Bull. Environm. Contam. Toxicol. 22,249-257 (1979)

Alkanes in Fish from the Buccaneer Oilfield

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

Circumstantial evidence is available which indicates that a natural hydrocarbon (3,6,9,12,15,18-heneicosahexaene) found in shark livers derives from zooplankton which, in turn, have ingested phytoplankton that biosynthesize the compound (BLUMER 1967, BLUMER et al. 1970). There is, however, no clear evidence that petroleum hydrocarbons can be magnified in a marine food chain in the same manner as, for example, some chlorinated hydrocarbons. LEE et al. (1972) have demonstrated the uptake of polycyclic aromatic hydrocarbons through the gills of fish, their temporary storage in the liver, and their eventual hydroxylation and excretion. Mullet with a kerosene-like taint were found to contain petroleum hydrocarbons both in the liver and subcutaneous fat (VALE et al. 1970, SHIPTON et al. 1970).

We have established that, in the Buccaneer oilfield, approximately 200g per day of alkanes are discharged into the sea from each of the two production platforms (MIDDLEDITCH et al. 1978). Fish might ingest the alkanes from water through their gills or by consuming plankton or barnacles, all of which contain petroleum-derived alkanes (MIDDLEDITCH et al. 1979a,b,c). We have therefore, examined 25 species of fish to determine whether they contain such alkanes. Flesh samples, including subcutaneous fat, were taken from each species. Liver samples from the larger species were also analyzed.

METHODS

All of the fish (Table 1) were caught for us by personnel of the National Marine Fisheries Service. The samples obtained on August 9-11, 1976 (I-XXI) and some of those collected on February 15-16, 1977 (XXVI-LIII) were obtained by trawling. A 12m nylon mesh semiballoon shrimp trawl was employed. A few samples (LIV-LIX) were obtained on February 16, 1977 from locations adjacent to the production platforms, using modified sablefish traps. Some sheepshead (March 2, 1977; LX-LXV) and bluefish (January 21, 1977; XXII-XXV) were speared by divers. Each specimen was frozen on board ship to minimize bacterial contamination.

0007-4861/79/0022-0249 $01.80

TABLE 1

Tabulation of fish samples

Sample	Date	Location (Fig. 1)	Species	Tissue	Alkanes (ppm)
I	8-9-76	S-2	sand seatrout	muscle	1.32
II			_Cynoscion arenarius_	liver	2.28
III	8-9-76	S-3	blackfin sea robin	muscle	0.10
IV			_Prionotus rubio_	liver	0.30
V	8-9-76	S-3	red snapper	muscle	0.75
VI			_Lutjanus campechanus_	liver	4.50
VII	8-9-76	V-4	southern kingfish	muscle	0.28
VIII			_Menticirrhus americanus_	liver	1.45
IX	8-9-76	V-4	inshore lizardfish	muscle	1.42
X			_Synodus foetens_	liver	0.14
XI	8-9-76	P-7	inshore lizardfish	muscle	2.46
XII			_Synodus foetens_	liver	1.26
XIII	8-9-76	P-7	red snapper	muscle	0.16
XIV			_Lutjanus campechanus_	liver	1.18
XV	8-9-76	P-7	sand seatrout	muscle	4.42
XVI			_Cynoscion arenarius_	liver	2.71
XVII	8-10-76	P-5	blackfin sea robin	muscle	3.80
XVIII			_Prionotus rubio_	liver	21.80
XIX	8-10-76	P-7	longspine porgy	muscle	0.84
			Stenotomus caprinus		
XX	8-11-76	J-9	atlantic midshipman	muscle	1.55
XXI			_Porichthys porosissimus_	liver	22.75
XXII	1-21-77	P-6	bluefish	muscle	0.62
XXIII			_Pomatomus saltatrix_	liver	0.52
XXIV	1-21-77	P-6	bluefish	muscle	1.94
XXV			_Pomatomus saltatrix_	liver	2.75
XXVI	2-15-77	Y-3	atlantic croaker	muscle	0.12
			Micropogon undulatus		
XXVII	2-15-77	Y-3	sea catfish	muscle	0.30
XXVIII			_Arius felis_	liver	3.20

