

## FOREWORD

Marine contamination by petroleum, whether by natural seepage or by spills from ships at sea, by accidents in harbour or at offshore installations or by atmospheric or terrigenous input is by no means a new or rare phenomenon. In recent years however, the problems have been highlighted not only by the increased utilisation and marine transport of oil but also by a number of spectacular accidents which have raised questions about possible effects on the ecosystem. A number of detailed studies have been carried out in an attempt to answer these questions. The demands for such knowledge have been further increased by the various questions raised as a result of expansion of offshore exploration and exploitation for oil, particularly in environments hostile to these operations, in regions as far apart as the northern North Sea and the coast of Alaska.

Consequently, diverse aspects of the problem are being studied in several parts of the world by chemists and biologists who are often asking the same questions but using different approaches and sometimes producing conflicting views. Against this background, it seemed timely therefore to bring together a group of scientists from university, industry and government, actively engaged in such work, to examine and discuss common problems relevant to petroleum hydrocarbon contamination of the marine ecosystem and so a Work-

shop was sponsored by the International Council for the Exploration of the Sea, and held in Scotland at Aberdeen in September 1975.

The Workshop considered methodology, occurrence and fate in the environment, and effects on the ecosystem of petroleum hydrocarbons in the sea. Most of the papers presented and updated where necessary, are brought together in the present volume together with an edited version of the recorded discussion that followed each session. Of necessity, the reportage of the discussion is very brief although the proportion of time available for discussion compared favourably with that set aside for formal presentation of the papers. In preparing the discussion reports, the editors were assisted in particular by Dr R. Hardy, Dr R. Johnston, Mr P. R. Mackie and Dr I. C. White, and by comments from several contributors.

No attempt was made to produce specific recommendations but a study of the papers in this volume does give a clear indication of several lines of research which must be followed up before an adequate understanding can be reached of the effects of petroleum in the sea and it is evident that widespread monitoring operations will be fully effective only when the basis of our knowledge has been thus extended.

A list of participants to the workshop may be found in Appendix I.

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## PARTICULATE HYDROCARBON MATERIAL IN OCEAN WATERS\*

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Sea water samples collected in the Sargasso Sea near Bermuda between 1 and 100 m depth (with one station to 800 m) were filtered and the filters examined visually, extracted with pentane and benzene, and the pentane extract analyzed by gas chromatography. Filter extracts showed primarily normal alkanes in the range from 25 to 40 carbons, no odd-carbon predominance, and an unresolved envelope in about half the samples. Such characteristics are extremely similar to the paraffinic wax inclusions found in pelagic tar lumps but different from those expected from many biogenic sources. The number of black or brown "tar-like" particles (10 to 500  $\mu\text{m}$  diameter) visible on the filters decreased in most cases after solvent extraction. Their estimated quantities (1 to 6 particles per litre) account for only about 10% of the amount (1 to 6  $\mu\text{g/litre}$ ) of filterable non-polar hydrocarbons estimated by gas-liquid chromatography of the pentane extract. The total mass of these particles in the water column to 100 m is estimated to be about four times the standing crop of larger pelagic tar lumps at the sea surface.

## INTRODUCTION

Measurements of the hydrocarbon content of sea water often concern only the "dissolved" fraction, i.e. compounds that pass through a fine porosity filter with the sea water sample and are later partitioned into an organic solvent. Workers using gravimetric methods of hydrocarbon quantification (Barbier et al, 1973; Iliffe and Calder, 1974) filter the sea water before extraction, while others using gas chromatography or UV spectrophotometry or fluorescence (Keizer and Gordon, 1973; Gordon and Keizer, 1974; Brown et al, 1974; Zsolnay, 1972) have extracted unfiltered sea water with solvent.

The concentration of hydrocarbons bound in a particulate form and suspended in the ocean waters is not measured in filtered sea water. In unfiltered sea water samples, the efficiency of solvent extraction for removing material from the particulate fraction has not been assessed quantitatively, although some laboratory experiments have been conducted (Gordon et al, 1973).

Possible sources of hydrocarbon-bearing particulate material in the oceans are natural or petroleum-derived hydrocarbons contained in organisms, hydrocarbons adsorbed from the water on to particulate material, microscopic oil droplets, and particles of solid petroleum residues suspended in the water column.

Long lived petroleum residues ("pelagic tar") released on the surface of the sea by crude oil tankers in the process of tank cleaning and deballasting now commonly occur in many oceanic regions (Butler et al, 1973;

National Academy of Sciences, 1975). Highest concentrations occur in the Sargasso and Mediterranean Seas. In the Sargasso Sea during 1970-72, the concentration of tar lumps (several mm diameter or larger) collected with neuston nets averaged 9.4 mg/m<sup>2</sup> of ocean surface (Morris and Butler, 1973); in the Mediterranean Sea during December 1974-January 1975, the average amount of these larger tar lumps was 9.7 mg/m<sup>2</sup> (Morris, Butler, and Zsolnay, 1976).

Thus far, the fate of pelagic tar lumps such as those collected by neuston nets at the ocean surface is largely unknown. In the open ocean, especially in central oceanic gyres such as the Sargasso Sea, stranding on beaches cannot be a major removal mechanism. Evaporative weathering and microbial degradation (Blumer, Ehrhardt and Jones, 1973; Butler, 1975) appear to be the most likely modes of removal of at least part of the crude oil residue. However, evaporation is limited to the more volatile fractions (normally less than C<sub>16</sub>-C<sub>18</sub>) and microbial attack occurs most rapidly on the normal paraffins, with naphthenes and aromatics requiring much longer times to develop adequate cultures. In addition, all such weathering is primarily limited to the surface of the lump, with the interior remaining protected and relatively fresh.

As the surface of a tar lump is degraded, however, it appears to disintegrate to fine particles, thus exposing more of the lump. This process together with simple physical breakup in rough seas would continually reduce the size of pelagic tar lumps and would increase the rate of degradation by increasing the surface area

\* Contribution No. 685 from the Bermuda Biological Station.

per unit volume. Evidence from the evaporative weathering model (Butler, 1975) is that most pelagic tar lumps found near Bermuda in neuston tows are only a small fraction (e.g.  $10^{-4}$ ) of their original size.

Since this crustal material flakes off the lump but is not completely decomposed, it remains for some time in the form of particles which may become suspended deeper in the water column, and should be detectable there. Some preliminary samples of sea water showed small black tarlike particles when filtered. Gas chromatographic analysis of similar particles (Quinn, private communication) suggested that their composition was roughly the same as that of the larger pelagic tar lumps.

Sampling specifically for particulate hydrocarbon material in subsurface water was initiated in November 1972 to quantify the amounts of such material, to characterize its composition, and to determine its contribution to the solvent-extractable fraction of unfiltered water samples.

