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Alkanes in Seawater in the Vicinity of the Buccaneer Oilfield

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As part of an interdisciplinary multiinstitutional study, performed under the aegis of the National Marine Fisheries Service (NMFS), we are investigating the distribution of petroleum hydrocarbons in the vicinity of the Buccaneer oilfield: an active, isolated oilfield in the northwestern Gulf of Mexico which has experienced only a few minor oil spills in the 15 years of its existence. We have reported that the mean rate of discharge of petroleum alkanes from each of the two production platforms in the oilfield is less than 200 g per day (MIDDLEDITCH et al. 1978). We now present data for hydrocarbons in seawater in the region of the Buccaneer oilfield. 76 water samples were collected at locations up to 20 km from the center of the oilfield, between June, 1976 and March, 1977. Alkanes were extracted from the water samples by shaking with cyclohexane and were separated from other hydrocarbons by chromatography on silica gel. Quantitation was effected by gas chromatography (GC), while combined gas chromatography - mass spectrometry (GC-MS) was used to verify the identities of individual components of about 10% of the samples.

MATERIALS AND METHODS

Materials

All organic solvents were "nanograde" quality. Silica gel (60-200 mesh) for chromatography was heated at 170° for 24 hr or more prior to use.

Samples

The samples analyzed are listed in Table 1. The two production platforms, designated A and B by NMFS for the purpose of this study, are located at 28°53.5' N, 94°41.7' W, and 28°52.0' N, 94°41.8' W, respectively. All of the samples were collected for us by NMFS personnel. With the exception of sample III, the bottom water samples were collected by nansen bottle; the water depth is about 20 m throughout the study area. Some surface water samples were also collected by nansen bottle. Others were collected using a stainless steel bucket or glass bottles. Samples obtained by divers were collected in glass bottles. Surface water samples were collected from the bow of the boat to

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TABLE 1

Tabulation of water samples analyzed

Sample	Location	Depth	Collection Method	Total Alkanes(ppb)
I	28°53.5'N, 94°41.7'W	surface	diver	12.9
II	28°53.5'N, 94°41.7'W	mid-depth	diver	3.54
III	28°53.5'N, 94°41.7'W	bottom	diver	5.44
IV	28°54.3'N, 94°41.0'W	surface	bucket	5.03
V	28°55.6'N, 94°42.0'W	bottom	nansen	1.85
VI	28°54.0'N, 94°36.8'W	bottom	nansen	1.05
VII	28°48.9'N, 94°45.9'W	bottom	nansen	0.70
VIII	28°53.5'N, 94°41.5'W	surface	bucket	2.26
IX	28°53.5'N, 94°41.5'W	bottom	nansen	14.4
X	28°54.0'N, 94°41.2'W	surface	bucket	24.8
XI	28°54.1'N, 94°40.8'W	surface	bucket	1.21
XII	28°54.1'N, 94°40.8'W	bottom	nansen	10.5
XIII	28°48.3'N, 94°44.5'W	surface	bucket	42.8
XIV	28°48.3'N, 94°44.5'W	bottom	nansen	23.4
XV	28°49.8'N, 94°43.4'W	surface	bucket	22.7
XVI	28°49.8'N, 94°43.4'W	bottom	nansen	7.90
XVII	28°50.5'N, 94°42.5'W	surface	bucket	7.50
XVIII	28°50.5'N, 94°42.5'W	bottom	nansen	8.95
XIX	28°51.3'N, 94°42.3'W	surface	bucket	16.0
XX	28°51.3'N, 94°42.3'W	bottom	nansen	14.4
XXI	28°52.2'N, 94°41.4'W	surface	bucket	5.25
XXII	28°52.2'N, 94°41.4'W	bottom	nansen	17.8
XXIII	28°52.7'N, 94°41.5'w	surface	bucket	7.65
XXIV	28°52.7'N, 94°41.5'W	bottom	nansen	1.40
XXV	28°53.4'N, 94°41.1'W	surface	bucket	10.8
XXVI	28°53.4'N, 94°41.1'W	bottom	nansen	1.45
XXVII	28°54.3'N, 94°40.0'W	surface	bucket	6.50
XXVIII	28°54.3'N, 94°40.0'W	bottom	nansen	5.30
XXIX	28°55.2'N, 94°40.1'W	surface	bucket	6.95
XXX	28°55.2'N, 94°40.1'W	bottom	nansen	3.40
XXXI	28°56.0'N, 94°38.9'W	surface	bucket	19.4
XXXII	28°56.0'N, 94°38.9'W	bottom	nansen	3.90
XXXIII	28°57.4'N, 94°37.4'W	surface	bucket	33.7
XXXIV	28°57.4'N, 94°37.4'W	bottom	nansen	1.72
XXXV	29°00.0'N, 94°50.0'W	surface	bucket	0.15
XXXVI	29°00.0'N, 94°50.0'W	bottom	nansen	0.60
XXXVII	28°52.4'N, 94°41.6'W	surface	bucket	0.63
XXXVIII	28°52.4'N, 94°41.6'W	bottom	nansen	0
XXXIX	28°55.2'N, 94°37.4'W	surface	bucket	0.30
XL	28°55.2'N, 94°37.4'W	bottom	nansen	0.22
XLI	28°49.2'N, 94°46.1'W	surface	bucket	0.47
XLII	28°49.2'N, 94°46.1'W	bottom	nansen	0.23
XLIII	28°44.0'N, 94°35.0'W	surface	bucket	0.21
XLIV	28°44.0'N, 94°35.0'W	bottom	nansen	0.68
XLV	28°55.9'N, 94°45.5'W	surface	nansen	4.60
XLVI	28°55.9'N, 94°45.5'W	bottom	nansen	0
XLVII	28°48.7'N, 94°38.5'W	surface	nansen	0.80

