

Alkanes in Benthic Organisms from the Buccaneer Oil Field

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We have previously reported that about 200 g per day of alkanes are present in brine discharged from each of two production platforms in the Buccaneer oil field in the NW Gulf of Mexico (MIDDLEDITCH et al. 1978). These alkanes disperse rapidly in the water column, so that seawater concentrations of petroleum alkanes in this region are generally very low (MIDDLEDITCH et al. 1979a). They can be taken up to some extent by plankton, fish, and barnacles (MIDDLEDITCH et al. 1979b,c,d), but the petroleum alkane concentrations in these organisms are also relatively low. The largest pool of petroleum alkanes is in the surficial sediments, where concentrations of up to 25 ppm are observed, with concentration gradients extending more than 20 m from the production platforms (MIDDLEDITCH & BASILE 1978). We have therefore examined organisms which are exposed to these sediments and, for comparison, other specimens from control sites around structures from which there are no discharges.

METHODS

Production platform A (Pfm A) is officially designated Galveston 288-A. Qtr A and FSt A are the associated quarters platform and flare stack, respectively. Production platform B is Galveston 296-B, and it is also accompanied by a quarters platform (Qtr B) and a flare stack. The locations of these structures and of well jacket B (Jkt B), officially designated as Galveston 288-5, are shown in Fig. 1.

Samples were collected by personnel from the National Marine Fisheries Service or LGL Ecological Research Associates (under contract to NMFS: GALLAWAY et al. 1979) either by trawl or by divers. Samples were frozen after collection to minimize decomposition and bacterial contamination.

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TABLE 1: Tabulation of samples

| Sample | Date | Location (Fig. 1) | Species | Alkanes (ppm) |
|--------|----------|----------------------|--|------------------|
| I | 2-16-77 | Pfm A | brittle worm (<u>Chloeia viridis</u>) | 1.0 |
| II | 3-2-77 | Jkt K | sea urchin (<u>Arbacia unctulata</u>) | 0.67 |
| III | 7-29-77 | Jkt B | sea urchin (<u>Arbacia unctulata</u>) | <0.01 |
| IV | 8-12-77 | Pfm A | yellow coral (<u>Alcyonaria</u>) | 5.2 |
| V | 8-12-77 | Pfm A | brown hydroid (<u>Hydroida</u>) | 36 |
| VI | 8-12-77 | Pfm A | Atlantic winged oyster (<u>Pteria colymbus</u>) | <0.01 |
| VII | 8-16-77 | Pfm A | horse conch (<u>Pleuroploea gigantea</u>) | 0.20 |
| VIII | 8-16-77 | Pfm A | brown hydroid (<u>Hydroida</u>) | 1.1 |
| IX | 8-19-77 | Jkt B | Atlantic winged oyster (<u>Pteria colymbus</u>) | <0.01 |
| X | 8-19-77 | Jkt B | yellow coral (<u>Alcyonaria</u>) | 6.4 |
| XI | 8-19-77 | Jkt B | giant eastern murex (<u>Murex fulvescens</u>) | <0.01 |
| XII | 8-19-77 | FSt A | Florida horse conch (<u>Pleuroploea gigantea</u>) | <0.01 |
| XIII | 8-19-77 | FSt A | giant eastern murex (<u>Murex fulvescens</u>) | <0.01 |
| XIV | 8-19-77 | FSt A | hermit crab (<u>Pagurus floridanus</u>) | <0.01 |
| XV | 8-19-77 | FSt A | banded tulip shell (<u>Fasciolaria hunteria</u>) | <0.01 |
| XVI | 10-19-77 | Pfm A | Atlantic winged oyster (<u>Pteria colymbus</u>) | 0.15 |