Sample	Date	Location (Fig. 1)	Species	Tissue	Alkanes (ppm)
XXIX	2-15-77	Y-3	sand seatrout	muscle	16.03
XXX			*Cynoscion arenarius*	liver	0.54
XXXI	2-16-77	P-6	largescale lizardfish	muscle	0.17
XXXII			*Saurida brasiliensis*	liver	23.73
XXXIII	2-16-77	P-6	sea catfish	muscle	0.37
XXXIV			*Arius felis*	liver	0.78
XXXV	2-16-77	P-6	roughback batfish	muscle	0.07
XXXVI			*Ogcocephalus parvus*	liver	1.57
XXXVII	2-16-77	P-6	southern hake	muscle	0.08
XXXVIII			*Urophycis floridanus*	liver	0.17
XXXIX	2-16-77	P-6	rock sea bass	muscle	0.18
XL			*Centropristis philadelphica*	liver	1.01
XLI	2-16-77	P-6	dwarf sand perch	muscle	0.14
XLII			*Diplectrum bivittatum*	liver	1.01
XLIII	2-16-77	P-6	pigfish	muscle	0.09
XLIV			*Orthopristis chrysoptera*	liver	1.51
XLV	2-16-77	P-6	atlantic croaker	muscle	0.03
XLVI			*Micropogon undulatus*	liver	0.79
XLVII	2-16-77	P-6	gulf butterfish *Peprilus burti*	muscle	1.75
XLVIII	2-16-77	P-6	smoothhead scorpionfish *Scorpaena calcarata*	muscle	0.08
XLIX	2-16-77	P-6	bandtail searobin *Prionotus ophryas*	muscle	0.03
L	2-16-77	P-6	bay whiff *Citharichthys spilopterus*	muscle	0.05
LI	2-16-77	P-6	dusky flounder	muscle	0.07
LII			*Syacium papillosum*	liver	0.33
LIII	2-16-77	P-6	blackcheek tonguefish *Symphurus plagiusa*	muscle	0.96
LIV	2-16-77	P-5	pigfish	muscle	1.63
LV			*Orthropristis chrysoptera*	liver	2.20

Sample	Date	Location (Fig. 1)	Species	Tissue	Alkanes (ppm)
LVI	2-16-77	P-5	atlantic spadefish	muscle	1.63
LVII			Chaetodipterus faber	liver	2.82
LVIII	2-16-77	P-6	leopard toadfish	muscle	0.07
LIX			Opsanus pardus	liver	0.87
LX	3-2-77	N-6	sheepshead	muscle	0.17
LXI			Archosargus probatocephalus	liver	2.70
LXII	3-2-77	N-7	sheepshead	muscle	1.10
LXIII			Archosargus probatocephalus	liver	1.43
LXIV	3-2-77	P-7	sheepshead	muscle	1.51
LXV			Archosargus probatocephalus	liver	23.70

In the laboratory, a sample of dorsal flesh (including skin, subcutaneous fat, and muscle tissue) was excised from each specimen. With the exception of the smaller fish (bay whiff, gulf butterfish, bandtail searobin, blackcheek tonguefish, smoothead scorpionfish, longspine porgy, and one of the two atlantic croakers), livers were also analyzed.

Analytical procedures were similar to those employed for plankton (MIDDLEDITCH et al. 1979b). Tissue samples were homogenized. *n*-[$^2H_{42}$]Eicosane and *n*-[$^2H_{66}$]dotriacontane were added as internal standards (MIDDLEDITCH and BASILE 1976). The homogenate was saponified and extracted with ether. The extract was dried over anhydrous sodium sulfate and was subjected to silica gel chromatography. An alkane fraction was eluted in cyclohexane and aliquots were examined by gas chromatography (GC) or combined gas chromatography - mass spectrometry (GC-MS).

For GC, 2m x 6mm 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 instruments. The injector and detector temperatures were, respectively, 225 and 300°. A Hewlett-Packard 5982A instrument was employed for GC-MS.

RESULTS AND DISCUSSION

Alkane concentrations in muscle tissue ranged from 0 to 16ppm, and in livers from 0 to 1,300ppm. Most samples contained relatively large amounts of *n*-pentadecane, *n*-heptadecane, and pristane of biogenic origin.