#### METHODS

Sea water samples from various depths were collected aboard the RV "Panulirus II" at station "S" ( $32^{\circ} 10'N$   $64^{\circ}30'W$ ), located in 3000 m of water about 25 km SE of Bermuda. Station numbers, dates, and depths sampled are given in Table 31. All stations but one were taken in conjunction with the regular "Panulirus II" hydrographic stations (Schroeder and Stommel, 1969; Morris and Schroeder, 1973) and these station numbers have been used in Table 31.

Niskin bottles (5 or 8 litre) were used to collect water samples. To minimize shipboard contamination, the samplers were kept closed at all times except after mounting on the hydrowire, and were opened just prior to lowering. The bottles were rinsed only by the sea water flowing through them while being lowered to depth.

The full samples (5 or 8 litre) of sea water were gravity filtered directly from the Niskin bottle. Several types of fine porosity filters were tested, including glass fibre (Whatman GFC No. 3), polyethylene filter discs (SGA Scientific No. F2332), and Millipore ( $0.45 \mu m$ ) filters. Because of their smooth flat surface, the Millipore filters were superior for particle counts. After filtration, the filters were stored in Millipore Petri-slides, and dried under cover for 24 to 48 hours.

Filter blanks, when subjected to extraction and gas-liquid chromatography of the extracted materials, showed characteristic patterns of peaks but these were easily distinguishable from the pattern characteristic of the particles (see below). Normally, filters were pre-extracted with pentane before filtration of the sea water samples.

Table 31. Station data for "Panulirus II" Station "S" tar-particle samples

Station No.	Date	Depths sampled (m)	Filter type
372	28 Nov 72	5, 25, 100	M
373	11 Dec 72	5, 25, 50, 100	M
374	27 Dec 72	5, 25, 50	M
375	11 Jan 73	5, 25, 50, 100	M
376	7 Feb 73	5, 25, 50, 100	P
377	21 Feb 73	5, 25, 50, 100	P
378	12 Mar 73	5, 25, 50, 100	P
379	16 Apr 73	5, 25, 50, 100	P
381	23 May 73	5, 25, 50, 100	P
382	6 Jun 73	5, 25, 50, 100	P
383	17 Jul 73	5, 25, 50, 100	P
384	27 Jul 73	5, 25, 50, 100	P
385	8 Aug 73	5, 25, 50, 100	GF
385 a	22 Aug 73	1, 5, 25, 50, 75, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800	GF
386	3 Sep 73	5, 25, 50, 100	GF
387	10 Oct 73	5, 25, 50, 100	GF
388	14 Nov 73	5, 25, 50, 100	GF
389	26 Nov 73	5, 25, 50, 100	GF
397	31 Jan 75	5, 25, 50, 100	M
398	11 Feb 75	1, 5, 25, 50, 100	M
399	26 Feb 75	1, 5, 25, 50, 100	M
400	3 Apr 75	1, 5, 25, 50, 100	M
401	27 May 75	1, 5, 25, 50, 100	M
402	7 Jun 75	1, 5, 25, 50, 100	M

M = Millipore filter,  $0.45 \mu m$  porosity

P = polyethylene filter

GF = Whatman glass fibre filter

The possibility that filterable hydrocarbons in sea water came from fragments of pelagic tar lumps suspended in the water column was investigated by counting all the "tar-like" particles visible in microscopic examination of the filters, both before and after solvent extractions, as well as by gas chromatographic analysis of the extracts.

#### PARTICLE COUNTS

Particles visible on the filters under a dissecting microscope at  $50\times$  were counted while still within the petri-slide holder. Characteristics used to categorize the particles were colour, texture, and shape. Such particles varied in appearance from glossy to dull, in colour from brown to grey to black, and in texture from solid to porous. Shapes varied from thin flakes to spheroid granules. Figure 75 shows scanning electron micrographs of some of these particles.

All tar-like particles (black, brown or grey fragments, non-metallic in appearance) were tallied according to size (mean diameter of the particle as viewed if its cross-section was not round) determined by an ocular micrometer. Metallic or other inorganic-looking particles were not counted.

