The 2015 Refugio Beach Oil Spill: Polycyclic Aromatic Hydrocarbons in Nearshore Fish and Invertebrate Tissues

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INTRODUCTION

On May 19, 2015, an underground pipeline (Line 901), owned and operated by Plains All American Pipeline, L.P., and Plains Pipeline, L.P., sustained a release of crude oil near Refugio State Beach in Santa Barbara County, California. Oil from the pipeline flowed down a culvert and entered the Pacific Ocean in the nearshore environment. As a result, the California Department of Fish and Wildlife (CDFW) implemented a fisheries closure, as recommended by the Office of Health Hazard Assessment (OEHHA). CDFW and OEHHA sampled fish and invertebrates to establish the degree and geographic extent of seafood contamination in the impacted area (OEHHA, 2015). The contaminants of concern for human health were the 8 polycyclic aromatic hydrocarbons that have the potential to cause cancer (cPAHs), reported as benzo(a)pyrene equivalents. The concentrations of benzo(a)pyrene equivalents found in finfish and invertebrate tissues were presented in the seafood consumption risk assessment report prepared by OEHHA (2015). However, in addition to the PAHs of human health concern, the fish and invertebrate tissues were analyzed for several other PAHs found in oil for a total of 45 PAHs ($TPAH_{45}$).

This report provides a summary of the $TPAH_{45}$ concentrations measured in the tissues. The natural resource trustees for resources affected by the Refugio[1] (Trustees) utilized this information to further evaluate fish and invertebrate exposure in the spill affected area.

METHODS

Field Sampling Procedures

Nearshore finfish and invertebrates were collected from June 10-19, 2015, approximately 3-4 weeks after the spill, from the three CDFW Commercial Fishing Blocks in the closure area (Figure 1 and Table 1; OEHHA, 2015). Details of the sampling and analysis methods are provided in OEHHA (2015).

Chemical Analysis

Skinless filets from fish and edible portions from invertebrates (e.g., crab, prawn and lobster body meat and sea urchin roe) were composited (Table 1), extracted and analyzed for PAHs, as detailed in OEHHA (2015). The gut contents of the sea cucumbers were rinsed out before tissues were composited. As indicated above, the extracts were analyzed for 45 individual PAHs and alkylated homologue groups. Results for these 45 individual PAHs and alkylated homologue groups were summed to estimate total PAHs ($TPAH_{45}$): naphthalene (N0); C1-naphthalenes as 1-methylnaphthalene (N1-1) and 2-methylnaphthalene (N1-2); C2-naphthalenes (N2); C3-naphthalenes (N3); C4-naphthalenes (N4); biphenyl (B); acenaphthylene (AY); acenaphthene (AE); fluorene (F0); C1-fluorenes (F1); C2-fluorenes (F2); C3-fluorenes (F3); phenanthrene (P0); anthracene (A0); C1-phenanthrene/anthracene (PA1); C2-

[1] The natural resource trustees for the Refugio Beach Oil Spill include the California Department of Fish and Wildlife, the U.S. Department of Commerce through the National Oceanic and Atmospheric Administration, the U.S. Department of the Interior through the Fish and Wildlife Service, the California Department of Parks and Recreation, the California State Lands Commission, and the Regents of the University of California.

phenanthrene/anthracene (PA2); C3-phenanthrene/anthracene (PA3); C4-phenanthrene/anthracene (PA4); dibenzothiopene (DBT0); C1-dibenzothiophenes (DBT1); C2-dibenzothiophenes (DBT2); C3-dibenzothiophenes (DBT3); pyrene (P); fluoranthene (FL0); C1-fluoranthene/pyrenes (FP1); C2-fluoranthene/pyrenes (FP2); C3-fluoranthene/pyrenes (FP3); C4-fluoranthene/pyrenes (FP4); benz[a]anthracene (BA0); chrysene (BC0); C1-chrysenes (BC1); C2-chrysenes (BC2); C3-chrysenes (BC3); C4-chrysenes (BC4); benzo(b)fluoranthene (BBF); benzo(k)fluoranthene (BJKF); benzo(e)pyrene (BEP); benzo(a)pyrene (BAP); perylene (PER); indeno(1,2,3-c,d)pyrene (ICDP); dibenz(a,h)anthracene (DA); C1-dibenz(a,h)anthracene (DA1); C2-dibenz(a,h)anthracene (DA2); C3-dibenz(a,h)anthracene (DA3); and benzo(g,h,i)perylene (GHI). When calculating $TPAH_{45}$, non-detects were assumed to be zero. Tissue results are reported on a dry weight basis. Moisture content ranged from 71 to 92 percent.