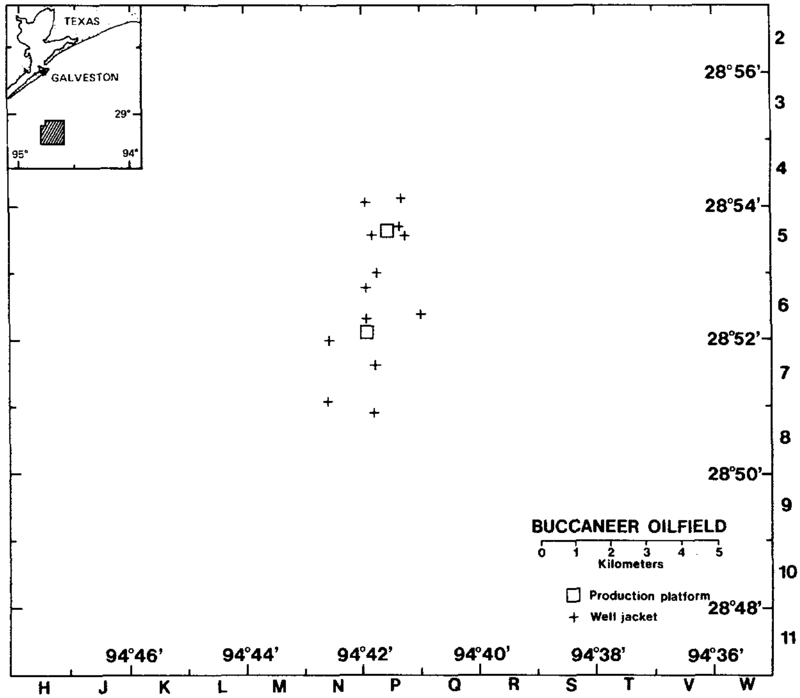

Figure 1. Map of region surrounding the Buccaneer oilfield, indicatng sample locations

In some samples, as noted below, there was evidence for the presence of petroleum alkanes.

Archosargus probatocephalus (sheepshead). Three specimens were examined. Petroleum hydrocarbons were found in muscle tissue from the first two specimens (LX, LXII), but not the third (LXIV). Curiously, these alkanes were present in liver from the third specimen (LXV), but not the first two (LXI, LXII).

Arius felis (sea catfish). Two specimens were examined. Muscle samples contained 295 (XXVII) and 367 (XXXIII) ppb of alkanes. The major alkanes were n-heptadecane and pristane, and there were no petroleum alkanes. The livers contained 3.2 (XXVIII) and 0.78 (XXXIV) ppb of alkanes. n-Heneicosane predominated. It is possible that the C-23 to C-30 alkanes (0.38ppm) in sample XXXIV were petroleum-derived.

Centropristis philadelphica (rock sea bass). Muscle tissue (XXXIX) contained only n-hexadecane (25ppb) and n-heptadecane (150ppb), while no alkanes were detected in the liver (XL).

Chaetodipterus faber (Atlantic spadefish). Both the muscle (LVI, 1.6ppm alkanes) and liver (LVII, 2.8ppm) were dominated by pristane (1.2 and 1.26ppm, respectively), and there was also a relatively large amount (0.9ppm) of n-heneicosane in the liver. The C-21 to C-28 alkanes in muscle (70ppb) and C-22 to C-27 alkanes in liver (280ppb) may have been petroleum-derived.

Citharichthys spilopterus (bay whiff). The muscle sample (L) analyzed contained only 51ppb, but the C-22 to C-31 alkanes (42ppm) exhibited the characteristic petroleum-like distribution. The liver was not examined.

Cynoscion arenarius (sand seatrout). Three specimens were analyzed. There was little pristane in muscle from the first two samples (I, 20ppb; XV, 40ppb), the major alkanes being n-pentadecane and n-heptadecane. Muscle from the third specimen (XXIX), however, contained 16 ppm of pristane. This sample also contained elevated levels of n-nonacosane (400ppb) and n-hentriacontane (100ppb). There was no clear evidence for petroleum contamination in any of these samples. Livers from the first two samples contained only 2.28 (II) and 2.71 (XVI) ppm, but the third (XXX) contained 542ppm of alkanes. The C-27 to C-31 alkanes in sample XXX (490ppm) were probably petroleum-derived.

