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ENVIRONMENTAL EFFECTS OF OFFSHORE OIL PRODUCTION: ALKANES IN THE REGION OF THE BUCCANEER OILFIELD

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SUMMARY

n-Alkanes, pristane, and phytane are among the hydrocarbons in discharged brine from production platforms in the Buccaneer oilfield. These compounds are detected in surface seawater samples, but hydrocarbons in bottom water samples are apparently of bacterial origin. Petroleum alkanes are also found in shrimp, fish, barnacles, plankton, and sediments.

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INTRODUCTION

Detailed studies have been made of the environmental effects of accidental oil spills from tankers and offshore wells¹. Little is known, however, of the possible effects of routine offshore oil production. In view of the mounting environmental concern over the proliferation of such activity, the National Marine Fisheries Service has initiated a multidisciplinary study of an established oilfield in the Northwestern Gulf of Mexico².

The Buccaneer oil field, operated by the Shell Oil Company, occupies blocks 288, 289, 295, and 296, approximately 50 km off Galveston, Texas, U.S.A. It was selected for this study because: (i) it is isolated from other active oil fields, (ii) it has been in production for about 15 years, sufficient time for the development of a dynamic climax marine community associated with the field, and (iii) there have been few reported oil spills (totaling less than 1000 l) during the history of the field.

This report is concerned with the routine discharge of alkanes from the two production platforms in the field, and the subsequent distribution of these compounds in the surrounding ecosystem.

A network of pipelines carries the gas-oil-brine mixture from satellite wells to the two production platforms. At each platform the gas is separated from the liquids, but some of the heavier components of the gas later condense. The crude oil is separated from the brine, and the polished brine is discharged into the sea. We have examined crude oil, condensate, and discharged brine samples from each of the platforms. Also reported here are data for alkanes in water, shrimp, fish, barnacles, plankton, and sediments.

EXPERIMENTAL

Materials

All organic solvents (except diethyl ether) were Mallinckrodt (St. Louis, Mo., U.S.A.) "nanograde" quality. Silica gel (60–200 mesh) for chromatography, obtained from J. T. Baker (Phillipsburgh, N.J., U.S.A.), was heated at 170° for at least 24 h before use. Hydrocarbon standards were purchased from Applied Science Labs. (State College, Pa., U.S.A.) or from Chem Service (West Chester, Pa., U.S.A.) and deuteriated hydrocarbons from Merck (Elmsford, N.Y., U.S.A.).

Samples

All of the samples described in this report were collected for us by personnel from the National Marine Fisheries Service, Gulf Fisheries Center, Galveston, Texas, U.S.A.

Use of internal standards

 $n-[^{2}H_{42}]$ Eicosane and $n-[^{2}H_{66}]$ dotriacontane were added to each sample prior to analysis so that quantitative data would not be impaired by variations in sample recovery, volume of solution injected into the gas chromatograph, or instrument parameters. The deuteriated alkanes were separated from alkanes on a conventional packed gas chromatographic (GC) column, so no mass spectrometer was required for their selective detection³.

Extraction of crude oil and condensate

Small samples $(1 \mu l, approx. 1 mg)$ of each sample were shaken with 1 ml of cyclohexane. The volumes were reduced by evaporation under nitrogen, and the concentrated solutions were fractionated by column chromatography.

Extraction of discharged brine and seawater

0.2-1.0 I was used for analysis. Hydrochloric acid was added to adjust the brine to pH 2. 100 ml of the brine were shaken with 100 ml of cyclohexane. The aqueous layer was discarded and the same 100 ml of cyclohexane were shaken with a further 100 ml of brine. This procedure was repeated until the entire brine sample had been extracted. In principle, it would have been more efficient to extract the brine sample several times with larger volumes of cyclohexane but this might have lead to greater contamination of the sample. Any possible reduction in recovery of hydrocarbons from the brine was offset by similar losses of the deuteriated hydrocarbons, so the results of the analyses were unimpaired. The extracts were reduced in volume using a Buchi-Brinkmann Rotavapor R rotating evaporator.

Extraction of shrimp and fish

Approx. 10-40 g of tissue from each animal was homogenized using a Brinkmann PT-35 Polytron power unit and a PT 20ST generator and then heated with 4 M sodium hydroxide solution (4 ml) at 90° for 2 h. The saponified material was extracted twice with 15-ml aliquots of diethyl ether and, each time, the supernatant was drawn off after centrifugation at 2000 rpm for 10 min. The combined extracts were dried over anhydrous sodium sulfate and evaporated using the Rotavapor prior to chromatography⁴.

