Bull. Environm. Contam. Toxicol. 21,421-427 (1979)

Alkanes in Plankton From the Buccaneer Oilfield

Brian S. Middleditch, Evelyn S. Chang, and Brenda Basile
Department of Biophysical Sciences, University of Houston, Houston, Tex. 77004

When an oil spill occurs at sea, the hydrocarbons initially accumulate at the air/sea interface. They can then be dispersed by evaporation, solution, oxidation, or microbial degradation (KOONS 1973). Zooplankton are known to ingest oil droplets and to incorporate them into fecal pellets, which sink to the ocean floor. It has been suggested that this process contributes significantly to the dispersion of spilled oil (CONOVER 1971).

We have found that the mean rate of discharge of alkanes from each of the two production platforms in the Buccaneer oilfield is approximately 200 g per day (MIDDLEDITCH et al. 1978a) and that most of these compounds are found (at concentrations up to 43 ppb) at the air/sea interface in the surrounding region (MIDDLEDITCH et al. 1978b). We have now examined sixteen samples of zooplankton, collected during May, August, and December of 1976, to determine whether they contain petroleum alkanes and whether they might contribute significantly to the dispersion of oil discharged from the production platforms.

METHODS

Bulk plankton samples were collected by J. H. Finucane and his colleagues of the National Marine Fisheries Service. Subsurface samples were obtained using paired 61 cm diameter bongo nets with mesh size of 0.333 and 0.505 mm. Timed double oblique tows were performed to sample the depth strata equally from the surface to about 1 m off the bottom. The water depth was 17-20 m throughout the study area. A neuston net, with a mouth opening of 0.5 x 1.0 m and a mesh size of 0.505 mm was used to collect surface samples. All samples were frozen in sea water in glass jars on board ship and were kept frozen until they were analyzed. Locations at which samples were collected are given in Table 1. The two production platforms in the Buccaneer oilfield, 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. No attempt was made to separate and analyze individual species; a copepod (*Acartia tonsa*), the sergestid shrimp (*Lucifer faxoni*), and a chaetognath (*Sagitta tenuis*) were among the major species obtained (FOTHERINGHAM, personal communication, see also FOTHERINGHAM and BRUNENMEISTER (1975)]. J. H. Finucane will report the ichthyoplankton abundance and species composition elsewhere.

0007-4861/79/0021-0421 $01.40

TABLE 1

Tabulation of zooplankton samples

Sample	Date	Collection Method	Location*
I	5-24-76	bongo	28°52'N, 94°42'W
II	5-24-76	bongo	28°51'N, 94°41'W
III	5-24-76	bongo	28°48'N, 94°38'W
IV	5-25-76	bongo	28°52'M, 94°41'W
V	8-16-76	bongo	28°55'N, 94°45'W
VI	8-16-76	bongo	28°52'N, 94°42'W
VII	8-17-76	bongo	28°52'N, 94°41'W
VIII	8-17-76	bongo	28°48'N, 94°38'W
IX	12-3-76	neuston	28°56'N, 94°47'W
X	12-3-76	neuston	28°54'N, 94°47'W
XI	12-3-76	neuston	28°53'N, 94°47'W
XII	12-3-76	neuston	28°52'N, 94°47'W
XIII	12-3-76	neuston	28°52'N, 94°42'W
XIV	12-3-76	neuston	28°51'N, 94°41'W
XV	12-3-76	neuston	28°52'N, 94°42'W
XVI	12-3-76	neuston	28°51'N, 94°42'W

*Plankton were collected in areas extending 1'N and 1'W from these locations.

The extraction procedure was based upon that described by WARNER (1976). A sample of plankton (about 10 g) was homogenized using a Brinkman PT 10-35 Polytron power unit equipped with a PT 20ST generator. The homogenate was transferred to a 50 ml centrifuge tube and n-[$^2H_{42}$]eicosane and n-[$^2H_{66}$]dotriactonane were added as internal standards (MIDDLEDITCH and BASILE 1976). Sodium hydroxide solution (4 ml, 4N) was added and the tube was heated at 90° for 2 hr. The saponified material was extracted with 15 ml and then 10 ml of diethyl ether. Each time, the supernatant layer was drawn off after centrifugation at 2000 rpm for 10 min. The combined extracts were dried over anhydrous sodium sulfate (1 g) and the solvent evaporated using a Buchi/Brinkman Rotavapor R rotating evaporator.

The extract was applied to a 1 x 20 cm column of activated silica gel (60-200 mesh) and an alkane fraction was eluted in 40 ml of cyclohexane ("nanograde"). This fraction was reduced in volume, again using the rotating evaporator, to 100-500 μl and 4 μl aliquots were used for gas chromatography (GC) or combined gas chromatography - mass spectrometry (GC-MS).