The Trustees also analyzed barred surfperch skinless filets collected on 23 May 2015 from Gaviota State Beach, Refugio State Beach and Campus Point (near Coal Oil Point) for the same 45 PAHs. Methods and results for this surfperch exposure assessment study are presented in Appendix G-3 of the DARP.

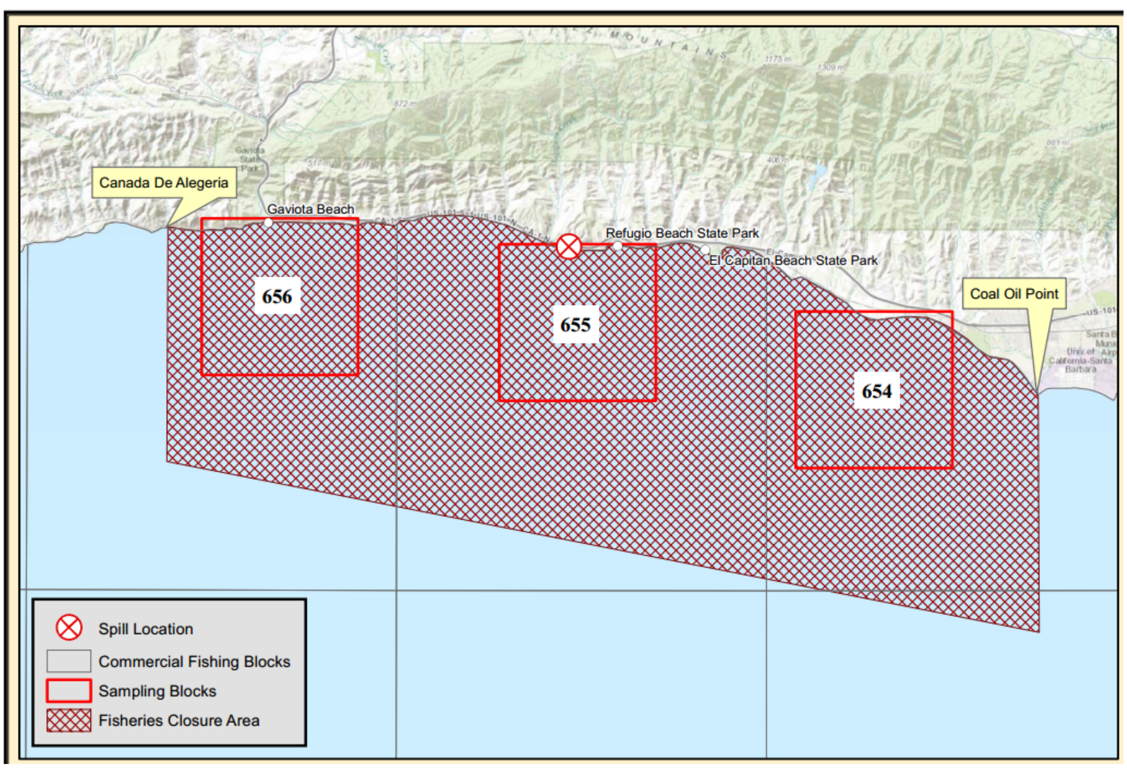

Figure 1. *Fishery closure area and sampling areas within the commercial fishing blocks (excerpted from Figure 1 of OEHHA, 2015).*

Table 1. *Number of fish and invertebrate individuals in composite samples collected from Fishing Blocks 654, 655 and 656 (excerpted from OEHHA, 2015). The 10 m depth column indicates whether a sampling location was inshore ("In") or further offshore, outside of the 10 m bathymetric line ("Out"), as depicted in Figure 2.*

Species	10 m Depth	654 – Coal Oil Pt	655 - Refugio	656- Gaviota
Invertebrates		**Number of Individuals per Composite –June 2015**		
CA Spiny Lobster *(Panulirus interruptus)*	In	**3**	**1**	**-**
Red Sea Urchin *(Strongylocentrotus franciscanus)*	In	**9**	**9**	**9**
Brown Rock Crab *(Cancer attennarius)*	In	**6**	**6**	**6**
Sheep Crab (Loxorhynchus grandis)	In	**9**	**9**	**6**
Warty Sea Cucumber (*Parastichopus parvimensis)*	In	**9**	**9**	**10**
Giant Red Cucumber (*Apostichopus californicus*)	Out	**8**	**12**	**-**
Ridgeback Prawn (Sicyonia ingentis)	Out	**12**	**11**	**-**
Yellow Rock Crab (Cancer anthonyi)	Out	**10**	**10**	**10**
Fish				
Barred Surfperch (*Amphistichus argenteus*)	In	**9**	**4**	**9**
Pacific Mackerel (*Scomber japonicas)*	In	**-**	**10**	**9**
Grass Rockfish *(Sebastes rastrelliger)*	In	**11**	**13**	**7**
Kelp Rockfish (Sebastes atrovirens)	In	**9**	**9**	**-**
Black and Yellow Rockfish *(Sebastes chrysomelas)*	In	**-**	**7**	**-**
Pacific Sanddab (deeper water) *(Citharichthys sordidus)*	Out	**9**	**11**	**12**
Pacific Sanddab (shallower water) *(Citharichthys sordidus)*	Out	**-**	**10**	**9**
Vermillion Rockfish (Sebastes miniatus)	Out	**8**	**9**	**9**
Bocaccio Rockfish *(Sebastes paucispinis)*	Out	**-**	**9**	**9**