Extraction of sediments

Approx. 100 g of sediment was transferred to a 300-ml lyophilization flask (Virtis F-121) and was freeze-dried. The dried sample was then transferred to a 45×130 mm glass extraction thimble in a modified soxhlet apparatus (Toe-Pre 807). The sample was extracted with cyclohexane (300 ml) for 6 h and the extract was reduced in volume prior to chromatography.

Extraction of barnacles

The barnacles grow in clusters, which were broken up using degreased pliers. The shells were broken open to remove the flesh, which was extracted in the same manner as for other biota.

Column chromatography

The "alkane" fraction of each extract was eluted in 40 ml of cyclohexane from a 1×20 cm silica gel column. Some lipid-rich samples, particularly biota, overloaded the column, and lipids eluted in this fraction. In such cases, indicated by a yellow coloration of the "alkane" fraction or anomalous GC peaks, column chromatography of these fractions was repeated.

Gas chromatography

GC was performed on Perkin-Elmer 3920B instruments equipped with flame ionization detectors and temperature programmers. Silanized glass columns (2 m \times 2 mm I.D.) were packed with 1% OV-1 on Supelcoport (100–120 mesh) and were programmed from 100 to 300° at 4°/min. The injector and detector temperatures were 225 and 300°, respectively.

Gas chromatography-mass spectrometry

A Hewlett-Packard 5982A instrument was used under similar conditions, except that the column temperature was limited to 270° since the instrument was equipped with a silicone membrane molecular separator. The instrument was interfaced to a Hewlett-Packard 5933A dual disc interactive data system with a Tektronix 4012 graphic display terminal and a Tektronix 4631 hard copy unit. Spectra were acquired and stored every 2 sec through a chromatogram and programs were available for a full range of data manipulation procedures.

Quality control

Strenuous efforts were made to minimize contamination of the samples, which would yield erroneous results. Periodically, "blank" analyses were performed, and washings from sample bottles before use (to check on contamination) and after use (to check on recovery) were examined.

Data archival

All analytical data have been submitted to the National Marine Fisheries Service for archival.

RESULTS AND DISCUSSION

The data selected for presentation in this report illustrate the nature of the liquid products of the oilfield and the distribution of petroleum alkanes in the vicinity of the production platforms. The analytical procedures employed were capable of routine measurement of as little as 10 ppt^{*} for individual alkanes in the 1.0-1 samples of brine or water, and 1 ppb^{*} in the 40-g samples of biota. Concentrations are reported only for those *n*-alkanes with twelve or more carbon atoms per molecule: those of lower molecular weight are too volatile to ensure quantitative recovery. Our use of the term "total alkanes" refers, therefore, only to those compounds with twelve or more carbon atoms per molecule.

Platform samples

The National Marine Fisheries Service, for the purpose of this study, has designated the two production platform as "platform A" ($28^{\circ}53.5'$ N, $94^{\circ}41.7'$ W) and "platform B" ($28^{\circ}52.0'$ N, $94^{\circ}41.8'$ W). A sample of crude oil and condensate from each platform, and 19 samples of discharged brine collected over a period of eleven months have been analyzed. Data from samples collected at platform B on July 16, 1976 are representative, and are shown in Table I.

The alkane composition of the crude oil is unremarkable, with concentration decreasing as chain length increases. The *n*-heptadecane-pristane ratio is 0.90, and the *n*-octadecane-phytane ratio is 2.44. The condensate, while containing a lower concentration of alkanes than the crude oil, contains relatively larger amounts of the lighter components. The *n*-heptadecane-pristane ratio is 1.30 and the *n*-octadecane-phytane ratio is 3.33. The difference between these ratios and those found for crude oil probably reflects the greater volatility of the C₁₇ and C₁₈ *n*-alkanes, compared with that of the C₁₉ and C₂₀ branched alkanes. Crude oil and condensate from platform. A are of similar composition.