| Sample | Date | Location (Fig. 1) | Species | Alkanes (ppm) |
|--------|----------|----------------------|--|------------------|
| XVII | 10-19-77 | Pfm A | Florida horse conch (<u>Pleuroploea gigantea</u>) | <0.01 |
| XVIII | 10-19-77 | Pfm A | Florida horse conch (<u>Pleuroploea gigantea</u>) | 2.3 |
| XIX | 10-27-77 | Pfm A | yellow coral (Alcyonaria) | 0.43 |
| XX | 10-27-77 | Pfm A | Atlantic winged oyster (<u>Pteria colymbus</u>) | <0.01 |
| XXI | 10-27-77 | Pfm A | brown hydroid (Hydroida) | 1.2 |
| XXII | 10-27-77 | Pfm A | Atlantic winged oyster (<u>Pteria colymbus</u>) | <0.01 |
| XXIII | 10-27-77 | Qtr A | yellow coral (Alcyonaria) | <0.01 |
| XXIV | 10-27-77 | Qtr A | brown hydroid (Hydroida) | 6.7 |
| XXV | 10-27-77 | Qtr A | Florida horse conch (<u>Pleuroploea gigantea</u>) | <0.01 |
| XXVI | 10-28-77 | Jkt B | yellow coral (Alcyonaria) | 3.1 |
| XXVII | 10-28-77 | Jkt B | brown hydroid (Hydroida) | 15 |
| XXVIII | 10-28-77 | Jkt B | Florida horse conch (<u>Pleuroploea gigantea</u>) | <0.01 |
| XXIX | 2-2-78 | Pfm B | Florida horse conch (<u>Pleuroploea gigantea</u>) | 0.10 |
| XXX | 2-2-78 | Pfm B | Florida horse conch (<u>Pleuroploea gigantea</u>) | 0.23 |
| XXXI | 2-2-78 | Pfm B | brown hydroid (Hydroida) | 4.2 |
| XXXII | 2-2-78 | Pfm B | brown hydroid (Hydroida) | 4.9 |

| Sample | Date | Location (Fig. 1) | Species | Alkanes (ppm) |
|---------|---------|----------------------|--|------------------|
| XXXIII | 2-2-78 | Pfm B | sea urchin (<u>Arbacia unctulata</u>) | 2.4 |
| XXXIV | 2-2-78 | Pfm B | yellow coral (Alcyonaria) | 3.6 |
| XXXV | 2-28-78 | Pfm B | Atlantic winged oyster (<u>Pteria colymbis</u>) | 0.42 |
| XXXVI | 2-28-78 | Pfm B | Atlantic winged oyster (<u>Pteria colymbus</u>) | <0.01 |
| XXXVII | 2-22-78 | Qtr B | Florida horse conch (<u>Pleuroploea gigantea</u>) | 0.22 |
| XXXVIII | 2-28-78 | Qtr B | Florida horse conch (<u>Pleuroploea gigantea</u>) | 4.6 |
| XXXIX | 2-28-78 | Qtr B | bushy hydroid (Hydroida) | 3.4 |
| XL | 2-28-78 | Qtr B | brown hydroid (Hydroida) | 10 |
| XLI | 2-28-78 | Qtr B | giant eastern murex (<u>Murex fulvescens</u>) | <0.01 |
| XLII | 3-10-78 | Jkt B | Florida horse conch (<u>Pleuroploea gigantea</u>) | <0.01 |
| XLIII | 3-10-78 | Jkt B | Florida horse conch (<u>Pleuroploea gigantea</u>) | 8.2 |
| XLIV | 3-10-78 | Jkt B | Atlantic winged oyster (<u>Pteria colymbus</u>) | 2.9 |
| XLV | 3-10-78 | Jkt B | Atlantic winged oyster (<u>Pteria colymbus</u>) | 2.7 |
| XLVI | 3-10-78 | Jkt B | sea urchin (<u>Arbacia unctulata</u>) | 1.7 |
| XLVII | 3-10-78 | Jkt B | yellow coral (Alcyonaria) | 3.0 |
| XLVIII | 3-10-78 | Jkt B | giant eastern murex (<u>Murex fulvescens</u>) | <0.01 |

In the laboratory, mollusc samples were removed from their shells and the muscle dissected with a degreased scalpel and scissors. Hydroid and alcyonaria samples were cut into small pieces with degreased scissors. Internal standards were added for quantitation (MIDDLEDITCH & BASILE 1976), and samples were extracted as previously described for plankton (MIDDLEDITCH et al. 1979b). The tissues were homogenized, saponified by heating with sodium hydroxide, extracted with diethyl ether, and dried over sodium sulfate. Alkane fractions were obtained by column chromatography on silica gel. Quantitative analyses were performed by gas chromatography using 30 m glass capillary columns coated with OV-101 programmed from 90 to 270° at 2° per min. Identities of individual components were confirmed using a gas chromatograph-mass spectrometer.

