D. McDermott-Ehrlich and George A. Alexander

CHEMICAL STUDIES OF OFFSHORE OIL PLATFORMS

During 1975, the Project conducted a series of field surveys of the marine life around two oil platforms, "Hazel" and "Hilda," in the Santa Barbara Channel. As described in Part 5, we found a diverse and abundant marine community on and near the platforms. As part of the effort to determine if the drilling and oil production operations at the platforms have had an effect on these organisms, we conducted chemical analyses of the nearby sediments and of the tissues of several marine animals found in the area. The methods and results of these analyses (presented in detail in Mearns and Moore 1976) are summarized here.

The platforms, which were installed in the late 1950's by Standard Oil Company, are about 2.5 km apart and located about 3 km offshore in 30 m of water (Figure 1). Each platform is about 30 m square and sits on legs of steel tubing in a pile of cuttings (rock chips and mud brought up in well drilling), which is now covered by a deep mantle of mussel and other shells from the tower. About 25 wells have been drilled from each platform, and the eight wells still in operation at Hazel and the seven at Hilda now produce around 600 barrels of oil per day.

For the Project's study, animals and sediments were collected at 14 sites within 0 to 240 m of each platform. Samples were also taken at two control sites at the same water depth, one rocky and one with a soft sandy bottom (Figure 1).

SEDIMENTS

In the Project's laboratories, sediment samples from all collection sites were analyzed for copper and zinc by Tsu-Kai Jan and for volatile solids and hexane extractable materials by Henry Schafer. The median values for these substances were similar to the average coastal background levels and well below levels in sediments contaminated by the discharge of municipal wastewaters (Table 1). In the cuttings pile immediately below the platforms, concentrations of all four materials were higher. For example, the zinc

concentration at one station under Platform Hazel was 1,500 mg/dry kg (the median of all zinc measurements taken around this platform was 61 mg/dry kg), and the hexane extractable level was 4,400 mg/dry kg (median, 665 mg/dry kg). The copper level at this station was 39 mg/kg (median, 12 mg/dry kg), and the volatile solids measurement was 5.2 percent (median, 3.9 percent) . The high zinc level was possibly the result of sediment contamination by metal flakes from the platform or by metal debris that we observed scattered under the tower. The high value for hexane extractable material may reflect oil contamination or the inclusion of small animals in the sample or a high fallout of fecal material from the biota attached to the legs of the structure.

Dr. J. Scott Warner (Battelle Laboratory, Columbus, Ohio) used three different chemical techniques to detect petroleum hydrocarbons in sediment samples taken at three stations along the eastern transect of each platform and at the soft-bottom control site; the results are given in Table 2. The infrared analysis indicated that the extractable material was primarily petroleum hydrocarbon in nature; this analysis also showed that a considerable amount of aromatic hydrocarbon was present, which explains why the infrared values were significantly lower than the gravimetric values. The agreement, however, between the infrared and gravimetric levels is quite satisfactory.

The total hydrocarbon values determined by the infrared and gravimetric methods were four to ten times higher than the gas chromatography results (Table 2). This difference is typically found when the three methods of analysis are used on samples of highly weathered oils from natural seeps; unlike the infrared and gravimetric methods, the gas chromatograph is not sensitive to asphaltenes and polar components, which are important constituents of such oils. In addition, higher molecular weight components (above carbon 35) are not detected in analysis by gas chromatography. The gas chromatographic fingerprints for the oil platform sediments showed a broad envelope with no significant individual peaks; this is also typical of a highly weathered oil and of the hydrocarbons from the sediments of Coal Oil Point, the nearby site of a natural oil seep.

MARINE ANIMALS

The tissues of marine animals collected near and away from the oil platforms were checked for metal and petroleum hydrocarbon levels. The analyses involved three species--the brown rockfish (*Sebastes auriculatus*), the white belly rockfish (*Sebastes vexillaris*) , and the yellow rock crab (*Cancer anthonyi*). Up to six specimens of each species were collected at each platform and at the rocky control station. (Predictably, these rockfishes were not present at the soft-bottom control station; however crabs were taken at this site.)

Trace Metals

Various tissues were excised from the animals and analyzed for the eleven metals listed on Table 3 at the UCLA laboratory using an optical emission spectrometric technique (described in Alexander et al., in press).

