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## DISCHARGE OF ELEMENTAL SULFUR AND ITS DISTRIBUTION IN SURFICIAL SEDIMENTS IN THE REGION OF THE BUCCANEER OIL FIELD\*

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### SUMMARY

The concentration of elemental sulfur in the produced water effluent from production platforms in the Buccaneer oil field was determined. In 15 samples collected between June, 1977 and May, 1978 the mean sulfur content was 457 ppm (range: <100 to 1200 ppm). The concentration of elemental sulfur in surficial sediment samples collected from the immediate vicinity of the production platforms in October, 1977 ranged from 0.30 to 11.85 ppm. There was no correlation between alkane and sulfur concentrations either in the effluents or the sediments.

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### INTRODUCTION

Gas chromatography (GC)<sup>1</sup> is the form of partition chromatography<sup>2</sup> which is most appropriate for the analysis of multicomponent mixtures of environmental origin. During the past several years we have been using GC and combined GC-mass spectrometry (MS) to study the hydrocarbon content of effluents from production platforms in the Buccaneer oil field and the distribution of these hydrocarbons in the surrounding environment<sup>3-9</sup>. In common with many environmental samples contaminated with petroleum residues, a number of our samples, particularly the surficial sediments, contained elemental sulfur<sup>10</sup>. The flame-ionization detector is insensitive to this substance, but it is detected by GC-MS. If a non-polar stationary phase (such as OV-1) is used for the analysis, sulfur coelutes with *n*-octadecane and interferes with the analysis of the latter. Thus, sulfur is usually removed from environmental hydrocarbon extracts prior to analysis<sup>11</sup>. Most of our knowledge of sulfur in the environment is restricted to oxides of sulfur<sup>12</sup>, so we decided to extend our studies of the environmental effects of offshore oil production to consider the sources, fates and effects of elemental sulfur. The concentration of sulfur in the production platform effluents was sufficiently high that a gravimetric procedure could be em-

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\* Dedicated to Professor A. J. P. Martin on the occasion of his seventieth birthday.

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ployed, but analyses of surficial sediments required the development of a more sensitive procedure based upon GC-MS. These procedures and the results obtained are discussed here.

## EXPERIMENTAL

### Materials

Sulfur enriched in  $^{34}\text{S}$  was obtained from Merck (Elmsford, NY, U.S.A.). All solvents were Mallinckrodt (St. Louis, MO, U.S.A.) Nanograde.

### Samples

Samples of the formation water discharge were collected from production platforms in the Buccaneer oil field, in the northwestern Gulf of Mexico. These structures are indicated as "Pfm A" and "Pfm B", respectively, in Fig. 1. Samples were collected monthly from June, 1977 to February, 1978. Specimens were obtained from both production platforms until October, 1977, when routine formation water discharge from platform 288-A ceased. These samples were collected directly into

