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Volatile Liquid Hydrocarbons around a Production Platform in the Northwest Gulf of Mexico

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Of the many sources of hydrocarbon pollution in the oceans, the catastrophic inputs (e.g., oil-tanker wrecks and offshore well blowouts) often receive the most attention, mainly due to the spectacular nature of the oil spills associated with these episodic events. Although such catastrophic inputs have received a great deal of study, they make relatively small contributions to the total amount of hydrocarbons entering the ocean each year (CLARKE and MACLEOD 1974). The more continuous inputs, such as those associated with normal transportation releases and offshore oil production, make the most significant contribution to the total petroleum hydrocarbon burden entering the ocean. Also, these continuous inputs probably have the greatest long term, sublethal effects on marine organisms. One of the more important continuous hydrocarbon sources in the northern Gulf of Mexico is via discharge of production brine associated with offshore oil production. During 1975, almost one-eighth of the world's offshore oil production occurred in the Gulf of Mexico, with an average discharge of 0.6 barrels of formation waters (brine) per barrel of oil (U.S. DEPARTMENT OF INTERIOR 1976). There are presently over 3500 offshore production platforms on the Louisiana and Texas continental shelf alone (U.S. DEPARTMENT OF INTERIOR 1980) discharging more than 350,000 barrels of brine daily into the outer continental shelf waters (U.S. GEOLOGICAL SURVEY 1981, personal communication). Land-based rigs operating within a few miles of the coast discharge an additional 325,000 barrels of formation waters (brine) daily into the outer continental shelf waters. The discharged brines usually have high concentrations of petroleum hydrocarbons, especially volatile liquid hydrocarbons.

Volatile liquid hydrocarbons (VLH) in the C_6 to C_{14} range, are preferentially partitioned from the produced oil into the discharge brine, due to their high solubilities in seawater relative to the higher molecular weight hydrocarbons. Thus VLH's are found in much higher concentrations in the discharged production brine than are the higher molecular weight hydrocarbons. Volatile liquid hydrocarbons are important environmentally, since

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these compounds include the light aromatics (benzene through naphthalene) which are the most immediately toxic components of petroleum (BAKER 1970; BLUMER 1971). Realizing the importance of examining possible VLH impacts from production brine discharges, the National Marine Fisheries Service added VLH measurements to the fourth year of their environmental study of an active gas and oil field in the Gulf of Mexico (the Buccaneer field). The discharge of high molecular weight alkanes from the Buccaneer field has been described previously (MIDDLEDITCH et al. 1978). This report describes the discharge and subsequent dilution of the volatile liquid hydrocarbons input into the surface seawater of the Buccaneer field.

METHODS

The Buccaneer Gas and Oil Field is located 50 km southwest of Galveston, Texas, in water about 21 m deep. The field has been in production for about 20 years. The two production platforms operated by Shell Oil Company in the Buccaneer field are separated by about 3 km and are located at 28°53.5'N, 94° 41.7'W (Platform 288-A) and 28°52.0'N, 94° 41.8'W (Platform 296-B). Production brine is discharged only from platform 296-B. Samples of discharge brine from platform 296-B were collected directly in two-liter bottles with ground glass stoppered tops. The glass sample bottles were combusted at 550°C prior to use. To examine the distribution patterns of VLH in the water column, surface water samples were taken directly below the discharge pipe and in a grid around platform 296-B, from which brine is discharged. A comparison, control grid was sampled around platform 288-A, where no brine is discharged. The grid study around platform 296-B was performed during two seasons. Samples of surface seawater were taken at stations 25 and 50 meters from platform 296-B and 10 meters from the control platform (288-A). Samples were taken from the bow of a small boat by lowering a two-liter bottle (closed) below the surface at arms length and opening the bottle and closing it after filling at that depth. A total of 45 samples were collected. Samples were stored in the sample bottles at 4°C and returned to the laboratory for analysis.