- Not sampled

RESULTS and DISCUSSION

Relative Tissue $TPAH_{45}$ Concentrations in Fishing Blocks and Depth Zones

Spatial and depth zone patterns of $TPAH_{45}$ concentrations in composited fish and invertebrate samples were evaluated. Fishing block 655 (labeled "Refugio") was closest to the oil release point, near Refugio State Beach, while Block 656 (labeled "Gaviota") was to the west in an area that included Gaviota State Beach and Block 654 (labeled "Coal Oil Point") was to the east in an area that included Coal Oil Point (Figure 2). There are active natural oil seeps offshore of Coal Oil Point (Lorenson, 2011).

The 10 m bathymetric line (Figure 2) is the approximate offshore extent of kelp forest and rocky reef habitat which provide critical habitat for fish and invertebrates. The Trustees determined that oil would mix throughout the water column to 10 meters depth through wave and tidal action. Accordingly, fish and invertebrates collected within the 10 m bathymetric line were likely to have experienced greater exposure to oil compared to fish and invertebrates collected farther offshore.

Figure 2. *Samples collected within the three fishing blocks in relationship to the 10 m bathymetric line. The red star is the approximate location of the oil release point.*

The highest $TPAH_{45}$ tissue concentrations were measured in the warty sea cucumber and red sea urchin composite samples near Refugio State Beach (Figure 3). Lower concentrations for these two species were measured in the fishing blocks to the west (Gaviota State Beach) and the east (Coal Oil Point). The giant red sea cucumber, collected outside of the 10 m bathymetric line in Fishing Block 655 (Figure 4), had $TPAH_{45}$ concentrations over ten times lower than the warty sea cucumber collected closer to shore in this block.

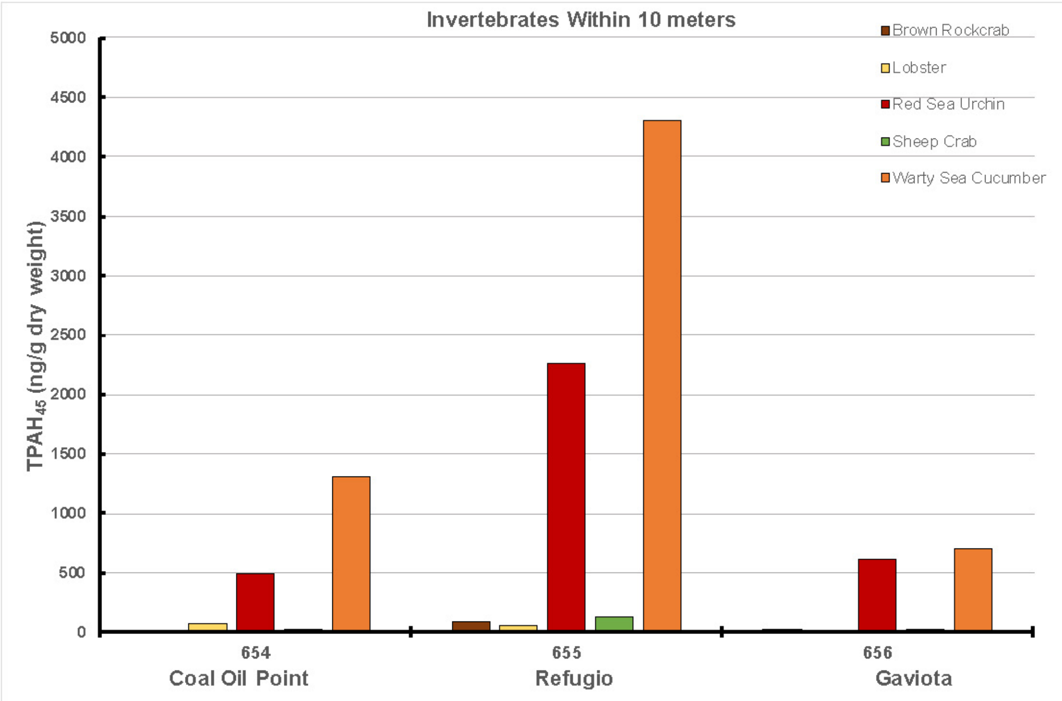

Figure 3. *Total polycyclic aromatic hydrocarbon concentrations ($TPAH_{45}$; ng/g dry weight) in invertebrates collected at or within the 10 m bathymetric line in Fishing Blocks 654, 655 and 656.*