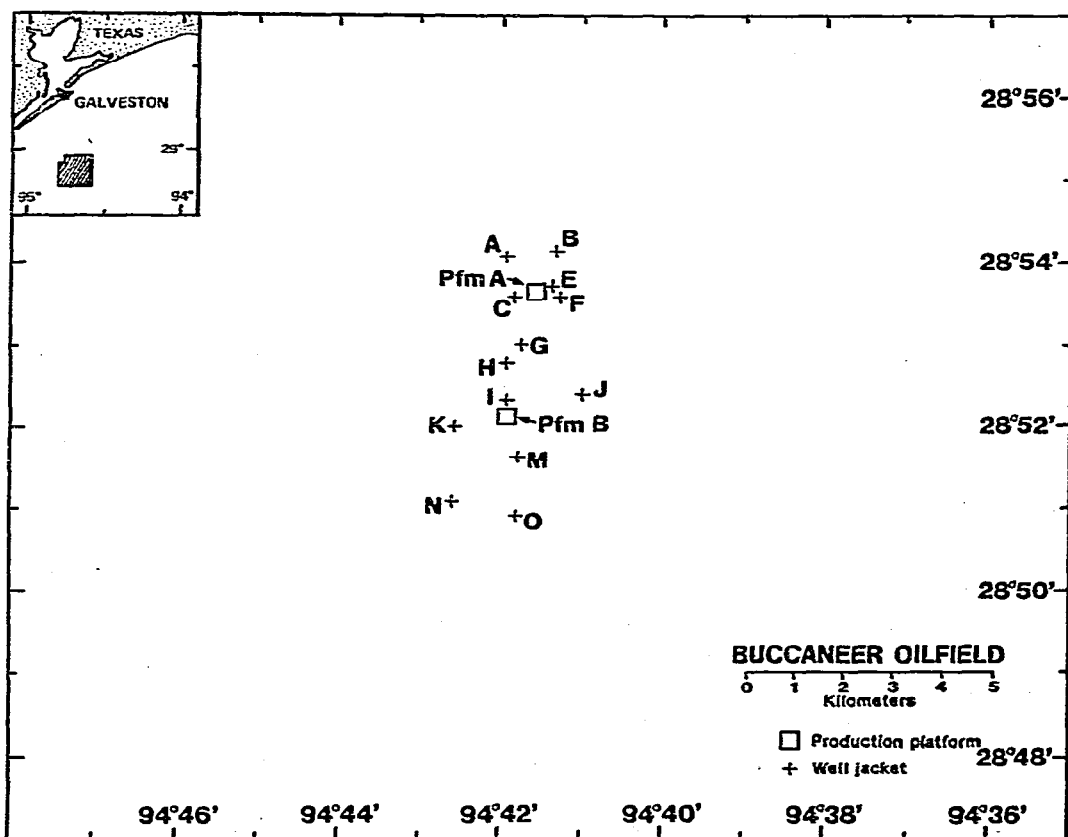


Fig. 1. Map showing location of structures in the Buccaneer oil field. "Pfm A" and "Pfm B" are, respectively, production platforms 288-A and 296-B. "B" is well jacket 288-5.

1-l glass bottles with ground glass stoppers. They were frozen as soon as possible after collection to minimize contamination that might otherwise have been caused by bacterial growth. They were kept frozen until analyzed.

Surficial sediments were collected from the vicinity of production platform 288-A and well jacket 288-5 (shown as "B" in Fig. 1). For each of the two structures 15 samples were collected from along a transect extending from a point 600 ft. (183 m) to the west of the midpoint of the western edge of the platform to a point 600 ft. (183 m) to the east of the midpoint of the eastern edge of the platform. Samples are numbered according to their distance in feet to the east or west of the platforms. Thus, E100, E150 and E300 are, respectively, 100, 150 and 300 ft. (30.5, 45.7 and 91.4 m) east of the midpoint of the eastern edge of the platform. Location C is below the platform. These samples were collected directly into 250-ml glass bottles, also with ground glass stoppers, by divers. The samples were frozen as for the formation water discharge samples.

### *Instruments*

GC was performed using Perkin-Elmer 3920B instruments equipped with flame-ionization detectors and 10-m glass capillary columns coated with OV-101. The injection and interface temperatures were, respectively, 250 and 290°C, and a temperature program of 100 to 290°C at 4°C/min was employed.

Combined GC-MS was performed using a Hewlett-Packard 5992A instrument equipped with a 1 m × 1 mm I.D. silanized glass column containing 3% OV-17 on Gas-Chrom Q (100-120 mesh), maintained isothermally at 220°C. The silicone membrane molecular separator used as the GC-MS interface was located inside the GC oven and was also at 220°C. The injection port temperature was 250°C.

### *Analysis of formation water discharge samples*

The alkane content of these samples was determined as previously described<sup>3,4</sup>. Fully deuteriated alkanes were used as internal standards to facilitate the quantitation<sup>13</sup>.

Elemental sulfur was recovered from these samples by filtration through glass fiber filters. The smallest quantity of sulfur which could be recovered and weighed by this procedure was about 50 mg, which corresponds to a concentration of 50 ppm in 1 l. All but two of the samples contained at least this quantity of sulfur.

### *Analysis of sediment samples*

The determination of alkanes in these sediment samples has been described previously<sup>5</sup>. In the previous report, concentrations of individual alkanes were given; only the total alkane concentration is discussed in the present report.

Concentrations of elemental sulfur in the surficial sediment samples were too low for quantitation by conventional procedures. It had already been demonstrated that elemental sulfur from marine sediments could be determined by GC<sup>10</sup>. Since sulfur enriched in <sup>34</sup>S was commercially available, we explored the use of this material as an internal standard for quantitation by GC-MS<sup>14</sup>. The detection limit of this technique was about 5 μg, which corresponds to 0.5 ppm in 10 g of sediment. At these low concentrations, the elemental sulfur was fully dissolved in the cyclohexane employed for the extraction of alkanes; the solubility of sulfur in cyclohexane at

22°C is 1.02%<sup>12</sup>. Sulfur coeluted with the alkanes during the column chromatography on silica gel, which was employed to separate alkanes from aromatic hydrocarbons and lipids. We were able, therefore, to examine the "alkane" fraction by GC to determine alkane concentrations and by GC-MS to determine sulfur concentrations. Selective ion monitoring at *m/e* 64 (<sup>32</sup>S<sub>2</sub><sup>+</sup>) and *m/e* 66 (<sup>32</sup>S<sup>34</sup>S<sup>+</sup>) was performed to obtain data for quantitation.