To prevent possible contamination during sample transfer, the volatile liquid hydrocarbon samples were processed in the same bottles used for sampling. Our analysis technique was a modification of the dynamic headspace stripping technique of SAUER (1980). Briefly, the volatile organics were stripped from a heated (70°C), stirred seawater sample by purging with pure helium for 90 min. Volatile organics were trapped on a 0.5 cm I.D. x 15 cm column of solid polyphenyl ether absorbent (Tenax-GC) which has excellent retention characteristics for VLH, retains very little water and exhibits negligible column bleed at temperatures under 300°C (BUTLER and BURKE 1976). The trapped volatiles were subsequently desorbed by heating to 250°C, consolidated on a liquid nitrogen trap, and transferred by heating (100°C) to a gas chromatographic column for analysis. Gas chromatography was performed using a 305 cm x 0.3 cm I.D. stainless steel column packed with 10% SP-2100 on 80/100 Supelcoport. The column was temperature programmed at 50°C for 10 min, from 50 to 180°C at 4°C/min, and at 180°C for 20 min. Brine samples were analyzed using a Hewlett-Packard 7675 purge and trap system. Samples of the produced oil were analyzed using the same gas chromatograhic conditions, but the oil was injected directly onto the chromatographic column via an injector port heated to 250°C.

RESULTS AND DISCUSSION

Figure 1 shows representative gas chromatograms of volatile liquid hydrocarbons (VLH) in Buccaneer field produced oil and brine. Although all VLH's were originally part of the oil, these hydrocarbons are found in high concentrations in the brine, since it is in contact with petroleum both in the reservoir and as it rises in the well stem. Since C_1-C_{14} hydrocarbons, and particularly the light aromatics, are the most soluble components of petroleum, they are found in very much larger concentrations in the brine than are the heavier hydrocarbons. For example, benzene is at least 5 or 6 orders of magnitude more soluble in brine than the heavy hydrocarbon octadecane (C_{18}). The gas chromatograms reflect these solubility differences.

VLH concentrations measured in two oil and brine samples are given in Table 1. A total of four oil and brine samples from different days were analyzed. VLH in oil are dominated by n-alkanes. Relative to the high concentration of n-alkanes, few light aromatic compounds are present in the oil. The n-alkanes comprised 30 to 40% of the VLH fraction in oil, while the aromatics comprised only a few percent. The percentages of alkanes and aromatic compounds in oils results from selectivity during the maturation process which produces petroleum (see, for example, HUNT 1979). The percentage distributions that we observed are not unusual for Gulf of Mexico oils. The data in Table 1 indicate that there are large variations, both daily and seasonally, in the concentration of all components in both brine and oil. This is probably due to the fact that thirteen different wells discharge brine at platform 296-B and all the wells are not producing at the same time. Averaged data from our four samples will be used to assess inputs.

The data in Figure 1 and Table 1 show that one-ring aromatics (e.g., benzene, toluene, ethylbenzene, xylenes) are the major components in the discharge brine. Benzene, the most soluble VLH, comprised from 40 to 50% of the volatile hydrocarbons in the brine. Toluene concentrations were about half the benzene values, with decreasing amounts of the higher molecular weight, one-ring aromatics. The one-ring aromatics comprised 70 to 90% of the VLH in the brine while n-alkanes comprised only 4 to 16%. Although the concentrations of total VLH in the brine varied considerably, one-ring aromatics were always the major

