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Discharge of Alkanes During Offshore Oil Production in the Buccaneer Oilfield

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The adverse effects of accidental oil spills are well documented (NELSON-SMITH, 1972), yet little is known of the environmental effects of routine offshore oil production. The National Marine Fisheries Service has, therefore, initiated a multidisciplinary study of an active oilfield (the Buccaneer field) in the northwestern Gulf of Mexico. This oilfield is particularly suitable for such a study since it is isolated from other active oilfields and, during its 15 year history, less than 1,000 ℓ of crude oil has been spilled.

During normal production activity, subterranean brine is separated from the gas and crude oil and is discharged into the sea. This brine inevitably contains petroleum hydrocarbons. Many hydrocarbons, principally alkanes, are produced by marine biota. The purpose of this report is to document the types and quantities of alkanes in the discharged brine so that a realistic estimate of the environmental impact of these compounds can be made.

METHODS

Two production platforms, designated A and B by NMFS for the purpose of this study, are situated at 28°53.5'N, 94°41.7'W and 28°52.0'N, 94°41.8'W, respectively, in the Buccaneer field. Samples of discharged brine (Table 1) were collected directly in 250 ml or 1 ℓ wide-mouthed glass bottles fitted with ground glass stoppers. Samples transported by boat were frozen on board, and those transported by helicopter were frozen upon arrival at the laboratory; they were stored at -20°C to minimize bacterial growth.

Alkanes were isolated and analyzed as previously described (MIDDLEDITCH et al., 1977). n-[$^2H_{42}$]Eicosane and n-[$^2H_{66}$]dotriacontane, used as internal standards (MIDDLEDITCH and BASILE, 1976), were added to the brine samples. A cyclohexane extract was fractionated by chromatography on silica gel, the alkane fraction being eluted in cyclohexane. Gas chromatography was

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TABLE 1

Tabulation of samples of discharged brine

Sample	Date	Platform	Volume (ml)	Notes
I	4-21-76	A	200	
II	7-16-76	B	220	
III	10-30-76	B	800	
IV	12-17-76	A	950	
V	12-17-76	A	800	
VI	12-17-76	B	800	
VII	1-30-77	A	205	
VIII	1-30-77	B	165	
IX	2-1-77	A	200	
X	2-1-77	B	195	
XI	3-8-77	B	240	1300, 21°C
XII	3-8-77	B	220	1400, 21°C
XIII	3-8-77	B	236	1500, 21°C
XIV	3-8-77	B	232	1600, 21°C
XV	3-8-77	A	250	1415, 30°C
XVI	3-8-77	A	250	1515, 30°C
XVII	3-8-77	A	250	1615, 30°C
XVIII	3-8-77	A	260	1715, 30°C

performed using 6 ft x 0.25 in silanized glass columns containing 1% OV-1 on Supelcoport (100-120 mesh), programmed from 100 to 300° at 4° per min. Some samples were further analyzed by combined gas chromatography - mass spectrometry using a Hewlett-Packard 5982A instrument under similar conditions, except that the column temperature was limited to 270°.

RESULTS AND DISCUSSION

Concentrations of alkanes in 18 samples collected over a period of eleven months are tabulated in Table 2. We have not reported concentrations of alkanes lighter than dodecane since the more volatile compounds are not recovered quantitatively. The only branched alkanes observed in any appreciable concentration are pristane and phytane. The term "total alkane concentration" refers, therefore, only to those compounds listed in Table 2.

TABLE 2

Concentrations (ppb) of alkanes in discharged brine

Alkane	I	II	III	IV	V	VI
n-$C_{12}H_{26}$	259					
n-$C_{13}H_{28}$	195				11	56
n-$C_{14}H_{30}$	169	0.5		0.25	17	88
n-$C_{15}H_{32}$	153	3.5	41	0.25	19	86
n-$C_{16}H_{34}$	119	6.5	48	1	19	73
n-$C_{17}H_{36}$	91	8	61	2	17	56
n-$C_{18}H_{38}$	65	7	43	3	13	42
n-$C_{19}H_{40}$	55	6	34	2	10	32
n-$C_{20}H_{42}$	45	5	22	3	8	25
n-$C_{21}H_{44}$	37	3.5	16	0.5	5	17
n-$C_{22}H_{46}$	28	3	12	1	4	14
n-$C_{23}H_{48}$	23	2.5	8		3	10
n-$C_{24}H_{50}$	15	2	5	0.5	2	7
n-$C_{25}H_{52}$	18	2	5	0.5	2	5
n-$C_{26}H_{54}$	10	1	3	1	1.5	5
n-$C_{27}H_{56}$	10	1	2	0.25	0.5	2
n-$C_{28}H_{58}$	10	2	1			2
n-$C_{29}H_{60}$	10	1	1	0.25		1
n-$C_{30}H_{62}$	3	1	0.5	0.25	0.5	1
n-$C_{31}H_{64}$	3	1	0.5	0.25	0.25	1
n-$C_{32}H_{66}$	3	0.5	0.5	0.25	0.25	2
n-$C_{33}H_{68}$	2	0.5		0.25	1	0.5
n-$C_{34}H_{70}$	3	0.5		0.5	0.5	1
n-$C_{35}H_{72}$	2					
n-$C_{36}H_{74}$	1					
pristane	69	6.5	47	2.0	14	45
phytane	15	2	11	1.0	4	10
total	1413	66.5	436.5	20	152.5	581.5