Sample	Location	Depth	Collection Method	Total Alkanes(ppb)
XLVIII	28°48.7'N, 94°38.5'W	bottom	nansen	1.13
XLIX	28°55.2'N, 94°37.4'W	surface	nansen	2.46
L	28°55.2'N, 94°37.4'W	bottom	nansen	0.95
LI	28°49.2'N, 94°46.1'W	surface	nansen	0
LII	28°49.2'N, 94°46.1'W	bottom	nansen	0
LIII	28°52.9'N, 94°42.6'W	surface	nansen	0
LIV	28°52.9'N, 94°42.6'W	bottom	nansen	0
LV	28°51.4'N, 94°41.1'W	surface	nansen	0
LVI	28°51.4'N, 94°41.1'W	bottom	nansen	0
LVII	28°52.8'N, 94°41.0'W	surface	nansen	0.70
LVIII	28°51.4'N, 94°42.7'W	surface	nansen	11.8
LIX	28°51.4'N, 94°42.7'W	bottom	nansen	0
LX	28°53.7'N, 94°41.6'W	surface	bottle	2.85
LXI	28°53.4'N, 94°41.7'W	surface	bottle	2.35
LXII	28°52.9'N, 94°41.8'W	surface	bottle	3.00
LXIII	28°52.2'N, 94°41.8'W	surface	bottle	4.97
LXIV	28°51.9'N, 94°41.9'W	surface	bottle	0.95
LXV	28°53.0'N, 94°42.7'W	surface	bottle	3.40
LXVI	28°53.0'N, 94°42.1'W	surface	bottle	3.10
LXVII	28°52.9'N, 94°41.2'W	surface	bottle	1.10
LXVIII	28°52.8'N, 94°40.7'W	surface	bottle	4.35
LXIX	28°55.2'N, 94°37.4'W	surface	bucket	1.80
LXX	28°55.2'N, 94°37.4'W	bottom	nansen	1.50
LXXI	28°52.4'N, 94°41.6'W	surface	bucket	0
LXXII	28°52.4'N, 94°41.6'W	bottom	nansen	4.80
LXXIII	28°49.2'N, 94°46.1'W	surface	bucket	0.70
LXXIV	28°49.2'N, 94°46.1'W	bottom	nansen	1.10
LXXV	28°51.1'N, 94°42.5'W	surface	diver	0.33
LXXVI	28°52.0'N, 94°41.8'W	surface	diver	0.18

minimize contamination. All of the samples were frozen in glass bottles (with ground glass stoppers) on board ship and were maintained in this state until they were analyzed.