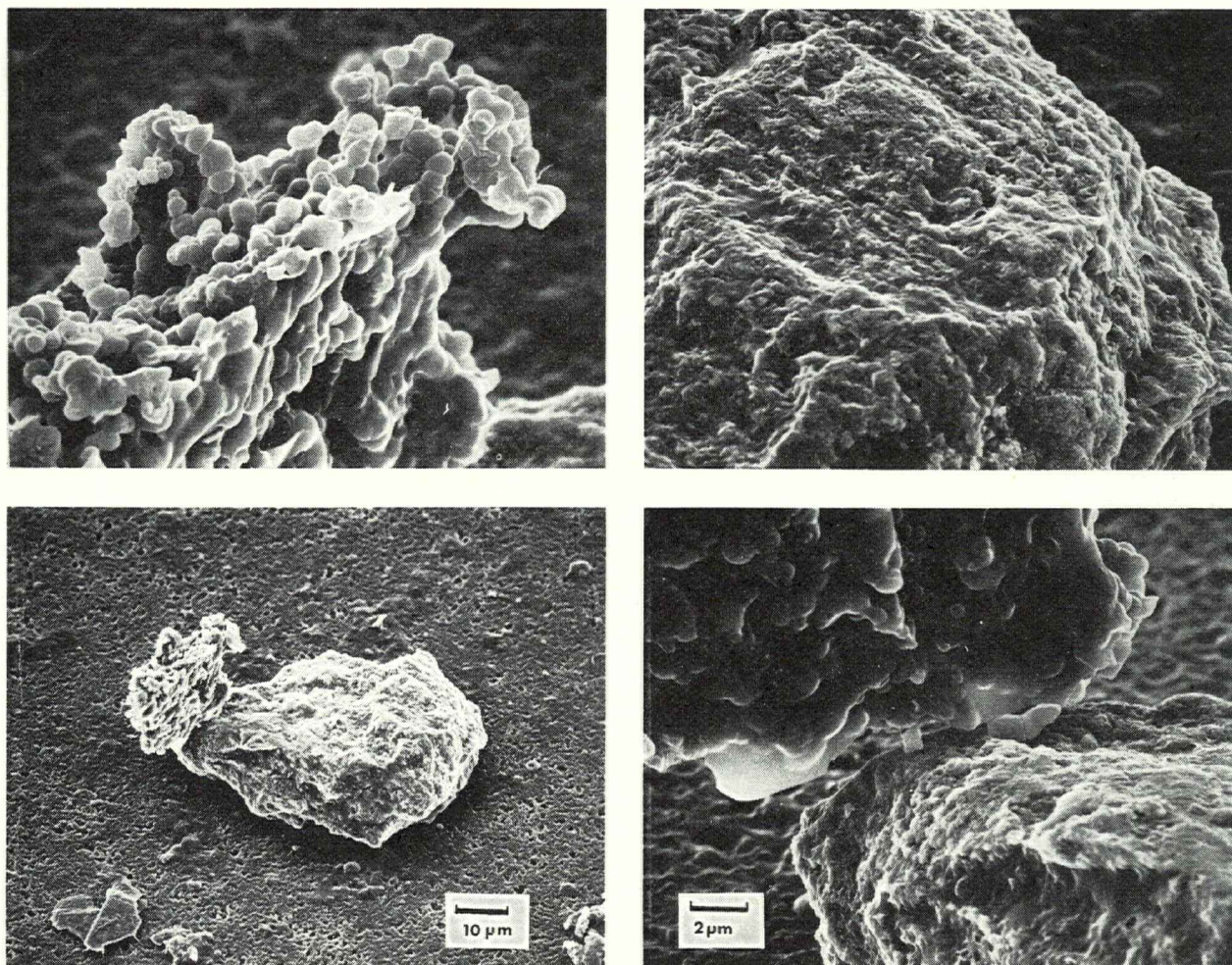


Figure 75. Scanning electron micrographs of two joined tar-like particles retained on millipore filters. Sampling depth 1 meter, 20 August 1975. General view, 667 x; closeups of surface of two particles and junction between the particles 3533 x.

This visual distinction was not always reliable. For example, light-coloured particles that may have been paraffinic wax were difficult to distinguish from other organic particles of similar colour, and were not counted. Similarly, not all particles counted proved to be soluble in either pentane or benzene. Many that had every superficial appearance of being a petroleum speck were not removed by solvent. Others were only partially soluble, suggesting that perhaps the hydrocarbon material was bound to some less soluble matrix. After extraction, some of these complex particles left a brownish halo on the filter. No attempt was made to determine the chemical composition of the brownish halo; it may have been inorganic (e.g. ferric oxide, which has been found in larger pelagic tar lumps) or a relatively polar organic residue.

After the initial count, the filter was placed in a flat glass funnel and extracted with 25 ml of pentane. This procedure was about 90 % efficient, since a second portion of pentane gave only about 10 % additional *n*-alkanes. An extraction with benzene was also made to dissolve any aromatic compounds. For the 1972–73 samples, only initial counts and final counts following both the pentane and benzene extractions were made (Sta. 372–386). Later (Sta. 397–402), counts were also made after the pentane extraction. The number of soluble particles was determined in all samples as the difference in counts between the initial filter and the benzene-extracted filter.

Table 32 presents two examples of data on the loss in particles of each size class between the initial count and after extraction. Sizes (average of length and

Table 32. Examples of counts of tar-like particles on filters and the effect of solvent extraction. The difference between counts represents dissolution of particles

Depth (m)	Size class ( $\mu\text{m}$ )								
	< 20		20-40		40-80	80-140	140-300		
Total number of particles in filter: (I), after pentane extraction: (P), after benzene extraction: (B).									
Station 382, 6 June 1973. Pentane extraction not counted									
	I	B	I	B	I	B	I	B	
5	14	52	8	15	6	3	4	0	
25	24	34	14	14	8	7	3	0	
50	29	34	30	16	33	7	16	2	
100	38	70	39	49	58	19	32	3	
Station 402, 7 June 1975. Pentane extraction counted									
	I	P	B	I	P	B	I	P	B
1	19	17	16	11	10	4	0	1	1
5	27	22	25	13	18	10	5	6	4
25	17	11	19	18	13	6	7	3	2
50	24	15	20	17	14	8	8	3	1
100	6	5	26	5	7	4	2	2	3
Station 385a, 22 August 1973. Pentane and benzene extractions both counted.									
1	74	105	23	36	42	13	8	9	6
5	27	20	11	10	10	2	2	1	1
25	71	27	20	37	13	13	10	2	6
50	40	16	8	16	5	0	5	1	0
75	52	19	16	21	12	10	3	1	1
100	57	32	18	17	12	7	5	5	5
150	39	8	5	12	6	5	10	4	4
200	33	18	7	10	0	3	1	1	3
250	57	29	18	21	20	16	8	10	4
300	61	34	25	34	27	17	8	7	2
350	17	21	8	8	11	3	4	1	1
400	66	37	18	33	29	15	10	4	1
500	95	53	34	29	39	15	14	9	5
600	55	41	22	26	28	14	10	3	3
700	43	40	29	26	21	9	9	8	5
800	34	30	12	19	21	9	6	8	7

width, disregarding thickness) were grouped into six ranges: < 20  $\mu\text{m}$ , 20-40  $\mu\text{m}$ , 40-80  $\mu\text{m}$ , 80-140  $\mu\text{m}$ , 140-300  $\mu\text{m}$ , and 300-500  $\mu\text{m}$ .

#### GAS CHROMATOGRAPHY

The extracts were evaporated to near dryness and kept frozen until analyzed by gasliquid chromatography. Pentane extracts were analyzed for non-polar hydrocarbon compounds by redissolving the residue in 100  $\mu\text{l}$  carbon disulfide and injecting 1 to 10  $\mu\text{l}$  of this solution into the gas chromatograph.

The chromatograph used was a Varian Model 1440 with a 10 ft  $\times$  1/16 inch column of 3% SE-30 on Varaport 30 100/120 mesh, or a 6 ft  $\times$  1/16 inch column of 3% SP 2100 on Supelcoport 100/120 mesh. Operating conditions were:  $\text{N}_2$  carrier gas, 30 ml/min; temperature programmed from 75 to 300°C at 6°/min with a

