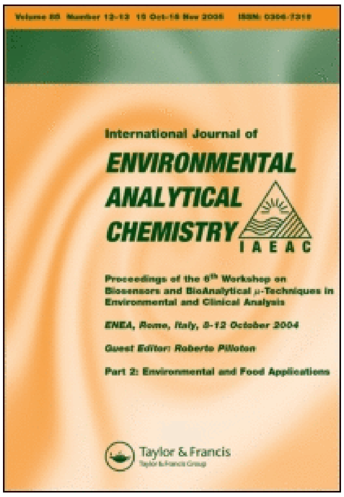

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Jones, D. M. , Rowland, S. J. , Douglas, A. G. and Howells, S.(1986) 'An Examination of the Fate of Nigerian Crude Oil in Surface Sediments of the Humber Estuary by Gas Chromatography and Gas Chromatography-Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 24: 3, 227 — 247

To link to this Article: DOI: 10.1080/03067318608076473

URL: http://dx.doi.org/10.1080/03067318608076473

Intern. J. Environ. Anal. Chem., 1986, Vol. 24, pp. 227–247
0306-7319/86/2403-0227 $18.50/0

Printed in Great Britain

An Examination of the Fate of Nigerian Crude Oil in Surface Sediments of the Humber Estuary by Gas Chromatography and Gas Chromatography-Mass Spectrometry[†]

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The hydrocarbon composition of surface sediments at two lithologically different sites in the Humber Estuary (U.K.) has been examined by gas chromatography and gas chromatography-mass spectrometry. The sediments were sampled 5, 7 and 12 months after the accidental spillage of 6000 tonnes of a Nigerian light crude oil into the estuary from the tanker "Sivand". The occurrence of distinctive marker compounds in the Nigerian oil facilitated the identification of residues of the "Sivand" cargo in the sediments up to 12 months after the spill.

Interpretation of chromatograms revealed several other sources of hydrocarbons contributing to the sediments including those from algae, higher plants and fossil fuel combustion products. Field observations and laboratory studies indicated that the latter compounds were less readily biodegraded in sediments than the oil-derived hydrocarbons. Possible reasons are discussed.

KEY WORDS: Hydrocarbons, Humber Estuary, Nigerian crude, Biodegradation, Oil spill.

[†] Presented at the Workshop on Chemistry and Analysis of Hydrocarbons in the Environment, Barcelona, November 1984.

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INTRODUCTION

The fate of crude oil spilled into the marine environment is dependent on a number of physico-chemical and biological factors, including evaporation, dissolution, photooxidation, biodegradation and (for beached oil) the effects of sediment turnover due to tidal action.[1-3] These processes gradually reduce the concentration and alter the composition of hydrocarbons in sediments, sometimes making positive identification of a spilled oil very difficult. However, some oils are readily recognised even after extensive alteration; for example, certain constituents of Nigerian crudes persist for long periods in surficial sediments and have been used to detect oily residues several months after small experimental oil spills.[4]

In September 1983, 6000–7000 tonnes of Nigerian crude oils was accidentally spilled from the tanker "Sivand" into the Humber Estuary, on the east coast of England. The resulting slick was sprayed with about 30 tonnes of two types of dispersant but successive tides distributed the oil over the entire 50 miles of the estuary.[5,6]

We have examined the concentration and composition of hydrocarbons in sediments at two sites in the estuary, five, seven and twelve months after the spill and report here our initial findings.

EXPERIMENTAL

Samples

Sediments were collected from Humberston Fitties (HF) and Blacktoft (HB) on the Humber Estuary (Figure 1). Site HF is a fairly flat beach in which the sediments are predominantly sandy (~9% clay) and which is bounded on the landward side by salt marsh. The sediments at site HB, a steeply sloping bank of the River Humber backed by extensive reed beds, consist mainly of dark sticky muds (~90% clay).[7] Sediments were collected with hand corers, the cores were divided into sections, transferred to the laboratory within a few hours and kept frozen until analysed.