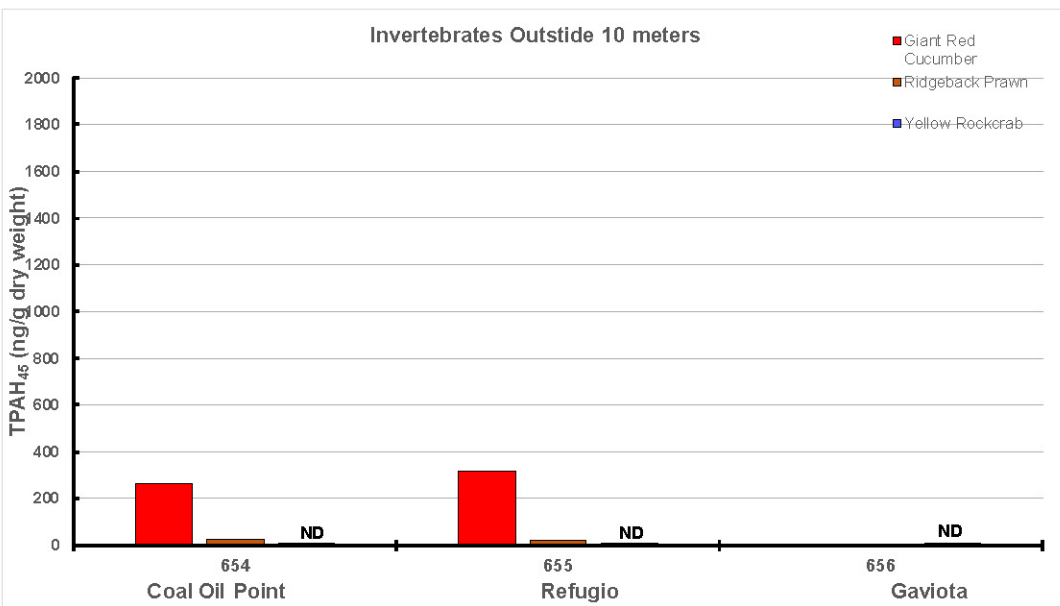

Figure 4. *Total polycyclic aromatic hydrocarbon concentrations ($TPAH_{45}$; ng/g dry weight) in invertebrates collected outside the 10 meter bathymetric line in Fishing Blocks 654, 655 and 656. ND = not detected.*