A somewhat different distribution of *n*-alkanes was found in the discharged brine. The odd-even preference (OEP) ratio for the *n*-alkanes (1.01) was indicative of an abiogenic origin but a concentration maximum appeared at $n-C_{17}H_{36}$. The lighter *n*-alkanes were apparently subject to preferential evaporation. The *n*-heptadecanepristane ratio was 1.23, and the *n*-octadecane-phytane ratio was 3.50. Other samples of discharged brine were found to contain up to 8.8 ppm of *n*-alkanes. Our data are insufficient to determine the total hydrocarbon content of the discharged brine since (i) we are not measuring the amounts of *n*-alkanes lighter than dodecane, and (ii) it cannot be assumed that the non-alkane hydrocarbons in the crude oil are of comparable solubility to the *n*-alkanes. It has been suggested that *n*-alkane-isoprenoid alkane ratios be used to determine the origin of marine hydrocarbon pollutants⁵. Since the major source of hydrocarbon pollutants in the oilfield is the discharged brine, the *n*-heptadecane-pristane and *n*-octadecane-phytane ratios from the discharged brine would be the most appropriate to use for this purpose: there have been only a few small accidental spills of crude oil or condensate in this field.

^{*} Throughout this article the American billion (10⁹) and trillion (10¹²) are meant.

TABLE I

ANALYTICAL DATA FOR ALKANES IN SAMPLES COLLECTED FROM PLATFORM B ON JULY 16, 1976

Component	Crude oil	Condensate	Discharged brine
	(%)	(%)	(ppb)
n-C12H26	2.61	5.44	
n-C13H28	2.40	2.72	
n-C14H30	2.21	1.40	0.5
n-C15H32	2.21	0.70	3.5
n-C16H34	1.86	0.33	6.5
n-C17H36	1.37	0.13	8.0
n-C18H38	1.10	0.05	7.0
n-C19H40	1.00	0.02	6.0
n-C20H42	0.75	0.005	5.0
<i>n</i> -C ₂₁ H ₄₄	0.60		3.5
n-C22H46	0.48		3.0
$n - C_{23} H_{48}$	0.38		2.5
$n-C_{24}H_{50}$	0.29		2.0
n-C-5H52	0.24		2.0
n-C25H54	0.16		1.0
n-C27H56	0.12		1.0
<i>n</i> -C28H58	0.07		2.0
n-C29H60	0.06		1.0
n-C30H62	0.03		1.0
n-C31H64	0.025		1.0
n-C32H65	0.015		0.5
n-C33H08	0.010		0.5
n-C34H70	0.005		0.5
Pristane	1.53	0.10	6.5
Phytane	0.45	0.015	2.0
To	tal 19.98	10.91	66.5

Water samples

Hydrocarbons are sufficiently insoluble in sea water for the bulk of these pollutants to float to the air-sea interface. We have examined 43 surface water samples collected over a period of nine months by steel bucket, Nansen bottle, or glass sample jar.

The highest concentration of *n*-alkanes in water samples was found on August 31 and September 1, 1976. A sampling cruise was made from a point (28°48.3' N, 94°44.5' W) approx. 5 km southwest of the center of the oilfield to a point (28°37.4' N, 94°37.4' W) a similar distance to the northeast. Analytical data for alkanes in surface water samples at both ends of this transect are given in Table II. Lower levels (less than 5 ppb) of alkanes were found near the center of the oilfield at that time. The sample from the SW location exhibited a concentration maximum at $n-C_{19}H_{40}$, an *n*-heptadecane-pristane ratio of 1.44, and an *n*-octadecane-phytane ratio of 1.93, while the sample from the NE location exhibited a concentration maximum also at $n-C_{19}H_{40}$, an *n*-heptadecane-pristane ratio of 1.39, and an *n*-octadecane-phytane ratio of 1.94. It is apparent that the hydrocarbons in these two samples derive from the same source and that they are similar in character to those in the discharged brine from the production platforms. These data indicate that there was a relatively heavy