Diplectrum bivittatum (dwarf sand perch). The muscle (XLI) and liver (XLII) contained, respectively, 140ppb and 1ppm of biogenic alkanes.

Lutjanus campechanus (red snapper). Two specimens were examined. Muscle tissue contained 750 (V) or 160 (XIII) ppb of biogenic alkanes, principally n-pentadecane, n-heptadecane, and pristane. Liver tissue contained 4.5 (VI) or 1.18 (XIV) ppm of alkanes and, again, there was no evidence of petroleum contamination.

Menticirrhus americanus (southern kingfish). The muscle (VII) and liver (VIII) tissue contained 275ppb and 1.5ppm, respectively, of alkanes. The C-22 to C-26 alkanes may have been petroleum-derived.

Micropogon undulatus (atlantic croaker). Muscle from two specimens and a liver from one of them was examined. Muscle from the first sample (XXVI) contained 120ppb of biogenic alkanes, whereas muscle from the second specimen (XLV) contained only petroleum-like alkanes (C-24 to C-28, 25ppb). Liver from the second sample (XLVI) contained 790ppb of alkanes of which 550ppb (C-22 to C-30) may be petroleum-derived.

Ogcocephalus parvus (roughback batfish). The muscle (XXXV) contained 70ppb and the liver (XXXVI) contained 1.6ppm of *n*-alkanes. There was no clear evidence of petroleum contamination.

Opsanus pardus (leopard toadfish). The muscle tissue (LVIII) contained 66ppb of alkanes, of which 24ppb (C-23 to C-27) may be petroleum-derived. The liver (LIX) contained 870ppb of alkanes, probably biogenic and dominated by pristane (430ppb).

Orthopristis chrysoptera (pigfish). Two specimens were examined. Muscle from the first (XLIII) contained only 90ppb of alkanes, and these compounds were absent from muscle of the second (LIV). Liver from the first (XLIV) contained only *n*-pentacosane (670ppb) and *n*-heptacosane (840ppb), while liver from the second (LV) contained 2.2ppm of C-25 to C-31 alkanes.

Peprilus burti (gulf butterfish). The muscle tissue (XLVII) contained 1.75ppm of alkanes, principally pristane, *n*-pentadecane, and *n*-nonadecane. There were no petroleum-derived alkanes. The liver was not examined.

Pomatomus saltatrix (bluefish). Two specimens were examined. Muscle from the first (XXII) contained 616ppb of alkanes, principally *n*-pentadecane and *n*-heptadecane. The C-21 to C-35 alkanes (207ppb) exhibited a typical petroleum-like distribution. The second sample (XXIV; total alkanes, 1.9ppm) contained much more *n*-heptadecane (1.3ppm) but the C-22 to C-35 alkanes (190ppb) were also petroleum-derived. Similar alkane distributions were observed in the livers. 180ppb (C-20 to C-30) of the 520ppb of alkanes in the first specimen (XXIII) were petroleum derived, as were 350ppb (C-22 to C-27) of the 2.8ppm of alkanes from the second sample (XXV).

Porichthys porosissimus (atlantic midshipman). The muscle (XX) contained 1.6ppm of biogenic *n*-alkanes, principally *n*-pentadecane, pristane, and *n*-heptadecane. The liver (XXI; total alkanes, 23ppm) also contained large amounts of *n*-pentadecane and *n*-heptadecane, but the C-21 to C-27 alkanes (10ppm) were petroleum-derived.

Prionotus ophryas (bandtail searobin). The muscle tissue (XLIX) contained only 30ppb of C-15 to C-18 alkanes. The liver was not examined.

Prionotus rubio (blackfin sea robin). Two specimens were analyzed. Muscle from the first (III) contained only 100ppb of biogenic alkanes, whereas muscle from the second (XVII) contained 3.8ppm of alkanes. The C-23 to C-27 alkanes (230ppb) may have been petroleum-derived. Liver from the first (IV) contained only *n*-heneicosane (300ppb) whereas that from the second (XVIII) contained 22ppm of alkanes, dominated by *n*-pentadecane. There was no clear evidence for petroleum contamination.