Methods

Each sediment core section was extracted by ultrasonication with

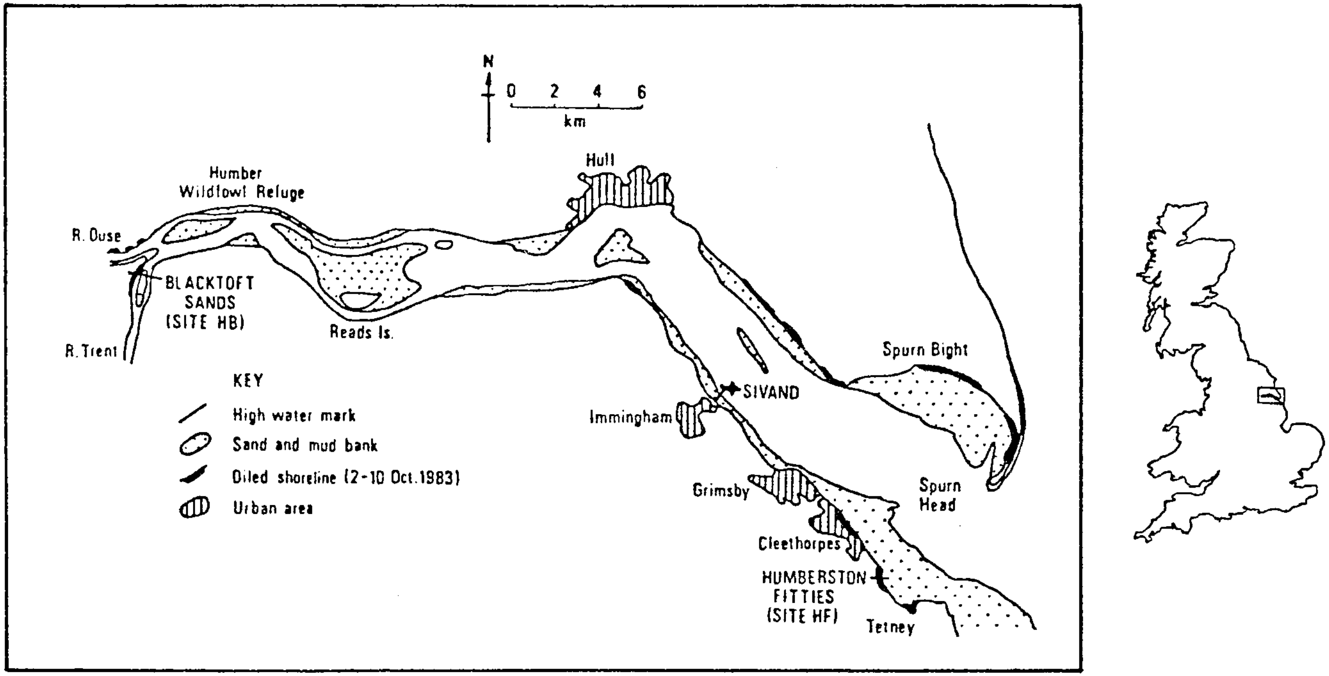


FIGURE 1 Location map of the Humber Estuary showing sampling sites, HB and HF.

methanol and dichloromethane. The resulting extracts and a sample of the oil from the "Sivand's" cargo were each divided into three aliquots: one was separated by column chromatography on alumina/silica into an aliphatic and an aromatic fraction using light petroleum (B.P. 40–60°) and 20% dichloromethane in light petroleum as eluants respectively.[8] A second aliquot was separated in the same way and the resulting aliphatic and aromatic fractions recombined to give a total hydrocarbon fraction. The third aliquot was weighed and stored.

Fractions were examined by gas chromatography on a 50 m × 0.3 mm i.d. fused silica column coated with OV-1 (total and aliphatic hydrocarbons) or on a 40 m × 0.15 mm i.d. glass capillary column coated[9] with SE-54 (aromatic hydrocarbons). Hydrogen was used as carrier gas; oven temperature was programmed from 50°C at 4°C min^{-1} to 310°C (total and aliphatic hydrocarbons) or 290°C (aromatic hydrocarbons).

The fractions were also analysed by combined gas chromatography-mass spectrometry (GC-MS) on a 25 m × 0.31 mm i.d. fused silica column coated with 5% phenylmethylsilicone. The oven temperature was programmed from 80°C to 280°C at 4°C min^{-1} using helium as carrier gas. The chromatograph was coupled to a VG Micromass 12B mass spectrometer and data were acquired and processed by a VG 2000 data-system. The operating conditions for the mass spectrometer were: 50 eV ionisation voltage, 40–460 amu mass range, 2–2.5 secs scan rate, 200 μA emission current.

Laboratory biodegradation studies were carried out using a method described previously[10] which involved the addition of crude oil to a fresh surface sediment–seawater slurry. Sediment from Bowness-on-Solway was used for the Nigerian oil (200 μl) degradation experiments and sediment from Dunstaffnage Bay near Oban, was used for the degradation experiments with North Sea Oil (100 μl).

Compounds were identified by co-chromatography with synthesised compounds or by comparison of retention times and mass spectra with those of the synthesized compounds. The pentacyclic triterpanes in the aliphatic hydrocarbon fractions were identified by GC-MS of the pentacyclane concentrate of Whitehead[11] under the same conditions as that of the samples. The bicyclic alkanes were identified by comparison of GC-MS results with published data.[12]

RESULTS AND DISCUSSION

Concentrations of total hydrocarbons in the Humber sediments for the 12 month period of the study are shown in Table I. Gas chromatograms of total and aromatic hydrocarbon fractions isolated from "Sivand" oil and from the sediments after 7 and 12 months are shown in Figures 2, 3 and 4. Gas chromatograms of crude oils degraded in the laboratory are shown in Figures 5 and 6. Peak identities are listed in Table II and in figure legends.