TABLE II

ANALYTICAL DATA (ppb) FOR ALKANES IN WATER SAMPLES COLLECTED ON AUGUST 30 AND SEPTEMBER 1, 1976

Component	20°48.3' N, 94°44.5' W		28°37.4' N, 94°37.4' W	
	Surface	Bottom	Surface	Bottom
n-C14H30			0.60	
n-C15H32	0.10	0.05	1.40	0.25
n-C16H34	0.75	0.10	2.40	0.025
n-C17H36	6.50	0.20	3.20	0.025
n-C18H38	5.80	0.20	3.30	
n-C19H40	8.20	0.40	3.80	0.04
n-C20H42	6.30	0.40	3.20	0.04
$n-C_{21}H_{44}$	3.60	0.20	1.90	0.025
n-C22H46	1.90	0.10	1.40	0.05
n-C ₂₃ H ₄₈	0.80		1.20	0.05
n-C24H50	0.40	0.10	0.90	0.05
n-C25H52	0.30	0.15	1.00	0.11
n-C26H54	0.20	0.20	0.70	0.06
n-C27H56	0,05	0.40	0.50	· 0.10
n-C28H58	0.10	0.90	0.80	0.15
n-C29H60		1.10	0.60	0.10
n-C30H62		2.00	0.50	0.12
n-C31H64	0.075	3.60	0.70	0.20
n-C32H66	0.05	3.80	0.60	0.15
n-C33H68	0.05	4.30	0.50	0.15
n-C34H70	0.075	2.70	0.20	0.10
7-C35H72	0.05	2.20	0.20	0.05
7-C36H74			0.10	0.07
Pristane	4.50	0.10	2.30	0.025
Phytane	3.00	0.15	1.70	
Total	42.80	23.35	33.70	1.72

discharge of hydrocarbons from the oilfield during August, 1976. Less than 1 ppb of alkanes remained in further surface water samples collected on September 23, 1976.

We also examined 32 bottom water samples collected by Nansen bottle during this period. Most of the bottom water samples were collected concurrently with the surface water samples. As expected, there was little evidence for petroleum alkanes in the bottom water samples: those alkanes which were found are probably of biogenic origin. Most notable, again, are the samples collected on August 31 and September 1, 1976, (Table II). At the SW location, less than 2 ppb of petroleum alkanes ($C_{15}-C_{22}$; OEP, 1.06; n-heptadecane-pristane, 2.0; n-octadecane-phytane, 1.33) were observed. In the region C_{24} - C_{35} , however, more than 21 ppb of *n*-alkanes with a concentration maximum at $n-C_{33}H_{68}$ were found. The relatively low (1.21) OEP ratio for these alkanes suggests that they are of bacterial origin⁶. Some sponges and corals also contain such alkanes with a low OEP ratio⁷, but there is no evidence for their existence at this location. In contrast, there was an almost total absence of alkanes in the bottom water sample from the NE location. Since the bottom current through the oilfield runs from NE to SW, it appears that a nutrient was released at the same time as the relatively heavy discharge of alkanes. It is possible that this nutrient is sulfur, which supports a population of hydrocarbon-producing bacteria⁶.

Fauna samples

The recognition of petroleum alkanes in fauna samples was more difficult to accomplish. Most marine animals contain endogenous hydrocarbons and, since n-heptadecane, pristane, and phytane are often particularly abundant, it is impractical to rely upon n-heptadecane-pristane and n-octadecane-phytane ratios as indicators of a petroleum origin. Moreover, the lighter n-alkanes are more volatile and more susceptible to chemical and metabolic oxidation. Thus, the problem remains of distinguishing the residual petroleum-derived alkanes from those which might be produced by bacteria. We have attempted to minimize bacterial growth by freezing the samples on board ship immediately after collection, and maintaining them in this state until they were analyzed.

The most outstanding example of petroleum contamination was for a specimen of the brown shrimp (*Penaeus aztecus*), a species of commercial significance in the Gulf of Mexico, collected on August 10, 1976, by trawling in an area just south of platform B ($28^{\circ}51-52'$ N, $94^{\circ}41-42'$ W). Data for this specimen and for an uncontaminated specimen collected the previous day in an area ($28^{\circ}56-57'$ N, $94^{\circ}38-39'$ W) approx. 10 km NE of the center of the oilfield are given in Table III. The *n*alkanes from C₂₂ to C₃₀ are apparently of petroleum origin, with a concentration maximum at C₂₄-C₂₅; the total petroleum alkane content being about 2.25 ppm. A third specimen of *P. aztecus* examined was found to be contaminated with petroleum alkanes, but none were found in three additional species of shrimp.

