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Alkanes in Shrimp from the Buccaneer Oil Field

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The Buccaneer field area was a good shrimp ground before the initiation of oil and gas drilling activities, and it appears that it has remained productive (JACKSON 1977). The most important commercial species in the region is the brown shrimp, Penaeus aztecus. Due to the economic importance of the shrimping industry, we decided to examine the possibility that shrimp in the region of the oil field could be contaminated with petroleum hydrocarbons.

The mean rate of discharge of alkanes from the production platforms in the Buccaneer oil field is approximately 200g per day (MIDDLEDITCH et al. 1978), and these compounds are found (at concentrations up to 43ppb) at the air/sea interface in the surrounding water (MIDDLEDITCH et al. 1979a).The highest concentrations of petroleum alkanes in the region of the oil field are found in sediments below the production platforms (up to 25ppm), and these compounds can be detected at distances up to 0.1km from the production platform (MIDDLEDITCH & BASILE 1978). Since shrimp are bottom-feeders, it is possible that they could contain petroleum hydrocarbons. We have examined 36 samples of shrimp from the region of the Buccaneer oil field, eighteen of which were representatatives of the commercial species Penaeus aztecus (Table 1) and the rest were various other species: Penaeus duorarum (pink shrimp), Trachypenaeus duorarum (sugar shrimp), Squilla empusa (mantis shrimp), and Sicyonia dorsalis (chevron shrimp) (Table 2).

METHODS

Samples were collected by personnel from the National Marine Fisheries Service from various locations within the vicinity of the production platforms and their associated structures (Figure 1).

Samples were wrapped in aluminum foil and frozen immediately after collection. Internal standards for quantitation were added prior to extraction (MIDDLEDITCH & BASILE 1976), and the samples were extracted in a manner previously described for plankton (MIDDLEDITCH et al. 1979b). The tissues were homogenized, saponified by heating with sodium hydroxide, extracted with diethyl ether, dried over sodium sulfate, and reduced in volume prior to column chromatography.

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TABLE 1

Tabulation of Brown Shrimp (Penaeus aztecus)

Sample	Date	Location	Total Alkanes (ppm)
I	8-9-76	S-2	0.31
II	8-9-76	S-2	0.17
III	8-9-76	S-2	0.05
IV	8-9-76	S-2	0.04
V	8-9-76	S-2	0.39
VI	8-10-76	P-6	<0.01
VII	8-10-76	P-6	0.06
VIII	8-10-76	P-6	0.21
IX	8-10-76	P-7	2.5
X	8-10-76	P-7	0.13
XI	8-10-76	P-7	0.13
XII	8-10-76	P-7	0.12
XIII	2-16-77	P-6	0.14
XIV	10-18-77	P-6	0.72
XV	10-18-77	P-6	0.70
XVI	10-18-77	P-6	0.53
XVII	10-18-77	P-6	0.60
XVIII	3-10-78	P-7	<0.01

An alkane fraction was obtained from each extract by chromatography on a 1 x 20 cm activiated silica gel column. If the column was overloaded by lipid material, chromatography was repeated. The alkane fraction was reduced in volume to 50 to 100μL prior to analysis by GC.

Gas chromatography was performed using an instrument equipped with a 30m glass capillary column coated with OV-101, programmed from 90 to 270° at 2° per min, and a flame ionization detector. Injector and detector temperatures were, respectively, 250 and 300°.

The alkanes and deuteriated alkanes were completely separated by GC, so a mass spectrometer was not required for their detection and quantitation. To confirm the identities of individual compounds, however, some samples were examined by combined gas chromatography-mass spectrometry (GC-MS). A instrument was used under conditions similar to those employed for GC, except that a 70cm x 2mm silanized glass column containing 1% OV-1 on Supelcoport (100-200 mesh) was programmed at 4° per min.