2 m x 6 mm silanized glass columns containing 1% OV-1 on Supelcoport (100-120 mesh) were programmed from 100 to 300° at 4 per min in Perkin-Elmer 3920B gas chromatographs equipped with flame ionization detectors. The injector and detector temperatures were, respectively, 225 and 300°. A Hewlett-Packard 5982A instrument was employed for GC-MS under similar conditions, except that the column temperature was limited to 270° since the instrument was equipped with a silicone membrane molecular separator.

RESULTS AND DISCUSSION

Concentrations of alkanes (ppb, wet weight) in sub-surface plankton samples collected in May and August, 1976, are given in Table 2 and data for surface plankton samples collected in December, 1976, are given in Table 3. Alkanes lighter than n-dodecane are not tabulated because they are too volatile for accurate quantitation. The only branched alkanes detected are pristane and phytane so the term "total alkanes" refers only to those compounds listed in Tables 2 and 3.

The total alkane concentrations ranged from 250 ppb (XI) to 3.58 ppm (XIV). There was also a wide variation in the distribution of alkanes from sample to sample. These variations merely reflect species differences; our major interest is in the content of petroleum hydrocarbons.

The first two samples collected on May 24, 1976 (I, II) were from the NW and SE quadrants, respectively, of the Buccaneer oilfield. Their alkane contents were almost identical, with n-docosane and n-pentadecane predominating. There was no clear indication of the presence of petroleum-derived alkanes. Sample III was collected on the same day from a location 10 km SE of the oilfield. It contained large amounts of n-pentadecane and n-heptadecane, but no petroleum alkanes. On the following day, a sample from the NE quadrant of the oilfield (IV) contained very little n-pentadecane, and there was no clear evidence for petroleum contamination.

Four samples were collected during mid-August: from the NW quadrant (VI) and the NE quadrant (VII) of the oilfield and from points 10 km NW (V) and SE (VIII) of the center of the field. It is possible that the C_{19} to C_{23} alkanes in sample V were petroleum derived, although this cannot be stated with certainty. Samples VI and VII were very similar in composition, and the

TABLE 2

Concentrations (ppb) of alkanes in sub-surface plankton samples.

Alkane	I	II	III	IV	V	VI	VII	VIII
n-$C_{12}H_{26}$	40		40					
n-$C_{13}H_{28}$	25		30					
n-$C_{14}H_{30}$	20	30	30					
n-$C_{15}H_{32}$	100	140	450	8	170	250	120	120
n-$C_{16}H_{34}$	70	70	70	5	100	170	130	60
n-$C_{17}H_{36}$	90	90	110	30	220	200	200	90
n-$C_{18}H_{38}$	50	50	50	40	100	60	95	50
n-$C_{19}H_{40}$	50	20	40	20	70	40	50	30
n-$C_{20}H_{42}$			10	10	140	20	30	20
n-$C_{21}H_{44}$	10	10	30	10	100	20	25	20
n-$C_{22}H_{46}$	250	200	50	10	80	40	40	30
n-$C_{23}H_{48}$	20	20	30	20	50	50	35	30
n-$C_{24}H_{50}$	30	30	40	15	70	50	35	30
n-$C_{25}H_{52}$				15		50	30	80
n-$C_{26}H_{54}$		10	20	15		20	17	5
n-$C_{27}H_{56}$	20	50	30	5		30	12	30
n-$C_{28}H_{58}$	20	90	20	15		70	12	30
n-$C_{29}H_{60}$	20		20	20	40	20	5	20
n-$C_{30}H_{62}$	20	20	10	10	50	10	5	5
n-$C_{31}H_{64}$			10				7	
n-$C_{32}H_{66}$							3	
n-$C_{33}H_{68}$							5	
n-$C_{34}H_{70}$							3	
n-$C_{35}H_{72}$								
n-$C_{36}H_{74}$								
n-$C_{37}H_{76}$								
pristane	50	70	80	35	190	200	210	90
phytane	30	30	30	10	40	30	35	20
Total	915	930	1200	293	1420	1330	1104	760

TABLE 3

Concentrations (ppb) of alkanes in surface plankton samples.

Alkane	IX	X	XI	XII	XIII	XIV	XV	XVI
n-$C_{12}H_{26}$								
n-$C_{13}H_{28}$								
n-$C_{14}H_{30}$	5	5	2	3	2	10	3	
n-$C_{15}H_{32}$	20	40	20	30	12	15	10	30
n-$C_{16}H_{34}$	15	20	8	8	10	10	15	10
n-$C_{17}H_{36}$	20	50	35	70	20	40	85	170
n-$C_{18}H_{38}$	10	10	10	5	12	10	30	20
n-$C_{19}H_{40}$	10	20	8	10	10	15	40	20
n-$C_{20}H_{42}$	5		2		5	20	25	20
n-$C_{21}H_{44}$	3	5	2	2	5	40	27	5
n-$C_{22}H_{46}$	10	5	5	8	10	150	30	5
n-$C_{23}H_{48}$	10	5	5	10	12	300	35	5
n-$C_{24}H_{50}$	15	35	8	15	20	440	45	10
n-$C_{25}H_{52}$	25	40	8	20	20	520	50	10
n-$C_{26}H_{54}$	15	25	8	20	22	470	45	15
n-$C_{27}H_{56}$	15	230	5	15	10	510	40	10
n-$C_{28}H_{58}$	20	20	5	10	20	300	35	15
n-$C_{29}H_{60}$	5	220	2	2	10	150	25	5
n-$C_{30}H_{62}$	10	30	2		8	80	20	5
n-$C_{31}H_{64}$	3	1020	2		10	60	17	5
n-$C_{32}H_{66}$		30	2		2	90	15	5
n-$C_{33}H_{68}$		400	2		5	40	15	5
n-$C_{34}H_{70}$		10	2		2	30	10	10
n-$C_{35}H_{72}$		5			2	30	6	15
n-$C_{36}H_{74}$		5			2	20	5	20
n-$C_{37}H_{76}$						10		20
pristane	160	180	102	40	225	200	65	90
phytane	5	5	5	2	10	20	12	15
Total	381	2415	250	270	466	3580	705	540

