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ALKANES IN SURFICIAL SEDIMENTS FROM THE REGION OF THE BUCCANEER OILFIELD

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SUMMARY

Surficial** sediment samples collected from below the production platforms in the Buccaneer oilfield contain up to 25 ppm of petroleum alkanes. On one occasion, concentration gradients of fresh oil were observed below both platforms, extending at least 75 ft. (22.9 m) from the platforms. On another occasion, the oil was more weathered and dispersed. There was no clear evidence for similar profiles in the vicinity of a well jacket structure, and alkanes in sediment samples collected at distances of 0.7-11.0 km from the production platforms were mostly of recent biogenic origin.

INTRODUCTION

We have reported on a preliminary survey of the distribution of alkanes in the region of the Buccaneer oilfield¹. We have also provided results of more detailed studies of the alkanes in brine discharged from the production platforms², in seawater³, and in plankton⁴. The average quantity of alkanes in brine discharged during 1976-1977 was only 200 g per week. It appears that almost all of this material is rapidly dispersed by solution, evaporation, and currents flowing past the platforms. Thus, the concentration of alkanes in seawater and biota is usually extremely low.

It has frequently been suggested that oil may be transported to the sediment-water interface by particulate material such as fecal pellets of zooplankton. Incorporation of alkanes into sediments would render them less mobile, so that relatively high concentrations (compared with those in water) of alkanes might be anticipated in sediments. We have therefore examined surficial** sediment samples collected from various locations in the region of the oilfield to test this hypothesis and to assess the exposure of epibenthic fauna to petroleum hydrocarbons.

EXPERIMENTAL

Study area

The Buccaneer oilfield is situated approximately 50 km south of Galveston, (Texas, U.S.A.) in the northwestern Gulf of Mexico. There are 15 structures in the oilfield: two production platforms and 13 well jackets. The water depth is 18-20 m

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** Surficial = referring to sediments located at the sediment-water interface.

throughout the area. There have been only a few small oil spills during the 15-year history of the field, which is isolated from other active fields. Further details of the Buccaneer oilfield and preliminary findings resulting from other components of the interdisciplinary study (of which the present work is a part) of the area have recently been published⁵.

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 deuterated hydrocarbons from E. Merck (Elmsford, N.Y., U.S.A.).

Samples

Sediment samples collected during 1976 were obtained for us by J. B. Anderson and his colleagues (Department of Geology, Rice University, Houston, Texas, U.S.A.) during two cruises of the R.V. Gus III: June 5–6 and June 10–12. Most of the samples were collected using a 15-cm diameter coring device, while a ponar grab* was employed for the remainder. Locations from which the samples were taken are shown in Fig. 1. Station numbers assigned by the National Marine Fisheries Service (NMFS) are given to facilitate comparison with data for sedimentology and geochemistry⁵. Sediment samples were transferred to 250-ml glass jars fitted with ground-glass stoppers, and were frozen on board ship to minimize bacterial growth. They were maintained in this state until they were analyzed.

Additional samples were obtained for us by personnel from the National Marine Fisheries Service (Gulf Fisheries Center, Galveston, Texas, U.S.A.). Sediments were scooped directly into 250-ml glass jars by divers, and frozen for storage as described above.

Isolation of alkanes

Samples collected during 1976 were extracted as previously described¹. Approximately 100 g of sediment were transferred to a 300-ml lyophilization flask (Virtis F-121) and 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 by evaporation under nitrogen prior to column chromatography.

A more rapid procedure was employed for the extraction of samples collected during 1977. The sediment (approximately 150 g) was tumbled with cyclohexane (100 ml) in a 1-l glass bottle fitted with a PTFE-lined screw cap, on a modified rock polisher for 24 h. The cyclohexane solution was decanted and reduced in volume prior to column chromatography.

Analysis of alkanes

Gas chromatography (GC) was performed on Perkin-Elmer 3920B instruments equipped with flame ionization detectors and temperature programmers. The samples collected prior to October, 1977 were examined using silanized glass columns (2 m ×

* A device for collecting surficial sediment samples.

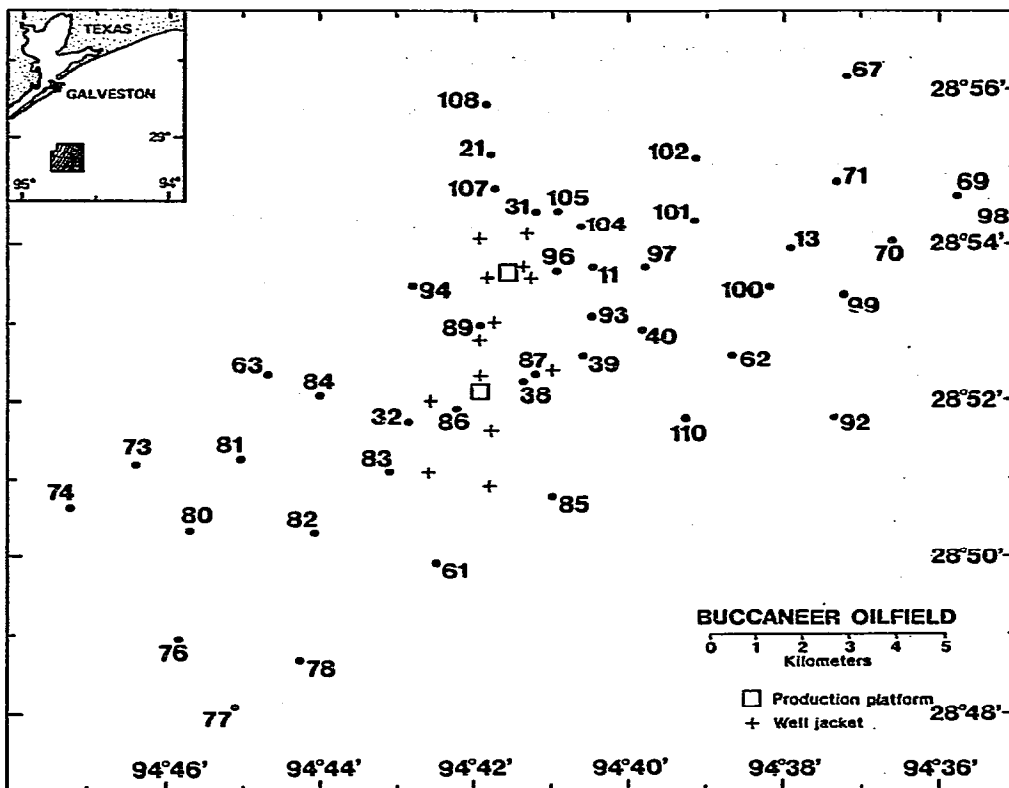


Fig. 1. NMFS station numbers for samples collected in June, 1976.