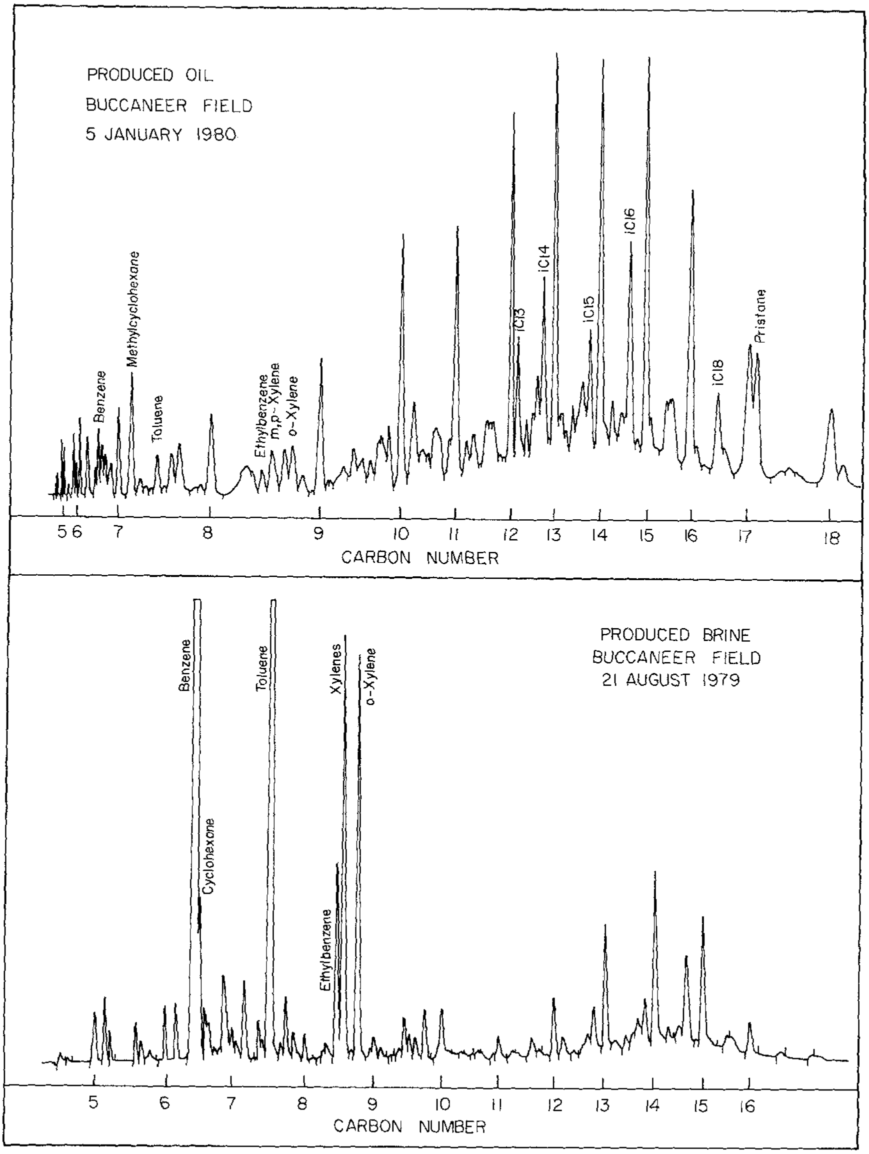

Figure 1. Representative gas chromatograms (flame ionization detector) of volatile liquid hydrocarbons extracted from Buccaneer field oil and produced brine (see text for details of chromatographic procedures).

TABLE 1

Volatile liquid hydrocarbons in Buccaneer field oil and discharge brine.

Compound	Oil (µg/g)		Brine (µg/L)	
	5 Jan 80	8 Apr 80	21 Aug 79	8 Jan 80
n-Pentane	580	4,600	-	-
n-Hexane	1,700	6,100	20	30
n-Heptane	3,900	10,000	21	39
n-Octane	3,700	14,000	19	130
n-Nonane	10,000	16,000	16	200
n-Decane	17,000	18,000	39	400
n-Undecane	20,000	19,000	18	880
n-Dodecane	22,000	17,000	35	1,000
n-Tridecane	26,000	19,000	77	1,050
n-Tetradecane	36,000	25,000	180	1,410
Benzene	2,200	6,000	6,200	17,700
Methylcyclohexane	6,800	15,000	62	340
Toluene	2,700	6,800	2,600	8,500
Ethylbenzene	3,500	5,500	220	1,100
m, p-Xylene	7,200	12,000	500	1,900
o-Xylene	7,060	11,000	480	1,800
Total n-C_5-C_{14}	140,000	150,000	420	5,100
Total Aromatic	23,000	41,000	10,000	31,000
Total VLH	420,000	490,000	11,300	44,400
% n-C_5-C_{14}	33.3	30.6	3.7	16.4
% Aromatics	5.5	8.4	88.5	70.0

component. The 8 January 1980 brine sample had the highest VLH concentrations and lowest aromatic percentage of the four samples we analyzed, probably due to dispersed oil in the sample. The average aromatic VLH concentration in the brine using our four samples was 16,600 µg/L. Assuming a mean rate of discharge of brine at 95,400 L/day (MIDDLEDITCH et al. 1978), the mean rate of discharge of VLH aromatic compounds is 1580 g/day. This compares to a discharge of 191 g/day for high-molecular-weight n-alkanes (MIDDLEDITCH et al. 1978).

