, altered enzyme levels, and abnormal muscular contractions (Eisler 1985). Although mammals and birds are comparatively

resistant to biocidal properties of cadmium, sublethal effects include growth retardation, anemia, and testicular damage (Eisler 1985). Mean concentrations of chromium exceeded the toxicity threshold of 1.0 µg g^{-1} wet weight in 22 of 98 Pacific sanddab, all from three natural areas (NA3, 7 of 10 fish; NA4, 10 of 10 fish, and NA5, 5 of 10 fish). Toxic effects from excess exposure to chromium may include decreased growth and body size, and also significant reduction in the rate of reproduction and survival of progeny (Moore and Ramamoorthy 1984).

Lead concentrations equaled the toxicity threshold of 0.4–8.8 µg g^{-1} wet weight (Hinck et al. 2009) in a single kelp rockfish from an oil platform (PL1, 1 of 10 fish). According to Eisler (1988b), lead is neither essential nor beneficial to living organisms, and all measured effects are adverse. Toxic effects in aquatic biota from excessive lead exposure include reduced survival, impaired reproduction, and reduced growth (Eisler 1988b). In birds and mammals feeding on lead-contaminated prey, sublethal effects can include impaired learning and abnormal social behavior (Eisler 1988b).

Mercury concentrations in 12 kelp bass, 11 kelp rockfish, and 10 Pacific sanddab equaled the toxic threshold of 0.1–3.0 µg g^{-1} wet weight for methylmercury (Hinck et al. 2009). Although total mercury was measured during our study, several investigators (Grieb et al. 1990, Bloom 1992, Wiener et al. 2003) reported that approximately 95%–99% of mercury in fish muscle tissues occurs as methylmercury. Nevertheless, Mason et al. (2006) reported methylmercury concentrations averaging only 28% ± 14% in axial muscle of planktivorous white perch, *Morone americana* (Gmelin, 1789), and 65% ± 22% in axial muscle of mostly piscivorous striped bass, *Morone saxatilis* (Walbaum, 1792), from tidal portions of Chesapeake Bay. During our study, kelp bass with high concentrations of mercury came from an oil platform (PL4, 3 of 8 fish) and a natural area (NA4, 9 of 10 fish), kelp rockfish came from an oil platform (PL2, 1 of 10 fish) and two natural areas (NA3, 8 of 10 fish; and NA5, 2 of 10 fish), and Pacific sanddab came from four oil platforms (PL2, 2 of 8 fish; PL3, 1 of 10 fish; PL4, 3 of 10 fish; and PL5, 1 of 10 fish) and a natural area (NA3, 3 of 10 fish). Although mercury is a potent neurotoxin capable of causing outright mortality in fish and wildlife, sublethal effects may include suppression of sex hormones, altered reproductive behavior, and impaired reproduction, along with maternal transfer of potentially toxic doses of mercury to embryos during oogenesis (Wiener et al. 2003, Scheuhammer et al. 2007).

Selenium concentrations in only two Pacific sanddab, both from a natural area (NA2, 2 of 10 fish), equaled or exceeded the toxicity threshold of 0.75–1.0 µg Se g^{-1} wet weight (Hinck et al. 2009). According to Maher et al. (1997), selenium recovered from fish muscle tissues are associated with proteins and consist mostly of selenocysteine. Lemly (2002) reported that adverse effects from excessive selenium concentrations in fishes can include severe tissue pathology, teratogenic deformities, and reproductive impairment, along with high mortality.

In summary, we selected three species that were likely to encounter and ingest prey containing elevated concentrations of trace elements, such as heavy metals, should they occur in the study sites. Because they not only ingest benthic infauna, but also lie on sediment, it might be expected that the Pacific sanddab, in particular, would accumulate these pollutants. However, our findings generally were not consistent with the hypothesis that oil platforms off California are major sources of trace element contamination in resident marine fishes.

Acknowledgments

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