2 mm I.D.) containing 1% OV-1 on Supelcoport (100–120 mesh), programmed from 100° to 300° at 4°/min. The remaining samples were examined using a 30-m glass capillary column (purchased from Perkin-Elmer) coated with OV-101, programmed from 90° to 270° at 2°/min. The injector and detector temperatures were 250° and 300°, respectively, for all analyses.

Representative samples were also examined by combined gas chromatography–mass spectrometry (GC–MS) to verify the identities of compounds characterized by GC. A Hewlett-Packard 5982A instrument was used for samples collected during 1976. This instrument was equipped with a silicone membrane molecular separator and a 2 m × 3 mm I.D. silanized glass column containing 1% OV-1 on Supelcoport (100–120 mesh), programmed from 100° to 270° at 4°/min. The instrument was interfaced to a Hewlett-Packard 5933A dual-disc interactive data system with a Tektronics 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. A Hewlett-Packard 5992A instrument was used for samples collected during 1977. This instrument was equipped with a single-stage glass-jet molecular separator and a 1 m × 2 mm I.D. silanized glass column containing 1% OV-1 on Gas-Chrom Q (100–120 mesh) programmed from 90° to 270° at 4°/min. Spectra were acquired every 2 sec, but only those from

TABLE I
ALKANE CONCENTRATIONS (ppb) IN SAMPLES COLLECTED DURING JUNE, 1976 (SEE FIG. 1 FOR SAMPLING SITES)

Alkane	Site	11	13	21	31	32	38	39	40	61	62	63	67	69	70	71	73	74	76	77	78	80	81
<i>n</i> -C ₁₃ H ₂₈	3	4	2	8	6	8	3	3	9	5	4	4	4	4	4	4	4	4	4	4	4	4	13
<i>n</i> -C ₁₄ H ₃₀	1	95	3	3	3	3	3	3	2	2	1	1	1	1	1	1	1	1	1	1	1	1	3
<i>n</i> -C ₁₅ H ₃₂	5	4	16	5	6	13	15	5	5	3	4	3	4	3	4	8	4	4	4	4	4	4	11
<i>n</i> -C ₁₆ H ₃₄	2	2	4	5	4	13	15	5	5	3	3	3	3	2	2	8	6	6	4	4	4	4	7
<i>n</i> -C ₁₇ H ₃₆	17	33	30	22	23	12	20	30	40	25	20	16	23	9	42	10	10	14	14	14	14	14	45
<i>n</i> -C ₁₈ H ₃₈	4	2	3	10	5	4	5	21	40	5	4	2	2	3	8	6	6	6	6	4	4	4	9
<i>n</i> -C ₁₉ H ₄₀	6	5	8	8	20	4	4	10	9	10	20	7	14	7	5	8	4	4	4	5	5	5	10
<i>n</i> -C ₂₀ H ₄₂			31	4	4	4	22	3	3	10	10		5	3	2	10	3	16	5	3	3	16	14
<i>n</i> -C ₂₁ H ₄₄	5	5	2	34	4	4	22	63	10	10	10		5	3	2	10	3	16	5	3	3	16	14
<i>n</i> -C ₂₂ H ₄₆	1	1	8	4	4	2	2	3	10				1	1	1	2	2	2	2	5	1	2	2
<i>n</i> -C ₂₃ H ₄₈			9	10	2	2	2	9							1	3	3	3	3	6	6	2	2
<i>n</i> -C ₂₄ H ₅₀	1	1	25	4	4	2	2	21	20				3	2	2	2	6	3	1	9	1	2	19
<i>n</i> -C ₂₅ H ₅₂	4	4	33	18		8	5	60		4	10	4	9	4	4	12	9	8	5	16	3	4	61
<i>n</i> -C ₂₆ H ₅₄	2	3	48	12	2	6	3	72		3	12	3	12	3	3	10	10	9	4	15	2	2	78
<i>n</i> -C ₂₇ H ₅₆	6	7	38	30	5	8	10	100		6	20	8	19	6	6	16	12	14	7	17	5	8	81
<i>n</i> -C ₂₈ H ₅₈	2		59	16	10	10	8	78		2	15	3	8	2	2	13	13	13	6	16	5	8	85
<i>n</i> -C ₂₉ H ₆₀	1	9	26	54	11	12	10	110		7	5	12	13	10	4	12	18	8	16	8	16	5	50
<i>n</i> -C ₃₀ H ₆₂			48	8	2	2	48	25					7	7	6	9	9	7	2	10	2	2	23
<i>n</i> -C ₃₁ H ₆₄	8	9	17	60		12	10	87		7	5	11	10	8	4	4	12	16	9	16	6	7	23
<i>n</i> -C ₃₂ H ₆₆	2		21	10		6	5	30		5	5	5	2	8	2	10	9	6	6	9	5	5	8
<i>n</i> -C ₃₃ H ₆₈	3	3	5	36		6	5	51		3	5	5	5	3	5	4	7	7	6	9	2	3	8
<i>n</i> -C ₃₄ H ₇₀	1	1	7			4		6					1	1	1	4	4	1	2	4	4	2	2
<i>n</i> -C ₃₅ H ₇₂	3	2			3	2		15					8	2	2	3	3	3	2	3	3	3	5
<i>n</i> -C ₃₆ H ₇₄	1																						
Pristane			28					52	60														
Phytane	1		5						3														
Total		76	97	527	393	104	156	158	904	215	116	122	112	126	85	140	116	172	63	154	67	68	547

the apices of GC peaks were stored on magnetic tape. Total-ion and selected-ion chromatograms were produced in real time on a line printer, and programs were available for a full range of data manipulation procedures.