## RESULTS AND DISCUSSION

### *Formation water discharges*

Concentrations of alkanes and sulfur in these samples are given in Table I.

TABLE I

ALKANES AND SULFUR CONCENTRATIONS IN FORMATION WATER DISCHARGES FROM PRODUCTION PLATFORMS 288-A AND 296-B

<i>Sample</i>	<i>Date</i>	<i>Platform</i>	<i>Alkanes (ppm)</i>	<i>Sulfur (ppm)</i>	<i>Sulfur/alkanes</i>
B-1	6-26-77	296-B	3.12	300	96
A-1	6-26-77	288-A	0.53	200	377
B-2	7-15-77	296-B	9.02	1000	111
A-2	7-15-77	288-A	12.11	<50	—
B-3	8-21-77	296-B	1.29	1200	930
A-3	8-21-77	288-A	3.70	<50	—
B-4	9-18-77	296-B	2.01	600	299
A-4	9-18-77	288-A	1.07	500	467
B-5	10-23-77	296-B	5.14	1100	214
A-5	10-23-77	288-A	0.94	300	319
B-6	11-14-77	296-B	3.48	600	172
B-7	12-22-77	296-B	3.41	200	59
B-8	1-29-78	296-B	2.62	400	153
B-9	2-05-78	296-B	0.56	60	107
B-10	2-05-78	296-B	1.57	400	255

The total alkane concentrations ranged from 0.53 to 12.11 ppm, while the sulfur concentrations were as high as 1200 ppm. The rate of discharge of formation water varies considerably from day to day, but averages about 1000 barrels (approx. 160,000 l) per day. The mean alkane content of these samples is 3.37 ppm, so the daily alkane discharge is approximately 540 g. The mean sulfur content of these samples is 457 ppm, so the daily sulfur discharge is approximately 73 kg, corresponding to almost 27 metric tons per year, compared with less than 200 kg per year of alkanes.

The ratio of sulfur to alkanes in the formation water samples which contained sulfur ranged from 59 to 930. Fig. 2 shows that there is no clear correlation between alkane and sulfur concentrations.

Sulfur is the major contaminant in the formation water discharges, so we have performed measurements to determine its fates and effects in the environment surrounding the oil field. It has a specific gravity of 2.1, so it can be expected to sink through the water column and become incorporated into the sediments. We have therefore examined the surficial sediments to determine their sulfur content.

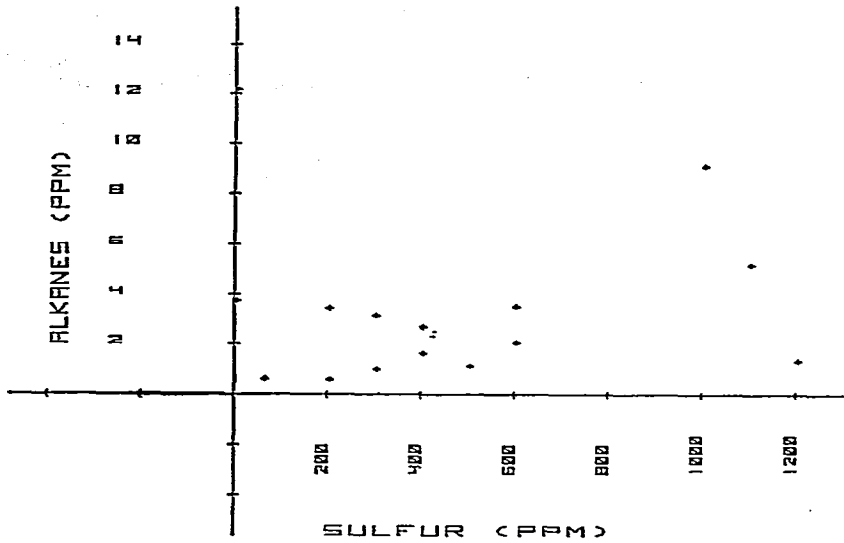


Fig. 2. Relationship between alkane and sulfur concentrations in formation water discharges.