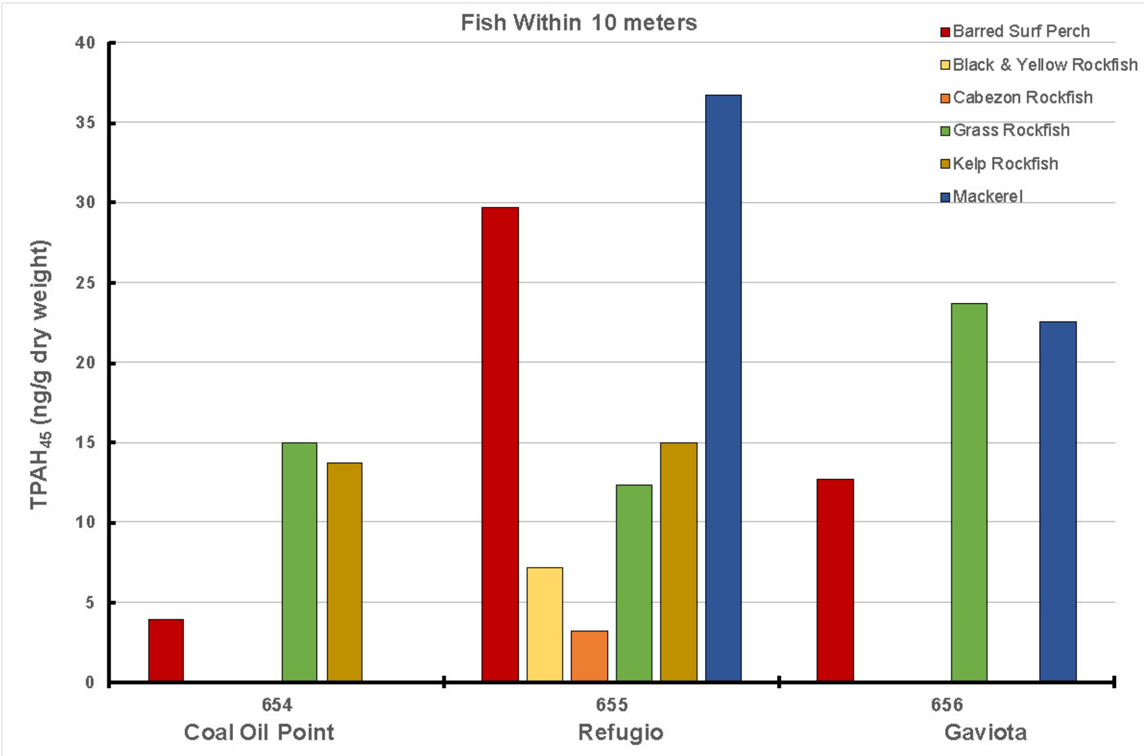

Figure 5. *Total polycyclic aromatic hydrocarbon concentrations ($TPAH_{45}$; ng/g dry weight) in fish collected at or within the 10 m bathymetric line in Fishing Blocks 654, 655 and 656.*

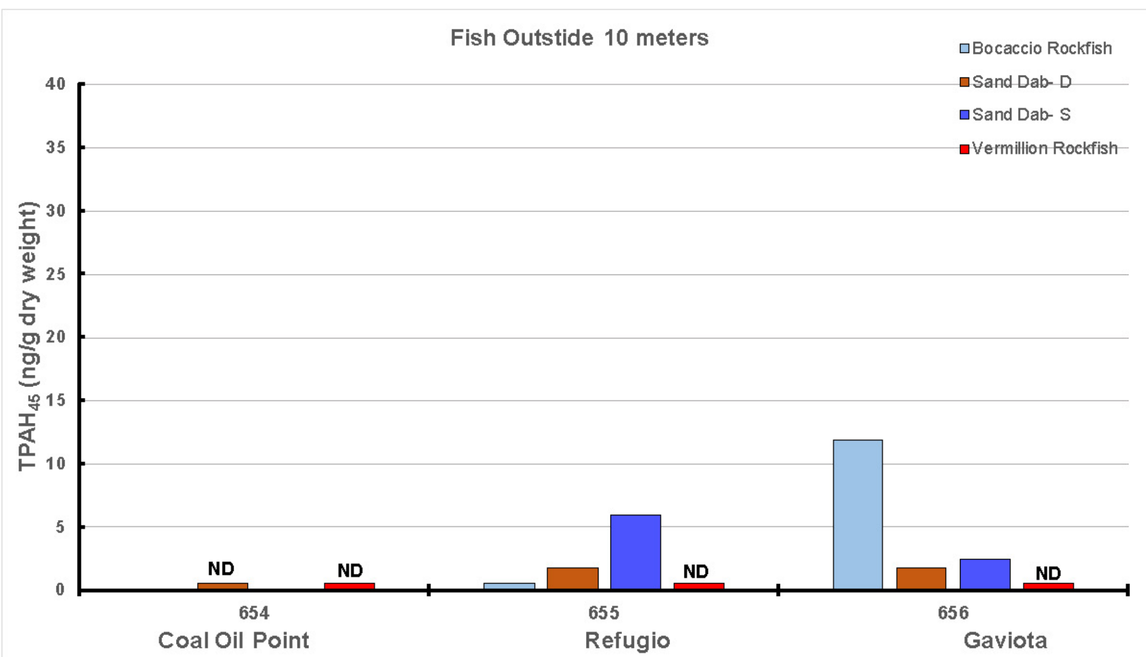

Figure 6. *Total polycyclic aromatic hydrocarbon concentrations ($TPAH_{45}$; ng/g dry weight) in fish collected outside the 10 m bathymetric line in Fishing Blocks 654, 655 and 656. ND = not detected.*

A similar spatial pattern was seen in fish where there were higher $TPAH_{45}$ concentrations in filets from fish collected within the 10 m bathymetric line (Figure 5), compared to filets from fish collected outside this depth zone (Figure 6). The highest $TPAH_{45}$ concentrations in fish were measured in mackerel and barred surfperch composite samples near Refugio State Beach (Figure 5), relative to the other fishing blocks. Surfperch filet concentrations from fish collected at Refugio State Beach approximately 22 days after the spill ($TPAH_{45}$ = 30 ng/g dry weight), were lower than surfperch filet composites from fish collected 4 days after the spill, from the same location (88 ng/g dry weight; Anulacion et al, 2019; see Appendix G-3 for study details). Since the tissue samples collected to evaluate seafood contamination in the impacted area were collected 3-4 weeks after the spill, $TPAH_{45}$ concentrations likely underestimated fish and invertebrate tissue concentrations that occurred immediately after the spill. Overall, results indicate exposures were higher within the 10 m depth zone and adjacent to the oil spill release site.