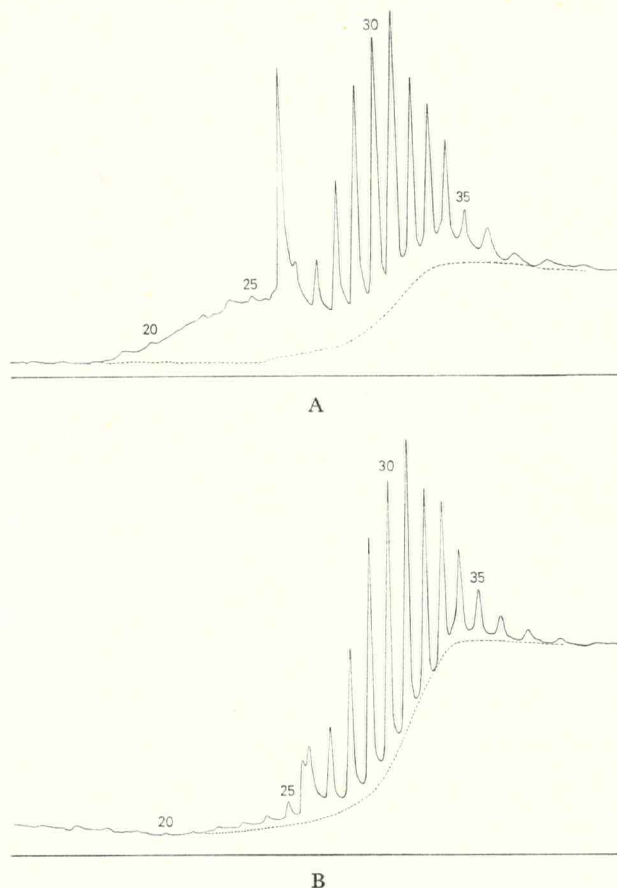


Figure 76. Chromatograms of filter extracts with high *n*-alkane concentrations. A. Sample 399-50 m showing large peak between  $\text{C}_{25}$  and  $\text{C}_{26}$ . Attenuation  $2^{-10}$ . B. Sample 399-100 m with similar distribution but smaller unresolved envelope. Attenuation  $1^{-10}$ .

final temperature of 300°C maintained until all peaks were eluted.

Quantitative standards of *n*-alkanes ( $\text{C}_{14}$  to  $\text{C}_{36}$ ) were regularly run and amounts of each resolved component determined by comparison of peak areas. Unresolved peaks below the principal alkanes formed an "envelope" which was measured by planimetry and quantified by assuming the calibration factor was the same as for the alkane of comparable retention time.

#### RESULTS

##### GAS CHROMATOGRAPHIC ANALYSES

Some typical chromatograms of pentane extracts are shown in Figures 76, 77, and 78. In 43% of the chromatograms, an unresolved envelope was detected; in the remainder, only alkane peaks appeared, with an occasional additional peak probably corresponding to a branched-chain hydrocarbon present between normal  $\text{C}_{25}$  and  $\text{C}_{26}$ .

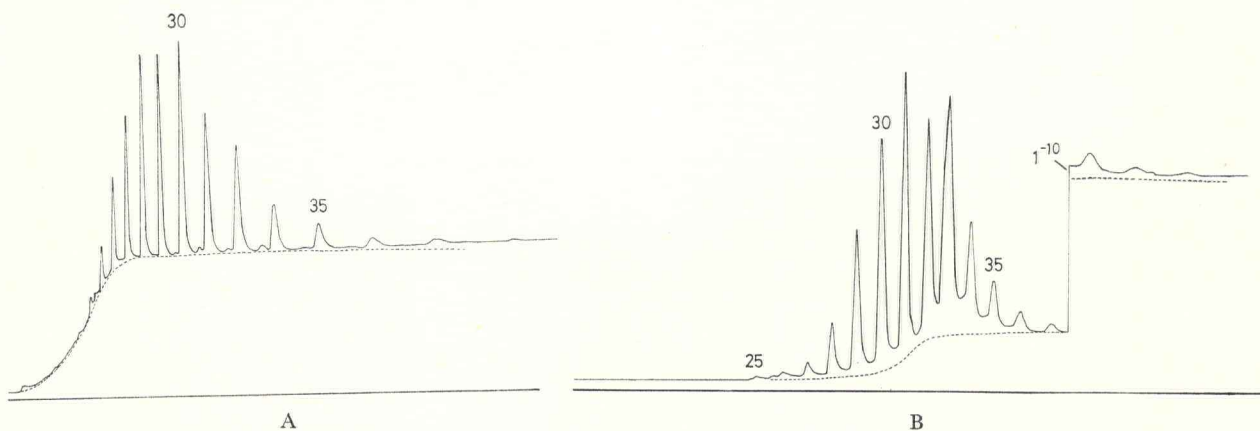


Figure 77. Chromatograms of samples with medium *n*-alkane concentrations. A. Sample 388—50 m lacking unresolved envelope. Attenuation  $2^{-10}$ . B. Sample 401—5 m with small unresolved envelope. Attenuation  $4^{-10}$ — $1^{-10}$ .

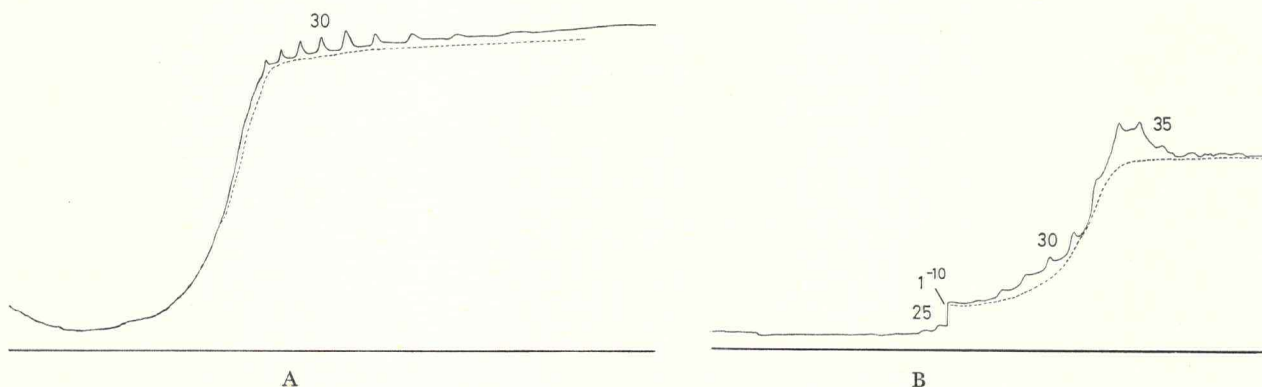


Figure 78. Chromatograms of samples with low *n*-alkane concentrations. A. Sample 387—5 m, lacking an unresolved envelope. Attenuation  $1^{-10}$ . B. Sample 401—50 m with unresolved envelope. Attenuation  $2^{-10}$ — $1^{-10}$ .

The particulate and adsorbed non-polar hydrocarbons retained on the filter and extractable by pentane contained normal alkanes primarily in the range from  $C_{25}$  to  $C_{36}$  with trace amounts down to  $C_{14}$  and up to  $C_{40}$ . This pattern was essentially independent of the sampling depth (Fig. 79). The predominant *n*-alkanes were  $C_{30}$  to  $C_{33}$  with typical concentrations between 0.3 and 0.9  $\mu\text{g/litre}$  for these compounds. (Chromatograms of the benzene extracts were complex, containing not only hydrocarbons but fatty acids, and their analysis is too incomplete to be reported at this time.)