Saurida brasiliensis (largescale lizardfish). The major alkanes from muscle of this specimen (XXXI; total alkanes, 170ppb) were *n*-pentadecane and *n*-heptadecane, but C-22 to C-30 petroleum alkanes were present to the extent of 81ppb. The liver (XXXII) contained 24ppm of alkanes, dominated by *n*-pentadecane and pristane. There was no evidence for petroleum contamination.

Scorpaena calcarata (smoothhead scorpionfish). The muscle (XLVIII) contained 80ppb of biogenic alkanes, and the liver was not examined.

Stenotomus caprinus (longspine porgy). The muscle (XIX) contained 840ppb of alkanes, mainly pristane, *n*-pentadecane, and *n*-heptadecane. The C-21 to C-25 alkanes (90ppb) may be petroleum-derived. The liver was not analyzed.

Syacium papillosum (dusky flounder). All of the alkanes (C-20 to C-31) in the muscle (LI) are probably petroleum-derived (67ppb). It is also likely that the C-23 to C-31 alkanes (180ppb) in the liver (LII; total alkanes, 330ppb) are from petroleum.

Symphurus plagiusa (blackcheek tonguefish). The muscle (LIII; total alkanes, 960ppb) from this specimen was heavily contaminated with petroleum alkanes. It is probably that most, if not all, of the *n*-alkanes (840ppb) were petroleum-derived. The liver was not examined.

Synodus foetens (inshore lizardfish). Two specimens were examined. The muscle samples (IX, XI) contained 1.4 and 2.5ppm, respectively, of alkanes, principally *n*-pentadecane, *n*-heptadecane, and pristane. The C-20 to C-27 alkanes of the first sample (120ppb) exhibited the typical petroleum-like distribution. Muscle from the second specimen was uncontaminated. Liver samples (X,XII) contained 140ppb and 1.3ppm, respectively, of alkanes, dominated by *n*-pentadecane. There was no clear evidence for petroleum contaminaton in the livers of either specimen.

Urophycis floridanus (southern hake). It is possible that the C-24 to C-26 alkanes (25ppb) in the muscle (XXXVII; total alkanes, 75ppb) were petroleum-derived. There is clearer evidence that the C-22 to

C-28 alkanes (120ppb) in the liver (XXXVIII; total alkanes, 170ppb) resulted from petroleum contamination.

CONCLUSIONS

There was good evidence for petroleum alkanes in *A. probatocephalus*, *C. spilopterus*, *C. arenarius*, *M. undulatus*, *P. saltatrix*, *P. porosissimus*, *P. rubio*, *S. brasiliensis*, *S. caprinus*, *S. papillosum*, *S. plagiusa*, *S. foetens*, and *U. floridanus*. It was also possible that *A. felis*, *C. faber*, and *O. pardus* were contaminated, but there were no petroleum alkanes in the other nine species examined. Levels of petroleum alkanes were usually higher in livers than in muscle tissue.

ACKNOWLEDGMENTS

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.: Science 156, 390 (1967).
BLUMER, M., M.M. MULLIN, and R.R.L. GUILLARD: Marine Biol. 6, 226 (1970).
LEE, R.F., R. SAUERHEBER, and G.H. DOBBS: Marine Biol. 17, 201 (1972).
MIDDLEDITCH, B.S., and B. BASILE: Anal. Lett. 9, 1031 (1976).
MIDDLEDITCH, B.S., B. BASILE, and E.S. CHANG: Bull. Environ. Contam. Toxicol., in press (1978).
MIDDLEDITCH, B.S., B. BASILE, and E.S. CHANG: Bull. Environ. Contam. Toxicol., in press (1979a).
MIDDLEDITCH, B.S., E.S. CHANG, and B. BASILE: Bull. Environ. Contam. Toxicol., in press (1979b).
MIDDLEDITCH, B.S., E.S. CHANG, and B. BASILE: Bull. Environ. Contam. Toxicol., in press (1979c).
SHIPTON, J., J.H. LAST, K.E. MURRAY, and G.L. VALE: J. Sci. Food Agr. 21, 433 (1970).
VALE, G.L., G.S. SIDHU, W.A. MONTGOMERY, and A.R. JOHNSON: J. Sci. Food Agr. 21, 429 (1970).