Internal standards were added to each sample prior to analysis to ensure that quantitative data would not be impaired by variations in sample recovery, volume of solution injected into the gas chromatograph, or instrument parameters. The compounds used as internal standards were n - $[^2\text{H}_{42}]$ icosane and n - $[^2\text{H}_{66}]$ dotriacontane. The deuterated alkanes were separated from alkanes even on the packed GC columns, so no mass spectrometer was required for their selective detection⁶.

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.

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

RESULTS AND DISCUSSION

Three groups of samples were collected during this study: June 5–12, 1976, December 17, 1976, and October 5, 1977. Each is discussed in turn.

Analytical data are given for n -alkanes with 13–36 carbon atoms per molecule. Those of lower molecular weight were too volatile for quantitative recovery, while no n -alkanes with more than 36 carbon atoms per molecule were detected. Pristane and phytane were the major branched alkanes in brine discharged from the production platforms², so the term "total alkanes" refers only to those compounds mentioned in this paragraph.

June, 1976 samples

A total of 44 samples was collected from locations (Fig. 1) at distances of 0.7–11.0 km from the production platforms (Tables I and II).

The total alkane content ranged from 30 ppb* (sample 97) to 3.0 ppm (sample 108).

Most of the alkanes in almost all of these samples can be recognized as having a recent biogenic origin. Notable in this category are the odd-chain C_{15} – C_{21} alkanes formed by decarboxylation of C_{16} – C_{22} even-chain fatty acids. The prominent odd-chain C_{25} – C_{35} n -alkanes in sample 40, for example, are characteristic of higher plants^{7–10}, and have frequently been reported as such in sediments from the Gulf of Mexico^{11,12} and elsewhere^{13,14}. The only alkanes which are likely to be of petroleum origin are those which occur with a range of chain lengths exhibiting a low odd–even preference (OEP) value¹⁵. Sample 108 could be considered in this category, since the C_{22} – C_{35} alkanes have an OEP value of only 1.15. Some caution is required, however, in ascribing an origin to these alkanes. A low OEP has been found for bacterial alkanes^{7,16–18} and such compounds are also produced by some corals and sponges¹⁹. Moreover, microbial action upon plant lipids has been shown to produce similar profiles¹⁸. Thus, these alkanes in the sediment sample can only tentatively be ascribed

* Throughout this article the American billion (10^9) is meant.

TABLE II
ALKANE CONCENTRATIONS (ppb) IN SAMPLES COLLECTED DURING JUNE, 1976 (SEE FIG. 1 FOR SAMPLING SITES)

Alkane	Site	82	83	84	85	86	87	88	89	92	93	94	96	97	98	99	100	101	102	104	105	107	108	110	
<i>n</i> -C ₁₃ H ₂₈					3		8	5			3	5					3	50		50		4		5	
<i>n</i> -C ₁₄ H ₃₀				1		102					3	3					1	25		22	69	4		3	
<i>n</i> -C ₁₅ H ₃₂			50	4	5	21	10				7	6	7				3	100	6	14	10	20	10	4	
<i>n</i> -C ₁₆ H ₃₄			140	5	5	11	5				8	4	5			5	2	130	8	5	10	20	21	3	
<i>n</i> -C ₁₇ H ₃₆			200	28	20	36		40		40	15	10	10	10	15	37	15	600	68	12	25	40		14	
<i>n</i> -C ₁₈ H ₃₈			140	3	5	6	3	40	3	40	3	6	3	10	5	7	4	100	24	4	5	12	5	4	
<i>n</i> -C ₁₉ H ₄₀			50	9		2					6	4	5		10	3	200	2	1	4	12	3		3	
<i>n</i> -C ₂₀ H ₄₂				1				10		10					3	3						6		2	
<i>n</i> -C ₂₁ H ₄₄	13	16		5	25	38	4	20	5	20	5	14				10	4	150	12	4	24	68	29	4	
<i>n</i> -C ₂₂ H ₄₆			20	1				10				8		10		3	1		3	3	3	4	10	1	
<i>n</i> -C ₂₃ H ₄₈			20		5	7					1	20				3	1			9	5	8	28	2	
<i>n</i> -C ₂₄ H ₅₀	3		20	1	5	9						1				3	1			2	20	6	4	96	
<i>n</i> -C ₂₅ H ₅₂	3	6	140	5	20	22	5	5	5	20	6	170	5			5	4	130	8	54	16	20	250	5	
<i>n</i> -C ₂₆ H ₅₄	3	2	25	3	30	26	3	3	3	30	7	270	3			3	3	100	10	65	16	16	370	3	
<i>n</i> -C ₂₇ H ₅₆	13	12	25	6	40	40	7				12	330	7			7	7	130	20	100	29	28	440	7	
<i>n</i> -C ₂₈ H ₅₈	13	12	100		40	31	5	20		20	4	310	4		3	13	1	130	50	86	20	4	410	1	
<i>n</i> -C ₂₉ H ₆₀	6	8	25	2	40	52	10	40	40	40	12	300	10	10	10	1	1	200	50	110	40	64	410	11	
<i>n</i> -C ₃₀ H ₆₂	6	2	25		15	22	3	20	3	20	10	200	3		3	5	5		66	11	12	300		8	
<i>n</i> -C ₃₁ H ₆₄	13	10		2	30	46	10	10	10	10	10	170	10			9	9		40	89	41	52	290	8	
<i>n</i> -C ₃₂ H ₆₆	6	6			15	15					3	90			6	2	2			31	11	4		3	
<i>n</i> -C ₃₃ H ₆₈	6	4			10	28	3		3	74	3	74	3			4	4		4	41	25		120	4	
<i>n</i> -C ₃₄ H ₇₀	3				5	5					4	24	3			1	1		10	10			48		
<i>n</i> -C ₃₅ H ₇₂	3				5	10					4	14	3			3	3		11	11	5		40	3	
<i>n</i> -C ₃₆ H ₇₄			200		5					6													60		
Pristane											20	14	12												
Phytane																									
Total		91	78	1180	76	328	541	69	210	210	137	2114	90	30	39	115	79	2070	254	807	375	458	3023	90	