Component .	P. aztecus		P. porosissimus	
	Contaminated (ppb)	Control (ppb)	Muscle (ppb)	Liver (ppm)
<i>n</i> -C ₁₃ H ₂₈		20		
<i>n</i> -C ₁₄ H ₃₀		10		
n-C15H32		20	500	3.8
<i>n</i> -C ₁₆ H ₃₄		30	50	
<i>n</i> -C ₁₇ H ₃₆	33	50	250	8.6
$n-C_{18}H_{38}$		15	50	0.5
<i>n</i> -C₁9H₄0	165	10	25	
<i>n</i> -C ₂₀ H _{≠2}	17	15	25	
n-C21H44	33	10		0.5
<i>n</i> -C ₂₂ H₄₀	132	10	25	0.5
n-C ₂₃ H ₄₈	300	10	25	1.0
n-C24H50	430	10		2.3
n-C25H52	430	10	25	2.3
n-C ₂₆ H ₅₄	365	10 -	25	2.3
n-C27H56	265		25	1.0
n-C28H58	165	10		
n-C29H60	100			
n-C30H62	17			
Pristane	17	50	400	
Phytane	33	20	50	
Tot	al 2502	310	1475	22.8

TABLE III

ANALYTICAL DATA FOR ALKANES IN SHRIMP AND FISH SAMPLES

Analyses were performed on muscle and liver tissue from 20 species of fish. Data for the atlantic midshipman (*Porichthys porosissimus*) caught on August 11, 1976, by trawl in the area $28^{\circ}49-50'$ N, $94^{\circ}46-47'$ W, are given in Table III. While the muscle tissue contained 1.5 ppm of *n*-alkanes, these were apparently of biogenic origin. It seems likely, however, that the C₂₁-C₂₇ *n*-alkanes (9.9 ppm) in the liver were petroleum-derived.

The predominant organism attached to the production platforms and the well jackets is the large barnacle, *Balanus tintinnabulum*. Pristane comprises more than 60% of the alkanes in the flesh of a specimen collected from platform A, at the water surface, on September 25, 1976. It is possible that the C_{22} - C_{30} *n*-alkanes (64 ppb) in this specimen are petroleum-derived. Such compounds were found in barnacle flesh of other specimens collected at the surface on this date but were absent from surface specimens collected on January 21, 1977, and were not encountered in submerged barnacles at any time.

Several bulk zooplankton samples were analyzed. The data in Table IV are for a sample collected on December 3, 1976, in the area 28°53–54' N, 94°47–48' W. A neuston net was employed to obtain plankton from near the air-sea interface, since

TABLE IV

ANALYTICAL DATA (ppb) FOR ALKANES IN BARNACLE, PLANKTON, AND SEDIMENT SAMPLES

Component	B. tintinnabulum	Plankton	Sediment I	Sediment II
n-C12H26	17		3	
n-C13H28	24		3	5
<i>n</i> -C ₁₄ H ₃₀	30	2.0	3	2.5
n-C:5H32	110	20.0	15	6
n-C16H34	26	7.5	15	4
n-C17H36		35.0	30	10
$n - C_{18} H_{38}$	14	10.0	21	6
n-C19H40	13	7.5	9	4
$n-C_{20}H_{42}$	8	2.0	3	
<i>n</i> -C ₂₁ H ₄₄	57	2.0	63	14
$n - C_{22}H_{46}$	7	5.0	3	8
n-C23H48	10	5.0	9	20
<i>n</i> -C ₂₄ H ₅₀	10	7.5	21	62
n-C25H52	12	7.5	60	174
n-C26H54	7	7.5	72	268
n-C27H56	7	5.0	102	334
n-C ₂₈ H ₅₈	7	5.0	78	310
n-C29H60	3	2.0	114	300
n-C30H62	1	2.0	48	200
n-C31H64	7	2.0	87	174
n-C32H66	3 7	2.0	30	90
n-C33H68	7	2.0	51	74
n-C34H70		2.0	6	24
n-C35H72	•		15	14
n-C36H74				6
Pristane	680	102.0	52	14
Phytane	30	5.0		
Tota	l 1090	247.5	913	2123.5

these were most likely to be contaminated. Again, pristane was the major alkane, and there is a possibility that the C_{20} - C_{34} *n*-alkanes (58.5 ppb) are petroleum-derived. It is not known whether such alkanes are contained only in specific species or whether they are from residual seawater.

Sediment samples

Not surprisingly, a variety of alkane distributions was found in the sediment samples. Two representative profiles are given in Table IV. Sediment I, from a core sample collected on June 10, 1976, at a site 3,000 m ESE of platform A (28°52.9' N, 94°40.0' W), contains alkanes in the C_{22} - C_{35} region with a relatively high OEP ratio, indicative of a biogenic origin. Sediment II, collected two days later at a location 2,000 m W of platform A (28°53.4' N, 94°42.9' W) contains similar alkanes with no discernible odd-even preference. By analogy with the data for the shrimp samples, it seems likely that the alkanes in sediment II are petroleum-derived.

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