Extraction

The frozen samples were thawed in a refrigerator n-[$^{2}H_{42}$]-Eicosane and n-[$^{2}H_{66}$]dotriacontane, employed as internal standards, were added to the bottles (MIDDLEDITCH and BASILE 1976). Hydrochloric acid was used to adjust the water to pH 2. Hydrocarbons were extracted by shaking with cyclohexane, and the extract was reduced in volume to 1 ml using a Buchi/Brinkman Rotavapor R rotating evaporator. An alkane fraction was eluted in 40 ml of cyclohexane from a 1 x 20 cm column of silica gel. The eluate was reduced in volume, first using the rotating evaporator and then under a nitrogen stream on a hot plate, to 50-100 µl. Aliquots (4 µl) were examined by GC or GC-MS.

Analysis

Gas chromatography was performed using Perkin-Elmer 3920B instruments equipped with flame ionization detectors and 2 m x 6 mm silanized glass columns containing 1% OV-1 on Supelcoport (100-120 mesh), programmed from 100 to 300° at 4° per min. The injector and detector temperatures were 225 and 300°, respectively.

For GC-MS, 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.

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 NMFS for archival.

RESULTS AND DISCUSSION

Concentrations were determined only for those alkanes with molecular weights greater than that of dodecane, since the lighter compounds were too volatile to be recovered quantitatively. The only branched saturated alkanes encountered were pristane and phytane. The term "total alkanes," therefore, refers only to these compounds.

Samples I-III were collected by divers below the brine discharge pipe at platform A on June 5, 1976. As might be expected, since alkanes are less dense than water, the alkane levels were highest at the surface. In each sample, the n-heptadecane/pristane and n-octadecane/phytane ratios were about 1.2 and 3.7, respectively. These ratios approximate those (1.3, 4.3) in a brine sample collected from platform A on April 21, 1976 (MIDDLEDITCH et al. 1978). The surface sample (I) exhibited a typical "petroleum" distribution in the region C_{12} to C_{21}, with concentration of n-alkanes decreasing with chain length. Weathered oil contains lowered concentrations of lighter alkanes, presumably because they undergo preferential evaporation, oxidation, and metabolism. Consequently, the concentration maximum for the C_{12} to C_{23} petroleum alkanes in the mid-depth (II) and bottom (III) water samples is at C_{16}. There is a bimodal distribution of n-alkanes in these two samples with a second, and more pronounced, concentration maximum at C_{32}. The n-alkanes in the region C_{26} to C_{37} exhibit no odd-even preference, so it is possible that they are of bacterial origin (DAVIS 1968; MIDDLEDITCH et al. 1977).

During June and July, 1976, several water samples were collected at random locations (IV-XII). Alkane concentrations were 0.7 (VII) to 24.8 (X) ppb. There was some evidence for petroleum alkanes in the surface samples (IV, VIII, X, XI) and for bacterial hydrocarbons in bottom samples (V-VII, IX, XII). In particular, with the exception of sample IX, the branched alkanes pristane and phytane were absent from bottom samples. It is also of interest to note that, where both surface and bottom samples were analyzed (VII, IX; XI, XII) alkane concentrations were greater in the former.

During August 31 and September 1, 1976, water samples were collected along a transect running from a point 10 km SW of the center of the oilfield to a point 10 km NE (Fig. 1). Both surface and bottom samples were collected at each of eleven locations (XIII- XXXIV). Several trends in these data can be discerned. Surface alkane concentrations were higher at the SW (42.8 ppb) and NE (33.7 ppb) ends of the transect than near the center of the oilfield (5.25-10.8 ppb). This was contrary to expectation, but may merely reflect variation in the concentration of alkanes in brine discharged from the production platforms; we have observed that such concentrations vary over at least three orders of magnitude (MIDDLEDITCH et al. 1978). The C_{15} to C_{25} surface alkanes can confidently be classified as petroleum derived, but it should be noted that these samples also contained smaller amounts of C_{26} to C_{36} alkanes of apparent bacterial origin, with concentration maxima around C_{32}. The distribution of alkanes in the bottom samples was strikingly different. To the SW, alkane concentrations ranged from 23.4 (XIV) to 7.9 (XVI) ppb, again with maximum concentration at the end of the transect. To the NE, however, alkane concentrations were only in the range 1.4 (XXIV) to 5.3 (XVIII) ppb. A bimodal alkane distribution is most apparent to the SW. The major components, around C_{33}, are apparently of bacterial origin, whereas those around C_{20} exhibit a distribution characteristic of petroleum alkanes. A bottom current flows through the region of the oilfield from NE to SW, so the greater concentration of bacterial hydrocarbons is downstream. There is no prevailing surface current.