Hydrocarbon composition of "Sivand" Nigerian crude oil

The hydrocarbon composition of "Sivand" crude was similar to that of other Nigerian crude oils.[13,14] Particularly notable features that distinguished it from many other oils were (Figure 2) the high pristane content, the presence of an unusual distribution of triterpanes (e.g. squalane (S),[15] 18α(H)-oleanane (O))[11,13,16,17] and the unusual abundance and distribution of bicyclic sesquiterpanes[18] (e.g. bc2, bc3). Steranes, which are another group of hydrocarbons commonly used for "fingerprinting" oils,[19] were very minor components of "Sivand" oil. In addition, the oil was distinguishable from other oils of different thermal maturity by the relative proportions of alkylnaphthalenes and alkylphenanthrene isomers.[20,21] Whilst individual Nigerian crudes differ somewhat in their hydrocarbon composition, it is generally accepted that many of them were derived from source rocks with a significant input of terrestrially-derived organic matter deposited in a deltaic environment.[13,16,17] When undegraded, such oils can be readily differentiated from oils whose source is marine-derived organic matter,[17] and from those which also have a different thermal history. However, after spillage into the marine environment various processes alter the composition of crudes and limit the use of certain compound classes as "fingerprints".

Concentration and composition of hydrocarbons in intertidal sediments of Humberston Fitties

Five months after the spill of 6–7000 tonnes of oil from the tanker "Sivand", over 50,000 $\mu g\,g^{-1}$ (dry weight sediment) of total hydrocarbons were still present in the sandy sediments at Humberston

TABLE I

Concentrations of total hydrocarbons ($\mu g\, g^{-1}$ dry weight of sediment) in Humber estuary sediments

Site (Period post spill)	Humberston Fitties (HF)				Blacktoft (HB)		
	(5 months)	(7 months)	(12 months)		(5 months)	(7 months)	(12 months)
Depth							
2 cm	53660	2204	4913	5 cm	2364	3371	325
7 cm	3766	200	2277	10 cm	1365	1246	988
12 cm	174	47	62	15 cm	1545	773	2185
17 cm	32	35	36	20 cm	742	731	645
22 cm	40	37	—	25 cm	ns	594	—

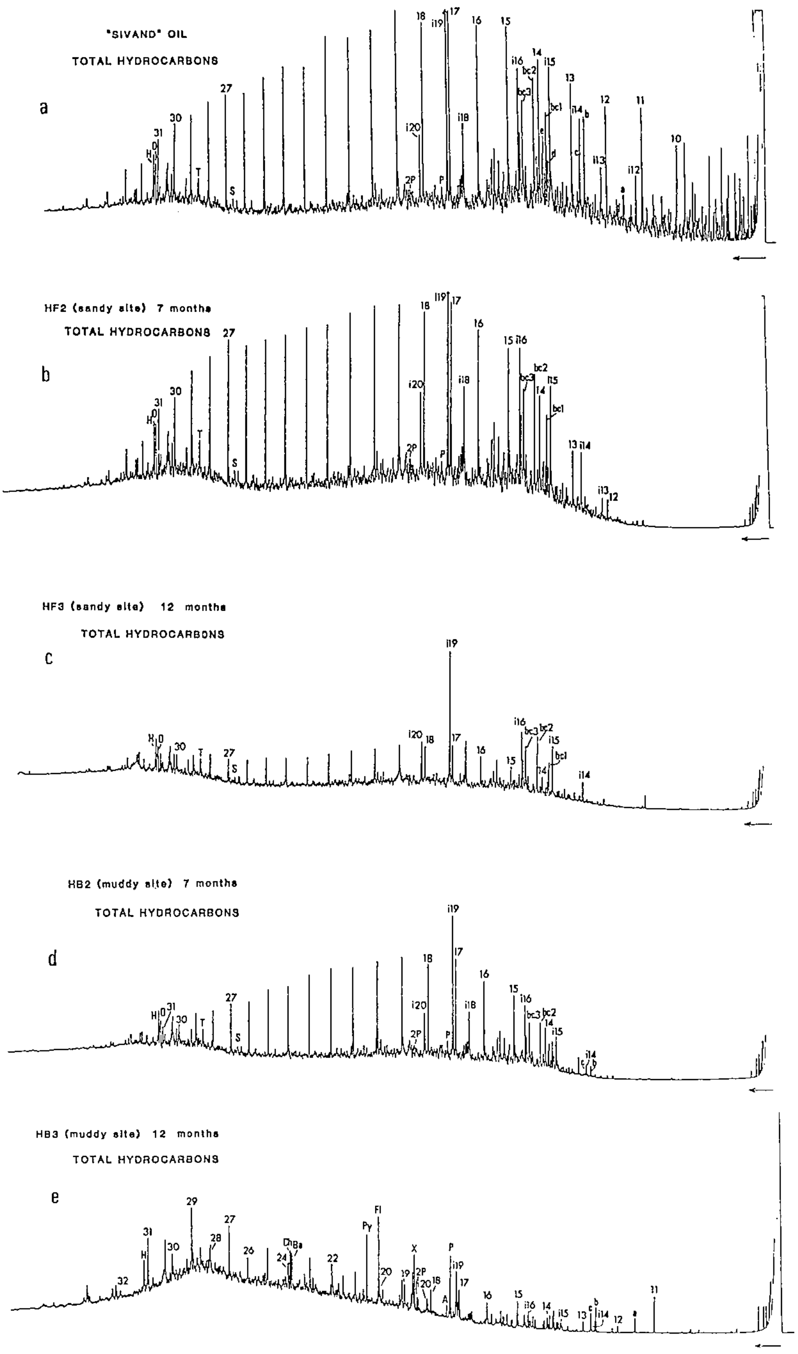


FIGURE 2 Gas chromatograms of total hydrocarbon fractions isolated from "Sivand" oil and HF (0–2 cm) and HB (0–5 cm) sediments. Peaks labelled 10–32 are *n*-alkanes and i12–i20 are isoprenoid alkanes with that number of carbon atoms. Other peak identification as in Table II.