TABLE 2

Tabulation of chevron shrimp (Sicyonia dorsalis), mantis shrimp (Squilla empusa), pink shrimp (Penaeus duorarum), and sugar shrimp Trachypenaeus similis)

Sample	Date	Location	Species	Total Alkanes (ppm)
XIX	2-16-77	P-6	P. duorarum	0.07
XX	2-16-77	P-6	P. duorarum	0.09
XXI	2-16-77	P-6	P. duorarum	<0.01
XXII	2-16-77	P-7	S. empusa	0.05
XXIII	2-16-77	P-6	S. empusa	0.30
XXIV	2-16-77	P-6	S. empusa	0.16
XXV	2-16-77	P-6	T. similis	0.11
XXVI	2-16-77	P-6	T. similis	0.23
XXVII	2-16-77	P-6	T. similis	0.53
XXVIII	10-18-77	P-6	T. similis	2.4
XXIX	10-18-77	P-6	T. similis	1.4
XXX	3-10-78	P-5	S. dorsalis	7.4
XXXI	3-10-78	P-5	T. similis	<0.01
XXXII	3-10-78	P-5	T. similis	0.23
XXXIII	3-10-78	P-5	T. similis	0.63
XXXIV	3-10-78	P-7	T. similis	0.43
XXXV	3-10-78	P-7	T. similis	0.68
XXXVI	3-10-78	P-7	T. similis	1.2

RESULTS AND DISCUSSION

Analytical data are given for n-alkanes with 12 to 36 carbon atoms per molecule. Those of lower molecular weight were too volatile for quantitative recovery, while n-alkanes with more than 36 carbon atoms per molecule were not detected. Pristane and phytane were the only branched alkanes observed. The term "total alkanes" refers only to these compounds mentioned in this paragraph.

Penaeus aztecus (brown shrimp). Only one of the five shrimp caught on August 9, 1976 at a location 10km NE of the center of the oil field contained petroleum hydrocarbons (V, 0.39ppm). The other four, collected at the same location, contained only biogenic hydrocarbons (I, 0.31ppm; II, 0.17ppm; III, 0.05ppm; IV, 0.04ppm). Figure 2 is a chromatogram for specimen IV: the large peaks are deuteriated internal standards.

Eight samples were obtained by trawling in the vicinity of the production platforms on August 10, 1976 and February 16, 1977. Two of the samples were contaminated with C_{20}-C_{30} petroleum alkanes (IX, 2.5ppm; XIII, 0.14ppm). Figure 3 is a chromatogram