a petroleum origin. Such petroleum-like profiles are also found in samples 81 (420 ppb), 73 (70 ppb), and 63 (65 ppb) and, less distinctly, in samples 40, 69, 74, 77, 86, 87, 104, and 105.

Even if these alkanes are petroleum-derived, their origin is obscure; there is no evidence to suggest that their presence in the sediments is related to activities in the Buccaneer oilfield.

The C_{14} – C_{18} *n*-alkanes from sample 101 and C_{15} – C_{19} *n*-alkanes from sample 84 are also petroleum-like. However, the pristane–*n*-heptadecane and phytane–*n*-octadecane ratios are very different from those of oil from the Buccaneer oilfield.

Some additional comments can be made concerning the biogenic hydrocarbons in the sediments:

(i) Pristane has been reported in plankton^{20,21}, fish^{22,23}, and many organisms from the region of the Buccaneer oilfield itself¹. It is also used as an indicator of petroleum pollution^{15,24,25}. Surprisingly, only eleven of the 44 sediment samples were found to contain pristane.

(ii) As previously reported²⁶, the greatest concentrations of *n*-alkanes were found to the north-east of the production platforms. This is not necessarily an indication of a greater biomass in this region of the study area, since there is great diversity in sediment texture throughout the area⁵.

(iii) Some bottom water samples from the study area have been found to contain C_{25} – C_{37} alkanes with concentration maxima around C_{33} and a low OEP value. We have suggested³ that these alkanes are derived from sulfur-utilizing bacteria¹⁶. Only one sediment sample (73) was found to contain such compounds; it also contained petroleum-like C_{22} – C_{30} alkanes.

December, 1976 samples

Our failure to find convincing evidence for petroleum alkanes in the 44 sediment samples collected during June, 1976 prompted us to examine samples collected from locations closer to the production platforms. The presence of pipelines (15 radiating from each production platform) precluded the use of coring devices or grabs for collecting these samples, which were therefore collected by divers.

Analytical data for surficial sediments collected in the vicinity of platform A (Fig. 2) are given in Table III. The platform measures 142 ft. (43.3 m) × 112 ft. (34.1 m), with the longer dimension oriented east-west. Location W is at the midpoint of the west side, below the brine discharge. Location C is below the center of the platform, and location E is at the midpoint of the east side. Locations E25, E50, and E75 are, respectively, 25, 50, and 75 ft. (7.6, 15.2, and 22.9 m) east of E. Location NE is below the northeast corner of the platform, and NE25, NE50, and NE75 are north of this point. Similarly, SE is below the southeast corner of the platform and SE25, SE50, and SE75 are south of that point. An asterisk (*) in Table III indicates that *n*-octacosane was obscured by the presence of squalene. This compound, a precursor of sterols, is present in brine discharged from the production platforms², but its presence in the sediments probably reflects an alternative source.

Fig. 3 is a chromatogram of one of these samples, from location C. There are several striking features of these data:

(i) The highest concentration of alkanes (24.5 ppm) is found below the center

TABLE III
 ALKANE CONCENTRATIONS (ppb) FOR SAMPLES COLLECTED DURING DECEMBER, 1976 IN THE IMMEDIATE VICINITY OF
 PLATFORM A (SEE TEXT FOR SAMPLING SITES)

* = *n*-Octacosane obscured by squalene.

Alkane	Site	W	C	E	E25	E50	E75	NE	NE25	NE50	NE75	SE	SE25	SE50	SE75
<i>n</i> -C ₁₃ H ₂₈		440	910			180		420		45	15				10
<i>n</i> -C ₁₄ H ₃₀		480	1400	15	15	300	3	810	30	80	30	360	260	15	40
<i>n</i> -C ₁₅ H ₃₂		600	2200	70	50	400	20	1000	50	180	60	600	440	30	25
<i>n</i> -C ₁₆ H ₃₄		640	2700	120	100	390	40	1200	60	270	85	760	520	40	35
<i>n</i> -C ₁₇ H ₃₆		800	3300	200	170	350	65	1200	80	320	130	900	530	50	60
<i>n</i> -C ₁₈ H ₃₈		900	2700	220	170	320	65	900	50	240	130	900	500	40	50
<i>n</i> -C ₁₉ H ₄₀		1200	2900	190	200	390	80	820	50	210	150	1400	650	50	50
<i>n</i> -C ₂₀ H ₄₂		1200	2300	380	180	360	70	520	30	140	100	1400	550	35	40
<i>n</i> -C ₂₁ H ₄₄		980	1400	350	150	290	60	400	30	90	60	1200	430	30	40
<i>n</i> -C ₂₂ H ₄₆		750	650	250	110	200	50	340	15	70	30	800	270	20	35
<i>n</i> -C ₂₃ H ₄₈		550	390	230	70	130	35	200	10	50	20	620	170	10	20
<i>n</i> -C ₂₄ H ₅₀		330	130	180	40	65	25	140	10	35	20	340	85	5	15
<i>n</i> -C ₂₅ H ₅₂		230	66	150	20	30	20	120	10	25	15	200	45	2	12
<i>n</i> -C ₂₆ H ₅₄		85		50	10	10	10	40		10	7	100	20	2	5
<i>n</i> -C ₂₇ H ₅₆		30		20	5	10	7	20		8	7	50	5	5	10
<i>n</i> -C ₂₈ H ₅₈		30			10		*	30		*	*	40		5	*
<i>n</i> -C ₂₉ H ₆₀					5		5	80		20	12	20		2	10
<i>n</i> -C ₃₀ H ₆₂		10						20			3				5
<i>n</i> -C ₃₁ H ₆₄															
<i>n</i> -C ₃₂ H ₆₆															
<i>n</i> -C ₃₃ H ₆₈															
<i>n</i> -C ₃₄ H ₇₀															
<i>n</i> -C ₃₅ H ₇₂															
<i>n</i> -C ₃₆ H ₇₄															
Pristane		800	3500	170	140	350	60	1500	90	230	100	1000	630	55	65
Phytane		450		100	60	100	25	460	20	95	60	440	230	20	20
Total		10505	24546	2695	1505	3875	645	10220	525	2118	1034	11130	5395	416	547