Comparison of Fish and Invertebrate PAH Concentrations

Fish filet $TPAH_{45}$ concentrations were generally lower than what were measured in invertebrate edible tissues (Figures 3-6). Fish have been reported to have greater ability to metabolize and eliminate PAHs, compared to invertebrates (Meador et al, 1995). Additionally, fish muscle tends to have lower PAH concentrations than other fish tissues, such as the liver (Meador et al., 1995; Ylitalo et al., 2012). Another factor potentially contributing to the difference is that some fish are more mobile than invertebrates and some may have been able to move away from the oil contaminated area, or may live and feed in habitats with less oil contamination (Graham et al, 2015; Law and Hellou, 1999). For example, the warty sea cucumber is an epibenthic detritivore that feeds on organic detritus and small organisms within the sediment, a potential depositional zone for the spilled oil (Leet et al., 2001). This feeding strategy may have contributed to the higher $TPAH_{45}$ concentrations in their tissues.

A wider array of PAHs were detected in invertebrate tissues (Figure 7) compared to fish tissues (Figure 8). In invertebrates, naphthalenes, phenanthrenes and dibenzothiophenes contributed the largest percentages to the $TPAH_{45}$ concentration, which is similar to other invertebrates analyzed following the Line 901 release (Stout, 2016). Elevated levels of naphthalenes and phenanthrenes in invertebrate tissues have been reported following other oil spills (Boehm et al, 2004; Rumney et al., 2011). Naphthalenes were the predominant PAHs detected in fish, which is consistent with other studies of fish contamination following oil spills (Incardona et al, 2011; Xia et al, 2012; Murawski et al., 2014).