The total concentrations of non-polar (pentane-extractable) hydrocarbons removed from the filters are given in Table 33. Highest concentrations occurred at the 1 m sampling depth, with slightly lower concentrations occurring at greater depths.

At Station S-385a, we sampled the water column to a depth of 800 m (Fig. 80). Despite the considerable variability in filterable hydrocarbons in the upper layer, a pronounced decrease in concentration occurred beneath the 100 m depth, corresponding to the bottom of the seasonal pycnocline.

#### TAR PARTICLE COUNTS

The count data for each sampling depth are summarized in Figure 81. The total for all depths of solvent-soluble particles averaged from 1.4 to 6.3 particles per litre. Highest average counts were at the 50 m depth and lowest just beneath the surface (1 m).

A progressive increase in the apparent solubility of the particles occurred with increasing size of particle. The correlation between size and solubility is strong (Fig. 82). The true extent to which the smaller particles are less soluble in the organic solvents is uncertain, since dissolution of the larger particles seemed to leave some small insoluble particles behind, and these were picked up in the final count. This perhaps explains why the smallest size class ( $< 20 \mu\text{m}$ ) sometimes increased in number after the extraction procedure.

However, the decrease in number of particles was statistically significant for most particle sizes. Using a paired observation *t*-test on the counts before and after extraction we obtained  $p < 0.05$  to 0.001 that extraction did not result in solution of particles. The largest

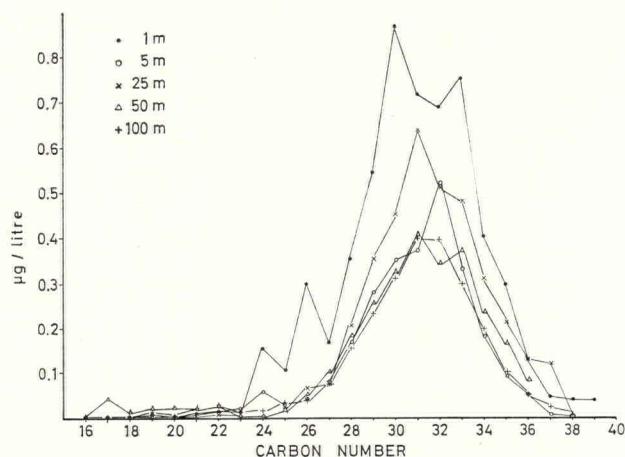


Figure 79. Average distribution (all stations) of *n*-alkane concentrations from pentane extracts of filterable material from five depths in the Sargasso Sea off Bermuda.

size class did not show a significant decrease because of the infrequency of such particles: generally less than one particle per hundred litres (or 20 samples).

A conversion of the counts to weight of particles per filter is desirable to compare with the amount of hydrocarbon found in the gas chromatographic analyses. Simple weighing of the filters was too imprecise to give usable data. Because of the varying shapes and porosity of the particles it is impossible to give an exact estimate from geometric shape, but with some simplifying assumptions we have obtained approximate values. Most particles are oblong, rectangular or round flakes or lumps whose product of length and width can be approximated by  $D^2$ . The thickness of the particles was less variable than diameter; the larger ones tended to

Table 33. Estimates by gas-liquid chromatography of non-polar hydrocarbon concentrations ( $\mu\text{g}/\text{litre}$ ) at different sampling depths retained on filters and recovered by pentane extraction

Depth (m)	<i>n</i>	<i>n</i> -Alkanes median (range)	Unresolved envelope median (range)	Total median (range)
1	5	4.38 (0.67–12.7)	0.39 (0–4.8)	6.15 (0.67–13.1)
5	21	1.13 (0–18.8)	0.13 (0–7.6)	1.23 (0–23.0)
25	21	0.65 (0–18.2)	0 (0–3.0)	0.98 (0–18.6)
50	21	1.15 (0–14.1)	0 (0–5.3)	1.69 (0–25.9)
100	22	0.89 (0–9.9)	0 (0–91.3)	1.78 (0–96.2)

*n* = No. of samples.

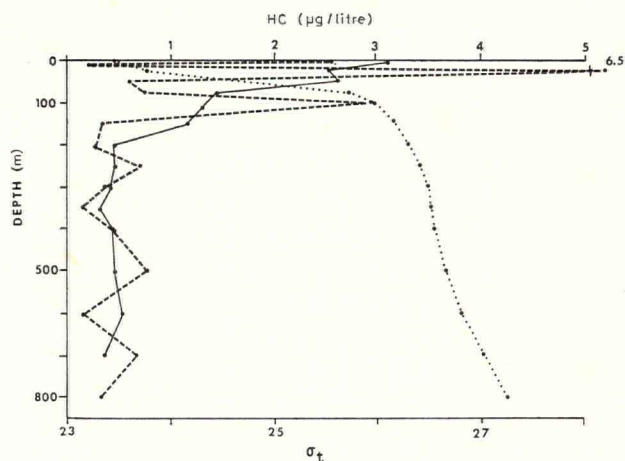


Figure 80. *n*-Alkane concentrations of water column between 0 and 800 m on August 22, 1973. Actual concentrations: dashed line; three-point moving average: solid line; density profile: dotted line. Note pycnocline at 50 to 100 m.

be flakes rather than lumps. Thickness was not measured quantitatively, but because the larger particles were relatively flatter, we assumed it to be approximately  $D^{0.5}$ . Thus the approximate weight  $\hat{Q}$  (in  $\mu\text{g}$ ) of tar particles on the filter is estimated by the expression:

$$\hat{Q} = \sum_i 10^{-6} N_i D_i^{2.5},$$

where  $N_i$  is the number of particles in each size class dissolved from filters by pentane-benzene, and  $D_i$  is the average diameter in  $\mu\text{m}$  of each size class  $i$ . The specific gravity of the particles was assumed to be 1.0.

Estimated weights of soluble particles in the water column derived from this equation are given in Figure 83. The average at 1 m may be too low because only 5 samples were available.

Comparison of the probable number of tar particles per litre of water at each depth (Fig. 81) with the weight of the same particles (Fig. 83) shows that although the most common size is in the 40–80  $\mu\text{m}$  size class (0.4 to 3.3 particles per litre), by weight the particles  $> 80 \mu\text{m}$  were most important and the presence of only one particle  $> 300 \mu\text{m}$  could contribute as much as half the total weight. However, both the greatest number of particles (6.4 per litre) and the greatest weight (1.0  $\mu\text{g}/\text{litre}$ ) occurred at 50 m depth. This is near the bottom of the seasonal thermocline and tar particles (as well as other detritus) could accumulate there during part of the year. Just below the surface (where one might expect a large number of particles from disintegration of surface tar lumps) only small particles ( $< 140 \mu\text{m}$ ) were found, and the least concentration by weight (0.03  $\mu\text{g}/\text{litre}$ ) also occurred.