### *Surficial sediments*

Concentrations of alkanes and sulfur in surficial sediments from the vicinity of production platform 288-A are given in Table II, while concentrations of these substances in surficial sediments from the vicinity of well jacket 288-5 are given in Table III. Formation water was still being discharged from platform 288-A when these samples were collected. There are no discharges from well jackets. Well jacket 288-5 was chosen for this study since the prevailing bottom current during most of the year is from NE to SW, and this well jacket is to the NE of the production platforms (see Fig. 1). Data for alkanes in Tables II and III are taken from ref. 5, which also contains data for individual alkanes.

In general, we have found concentration gradients for alkanes in surficial sediments in the immediate vicinity of the production platforms: concentrations decreasing with increasing distance from the discharge. Anomalously low concentrations are sometimes found in sediments from below the structures, presumably due to the scouring effects of currents round the legs of the structures. In Table II, relatively high concentrations (greater than 1 ppm) of alkanes are found within 50 ft. (15.2 m) to the west of the platform and within 25 ft. (7.6 m) to the east. The only high value from this set of samples was in the W600 sample.

Relatively high concentrations of elemental sulfur were encountered immediately to the west of the structure, but the concentration gradients were not as pronounced as for the alkanes. The mean sulfur/alkane ratio was 17.4, considerably lower than in the formation water discharge. The maximum sulfur/alkane ratio observed was only 83.0. As in the case of the formation water discharge, there was no clear correlation between alkane and sulfur content (Fig. 3).

Since there are no discharges from the well jackets, samples were taken from one such structure to determine whether there is any seepage of oil along the well pipes which might result in an additional input of petroleum hydrocarbons into the environment. Sulfur levels were also determined for these samples (Table III). There

TABLE II

ALKANES AND SULFUR CONCENTRATIONS FOR SAMPLES COLLECTED DURING OCTOBER, 1977 IN THE IMMEDIATE VICINITY OF PRODUCTION PLATFORM 288-A

See text for sampling sites.

<i>Sample</i>	<i>Date</i>	<i>Alkanes (ppm)</i>	<i>Sulfur (ppm)</i>	<i>Sulfur/alkanes</i>
W600	10-28-77	4.14	3.45	0.83
W300	10-28-77	0.27	3.11	11.52
W150	10-28-77	0.16	1.45	9.35
W100	10-06-77	<0.01	0.30	—
W75	10-06-77	0.35	3.47	9.91
W50	10-06-77	4.65	9.07	1.95
W25	10-05-77	6.61	11.85	1.79
C	10-05-77	0.20	0.87	4.35
E25	10-05-77	3.42	1.12	0.33
E50	10-05-77	0.02	1.33	66.50
E75	10-05-77	0.27	0.96	3.55
E100	10-05-77	0.03	2.49	83.00
E150	10-28-77	0.38	3.83	10.08
E300	10-28-77	0.11	3.26	29.64
E600	10-28-77	0.29	3.25	11.21

was no alkane concentration gradient in the vicinity of the well jacket. The mean alkane concentration for these samples was 0.12 ppm, less than 10% of the mean concentration (1.39 ppm) for the 15 samples collected from the vicinity of the production platform, and considerably less than that of the samples collected very close to the production platform. Surprisingly, the sulfur concentrations near the well jacket (mean, 4.10 ppm) are comparable to those near the production platform (mean, 3.32 ppm). Thus, the sulfur/alkane ratios for the well jacket site are much higher than at the production platform site.

TABLE III

ALKANES AND SULFUR CONCENTRATIONS FOR SAMPLES COLLECTED DURING OCTOBER, 1977 IN THE IMMEDIATE VICINITY OF WELL JACKET 288-5

See text for sampling sites.

<i>Sample</i>	<i>Date</i>	<i>Alkanes (ppm)</i>	<i>Sulfur (ppm)</i>	<i>Sulfur/alkanes</i>
W600	10-28-77	<0.01	3.00	—
W300	10-28-77	1.13	7.33	6.5
W150	10-28-77	<0.01	6.28	—
W100	10-07-77	0.01	9.50	950.0
W75	10-07-77	0.26	4.43	17.0
W50	10-07-77	0.01	4.18	418.0
W25	10-07-77	0.01	0.44	44.0
C	10-06-77	<0.01	3.96	—
E25	10-06-77	0.05	3.70	74.0
E50	10-06-77	0.15	1.92	12.8
E75	10-06-77	<0.01	3.05	—
E100	10-06-77	<0.01	0.57	—
E150	10-28-77	0.04	4.64	116.0
E300	10-28-77	1.08	36.0	36.0
E600	10-28-77	0.05	7.36	147.2