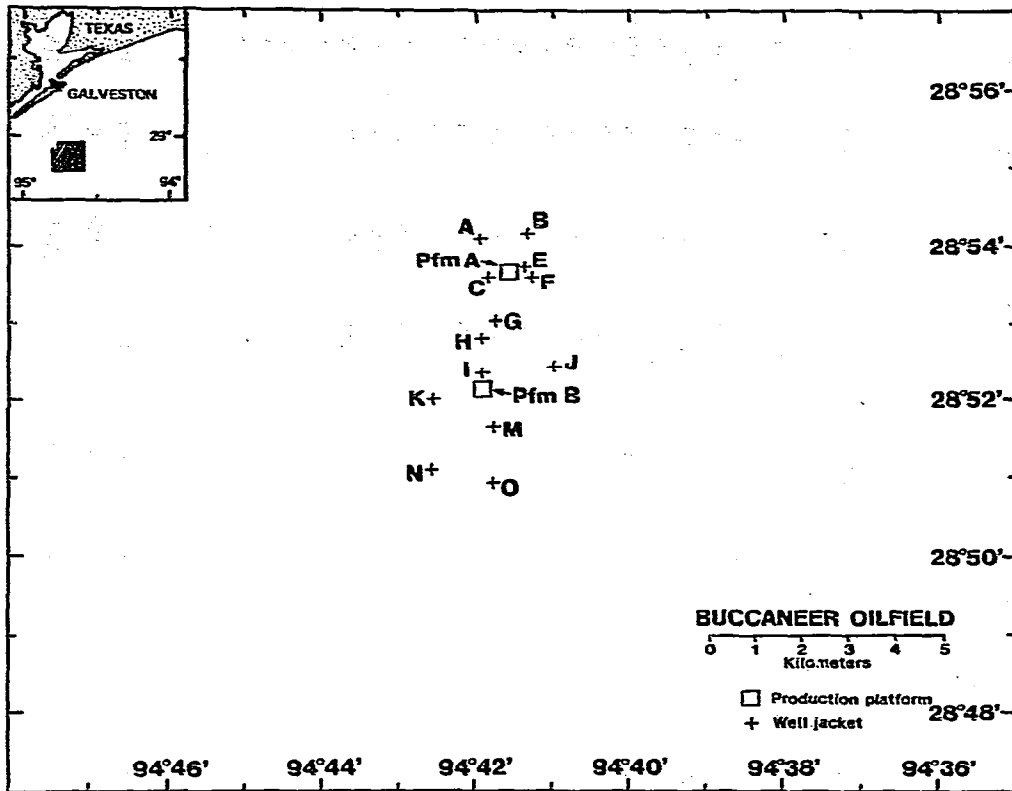


Fig. 2. Map showing locations of the production platforms and the well jackets in the Buccaneer oilfield.

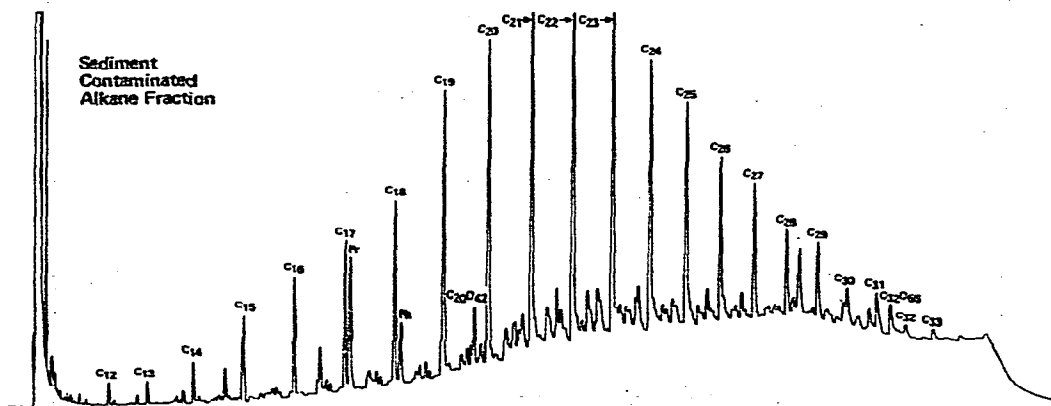


Fig. 3. Gas chromatogram for alkanes in a sediment sample collected from below the center of platform A during December, 1976. Glass capillary column (30 m) coated with OV-101, programmed from 90° to 270° at 2°/min in a Perkin-Elmer 3920B instrument. Numbering on peaks indicates chain length of *n*-alkanes. C₂₀D₄₂ and C₃₂D₆₄ are internal standards. Pr = pristane; Ph = phytane.

TABLE IV
ALKANE CONCENTRATIONS (ppb) FOR SAMPLES COLLECTED DURING DECEMBER, 1976 IN THE IMMEDIATE VICINITY OF
PLATFORM B (SEE TEXT FOR SAMPLING SITES)

* = *n*-Octacosane obscured by squalene.