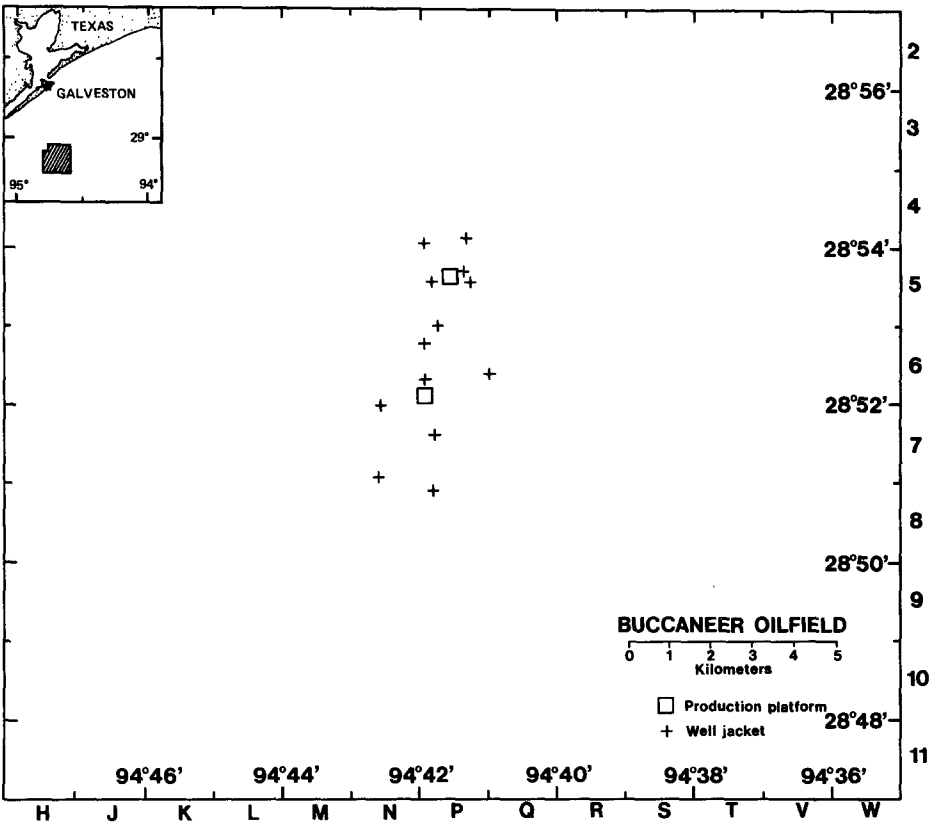

Figure 1. Structures in the Buccaneer oil field

for specimens IX: compare with Figure 2. The other six specimens collected on these dates contained hydrocarbons of biogenic origin only.

Four additional samples were obtained by trawling between the production platforms on October 18, 1977. Two of them contained C_{23}-C_{31} petroleum alkanes (XIV, 0.72ppm; XV, 0.70ppm), whereas the other two had alkane profiles dominated by C_{27}, C_{29}, and C_{31} compounds (XVI, 0.53ppm; XVII, 0.60ppm). These odd-chain alkanes are apparently of biogenic origin.

One additional specimen (XVIII), caught at a location adjacent to platform 296B on March 10, 1978, was devoid of alkanes.

Sicyonia dorsalis (chevron shrimp). The sole specimen of this species (XXX) was caught in the vicinity of platform 288A on March 10, 1978. It contained 7.4ppm of petroleum alkanes.

Squilla empusa (mantis shrimp). All three specimens were collected on February 16, 1977. They contained only biogenic alkanes (XXII, 0.05ppm; XXIII, 0.30ppm; XXIV, 0.16ppm).