We were surprised to find such high concentrations of alkanes on August 31 and September 1, 1976, particularly at locations 10 km from the center of the oilfield so, on September 23, 1976, additional samples were collected at five locations around the oilfield: 20 km NW (XXXV, XXXVI), at the center of the oilfield (XXXVII, XXXVIII), 10 km NE (XXXIX, XL), 10 km SW (XLI, XLII), and 20 km SE (XLIII, XLIV). By this time, the high concentrationsof alkanes previously observed had dispersed; none of these samples contained more than 0.7 ppb of alkanes.

Surface and bottom samples were collected at eight locations on December 3, 1976: 10 km NW (XLV, XLVI), 10 km SE (XLVII, XLVIII), 10 km NE (XLIX, L), 10 km SW (LI, LII), 2 km NW (LIII, LIV), 2 km SE (LV, LVI), 2 km NE (surface only: LVII), and 2 km SW

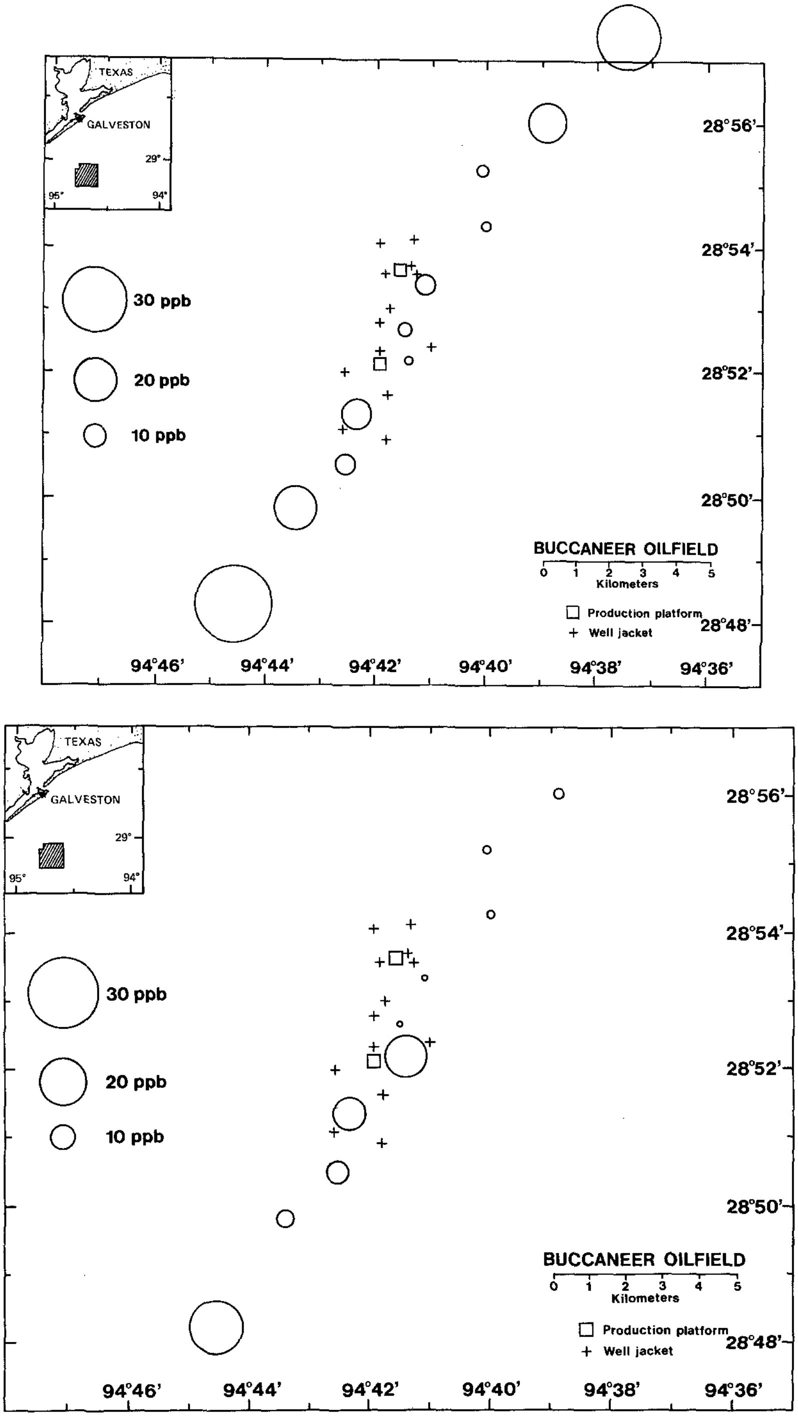

Figure 1: Alkane concentrations in surface (upper) and bottom (lower) water samples. August 31 - September 1, 1976.