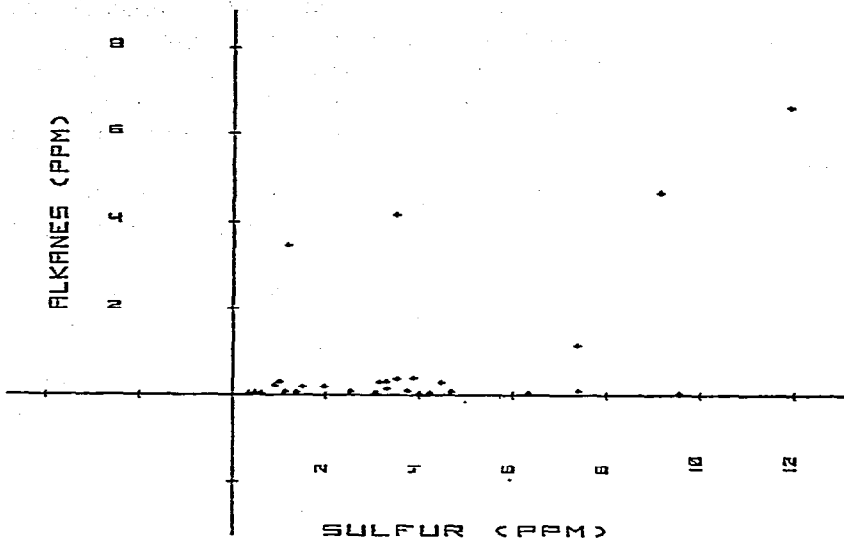


Fig. 3. Relationship between alkane and sulfur concentrations in surficial sediments from the vicinity of production platform 288-A.

## CONCLUSIONS

Sulfur concentrations in the formation water discharges from production platforms are considerably higher than alkane concentrations. Concentration gradients for alkanes are more pronounced than for sulfur in the vicinity of the production platform from which surficial sediments were collected. There were no discernable concentration gradients for either alkanes or sulfur around the well jacket selected for study. Sulfur concentrations were somewhat higher than alkane concentrations around the production platform, but the sulfur/alkane ratio was much lower than in formation water discharges. Sulfur concentrations in surficial sediments around the well jacket are comparable to those around the production platform. Since alkane concentrations were lower at the well jacket site than at the production platform site, sulfur/alkane ratios were higher at the former location.

Since sulfur is present in the formation water discharges at a much higher concentration than alkanes, and since sulfur has a higher specific gravity than water while oil does not, one might expect to find very much higher concentrations of sulfur than alkanes in the surficial sediments. This is not the case. In considering the mode of transport of alkanes to the surficial sediments<sup>5</sup>, we suggested that incorporation into fecal pellets of zooplankton may play a role<sup>15</sup> and we also suggested that sulfur in the formation water discharge could be implicated as a carrier. The latter possibility now seems less likely unless sulfur is rapidly degraded or efficiently dispersed once it reaches the sediments. Periodic resuspension of surficial sediments does take place, but it is difficult to envision how this process would lead to more efficient dispersion of sulfur than alkanes. However, since sulfur concentrations at the

production platform site are similar to those at the well jacket site, it appears that sulfur is indeed transported some distance away from the discharge point.

It is tempting to speculate that the alkanes found in sediments in the vicinity of the production platform derive from a source other than the formation water discharge. This could be by seepage along well pipes (although this was not observed at the well jacket site) or, perhaps, in conjunction with the jettison of other wastes from the platform. We have no evidence for the latter, and should point out that we are unaware of any harmful effects that can be ascribed to the small pools of alkanes below the production platforms.

Several hundred metric tons of sulfur have been discharged from the production platforms during the time that the field has been in operation, assuming that the discharge rate has been relatively constant during this time. Current concentrations in the sediments do not reflect this. Thus, it can be assumed that the sulfur is being degraded. Indeed, we have occasionally observed<sup>6</sup> alkane profiles in seawater collected near the water/sediment interface which are very similar to those of sulfur utilizing bacteria<sup>16</sup>. Sulfur utilizing bacteria are found throughout the region of the oil field, and their populations are not strikingly dense near the production platforms<sup>17</sup>. Thus the distributions of sulfur and the bacteria which utilize this substance are not dissimilar. We hope to further investigate the hypothesis that sulfur discharged from the production platforms supports a population of bacteria at the base of the food web which, in turn, supports the abundant fish and shrimp populations in this region. If this were the case, sulfur could be considered as a nutrient rather than a pollutant.

#### ACKNOWLEDGEMENTS

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