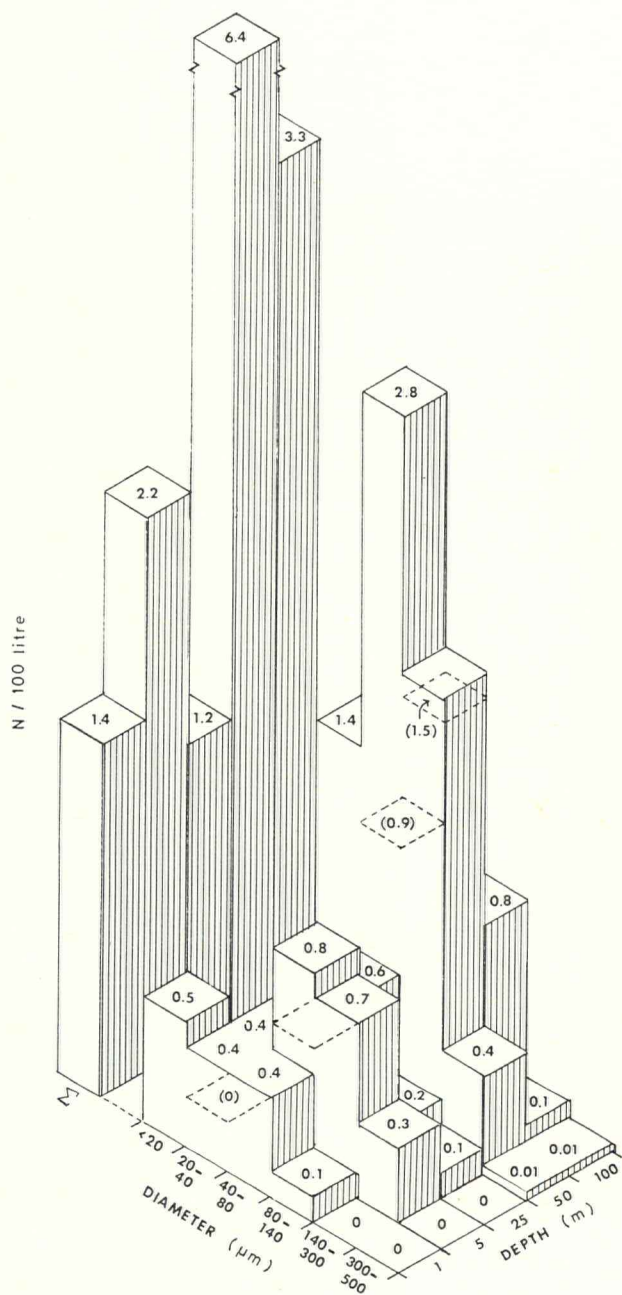


Figure 81. Isometric three-variable graph of number of particles vs. depth and size class.

At Station S-385a, where the water column was sampled at 16 depths between 1 m and 800 m, estimates of weight (Fig. 84) range between 0.05 and 0.42 µg/litre with an apparent maximum at 250 to 300 m depth. This was due to the presence on these two filters of large (> 140 µm) particles that were absent on all other filters. An alternate profile omitting those two

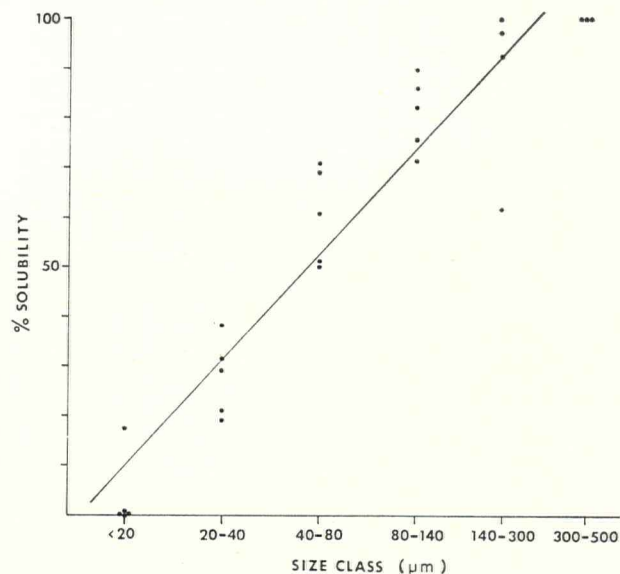


Figure 82. Correlation of solubility and size class of "tar-like" particles.

large particles (Fig. 84) does not show any special depth maximum. On this occasion, however, concentrations in the 0 to 100 m range were considerably below average, and thus the profile is probably not representative of average distributions.

#### DISCUSSION

Measurement by gas chromatography of the amount of hydrocarbon material obtained from filter extracts gives much higher concentrations than estimates from particle counts. The values differ by an order of magnitude for most depths (Fig. 85). The greatest discrepancy is at one metre depth where the highest gas chromatography (6.2 µg/litre) and lowest count (0.03 µg/litre) estimates occurred. Although the variation of concentrations by either estimate is large, the differences are statistically significant at the 99 % confidence level and cannot be reconciled by allowing for greater inaccuracy in the count estimates. Hydrocarbons other than those contained in the tar particles must be present on the filter.

It is possible that some of the filterable hydrocarbons came from the adsorption of dissolved or colloiddally dispersed compounds. Measurement of dissolved hydrocarbons from *filtered* sea water (Barbier et al, 1973; Iliffe and Calder, 1974) has shown higher *n*-alkane concentrations in the dissolved fraction than we measure from the particulate material. This suggests that our analyses may overestimate the concentrations of particulate hydrocarbons by including dissolved compounds or colloidal particles smaller than the filter