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 none with more than 36 carbon atoms per molecule was detected. Pristane and phytane were the only branched alkanes observed. The term "total alkanes" refers to the sum of these alkanes.

Yellow coral (Alcyonaria). Samples obtained near the production platforms (IV, 5.2 ppm; XIX, 0.43 ppm; XXXIV, 3.6 ppm) all had similar alkane profiles. C₂₂ to C₃₂ alkanes were present with low odd-even preference (OEP) ratios (1.0-1.2), and concentration maxima were at C₂₆. The sample collected from a quarters platform (XXIII) contained no alkanes. Samples from the vicinity of the well jacket (X, 6.4 ppm; XXVI, 3.1 ppm; XLVII, 3.0 ppm) had alkane profiles similar to those from the production platforms, with OEP ratios of 0.99-1.2. OEP values near unity are normally indicative of a petroleum origin. However, KOONS et al. (1965) have reported that the biogenic alkanes in Coelenterata (horny coral) have low OEP values. Moreover, since the samples from all locations in the oil field have similar profiles, it can be concluded that these alkanes are of biogenic origin.

Brown hydroid (Hydroida). Five samples (V, 36 ppm; VIII, 1.1 ppm; XXI, 1.2 ppm; XXXI, 4.2 ppm; XXXII, 4.9 ppm) were collected from the production platforms. They contained C₂₆ to C₃₁ alkanes, with concentration maxima around C₂₈ and OEP ratios of 0.83-1.5. Two samples (XXIV, 6.7 ppm; XL, 10.3 ppm) from the

quarters platforms had similar profiles, with OEP ratios of 0.83 and 1.1. The sample from a well jacket (XXVII, 15 ppm) had an OEP ratio of 1.2. By analogy with the yellow coral, these were probably all biogenic alkanes.

Bushy hydroid (Hydroida). The sample from quarters platform B (XXXIX, 3.4 ppm) contained alkanes which could also be ascribed a biogenic origin.

Atlantic winged oyster (Pteria colymbus). Six specimens were obtained from the production platforms. Only two (XVI, 0.15 ppm; XXXV, 0.42 ppm) contained alkanes. These were in the region C_{23} to C_{31} and were petroleum-like with OEP ratios of 1.3 and 1.8. The other four samples (VI, XX, XXII, XXXVI) contained no alkanes. Three samples from the well jacket (IX, <0.1 ppm; XLIV, 2.9 ppm; XLV, 2.7 ppm) were analyzed. XLIV was dominated by the C_{21} alkane (of biogenic origin), but both samples with alkanes contained those in the C_{21} to C_{30} range with a low OEP ratios and concentration maxima at C_{26} . It is probable that samples XVI, XXXV, XLIV, and XLV contained petroleum alkanes.

Florida horse conch (Pleuroploea gigantea). Five specimens were obtained from production platforms (VII, 0.20 ppm; XVII, <0.1 ppm; XVIII, 2.3 ppm; XXIX, 0.10 ppm; XXX, 0.23 ppm), but only one (XXX) contained C_{24} to C_{31} petroleum alkanes. Samples XXXVII (0.22 ppm) and XXXVIII (4.6 ppm) from the quarters platforms both contained C_{23} to C_{31} alkanes with OEP ratios of 1.0 and 1.1, respectively. Sample XXV from the same location contained no alkanes. Sample XLIII from the well jacket contained 8.2 ppm of alkanes, but these were dominated by the biogenic C_{17} (61%) and C_{21} (20%) alkanes. Samples XXVIII and XLII from the well jacket and sample XII from flare stack A contained no alkanes. Thus, samples XXX, XXXVII, and XXXVIII contained petroleum alkanes, while the others did not.