Three tissues (muscle, liver, and kidney) were excised from the rockfish. The Wilcoxon rank-sum test (a nonparametric statistical method comparable to the parametric Student-t test) was used to determine if there were any statistically significant differences in the levels of each metal in the two species. Two of the results for the 99 statistical tests run (eleven metals in three tissues of specimens from three locations) were statistically significant: Kidney tissue from brown rockfish taken near Hazel had a higher concentration of iron than kidney tissue from white belly rockfish from the same location, and kidneys of white belly rockfish from the rocky control station had higher levels of zinc than those of brown rockfish from this site. When performing 99 tests, however, one would expect up to five statistically significant differences to appear as the random result of multiple testing. We therefore concluded that there was no significant difference between the trace element levels in the two species of rockfish and combined the rockfish results for each tissue. These data appear in Table 3.

The Wilcoxon rank-sum test was again used on the rockfish data to determine if the trace metal values varied significantly with location. Five statistically significant differences (less than or equal to 0.05) were found:

- Cadmium levels were higher in the liver of rockfish from Hazel than in the livers of specimens from Hilda.
- Vanadium levels were higher in kidney tissue of fish from Hazel than in the kidneys of specimens from the rocky control site.
- The vanadium levels in the liver of fish from the platforms were significantly higher than the values for the control specimens; the vanadium values for the two platforms also differed significantly from each other, with the livers of specimens from Hazel showing the higher level.

Again, 99 statistical tests were performed, and the results observed might be expected to have occurred as a random result of multiple testing: However, four of these five results involved vanadium, and it is highly improbable that these differences occurred by chance. The source of the vanadium to the rockfish is not known, although both oil and tunicates residing on the platforms are possibilities. Some species of tunicates naturally concentrate vanadium. It is not known whether or not the species present on the platforms (*Styela montereyensis*) also concentrates this element and whether or not the platform rockfish include these tunicates in their diet.

Two tissues (muscle and gonad) were excised from the yellow rock crab and analyzed for their trace element content. These results are presented in Table 4. There were too few data points from Hilda and the rocky control to

do statistical comparisons of the values for each location sampled. The Wilcoxon rank-sum test was utilized, however, to compare trace metal levels in tissues of crabs collected from Platform Hazel and the soft-bottom control site. The results indicated that there were no statistically significant differences between the trace metal levels in gonad or muscle tissue from crabs collected at these sites.

Petroleum Hydrocarbons

Dr. Warner determined the hydrocarbon content of tissue samples by gas chromatography. The analysis revealed no detectable hydrocarbons (petroleum or biogenic) in the crabs regardless of collection site but very high levels in the rockfish (Table 5). The gas chromatographic fingerprints show no indication of any petroleum hydrocarbons in the rockfish: All of the peaks can be reasonably attributed to biogenic hydrocarbons. One component in the rockfish, tentatively identified as squalene on the basis of retention time, accounts for over one-half of the total hydrocarbon content. Squalene is a natural lip id common to many marine organisms, especially fish.

Intertidal mussels (*Mytilus californianus*) were collected from the legs of each platform for another tissue analysis by gas chromatography (Table 5). The whole soft tissues of these animals contained no detectable petroleum or biogenic hydrocarbons.

Because of the overwhelming quantity of biogenic hydrocarbons found in the rockfish, it would not be possible to detect trace amounts of petroleum hydrocarbons. As mussels are generally good accumulators of petroleum hydrocarbons, and no detectable amounts of petroleum hydrocarbons were found in the mussels, it is unlikely that the rockfish from the same site would contain significant amounts of petroleum hydrocarbons.

SUMMARY

Levels of copper, zinc, hexane extractable materials, and volatile solids in sediments around the oil platforms were similar to average coastal background levels and were well below levels observed in sediments contaminated by the largest discharges of municipal wastewaters in southern California.

The petroleum hydrocarbon content of all sediment samples collected was higher than values observed in areas with no natural seeps. The platform levels were higher than the level measured at the soft control site; however, the gas chromatographic fingerprints for all samples were indicative of highly weathered oil, indicating no recent contamination of the sediments.

Of the 11 trace elements studied, only the vanadium levels in rockfish livers varied significantly with collection site. The ecological and biological significance of this contamination is not known. However, vanadium is naturally very highly concentrated in certain marine organisms--particularly

tunicates, which employ it in blood pigments—and tunicates are present on the towers. The rockfish may derive the high vanadium from this source.

No statistically significant differences in metals were observed for yellow rock crabs collected from the oil platforms and the control sites. No detectable amount of petroleum hydrocarbons were observed in any of the animals analyzed.

REFERENCES

Alexander, G.V., D.R. Young, D.J. McDermott, M.J. Sherwood, A.J. Mearns, and O.R. Lunt. Marine organisms in the Southern California Bight as indicators of pollution. In Proceedings of the Intl. Conference on Heavy Metals in the Environment, 27-31 October 1975, Toronto, Ontario, Canada, in press.