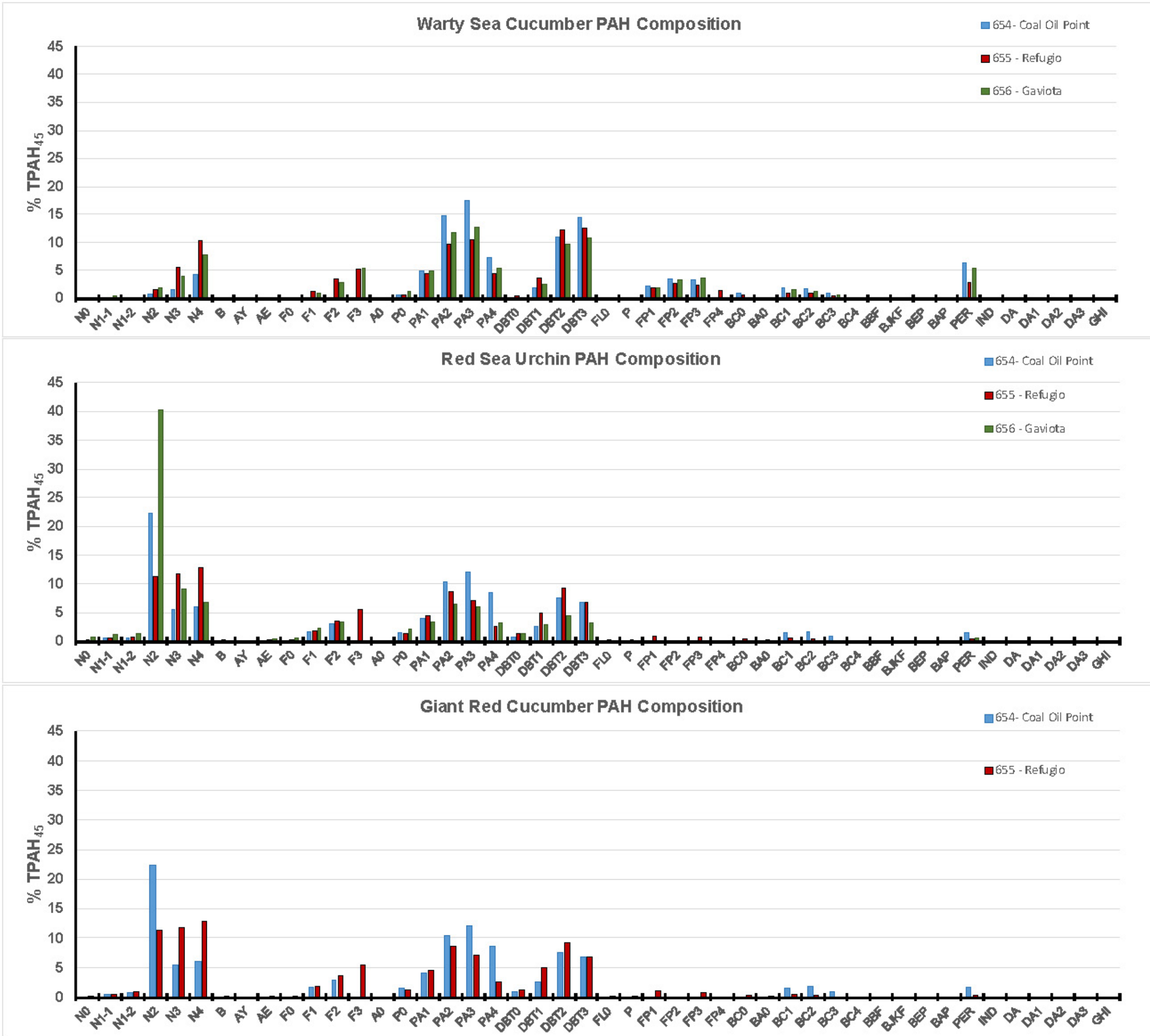

Figure 7. *Percent composition of polycyclic aromatic hydrocarbons (PAHs) in warty sea cucumber, red sea urchin and giant red sea cucumber in the three fishing blocks. See Methods for PAH abbreviations*.

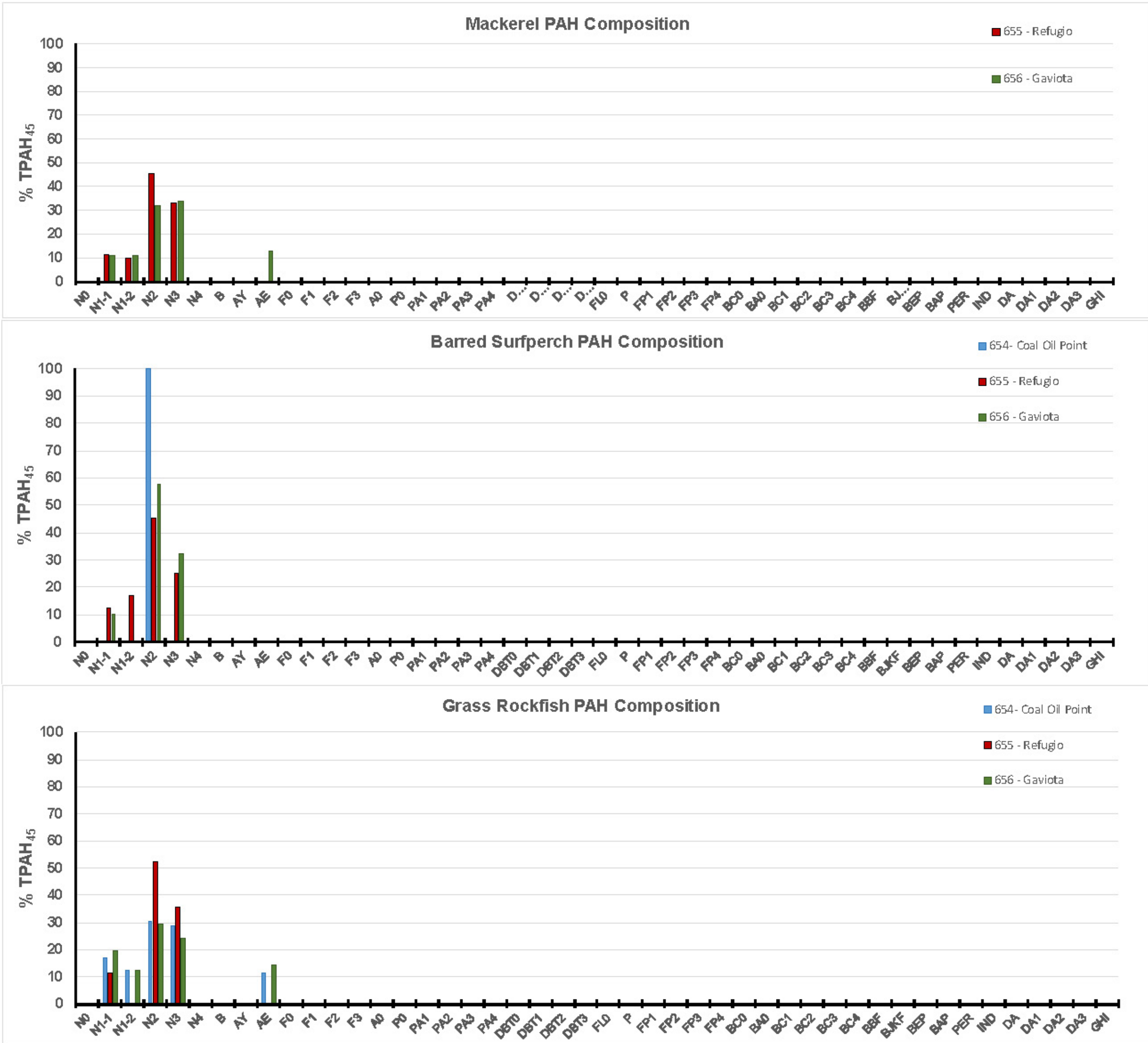

Figure 8. *Percent composition of polycyclic aromatic hydrocarbons in mackerel, barred surfperch and grass rockfish in the three fishing blocks. See Methods for PAH abbreviations.*