Alkane	Site	W	C	E	E25	E50	E75	NE	NE25	NE50	NE75	SE	SE25	SE50	SE75
<i>n</i> -C ₁₃ H ₂₈		150	600		5	5	2	80	5	7					5
<i>n</i> -C ₁₄ H ₃₀		320	800	13	15	25	8	160	20	7		12		15	40
<i>n</i> -C ₁₅ H ₃₂		620	1800	30	40	45	12	320	35	37		70		50	80
<i>n</i> -C ₁₆ H ₃₄		870	2100	45	60	80	14	410	55	53	95	120	95	90	120
<i>n</i> -C ₁₇ H ₃₆		1100	2300	70	60	65	18	380	30	30	47	120	95	85	80
<i>n</i> -C ₁₈ H ₃₈		1000	1900	60	70	70	18	550	25	23	47	160	95	110	60
<i>n</i> -C ₁₉ H ₄₀		1100	1900	70	70	70	18	390	5	4	95	100	95	70	25
<i>n</i> -C ₂₀ H ₄₂		840	1700	75	80	50	16	300	15	16	95	150	95	110	30
<i>n</i> -C ₂₁ H ₄₄		550	700	80	70	35	16	300	7	16	95	120	95	70	30
<i>n</i> -C ₂₂ H ₄₆		200	100	40	50	20	5	200	7	16	95	90		55	10
<i>n</i> -C ₂₃ H ₄₈		160	200	30	50	10	4	120	10	16		40	47	65	5
<i>n</i> -C ₂₄ H ₅₀		40	40	25	40	10	4	60	5	18		40	95	80	5
<i>n</i> -C ₂₅ H ₅₂		30	30	30	25	10	6	40	20	26		40	95	40	5
<i>n</i> -C ₂₆ H ₅₄		10	10	30	25	10	8	10	15	26		40	95	40	5
<i>n</i> -C ₂₇ H ₅₆				13	20	5	4		15	30		25	140	25	15
<i>n</i> -C ₂₈ H ₅₈				*	10	3	2		*	23		*	140	*	*
<i>n</i> -C ₂₉ H ₆₀				15	5	3	2		3	26		15	95	10	20
<i>n</i> -C ₃₀ H ₆₂					3	5	2		3	7		5			15
<i>n</i> -C ₃₁ H ₆₄							2		3	4					15
<i>n</i> -C ₃₂ H ₆₆							2								5
<i>n</i> -C ₃₃ H ₆₈															3
<i>n</i> -C ₃₄ H ₇₀															
<i>n</i> -C ₃₅ H ₇₂															
<i>n</i> -C ₃₆ H ₇₄															
Pristane		910	2200	70	60	75	40	370	57	50	95	120	47	90	100
Phytane		460	1100	35	30	40	10	160	20	17	47	55	95	40	50
Total		8410	17400	741	753	571	193	3810	345	456	616	1322	1514	1005	718

TABLE V
ALKANE CONCENTRATIONS (ppb) FOR SAMPLES COLLECTED DURING OCTOBER, 1977 IN THE IMMEDIATE VICINITY OF
PLATFORM A (SEE TEXT FOR SAMPLING SITES)

Alkane	Site															
	W600	W300	W150	W100	W75	W50	W25	C	E25	E50	E75	E100	E150	E300	E600	
<i>n</i> -C ₁₃ H ₂₈	390		8	0		130										
<i>n</i> -C ₁₄ H ₃₀	600		11		15	32	240						1			
<i>n</i> -C ₁₅ H ₃₂	450				45	130	390						2			
<i>n</i> -C ₁₆ H ₃₄	350		10		60		500	4					3			
<i>n</i> -C ₁₇ H ₃₆	270		21		5	32	600	5	6				4			1
<i>n</i> -C ₁₈ H ₃₈	230		22		180	130	680	5	12	1		1	4			1
<i>n</i> -C ₁₉ H ₄₀	190	5	12		5	390	840	5	15	1		1	6			2
<i>n</i> -C ₂₀ H ₄₂	160	5	7		5	330	730	5	51	2		1	8			4
<i>n</i> -C ₂₁ H ₄₄	160	10	6		5	330	600	9	160	2	2	1	15			10
<i>n</i> -C ₂₂ H ₄₆	160	20	3		5	330	470	14	340	2	7	1	26			20
<i>n</i> -C ₂₃ H ₄₈	160	20	4		20	460	310	22	490	2	18	2	26			20
<i>n</i> -C ₂₄ H ₅₀	160	30	5			390	240	28	540	3	32	3	44			35
<i>n</i> -C ₂₅ H ₅₂	130	40	5			390	160	30	550	3	43	5	58			46
<i>n</i> -C ₂₆ H ₅₄	85	40	5			330	80	23	460	2	52	5	69			55
<i>n</i> -C ₂₇ H ₅₆	60	30	3			260	70	23	360	2	45	4	56			47
<i>n</i> -C ₂₈ H ₅₈	45	50	7			330	20	10	240	1	35	4	42			33
<i>n</i> -C ₂₉ H ₆₀	20	10	4			200		7	120	1	21	2	25			20
<i>n</i> -C ₃₀ H ₆₂								2	48		11	1	11			7
<i>n</i> -C ₃₁ H ₆₄									15		4		5			3
<i>n</i> -C ₃₂ H ₆₆											2		2			1
<i>n</i> -C ₃₃ H ₆₈																
<i>n</i> -C ₃₄ H ₇₀																
<i>n</i> -C ₃₅ H ₇₂																
<i>n</i> -C ₃₆ H ₇₄																
Pristane	410		12		10		400	4	4				2			
Phytane	105		10			460	280	3	3				1			
Total	4140	270	155	0	350	4654	6610	199	3418	22	272	30	380	106		285