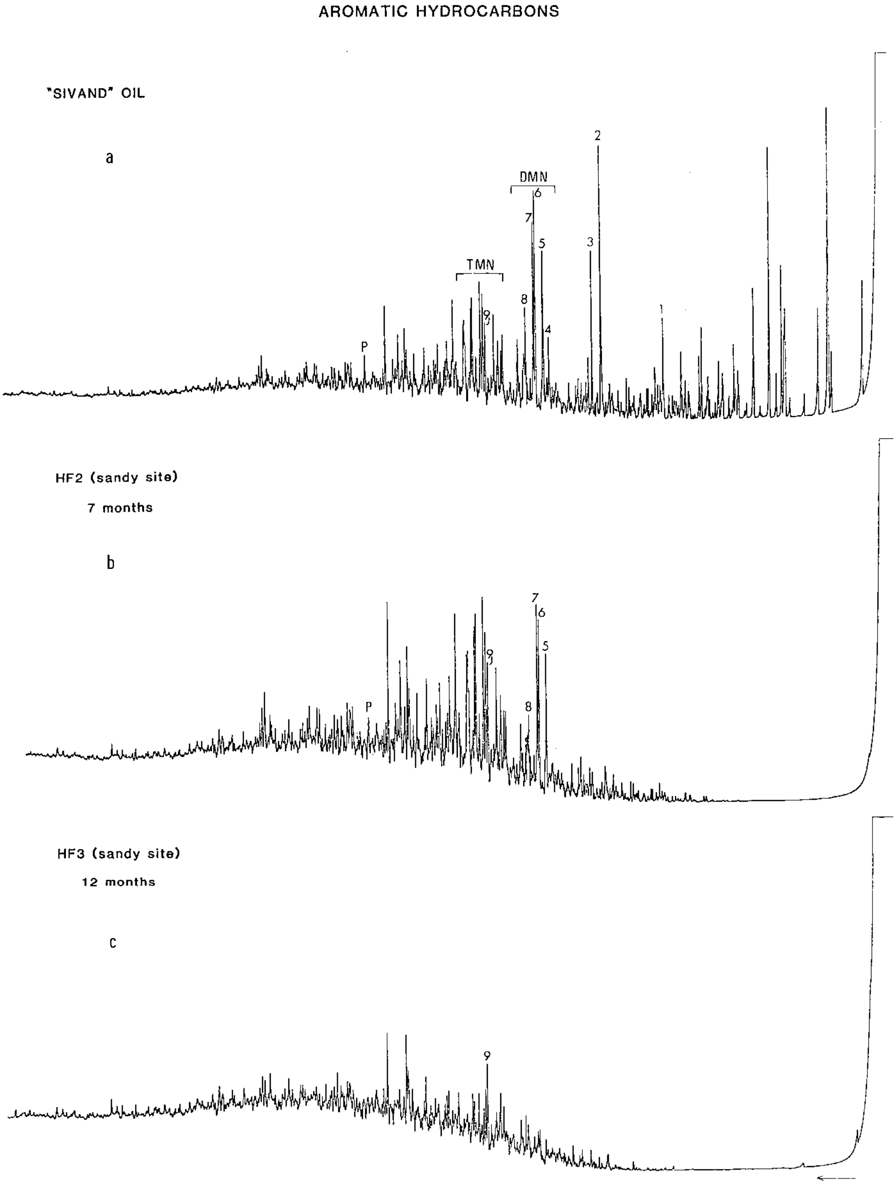


FIGURE 3 Gas chromatograms of aromatic hydrocarbon fractions isolated from "Sivand" oil and HF (0–2 cm) sediments. Peak identifications as in Table II.