REFERENCES

Anulacion, B., G. Ylitalo, R. Donohoe, D. Witting. 2019. The 2015 Refugio Beach Oil Spill: Assessment of Surfperch (Embiotocidae) Exposure. Technical Report for the Damage Assessment and Restoration Plan. (Appendix G-3)

Boehm, P.D., D.S. Page, J.S. Brown, J.M. Neff, W.A. Burns. 2004. Polycyclic aromatic hydrocarbon levels in mussels from Prince William Sound, Alaska, USA, document the return to baseline conditions. Environmental Toxicology and Chemistry 23:2916-2929.

Graham, L., C. Hale, E. Maung-Douglass, S. Sempier, L. Swann, M. Wilson. 2015. Oil Spill Science: The Deepwater Horizon Oil Spill's Impact on Gulf Seafood. MASGP-15-014.

Incardona, J., G. Ylitalo, M. Myers, N. Scholz, T. Collier, C. Vines, F. Griffin, E. Smith, G. Cherr. 2011. The 2007 Cosco Busan Oil Spill: Field and Laboratory Assessment of Toxic Injury to Pacific Herring Embryos and Larvae in the San Francisco Estuary. Final Report. September. Seattle, WA.

Law, R.J., J. Hellou. 1999. Contamination of fish and shellfish following oil spill incidents. Environmental Geosciences 6:90-98.

Leet, W.S., C.M. Dewees, R. Klingbeil, E.J. Larson. 2001. California's Living Marine Resources: A Status Report. California Department of Fish and Game. University of California Agriculture and Natural Resources Publication SG01-11.

Lorensen, T.D., I. Leifer, F.L. Wong, R.J. Rosenbauer, P.L. Campbell, A. Lam, F.D. Hostettler, J. Greinert, D.P. Finlayson, E.S. Bradley, and B.P. Luyendyk. 2011. Biomarker Chemistry and Flux Quantification Methods for Natural Petroleum Seeps and Produced Oils, Offshore Southern California. U.S. Geological Survey Scientific Investigations Report 2011-5210.

Meador, J. P., J.E. Stein, W.L. Reichert, U. Varanasi.1995. Bioaccumulation of polycyclic aromatic hydrocarbons in marine organisms. Reviews of Environmental Contamination and Toxicology 143: 79-165.

Murawski S.A., W.T. Hogarth, E.B. Peebles, L. Barbeiri. 2014. Prevalence of external skin lesions and polycyclic aromatic hydrocarbon concentrations in Gulf of Mexico fishes, post-Deepwater Horizon. Transactions of the American Fisheries Society 143:1084-1097.

Office of Environmental Health Hazard Assessment. 2015. Risk Assessment of Seafood Consumption Following the Refugio Beach Oil Spill Incident in Santa Barbara County. December. Sacramento, CA.

Rumney, H.S., F. Laruelle, K. Potter, P.K. Mellor, R.J. Law. 2011. Polycyclic aromatic hydrocarbons in commercial fish and lobsters from the coastal waters of Madagascar following an oil spill in August 2009. Marine Pollution Bulletin 62:2859-2862.

Stout, S.A. 2016. Refugio Beach Oil Spill NRDA Investigation: Trustees Forensic Oil Source Analysis. NewFields Government Services, Rockland, Massachusetts. December 19.

Xia, K., G. Hagood, C. Childers, J. Atkins, B. Rogers, L. Ware, K. Armbrust, J. Jewell, D. Diaz, N. Gatian, H. Folmer. Polycyclic aromatic hydrocarbons (PAHs) in Mississippi seafood from areas affected by the Deepwater Horizon Oil Spill. Environmental Science and Technology 46:5310-5318.

Ylitalo, G. M., M. M. Krahn, W. W. Dickhoff, J. E. Stein, C. C. Walker, C. L. Lassitter, E. S. Garrett, L. L. Desfosse, K. M. Mitchell, B. T. Noble, S. Wilson, N. B. Beck, R. A. Benner, P. N. Koufopoulos, and R. W. Dickey. 2012. Federal seafood safety response to the Deepwater Horizon oil spill. Proceedings National Academy of Sciences 109:20274-20279.