Sea urchin (Arbacia unctulata). These specimens contained only biogenic hydrocarbons. The sample from production platform B (XXXIII, 2.4 ppm) and one sample from the well jacket (II, 0.67 ppm) were dominated by C_{19} and C_{21} alkanes. A second sample from the well jacket (XVII, 1.7 ppm) contained mainly the C_{21} alkane, while a third sample from this location was devoid of alkanes.

Brittle worm (Chloeia viridis). This sample (I, 1.0 ppm) contained C_{20} to C_{22} alkanes. Their origin is obscure.

Giant eastern murex (Murex fulvescens). None of these samples (XI, XIII, XLI, XLVIII) contained alkanes.

Hermit crab (Pagurus floridanus). This specimen (XIV) did not contain alkanes.

Banded tulip shell (Fasciolaria hunteria). This specimen (XV) did not contain alkanes.

CONCLUSIONS

Alkane profiles of 48 benthic organisms from the Buccaneer oil field are reported. Coral samples contained biogenic alkanes in the C₂₂ to C₃₂ region (KOONS et al. 1965). Hydroid specimens exhibited similar profiles which were also ascribed a biogenic origin. Samples of one species of mollusc, Pleuroploea gigantea, from the production and quarters platforms contained petroleum alkanes, while corresponding samples from the well jacket did not contain these compounds. Some specimens of another mollusc, Pteria colymbus, contained petroleum hydrocarbons, while there was no evidence for petroleum hydrocarbons in any of the other species examined: Arbacia unctulata, Chloeia viridis, Murex fulvescens, Pagurus floridanus, and Fasciolaria hunteria.

Molluscs have been shown to sequester petroleum hydrocarbons after long periods of exposure (LEE et al. 1972). In the present study, however, petroleum alkanes were found only in Pleuroploea gigantea and Pteria colymbus, but even in these organisms such hydrocarbons were generally present in concentrations lower than those of the biogenic hydrocarbons.

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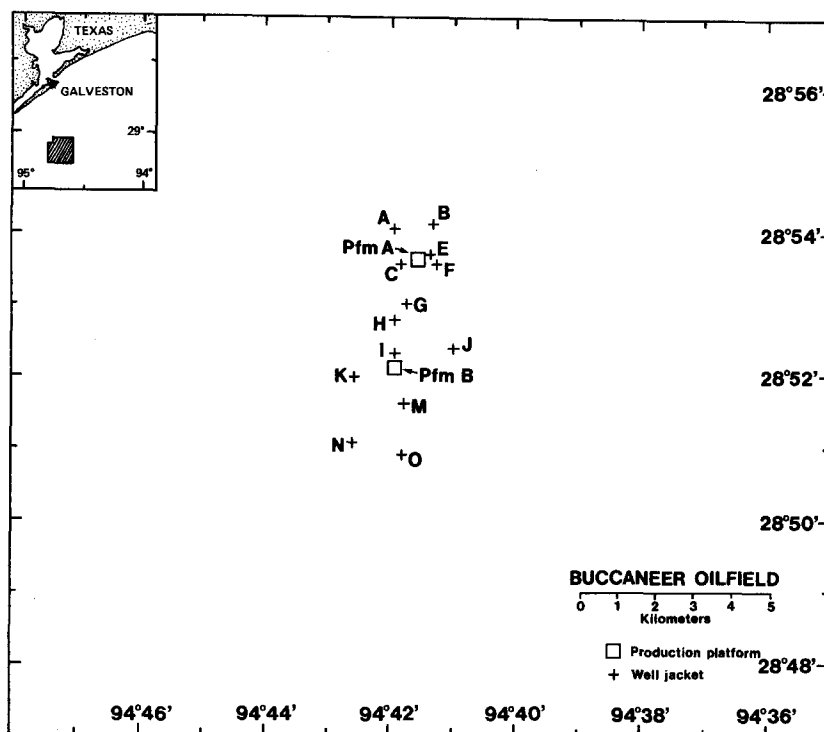


Figure 1. Production platforms and well jackets in the Buccaneer oil field. Quarters platforms and flare stacks are adjacent to the production platforms.