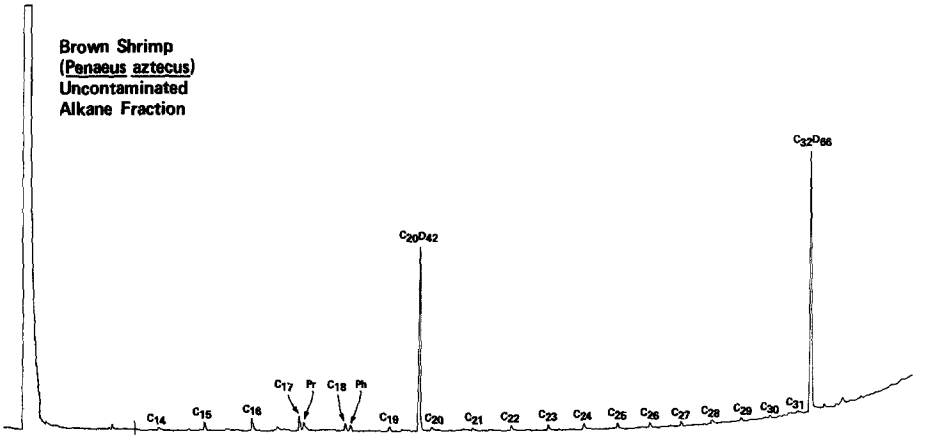

Figure 2. Chromatogram of sample IV

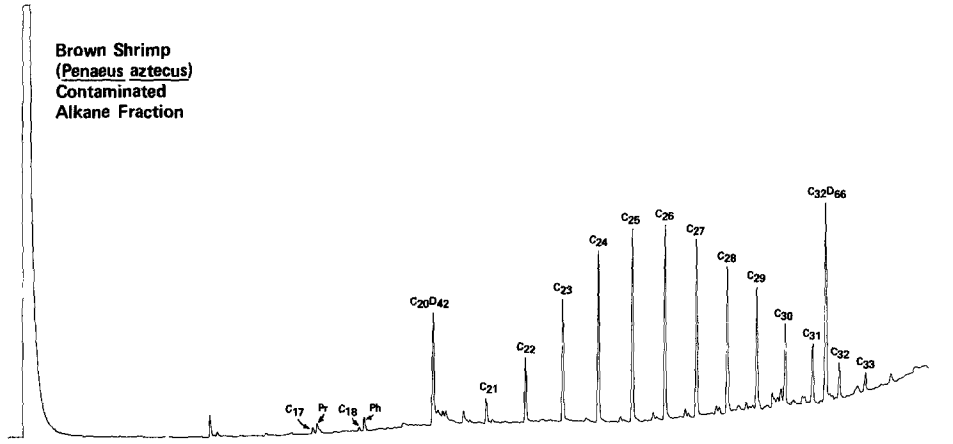

Figure 3. Chromatogram of sample IX

Penaeus duorarum (pink shrimp). The three specimens of this species were caught in the same trawl as the mantis shrimp. One specimen (XX) contained only a low concentration (0.09ppm) of petroleum alkanes, another (XIX) contained only biogenic alkanes, while the third (XXI) was devoid of alkanes.

Trachypenaeus similis (sugar shrimp). All three samples (XXV-XXVII) caught near the production platforms on February 16, 1977 contained only biogenic alkanes. However, both shrimp caught in this region on October 18, 1977 contained C_{23}-C_{31} petroleum alkanes (XXVII, 0.53ppm; XXVIII, 2.4ppm; XXIX, 1.4ppm). On March 10, 1978 three specimens were taken near platform 288A (XXXI-XXXIII) and three near platform 296B (XXXIV-XXXVI). One specimen from each location (XXXI, XXXIV) was uncontaminated, whereas the others contained C_{22}-C_{32} petroleum alkanes (XXXII, 0.23ppm; XXXIII, 0.63ppm; XXXV, 0.68ppm; XXXVI, 1.2ppm).

CONCLUSIONS

Only thirteen of the forty shrimp collected from the region of the Buccaneer oil field contained petroleum alkanes, and the majority of these were obtained from trawls immediately adjacent to the production platforms. It appears that shrimp caught in the region of the Buccaneer oil field are not appreciably tainted with hydrocarbons discharged from the production platforms.

GIAM et al. (1976) found that shrimp obtained from the Gulf of Mexico had a maximum alkane concentration at C_{31}. Four of our shrimp (XII, XIV, XVIII, XXXI) had similar hydrocarbon profiles. The other shrimp, which contained only biogenic hydrocarbons, had maximum alkane concentrations at C_{17} or C_{21}. The discrepancies in the analytical results can probably be ascribed to dietary variation.

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REFERENCES

GIAM, C. S., H. S. CHAN, & G. S. NEFF: Bull. Environ. Contam. Toxicol. 16, 37 (1976).

JACKSON, W. B. (ed). Environmental Assessment of an Active Oilfield in the Northwestern Gulf of Mexico, 1977-1978: A Report of NMFS/LGL Workshop 1, 1977-1978. National Marine Fisheries Service, Galveston, Texas.

MIDDLEDITCH, B. S., & B. BASILE: Anal. Lett. 9, 1031 (1976).

MIDDLEDITCH, B. S., B. BASILE, & E. S. Chang. Bull. Environ. Contam. Toxicol. 20, 59 (1978).

MIDDLEDITCH, B. S., & B. BASILE: J. Chrom. 158, 449 (1978).

MIDDLEDITCH, B. S., B. BASILE & E. CHANG: Bull. Environ. Contam. Toxicol. 21, 413 (1979a).

MIDDLEDITCH, B. S., B. BASILE & E. CHANG: Bull. Environ. Contam. Toxicol. 21, 421 (1979b).

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