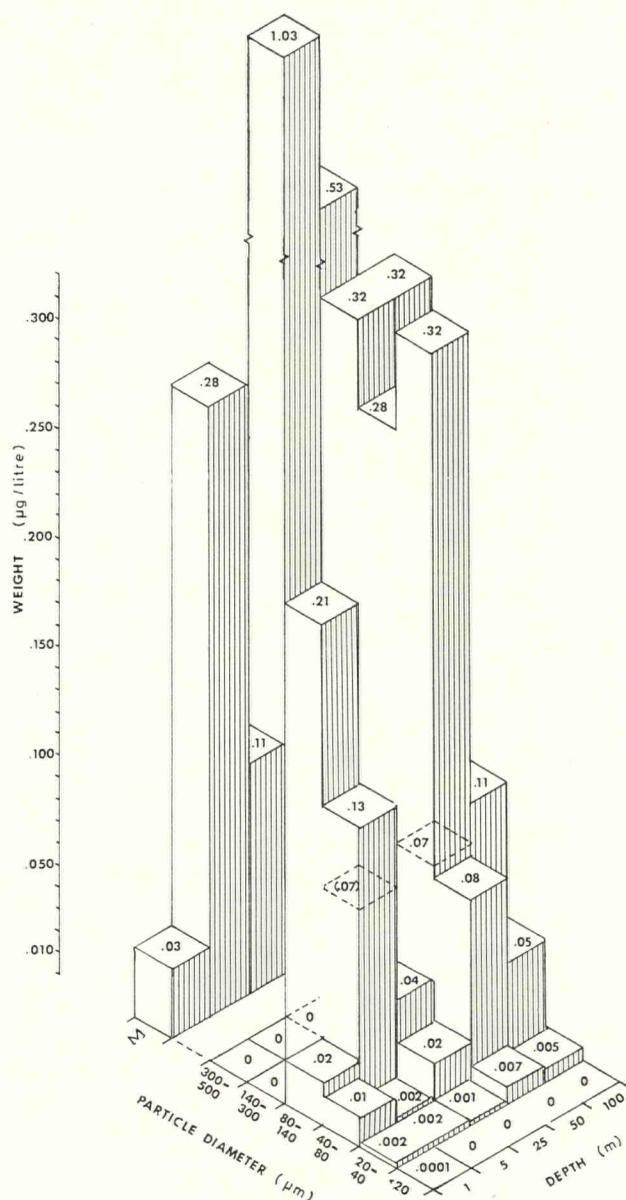


Figure 83. Isometric three-variable graph of estimated average weight of particles per litre vs. depth and size class. Note reversed order of size classes compared to Figure 81.

size, which adsorb on the filter. This would be a satisfactory explanation for the discrepancy between particle count estimates and gas-liquid chromatography measurement of the non polar hydrocarbons except for two reasons. First, both Brown et al. (1974) and Gordon and Keizer (1974) reported concentrations similar to ours by extracting *unfiltered* sea water. In this case higher values from the dissolved fraction would be expected. Second, the findings of Wade and Quinn (1975) support the use of non-gravimetric methods.

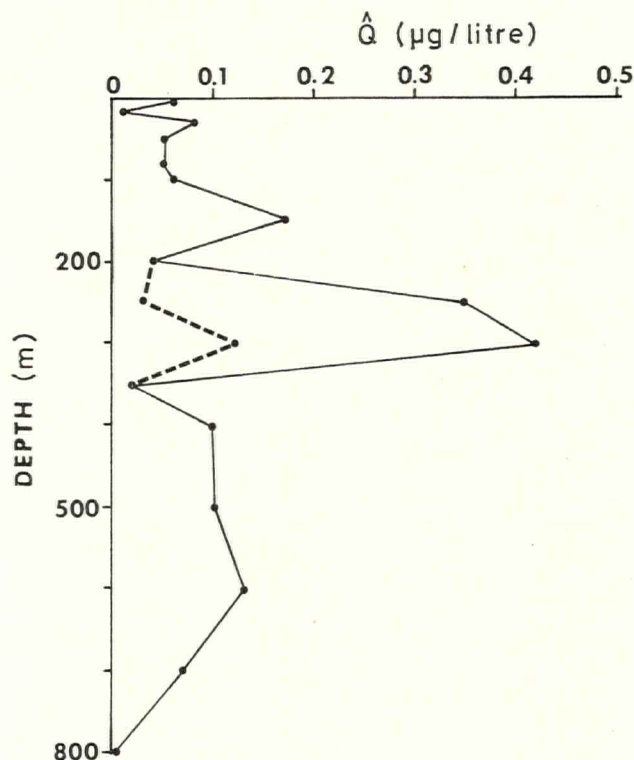


Figure 84. Estimated weights of tar particles retained on filters from sea water samples obtained 22 August 1973 between 1 and 800 m depth. Dashed line indicates results if occurrence of large particles ( $> 140 \mu\text{m}$ ) on the 250 and 300 m samples is excluded.

They found that filtering sea water resulted in retention of most of the hydrocarbons on the filter. The relative contribution of the particulate vs. adsorbed fractions is unresolved.

Our normal alkane distributions (e.g. Fig. 79) are similar to those reported by Barbier et al. (1973) from the dissolved fraction. They found a range of *n*-alkanes from  $\text{C}_{14}$  to  $\text{C}_{37}$  with maxima between  $\text{C}_{27}$  and  $\text{C}_{30}$ . No odd-carbon predominance occurred and the unresolved envelope was small. Our samples showed a somewhat higher *n*-alkane maximum (between  $n\text{-C}_{30}$  and  $n\text{-C}_{33}$ ) the frequent lack of an unresolved envelope, and an odd/even carbon preference index between 0.9 and 1.1.

Wade and Quinn (1975) have also reported finding black particles in surface and subsurface samples from the Sargasso Sea. By analogy with a laboratory experiment in which large pelagic tar lumps were shaken with filtered sea water, they concur that these particles were formed by the disintegration of pelagic tar.

The relative contribution of biogenic vs. petroleum sources to the filterable hydrocarbon fraction is a difficult question to address. Three criteria for distinguishing petroleum derived from biogenic hydrocarbons are

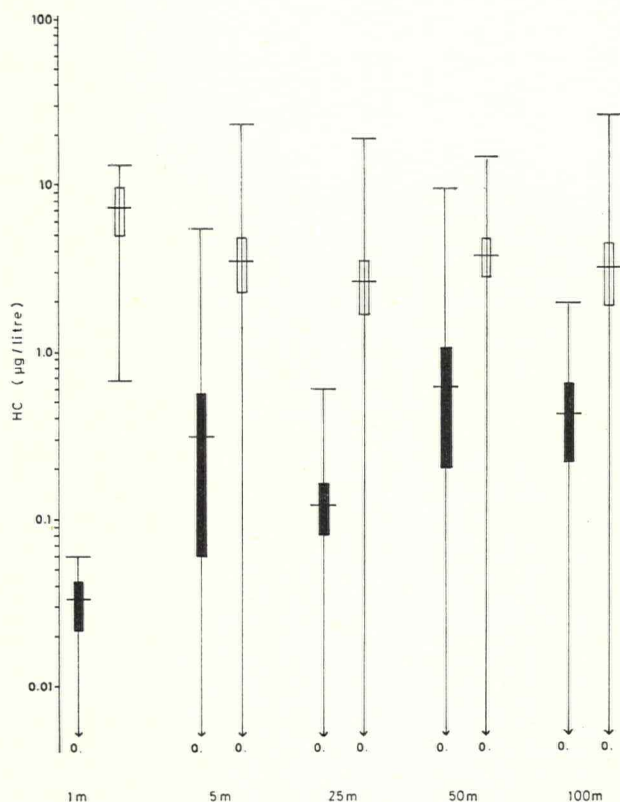


Figure 85. Comparison of estimated concentrations ( $\mu\text{g}/\text{litre}$ ) of particulate material on filters based on particle counts (dark bars) and on gas chromatographic analysis (white bars) at five sampling depths. Range of values indicated by end lines, mean by central horizontal line, and one standard error on either side of the mean by the wide vertical bar.

a) lack of odd-even carbon preference in the paraffins, b) the presence of the  $\text{C}_{18}$  to  $\text{C}_{20}$  isoprenoids, with pristane/phytane ratios of the order of 1/2, and c) the presence of a complex mixture of naphthenic, aromatic and heterocyclic compounds in an unresolved envelope of the chromatogram.