TABLE 2 (continued)

Alkane	VII	VIII	IX	X	XI	XII
n-$C_{12}H_{26}$						1100
n-$C_{13}H_{28}$		1			2440	1100
n-$C_{14}H_{30}$	14	2		71	1470	628
n-$C_{15}H_{32}$	21	2		73	1370	596
n-$C_{16}H_{34}$	30	3	10	61	1010	460
n-$C_{17}H_{36}$	37	5	52	51	747	346
n-$C_{18}H_{38}$	34		72	37	506	237
n-$C_{19}H_{40}$	34	1	90	31	382	191
n-$C_{20}H_{42}$	25	2	80	21	266	127
n-$C_{21}H_{44}$	21		70	16	191	91
n-$C_{22}H_{46}$	17		60	13	141	73
n-$C_{23}H_{48}$	12		50	9	104	55
n-$C_{24}H_{50}$	7		40	6	66	36
n-$C_{25}H_{52}$	5		25	5	50	27
n-$C_{26}H_{54}$	3		10	3	25	14
n-$C_{27}H_{56}$			5	1	8	7
n-$C_{28}H_{58}$			2.5			
n-$C_{29}H_{60}$						
n-$C_{30}H_{62}$						
n-$C_{31}H_{64}$						
n-$C_{32}H_{66}$						
n-$C_{33}H_{68}$						
n-$C_{34}H_{70}$						
n-$C_{35}H_{72}$						
n-$C_{36}H_{74}$						
pristane	35		52	48	622	291
phytane	14	3	35	16	141	64
total	309	19	653.5	462	9539	5443

TABLE 2 (continued)

Alkane	XIII	XIV	XV	XVI	XVII	XVIII
$n\text{-}C_{12}H_{26}$		585				
$n\text{-}C_{13}H_{28}$	1250	636	8	4	50	5
$n\text{-}C_{14}H_{30}$	1070	1300	24	12	84	14
$n\text{-}C_{15}H_{32}$	638	1390	40	40	132	17
$n\text{-}C_{16}H_{34}$	485	628	64	72	136	17
$n\text{-}C_{17}H_{36}$	366	473	96	88	116	18
$n\text{-}C_{18}H_{38}$	255	344	104	68	76	14
$n\text{-}C_{19}H_{40}$	196	275	112	56	60	15
$n\text{-}C_{20}H_{42}$	132	189	96	40	40	16
$n\text{-}C_{21}H_{44}$	94	138	80	28	26	21
$n\text{-}C_{22}H_{46}$	68	103	64	20	16	26
$n\text{-}C_{23}H_{48}$	51	77	40	16	10	29
$n\text{-}C_{24}H_{50}$	34	52	24	8	5	28
$n\text{-}C_{25}H_{52}$	26	34	16	6	2	25
$n\text{-}C_{26}H_{54}$	13	17	8	2	1	18
$n\text{-}C_{27}H_{56}$	19	9				13
$n\text{-}C_{28}H_{58}$		4				9
$n\text{-}C_{29}H_{60}$						5
$n\text{-}C_{30}H_{62}$						2.5
$n\text{-}C_{31}H_{64}$						2
$n\text{-}C_{32}H_{66}$						
$n\text{-}C_{33}H_{68}$						
$n\text{-}C_{34}H_{70}$						
$n\text{-}C_{35}H_{72}$						
$n\text{-}C_{36}H_{74}$						
pristane	298	417	88	72	100	17
phytane	68	95	32	24	24	4
total	5063	6766	896	556	878	315.5

The total alkane concentration was found to range from 19 ppb (VII) to 9.5 ppm (XI). It varied appreciable, even in samples collected on the same day. Two samples (IV,V) collected from platform A on December 19, 1976, contained 20 and 153 ppb; four samples (XV-XVIII) collected from platform A on March 8, 1977, contained 315-896 ppb; and four samples (XI-XIV) collected from platform B on March 8, 1977, contained 5.1-9.5 ppm of alkanes.

Some differences in the relative concentrations of individual alkanes were observed. Some samples, such as I, contained alkanes in concentrations decreasing with increasing chain length. Others exhibited a concentration maximum between tridecane and tricosane. It is probable that, in such cases, the lighter alkanes had evaporated preferentially. Indeed, samples collected at 21°C from platform B on March 8, 1977, exhibited a concentration maximum at C_{12}-C_{15}, whereas those collected at 30°C on the same day from platform A exhibited a concentration maximum at C_{16}-C_{23}.

It has been suggested that measurements of n-alkane/isoprenoid alkane ratios be used to determine the origin of marine hydrocarbon pollutants (EHRHARDT and BLUMER, 1972). The mean n-heptadecane/pristane ratio of discharged brine from platform A was 1.1, and from platform B was 1.2. The mean n-octadecane/phytane ratios for platforms A and B were, respectively, 3.2 and 3.6.

CONCLUSIONS

We have characterized the alkane content of the discharged brine from both production platforms in the Buccaneer oilfield over a period of eleven months, from April, 1976 to March, 1977. The mean concentration of C_{12}-C_{36} alkanes was approximately 2 ppm (2 mg/ℓ). The mean rate of discharge of brine in the field is approximately 600 bbl (95,400 ℓ) per day. The mean rate of discharge of alkanes per day, therefore, is 191 g. Additional research is required to determine the rate of dispersion of these alkanes, their pool size in the vicinity of the production platforms, and their significance relative to alkanes of biogenic origin.

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