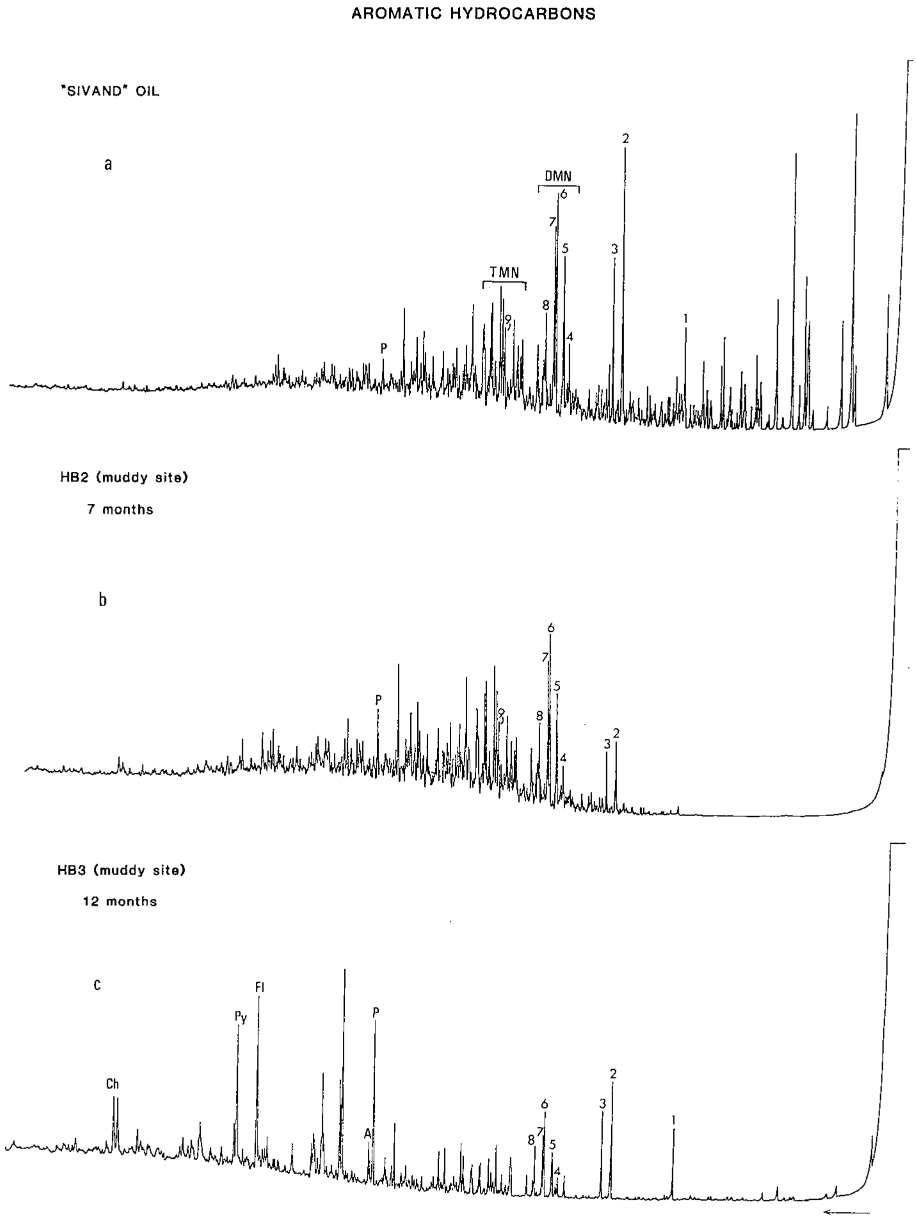


FIGURE 4 Gas chromatograms of aromatic hydrocarbon fractions isolated from "Sivand" oil and HB (0–5 cm) sediments. Peak identifications as in Table II.