Since the volatile liquid hydrocarbon fraction contains the most immediately toxic components of petroleum, the light aromatic compounds, the high toxicity of VLH could have special importance for marine organisms and might have contributed to the reduced biomass observed on the brine discharge leg (GALLOWAY 1980). The effect that a 1580 g/day input of VLH with the brine will have depends on the dispersion of the VLH after input; thus we measured the VLH's in the surface waters around both platforms. In order to effectively compare the grid stations without the complicating effects of directional advective transport, the grid study data was averaged by distance from the platform. The average concentrations of VLH components are presented in Table 2. As expected, the highest concentrations of total VLH in the surface waters (65,000 ng/L) were found below the discharge pipe at platform 296-B. This level was about 20 times the highest value reported at 25 m from the discharge and about 35 times the average concentration for the grid area. There was a rapid dilution of total VLH within 25 m of the discharge and the average concentrations remained essentially constant throughout the $\sim$ 16,000 m^2 grid area around the platform discharging brine. The VLH concentrations around the platform with no discharge (288-A) are a factor of four lower than around the discharging platform. Data from SAUER (1980) representing relatively clean (Caribbean Sea) and polluted (Mississippi River mouth) areas are shown for comparison.

Table 2 also contains a breakdown of total VLH into n-alkanes, cycloalkanes and aromatic compounds. The concentrations of the total benzene, toluene, ethylbenzene, and m-, p-, and o-xylylenes (BTX) fraction are also given along with percentages of VLH that were aromatics and BTX compounds. The n-alkanes and cycloalkanes make up only a small fraction of the total VLH. Between 81 and 88% of total VLH's in the grid area were aromatics. BTX's alone comprised 45 to 59% of the VLH around the two platforms. In the input brine (Table 1), the aromatics made up 70 to 88% of the VLH with the BTX compounds accounting for virtually all of the aromatics.

These data indicate that the VLH input is rapidly diluted in the area of the platform, and that the aromatic compounds are not preferentially lost to the atmosphere relative to the alkanes. The VLH levels around platform 296-B are greater than the 1 ug/L that could be harmful to marine organisms (SAUER 1980). The levels 3 km away, around platform 288-A, are half of that value, but still higher than values for polluted waters given by SAUER (1980). The initial results of the Buccaneer Oil and Gas Field study (JACKSON and WILKENS 1980) indicate few if any negative impacts of the discharge of VLH in this area. If our surface water values are representative of the entire water column, the concentration of VLH required to adversely impact

TABLE 2

Average concentrations of VLH (ng/L) in the surface waters around the two platforms studied in the Buccaneer field. Brine is discharged only from platform 296-B.

	Total				%
Location	n-alkanes	Cyclo-alkanes	Aromatics (BTX)[1]	VLH	Aromatics (% BTX)
Below 296-B Discharge	6060	1620	57200(46100)	64900	88(71)
25m from 296-B	298	25.5	1520(825)	1840	82(45)
50m from 296-B	372	15.7	1640(1190)	2020	81(59)
10m from 288-A	51.6	13.3	474(320)	539	88(59)
Caribbean Sea[2]	nd[3]	nd[3]	18.6(18.6)	18.6	100(100)
Miss. River[2] mouth	23.1	85.3	290(271)	397	74(69)

[1] BTX = the sum of benzene, toluene, ethylbenzene, m-, p-, and o-xylene.
[2] Data from SAUER (1980) for comparison.
[3] nd = none detected.

marine organisms over a long period (>20 years) may be greater than the levels that we observed. Further studies of VLH in the complete water column around a production platform would be valuable.

CONCLUSIONS

We have characterized the volatile liquid hydrocarbons in the oil, discharge brine and surface receiving waters from an oil and gas production platform discharging brine into the Gulf of Mexico. The mean VLH concentrations were 450,000 µg/g (oil), 21,600 µg/L (brine) and 1900 ng/L (surface waters). Light aromatic compounds comprised over 80% of VLH in the brine and surface waters, with benzene, toluene, ethylbenzene, m-, p-, and o-xylene being the predominant compounds. VLH concentrations around a control platform 3 km distant were four times lower, indicating rapid dilution. The 2 µg/L concentration of VLH around platform 296-B is twice the concentration that SAUER

(1980) suggested could be detrimental to the life processes of many marine organisms. If this value is representative of the complete water column and considering the fact that the Buccaneer field has been discharging brine at this location for over twenty years, with no obvious harm to the biota, the lower limit for VLH to cause detrimental long term effects on marine organisms may have to be reevaluated.

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