C_{20} to C_{27} alkanes may tentatively be ascribed to petroleum contamination. Sample VIII was probably uncontaminated.

Since we had established that petroleum hydrocarbons in the Buccaneer oilfield were found mainly at the air/sea interface (MIDDLEDITCH et al. 1978b), the other eight samples (IX-XVI) were collected using a neuston net, on December 3, 1976. Four samples (IX-XII) were collected along a transect running from a point 14 km NW of the oilfield to a point 10 km W of the oilfield. It is possible that the C_{20} to C_{35} alkanes in samples IX, XI, and XII were from petroleum. The alkanes in sample X were dominated by n-heptacosane, n-nonacosane, n-hentriacontane, and n-tritriacontane: the high odd/even chain length preference being characteristic of a biogenic origin. Samples XIII, XIV, XV, and XVI were collected, respectively, from the NW, SE, NE, and SW quadrants of the oilfield. It is almost certain that the C_{18} to C_{37} alkanes from sample XIV are petroleum-derived, and a similar distribution is observed, to a lesser extent, in samples XIII, XV, and XVI.

CONCLUSIONS

BLUMER et al. (1963, 1964) have reported the presence of pristane in relatively high concentrations in several copepods and have suggested that this compound has a role in the maintenance of buoyancy by these organisms. A number of unsaturated hydrocarbons have also been reported in zooplankton (BLUMER and THOMAS 1965, BLUMER et al. 1970). The major n-alkane in a sample of mixed zooplankton and phytoplankton from Tarpaulin Cove, Massachusetts was n-heptadecane, and lower concentrations of other C_{14} to C_{29} n-alkanes were found (CLARK and BLUMER 1967).

We have found pristane and other biogenic alkanes in each sample examined. The presence of large amounts of C_{18} to C_{37} alkanes in sample XIV is believed to be good evidence for petroleum contamination (MIDDLEDITCH et al. 1977). A similar distribution of alkanes is observed in several other samples.

In summary, one (XIV) of the nine samples from the center of oilfield was heavily contaminated with oil, two (XIII, XIV) were slightly contaminated, and another two (VI, VII) may have been contaminated. There is some evidence that two (V, XI) of the seven samples collected at distances of 10-15 km from the oilfield contained petroleum alkanes.

Further work is required to determine which species of plankton preferentially ingest the oil and whether they have a role in the dispersion of oil discharged from the production platforms by (i) incorporation into fecal pellets which sink to the ocean floor, or (ii) transport away from the region of the oilfield.

ACKNOWLEDGMENTS

We thank J. H. Finucane for obtaining the plankton samples and N. Fotheringham for identifying the major species. This work is a result of research sponsored by the NOAA, National Marine Fisheries Service, Department of Commerce, under Contract No. 03-6-042-35120.

REFERENCES

BLUMER, M., and D. W. THOMAS: Science 147, 1148 (1965).

BLUMER, M., M. M. MULLIN, and D. W. THOMAS: Science 140, 974 (1963).

BLUMER, M., M. M. MULLIN, and D. W. THOMAS: Helgoländer Wiss. Meeresuntersuch. 10, 187 (1964).

BLUMER, M., M. M. MULLIN, and R. R. L. GUILLARD: Marine Biol. 6, 226 (1970).

CLARK, R. C., JR., and M. BLUMER: Limnol. and Oceanogr. 12, 79 (1967).

CONOVER, R. J.: J. Fish. Res. Bd. Can. 28, 1327 (1971).

FOTHERINGHAM, N., and S. BRUNENMEISTER: Common Marine Invertebrates of the Northwestern Gulf Coast. Houston: Gulf Publishing Co. 1975.

KOONS, C. B.: Background Papers for a Workshop on Inputs, Fates, and Effects of Petroleum in the Marine Environment, Vol. II. NTIS Publication AD 783 990, 1973, pp. 475-484.

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

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

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

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

WARNER, J. S.: Anal. Chem. 48, 578 (1976).