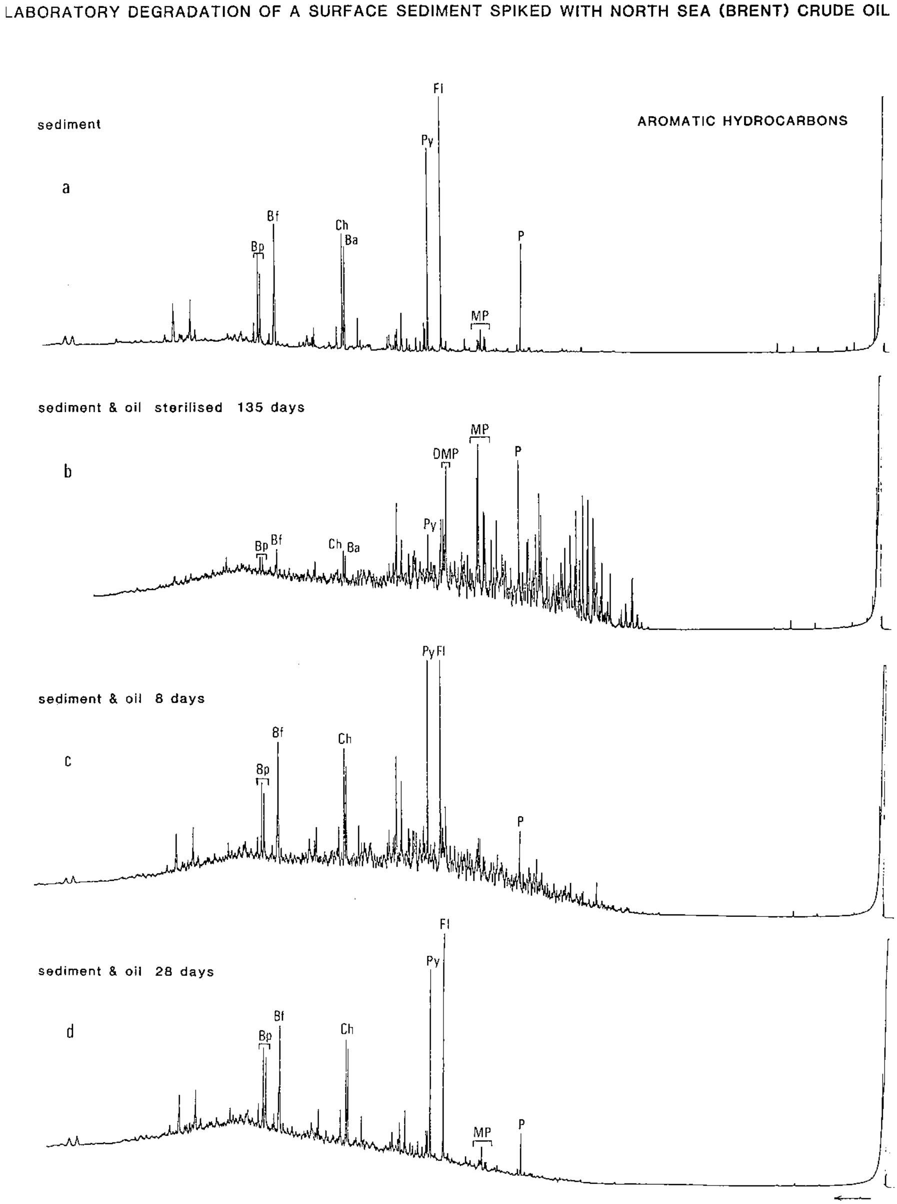


FIGURE 5 Gas chromatograms of aromatic hydrocarbon fractions isolated from laboratory-degraded crude oil. Peak identifications as in Table II.

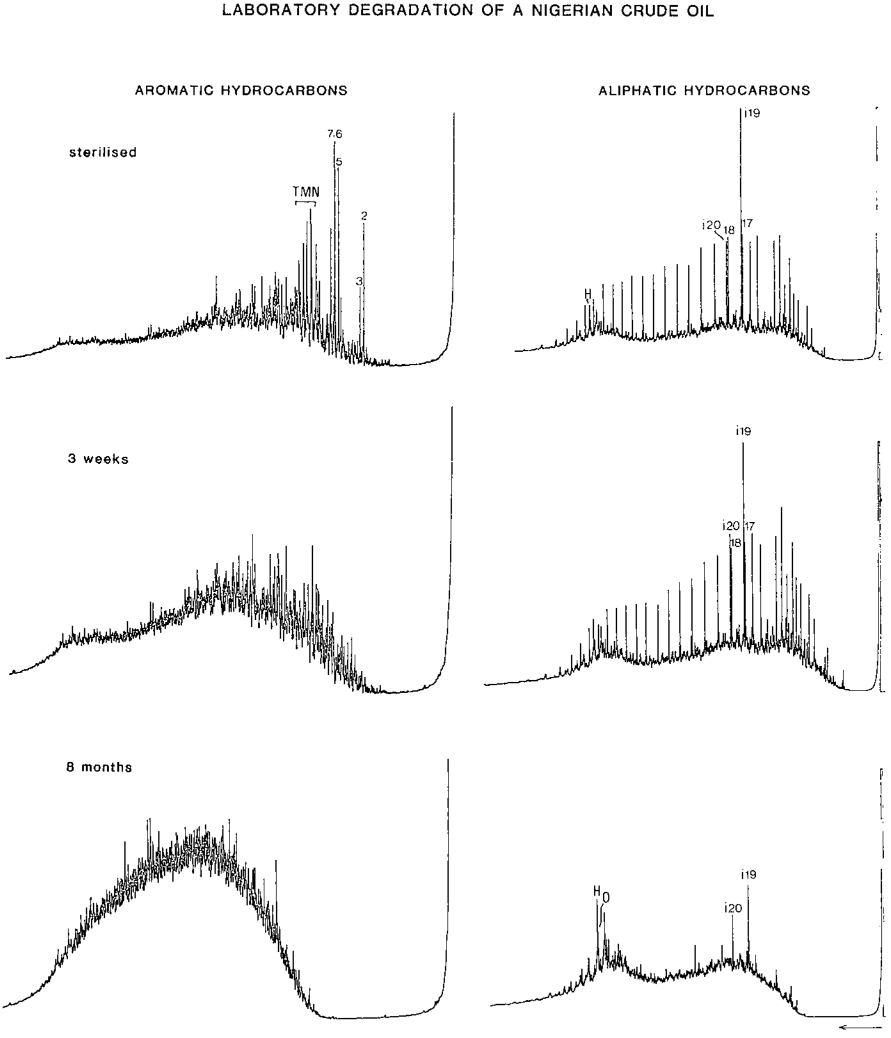


FIGURE 6 Gas chromatograms of aromatic and aliphatic hydrocarbon fractions isolated from laboratory-degraded Nigerian crude oil. Peak identifications as in Figures 2 and 3.