Our chromatograms (Figs. 76 to 78) lacked significant amounts of pristane, phytane, or normal paraffins below about  $\text{C}_{25}$ . The unresolved envelope was undetectable in about half the samples. In a few samples there were small peaks other than normal paraffins between  $\text{C}_{18}$  and  $\text{C}_{19}$  (but not phytane), between  $\text{C}_{19}$  and  $\text{C}_{20}$ , and a large peak between  $\text{C}_{25}$  and  $\text{C}_{26}$ .

Biogenic hydrocarbons extracted from unialgal phytoplankton cultures generally show only a few specific alkanes (Blumer et al, 1971) and those are often branched or cyclic. By comparison, the extracts of mixed plankton (Clark and Blumer, 1967; Blumer et al, 1971) usually show compounds most strongly in the  $\text{C}_{15}$  to  $\text{C}_{22}$  region. Although some mixtures of plankton show equal amounts of odd and even normal paraffins,

odd-carbon chain preference is more typical. In Fig. 79, only the 1 m average shows any indication of an alternation in amounts of successive  $n$ -paraffins.

The absence in our samples of these lower alkanes, or the isoprenoids, the carbon preference index near 1.0, the presence of a few dominant non-alkanes, and the partial presence of an unresolved envelope, suggest both a petroleum and a biogenic origin for the filterable fractions. Certainly the concentrations were much too high to be accounted for simply by the natural hydrocarbon content of the few organisms on the filter.

A distinct similarity exists between our profiles of  $n$ -alkanes from the filter extracts, and the profiles obtained from wax inclusions in pelagic tar lumps (Blumer et al, 1973; Butler et al, 1973). These may be a source of some of the  $\text{C}_{25}$  to  $\text{C}_{37}$  alkanes. Because of their light colour they would have been overlooked in the counts of black or brown "tar" particles.

That so few compounds of lower molecular weight were found in the filterable hydrocarbons is puzzling. Simple evaporative weathering (Butler, 1975) even for long periods of time, would not be expected to deplete the hydrocarbon profile above about  $\text{C}_{18}$ . Microbial attack degrades paraffins at approximately the same rate over a wide range of chain lengths, but branched or cyclic compounds are attacked much more slowly (National Academy of Sciences, 1975). A microbially degraded sample of petroleum-derived hydrocarbons would be expected to show an unresolved envelope with a few distinctive isoprenoid or other peaks, and not a regular succession of higher paraffins only. Thus some reason other than evaporation or microbial degradation is required to explain the absence of hydrocarbons below  $\text{C}_{25}$  in virtually all the samples we analyzed (Figs. 76 to 79).

Since longer chain  $n$ -alkanes are very insoluble in sea water and must be dispersed as micelles if at all, these longer molecules may be preferentially adsorbed on to the filter or suspended particulate material while the lower molecular weight hydrocarbons pass through in the dissolved or colloidal state. Analysis of the filtered water could test this hypothesis. However, the data of Barbier et al. (1973) do not show any special filter adsorption of the higher molecular weight hydrocarbons, while Wade and Quinn (1975) report almost total retention of hydrocarbons by the filter.

The large excess of extractable hydrocarbons of uncertain origin on the filter masked the chromatographic analysis of the composition of the smaller fraction of "tar" particles. Since their small size precluded the analysis of individual particles, their true composition is still unresolved. At present, the basic evidence we have for assuming the dark particles on the filter are "tar" is a) the knowledge that tar lumps do disintegrate into small particles, and b) the presence in the ocean of par-

ticles of similar appearance that are soluble in pentane and benzene. Other more sensitive and selective methods of analysis such as mass spectrometry (Giger and Blumer, 1974) or high performance liquid chromatography (Zsolnay, 1973) should provide further information.

Integrating the estimated concentrations of tar particles within the upper 100 m gives an estimate of 40 mg of tar particles beneath each square metre of ocean surface. The surface concentration of tar lumps in the Sargasso Sea is approximately 10 mg/m<sup>2</sup>, with a residence time of the order of a year (Morris and Butler, 1973). Tar particles in the water column, although derived from the surface tar lumps, may exceed the quantity of lumps floating on the surface at any given time simply by being more resistant to degradation, and thus having a longer residence time in the water column than the residence time of the parent lumps on the surface.

Considering the inaccuracies inherent in the tar particle estimates and the variability encountered during surface tar sampling (a factor of ten for individual samples, a factor of two for the geometric mean of 16 samples) the agreement seems plausible, and implies a residence time for the suspended particles of the order of several years.

#### SUMMARY

1. Sea water samples from the upper 100 m of the Sargasso Sea were analyzed for a particulate hydrocarbon fraction. Alkanes retained by fine porosity filters and extractable with pentane and benzene were measured by gas-liquid chromatography in concentrations averaging from 1 to 6 µg/litre.

2. The hydrocarbons consisted primarily of a series of *n*-alkanes from *n*-C<sub>25</sub> to *n*-C<sub>36</sub>. An unresolved complex mixture was measurable in 43 % of the filter extracts. Some contained a relatively strong peak falling between C<sub>25</sub> and C<sub>26</sub> in retention time.

3. Tar-like particles were visible on the filters. Abundance of these particles as determined by the decrease in counts in each size class after solvent extraction of the filter varied from 1 to 6 per litre. The most common particle size was 40 to 80 µm. Maximum abundance of particles occurred at 50 m depth.

4. The solubility of the particles increased with increasing size. All particles > 300 µm were soluble, but at this size, particles only occurred on the average of one per 100 litre of sea water.

5. Estimated quantities of tar particles suspended in the water column averaged between 0.03 and 0.6 µg/litre. This accounts for 10 % or less of the hydrocarbons extracted from the filter, but would account for about 4 times the standing crop of large pelagic tar lumps at the sea surface.

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