(LVIII, LIX) of the center of the oilfield. Small amounts of alkanes were found in only two (XLVIII, L) of the bottom samples, but these appeared to derive neither from petroleum nor bacteria. The greatest concentration of alkanes in surface samples was found 2 km SW of the center of the oilfield (LVIII, 11.8 ppb), but there was no clear evidence that these hydrocarbons were petroleum-derived.

Two weeks later, on December 17, 1976, surface water samples were collected from the center of the oilfield at various locations: 1.6 km N (LX), 1.2 km N (LXI), the center (LXII), 1.2 km S (LXIII), 1.6 km S (LXIV), and 1.6 km E (LXVIII). [Platform A is 1.4 km N and platform B is 1.4 km S of the center of the oilfield.] The alkane concentration in the surface water samples was within a fairly narrow range (1-5 ppb) and there was no discernible concentration gradient. In each of the nine samples, the C_{14} to C_{21} alkanes exhibited a petroleum-like distribution.

Surface and bottom water samples were collected at three locations on February 15-17, 1977: 10 km SW (LXIX, LXX), at the center of the oilfield (LXXI, LXXII), and 10 km NE (LXXIII, LXXIV). The principal alkane in these samples, n-heptadecane, was a compound of biogenic origin.

Two additional samples were collected on March 2, 1977. A sample from the vicinity of a well jacket (LXXV) and another adjacent to platform B (LXXVI) each contained less than 0.4 ppb of alkanes, with no indication of petroleum contamination.

CONCLUSIONS

Concentrations of alkanes in 76 water samples collected within 30 km of the Buccaneer oilfield between June, 1976, and March, 1977, were found to be as high as 43 ppb. It appears that petroleum alkanes discharged from the production platforms float at the air/sea interface and are dispersed. Further studies are required to determine their rates of dispersion and to investigate whether oxidation, metabolism, and other processes have a significant role in the removal of petroleum from the region of this oilfield. It seems likely that discharge from the production platforms of hydrocarbon-producing bacteria, or a nutrient which supports such bacteria, is responsible for the presence of bacterial hydrocarbons in bottom water samples down-current of the oilfield.

BARBIER et al. (1973) found alkane concentrations of 2-28 ppb in the eastern Atlantic Ocean. A concentration maximum at C_{27} to C_{30} indicated that these compounds derived from phytoplankton (BLUMER 1970). Levels of alkanes ranging from 0 to 75 ppb were found by ILIFFE and CALDER (1974) in the Gulf of Mexico and the Caribbean Sea. Most of these were C_{15} to C_{20} alkanes of petroleum origin, but others in the range C_{21} to C_{36} were observed. BROWN and HUFFMAN (1976) have reported that the mean concentration of alkanes at several locations in the Atlantic, Arctic, and Indian Oceans, the Mediterranean Sea, and the Persian Gulf is 4 ppb. It was concluded that most of the compounds were petroleum-derived.

Our data, by comparison with other reports in the literature, indicate that oil production in the Buccaneer field does not afford significant levels of alkanes in the surrounding seawater.

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REFERENCES

BARBIER, M., D. JOLY, A. SALIOT, and D. TOURRES: Deep-Sea Res. 20, 305 (1973).

BLUMER, M., in D. W. HOOD (Ed.): Organic Matter in Natural Waters. University of Alaska, 1970.

BROWN, R. A., and H. F. HUFFMAN, JR.: Science 191, 847 (1976).

DAVIS, J. B.: Chem. Geol. 3, 155 (1968).

ILIFFE, T. M., and J. A. CALDER: Deep-Sea Res. 21, 481 (1974).

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

MIDDLEDITCH, B. S., B. BASILE, and E. S. CHANG: J. Chromatog. 142, 777 (1977).

MIDDLEDITCH, B. S., B. BASILE, and E. S. CHANG: Bull. Environ. Contam. Toxicol. In press (1978).