TABLE II

Peak identifications

Peak	Assignment	
1	Naphthalene	(Peak a in Figure 2)
2	2-Methylnaphthalene	(Peak b in Figure 2)
3	1-Methylnaphthalene	(Peak c in Figure 2)
4	2-Ethylnaphthalene	
5	2,6-Dimethylnaphthalene + 2,7-Dimethylnaphthalene	(Peak d in Figure 2)
6	1,3-Dimethylnaphthalene + 1,7-Dimethylnaphthalene	(Peak e in Figure 2)
7	1,6-Dimethylnaphthalene	
8	2,3-Dimethylnaphthalene + 1,4-Dimethylnaphthalene	(Peak f in Figure 2)
9	α,β-Ethylmethylnaphthalene ?	
bc1	C_{15} bicyclane	
bc2	C_{15} bicyclane (tentatively identified as structure IV)	
bc3	C_{15} bicyclane (tentatively identified as structure V)	
DMN	Dimethylnaphthalenes	
TMN	Trimethylnaphthalenes	
P	Phenanthrene	
A	Anthracene	
2P	2-Methylphenanthrene	
MP	Methylphenanthrenes	
DMP	Dimethylphenanthrenes	
Fl	Fluoranthene	
Py	Pyrene	
Ba	Benz(a)anthracene	
Ch	Chrysene + triphenylene	
Bf	Benzofluoranthenes	
Bp	Benzopyrenes	
S	Squalane	(Structure I)
T	18α (H), 22, 29, 30-trisnorhopane	(Structure III; $R_1 = R_2 = H$)
O	18α (H)-oleanane	(Structure II)
H	17α (H), 21 β (H)-hopane	(Structure III; $R_1 = CH_3$, $R_2 = i-C_3H_7$)

Fitties (HF Table I). During the next seven months this value decreased substantially (Table I) but concentrations of nearly 5000 $\mu g\,g^{-1}$ still remained after 12 months. In some of the trial spills conducted with Nigerian crude on sandy sediments a similar decrease in hydrocarbon concentration was observed, i.e. only 10% of the spilled crude was retained after a year.[4] However, the lithological characteristics and hydrology of sediments are probably important in determining the amount of oil retained. During the year of the study, by far the greatest proportion of the oil was present in the top 7 cm of sand at Humberston Fitties.

The oily residue was recognisable as "Sivand" crude in all of the Fitties (HF) samples, by the presence of squalane, 18α(H)-oleanane, other characteristic triterpanes[11,16] and C_{15} bicyclanes (Figures 2a–c). However the distributions of other hydrocarbons in each of these sediment samples differed from that of the spilled oil, mainly due to the effects of bacterial action and weathering. For example, *n*-alkanes were present in decreased proportions relative to the acyclic and cyclic isoprenoids after 7 and 12 months (Figures 2a–c and Table III). These changes are attributed to the preferential oxidation of *n*-alkanes relative to isoprenoid alkanes by bacteria; a process for which there is a large body of evidence[22,23] and which was also demonstrated in the laboratory by degrading Nigerian crude for 8 months (Figure 6). Other differences between "Sivand" oil and that recovered from the sediments at Humberston Fitties included (after 7 months) the virtual removal of 2- and 1-methylnaphthalene (peaks 2 and 3) and the depletion of 2-ethylnaphthalene (peak 4), 1,3-

TABLE III

Ratios of aliphatic compounds showing the effects of biodegradation

	i19/nC_{17}	bc2/nC_{14}	S/nC_{27}	0/nC_{31}
Sivand oil	1.4	0.9	0.1	0.6
HF2 (7 months)	1.7	1.2	0.1	0.8
HF3 (12 months)	4.1	3.4	0.3	1.4
HB2 (7 months)	1.7	1.1	0.2	1.3
HB3 (12 months)	1.6	nm	nm	nm

nm = not measurable.
For compound identification see Table II.

and/or 1,7-dimethylnaphthalene (peak 6) and 2,3- and/or 1,4-dimethylnaphthalene (peak 8) (Figure 3b). Since 1- and 2-methylnaphthalene, 2-ethylnaphthalene, 1,3- and 1,4-dimethylnaphthalene all have higher solubilities than the other dimethylnaphthalenes for which data is available,[24] we suggest that water-washing has had a major effect on the composition of the oil in this sample. Although some biodegradation has also occurred, from the evidence available 2,3- and 1,4-dimethylnaphthalenes (peak 8) are not expected to be as rapidly degraded by bacterial action as other dimethylnaphthalenes.[25-27] While the effects of evaporation would be significant on compounds below C_{10} they are less so on higher boiling compounds. Thus *n*-undecane (C_{11}) and *n*-dodecane (C_{12}), which have higher vapour pressures than the corresponding C_{11} or C_{12} alkylnaphthalenes (i.e. the severely depleted methyl- and dimethylnaphthalenes), have not been entirely removed from this sample (Figure 2b) which perhaps suggests that evaporation of hydrocarbons is not the major process responsible for the observed changes in this molecular weight range. The sandy nature and intertidal situation of the Humberston Fitties sediments also make water-washing seem a reasonable explanation for some of the changes observed.

After 12 months, further changes were observed in the composition of hydrocarbons in the sediment (Figures 2 and 3), including the removal of many of the prominent peaks in the chromatogram (Figure 3c). A notable exception was a component tentatively identified as an ethylmethylnaphthalene (peak 9, Figure 3) which was found to be particularly resistant to biodegradation in our previous studies.[27] Further preferential degradation of the *n*-alkanes had occurred but the triterpanes (e.g. peak 0) were apparently unaffected as was noted in the laboratory studies (Figure 6). Such alkanes are therefore a good indication of the presence of residues of Nigerian crude oil (cf. ref. 4).