TABLE VI

ALKANE CONCENTRATIONS (ppb) FOR SAMPLES COLLECTED DURING OCTOBER, 1977 IN THE IMMEDIATE VICINITY OF WELL JACKET B (SEE TEXT FOR SAMPLING SITES)

Alkane	Site														Total	
	W600	W300	W150	W100	W75	W50	W25	C	E25	E50	E75	E100	E150	E300		E600
<i>n</i> -C ₁₃ H ₂₈	0							0								
<i>n</i> -C ₁₄ H ₃₀																
<i>n</i> -C ₁₅ H ₃₂																
<i>n</i> -C ₁₆ H ₃₄																
<i>n</i> -C ₁₇ H ₃₆																
<i>n</i> -C ₁₈ H ₃₈																
<i>n</i> -C ₁₉ H ₄₀																
<i>n</i> -C ₂₀ H ₄₂		2														2
<i>n</i> -C ₂₁ H ₄₄		6														1
<i>n</i> -C ₂₂ H ₄₆		24														4
<i>n</i> -C ₂₃ H ₄₈		59														1
<i>n</i> -C ₂₄ H ₅₀		110														2
<i>n</i> -C ₂₅ H ₅₂		150														3
<i>n</i> -C ₂₆ H ₅₄		180														5
<i>n</i> -C ₂₇ H ₅₆		170														6
<i>n</i> -C ₂₈ H ₅₈		160														7
<i>n</i> -C ₂₉ H ₆₀		120														6
<i>n</i> -C ₃₀ H ₆₂		80														6
<i>n</i> -C ₃₁ H ₆₄		40														6
<i>n</i> -C ₃₂ H ₆₆		20														2
<i>n</i> -C ₃₃ H ₆₈		7														2
<i>n</i> -C ₃₄ H ₇₀		2														2
<i>n</i> -C ₃₅ H ₇₂																2
<i>n</i> -C ₃₆ H ₇₄																2
Pristane																
Phytane																
Total	0	1130	0	13	262	7	14	0	54	153	0	0	38	27	47	

of the platform, and the concentration of alkanes decreases with increasing distance from the platform.

(ii) The alkanes derive from Buccaneer crude oil. The pristane-*n*-heptadecane and phytane-*n*-octadecane ratios are generally those found in oil in the discharged brine².

(iii) The oil in the sediments is relatively fresh. The weathering process, which involves evaporation, solution, oxidation and metabolism, preferentially affects the lighter components of oil, so that concentration maxima shift to compounds of greater chain length as these processes proceed. The concentration maxima of oil in the sediments are comparable to those in the discharged brine².

(iv) There are still significant amounts of oil (0.55–1.03 ppm) in sediments collected at distances of 75 ft. (22.9 m) from the platform.

A similar distribution of alkanes is found in the vicinity of platform B (Table IV). The concentrations were somewhat lower than at platform A, ranging from 17.4 ppm below the center of the platform to 190–720 ppb at distances of 75 ft. (22.9 m) from the platform. Each sample, however, contained relatively fresh Buccaneer crude oil.

October, 1977 samples

Additional samples were collected from the vicinity of platform A to determine whether fresh oil could still be observed in the sediments. Analytical data for these samples are given in Table V. Fifteen samples were collected along a transect extending from a point 600 ft. (183 m) to the west of the midpoint of the western edge of the platform to a point 600 ft. (183 m) to the east of the midpoint of the eastern edge of the platform. Sample locations were numbered as for the December, 1976 samples. Thus, locations E100, E150, and E300 are, respectively, 100, 150, and 300 ft. (30.5, 45.7, and 91.4 m) east of the midpoint of the eastern edge of the platform.

The concentration of alkanes below the platform was surprisingly low, only 200 ppb. The concentration maximum at C₂₆ is indicative either of weathered petroleum or of a biogenic origin for these compounds.

The alkanes in sample W25 (6.6 ppm), however, exhibit a typical petroleum-like profile, and the pristane-*n*-heptadecane and phytane-*n*-octadecane ratios correspond to those of Buccaneer crude oil.

It is difficult to ascribe a definite origin to the alkanes in the other samples. It is relatively safe to assume that the samples from locations within 50 ft. (15.2 m) of the platform are of petroleum origin, with most of them exhibiting evidence of weathering. The alkanes in sample W600 have the appearance of relatively fresh petroleum, but the pristane and phytane content is somewhat different from that of Buccaneer crude oil.

Comparing the results obtained during December, 1976 and October, 1977, it appears that sediments may become contaminated with fresh oil, and that weathering and dispersion can ensue to distort the concentration gradients.

The fresh oil found in the sediments during December, 1976 could have been transported from the air-sea interface, but it is also possible that it entered the sediments by seepage along the outside of well pipes. Since there are no discharges from well jacket structures, sediment samples from the vicinity of such a structure were collected to determine whether they were contaminated.

Analytical data for sediment samples collected along a transect running from a point 600 ft. (183 m) west of well jacket B to a point 600 ft. (183 m) to its east are given in Table VI. There were no alkanes in the sample collected from below the structure. Only three samples (W300, W75, and E50) contained alkanes in concentrations greater than 55 ppb. There was no concentration gradient of alkanes along the transect and, while it is possible that some samples contained weathered petroleum, it is also likely that the alkanes were of biogenic origin.

A further observation concerning the distribution of alkanes in October, 1977 can be made. Samples to the west of platform A contained a mean alkane content of 2.3 ppm, whereas those to the east contained 0.6 ppm. The corresponding mean concentrations for the well jacket samples were 0.2 ppm (west) and 0.05 ppm (east). This is consistent with the observation that the prevailing bottom current through the study area runs from northeast to southwest⁵.

CONCLUSIONS

While others have found evidence for petroleum hydrocarbons in surficial sediment samples in areas where offshore oil production was taking place²⁶⁻²⁸, this is the first report of a concentration gradient of such compounds in the vicinity of offshore production platforms. On one occasion, fresh petroleum was found in the vicinity of both production platforms in the Buccaneer oilfield and, on another occasion, somewhat weathered and dispersed oil was found in the vicinity of one of these platforms.