Mearns, A.J., and M.D. Moore. 1976. Biological study of Oil Platforms Hilda and Hazel, Santa Barbara Channel, California. Final report to the Institute of Marine Resources, University of California, San Diego, Research Contract 5L-21174.

Table 1. Median values of chemical parameters measured in sediments collected from various coastal sites, 1975.

Collection Site	Volatile Solids (%)	Hexane Extractable Materials (mg/dry kg)	Copper (mg/dry kg)	Zinc (mg/dry kg)
Coastal background	3 to 5	~1,000	16	63
Oil platforms (Santa Barbara Channel)				
Hazel	3.9	665	12	61
Hilda	4.8	–	14	68
Soft Control	3.3	470	9.8	61
Santa Monica Bay, end of 7-mile outfall	40	25,600	1,000	2,000

Table 2. Hydrocarbon concentrations (mg/l) in sediments collected near oil platforms and at a soft control site, Santa Barbara Channel, spring 1975.

Station*	Type of Analysis		
	Infrared**	Gravimetric	Gas Chromatography
Hazel			
Station 1	730	1,200	125
Station 2	620	1,050	170
Station 3	630	1,230	165
Hilda			
Station 1	980	1,870	135
Station 2	1,230	1,670	165
Station 3	660	1,200	265
Soft Control	550	980	150

*Station 1 is located just under the eastern edge of each platform; Stations 2 and 3 are 30 and 60 meters east (the direction of the prevailing currents).

**Absorption at 2,920 cm^{-1}.

Table 3. Median trace element concentrations (mg/dry kg) in tissues of rockfish* collected near the oil platforms and a control site, Santa Barbara Channel, spring 1975.

	Muscle			Liver			Kidney		
Element	Hazel	Hilda	Rocky Control	Hazel	Hilda	Rocky Control	Hazel	Hilda	Rocky Control
Silver	**	**	**	0.6	0.5	0.6	0.6	0.8	0.8
Cadmium	**	0.8	2.0	2.9	1.7	2.0	2.0	0.1	2.1
Chromium	**	**	**	0.2	0.3	1.0	**	**	**
Copper	**	**	**	9.4	5.0	7.8	3.2	3.0	4.2
Iron	3.0	7.1	9.0	550	230	260	550	640	560
Molybdenum	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.2
Nickel	2.5	2.4	2.1	2.0	1.4	1.5	2.1	2.6	2.4
Lead	1.2	1.2	1.0	0.9	**	0.2	0.2	0.6	0.8
Silicon	11	6.6	5.4	9.7	5.9	8.8	6.6	10	6.0
Vanadium	1.2	1.0	0.9	1.3	0.8	0.1 0.08	1.2	1.4	0.2
Zinc	12	11	13	54	42	42	66	61	77

*Brown rockfish (*Sebastes auriculatus*) and white belly rockfish (*Sebastes vexillaris*).
**Not detected.

Table 4. Median trace element concentrations (mg/dry kg) in muscle and gonad tissues of the yellow rock crab* collected from oil platforms, and two control sites, Santa Barbara Channel, spring 1975.

	Hazel		Hilda		Rocky Control		Soft Control	
Element	Muscle	Gonad	Muscle	Gonad	Muscle	Gonad	Muscle	Gonad
Silver	3.9	3.8	1.4	3.6	1.9	1.6	3.5	6.4
Cadmium	2.1	4.7	3.0	4.8	1.8	4.3	2.5	6.0
Chromium	0.6	1.1	**	0.4	0.1	2.4	1.1	3.0
Copper	41	30	33	43	35	17	41	45
Iron	22	67	21	73	15	62	22	43
Molybdenum	0.1	0.2	0.2	0.1	0.2	0.2	0.1	0.1
Nickel	1.4	1.6	2.0	3.6	2.0	3.0	1.5	2.4
Lead	0.7	0.4	1.0	0.7	0.8	0.6	0.7	0.5
Silicon	65	12	63	9.8	46	6.2	97	9.4
Vanadium	0.6	0.5	1.0	1.1	0.7	0.3	**	0.3
Zinc	65	81	82	90	72	100	88	91

Cancer anthonyi
**Not detected

Table 5. Hydrocarbon concentrations (mg/wet kg) in tissues of marine organisms collected near the oil platforms and control sites Santa Barbara Channel, spring 1975.

Tissue	Hazel	Hilda	Rocky Control	Soft Control
White belly rockfish liver	320	270	580	–*
Brown rockfish liver	420	1,000	1,100	–
Mussel whole soft tissues	<5**	<5**	–	–
Crab muscle	<5**	<5**	<5**	<5**

*No samples obtained.
**Limit of detection.

Figure 1. Location of Oil Platforms Hazel and Hilda and control sites in the Santa Barbara Channel, California.