The mode of transport of the petroleum hydrocarbons to the sediments remains obscure. Failure to find significant quantities of such compounds in the vicinity of the well jacket indicates that (at least for the wells drilled from that particular location) seepage along the well pipes does not take place. It seems more likely that the oil is transported from the air-sea interface. It has been suggested that this could be accomplished by incorporation into fecal pellets of zooplankton²⁹, and it is also possible that particulate matter (such as sulfur) in the discharged brine could play a role in this process.

Weathering of the fresh oil may proceed *via* preferential solution of the lighter components and by microbial action¹⁸. Dispersion probably takes place primarily by resuspension of the sediments into the water column. The amount of suspended particulate matter in the study area is frequently high⁵.

The area of the sea bed in the vicinity of the production platforms which is contaminated with oil is rather limited. It seems unlikely that it would pose a significant threat to bottom-feeding fauna. There is no convincing evidence for food-chain biomagnification of petroleum hydrocarbons³⁰, and depuration of contaminated animals is generally rapid³¹, so it is also unlikely that significant amounts of toxic petroleum components would accumulate in edible shrimp. Indeed, we have found that few specimens of the brown shrimp (*Penaeus aztecus*) from the Buccaneer oilfield contain petroleum alkanes¹.

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REFERENCES

- 1 B. S. Middleditch, B. Basile and E. S. Chang, *J. Chromatogr.*, 142 (1977) 777.
- 2 B. S. Middleditch, B. Basile and E. S. Chang, *Bull. Environ. Contam. Toxicol.*, in press.
- 3 B. S. Middleditch, B. Basile and E. S. Chang, *Bull. Environ. Contam. Toxicol.*, in press.
- 4 B. S. Middleditch, E. S. Chang and B. Basile, *Bull. Environ. Contam. Toxicol.*, in press.
- 5 E. F. Klima (Editor), *Environmental Assessment of an Active Oilfield in the Northwestern Gulf of Mexico, 1976-1977*, National Marine Fisheries Service, Galveston, Texas, 1977.
- 6 B. S. Middleditch and B. Basile, *Anal. Lett.*, 9 (1976) 1031.
- 7 J. Han and M. Calvin, *Proc. Nat. Acad. Sci. U.S.*, 64 (1969) 436.
- 8 D. H. Attaway, P. L. Parker and J. A. Mears, *Contrib. Mar. Sci.*, 15 (1970) 13.
- 9 J. R. Sever, T. F. Lytle and P. Haug, *Contrib. Mar. Sci.*, 16 (1972) 149.
- 10 T. F. Lytle, J. S. Lytle and P. L. Parker, *Gulf Res. Rep.*, 4 (1973) 214.
- 11 N. P. Stevens, E. E. Bray and E. D. Evans, *Bull. Amer. Ass. Petrol. Geol.*, 40 (1956) 975.
- 12 P. Gearing, J. N. Gearing, T. F. Lytle and J. S. Lytle, *Geochim. Cosmochim. Acta*, 40 (1976) 1005.
- 13 E. E. Bray and E. D. Evans, *Geochim. Cosmochim. Acta*, 22 (1961) 2.
- 14 S. J. Gaskell, R. J. Morris, G. Eglinton and S. E. Calvert, *Deep-Sea Res.*, 22 (1975) 777.
- 15 M. Ehrhardt and M. Blumer, *Environ. Pollut.*, 3 (1972) 179.
- 16 J. B. Davis, *Chem. Geol.*, 3 (1968) 155.
- 17 M. A. Rogers and C. B. Koons, in R. F. Gould (Editor), *Refining Petroleum for Chemicals*, American Chemical Society, 1970.
- 18 R. W. Johnson and J. A. Calder, *Geochim. Cosmochim. Acta*, 37 (1973) 1943.
- 19 C. B. Koons, G. W. Jamieson and L. S. Ciereszko, *Bull. Amer. Ass. Petrol. Geol.*, 49 (1965) 301.
- 20 M. Blumer and D. W. Thomas, *Science*, 147 (1965) 1148.
- 21 M. Blumer, R. R. L. Guillard and T. Chase, *Mar. Biol.*, 8 (1971) 183.
- 22 P. L. Parker, J. K. Winters and J. Morgan, in *Baseline Studies of Pollutants in the Marine Environment*, National Science Foundation, 1972.
- 23 P. R. Mackie, K. J. Whittle and R. Hardy, *Estuarine Coastal Mar. Sci.*, 2 (1974) 359.
- 24 W. Giger, M. Reinhard, C. Schaffner and W. Stumm, *Environ. Sci. Technol.*, 8 (1974) 454.
- 25 E. B. Overton, J. Bracken and J. L. Laseter, *J. Chromatogr. Sci.*, 15 (1977) 169.
- 26 D. E. Harper, Jr., R. J. Scudato and C. S. Giam, *Pilot Study of the Buccaneer Oil Field (Benthos and Sediments)*, National Marine Fisheries Service, Galveston, Texas, 1976.
- 27 *The Offshore Ecology Investigation*, Gulf Universities Research Consortium, Galveston, Texas, 1974.
- 28 R. M. Bean, J. W. Blaylock, E. A. Sutton, R. E. Wildung and F. M. Davidson, in T. F. Yen (Editor), *Chemistry of Marine Sediments*, Ann Arbor Sci. Publ., Ann Arbor, Mich., 1977, p. 39.
- 29 A. A. Nelson-Smith, *Oil Pollution and Marine Ecology*, Elek Science, London, 1972.
- 30 J. M. Teal, in D. A. Wolfe (Editor), *Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms*, Pergamon Press, Elmsford, N.Y., 1977, p. 71.
- 31 R. F. Lee, in D. A. Wolfe (Editor), *Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms*, Pergamon Press, Elmsford, N.Y., 1977, p. 60.