Concentration and composition of hydrocarbons in muddy estuarine sediments at Blacktoft

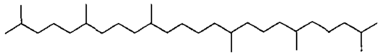
Five months after the spill of "Sivand" oil the concentration of hydrocarbons in the muddy sediments at Blacktoft was over 2000 $\mu g\, g^{-1}$ (dry weight sediment) in the top 5 cm. This is considerably lower than in the corresponding sandy sediment of

Humberston Fitties but since we did not sample either site immediately after the spill, we cannot state whether this difference is because Blacktoft was less contaminated in the first instance or if post-spill environmental differences were responsible.

Seven months after the "Sivand" spill the concentration of hydrocarbons in the Blacktoft sediments had increased somewhat compared to that at 5 months and was about 3000 $\mu g\,g^{-1}$ (dry weight sediment) in the top 5 cm. This change is much less dramatic than that observed in the sandy sediments at Humberston Fitties, although the concentrations in both sediments after 7 months were comparable. After a further 5 months (i.e. 12 months post-spill) the concentration of hydrocarbons was 325 $\mu g\,g^{-1}$ (dry weight sediment) in the top 5 cm Blacktoft (HB), though the maximum concentration in this sample (2185 $\mu g\,g^{-1}$) was at 10–15 cm depth.

The data suggest that the concentration of hydrocarbons in the Blacktoft muddy sediments is greatly affected by sediment deposition and turnover. For instance physical removal by tidal actions of a surface layer of oil or oiled mud or deposition of mud uncontaminated with "Sivand" oil on top of that originally present might explain the observations in the 12 month Blacktoft sample. Such variation in the concentrations of hydrocarbons in sediments, due to redistribution of spilled oil by physical processes, has been noted previously.[3] An additional possible explanation for the vertical hydrocarbon distribution seen in this sediment would be that seepage of oil into the sediments down the sides of plant shoots (which were abundant at this site) results in an accumulation of oil in the 10–15 cm depth range.

The compositional data support the above hypotheses; for example, examination of the hydrocarbons in the top 5 cm of Blacktoft sediment after 5 and 7 months, revealed the presence of the characteristic "Sivand" oil terpanes (e.g. structures I, II, IV and V) whereas after 12 months (0–5 cm) these could barely be detected even by more specific GC-MS "fingerprinting". Although some differences in the distribution of hydrocarbons in the 7 month sample compared with the "Sivand" oil were observed, these were attributed to preferential bacterial oxidation of non-isoprenoids (Table III); no such mechanism suffices to explain the major differences observed between the "Sivand" oil and the sediment sample after 12 months. The distributions of *n*- and isoprenoid alkanes in the 12 month



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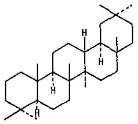

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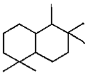
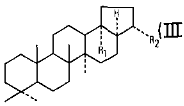
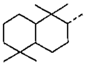


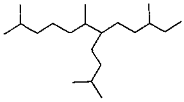
(IV)



(III)



(V)



(VI)

sample were very different from those in the "Sivand" oil and from the 5 and 7 month samples (Figure 2). The n-C_{27-31} alkanes present in the 12 month sediment sample showed a high odd over even carbon number predominance unlike those in the "Sivand" oil, 5 and 7 month samples; they are probably derived from higher plant cuticular waxes (e.g. from the adjacent reeds). The isoprenoid alkane, 2,6,10-trimethyl-7-(3-methylbutyl)dodecane (structure VI) was detected only in the 12 month sediment sample and not in "Sivand" oil or the 5 and 7 month sediment samples. This compound probably derives from green algae observed at the sampling site.[28]

The aromatic hydrocarbon distribution and particularly the distributions of C_2 and C_3 alkylnaphthalenes and C_{0-3} phenanthrenes in the Blacktoft sediment 7 months after the spill was similar to that of the "Sivand" oil (Figures 4a, b); components more volatile than the C_2 alkylnaphthalenes had been depleted as a result of the various weathering processes. In contrast, the aromatic hydrocarbon distribution in the 0–5 cm sample at 12 months after the spill was very unlike that of the "Sivand" oil (Figures 4c and a, respectively). Some alkylated aromatic hydrocarbons were present, including methyl-, dimethyl- and trimethylnaphthalenes, but their distributions (e.g. the ratios of 1-methyl to 2-methylnaphthalene and peak 5 to peak 8) were different from those in the "Sivand" oil. These differences could perhaps be explained by weathering or biodegradation effects but the virtual absence of the characteristic saturated hydrocarbons in this sample suggested that these alkylated aromatic compounds were not derived from the "Sivand" cargo; their origin remains unclear. However, the gas chromatogram of the aromatic hydrocarbon fraction of this sample (Figure 4c) was dominated by several prominent non-alkylated aromatic hydrocarbons (e.g. fluoranthene, pyrene, anthracene) which were not present in the oil and were in low concentration relative to the oil-derived aromatic compounds in the other sediments. These compounds are probably derived from partially combusted fossil fuel particulates.[31,32]

The high abundance of the non-alkylated (combustion derived) polycyclic aromatic hydrocarbons (PAH) in the HB3 (12 months) sediment sample, relative to alkylated aromatic hydrocarbons (typical of petrogenic sources), is thought to be due to removal of the latter compounds by weathering processes. However a further subsequent input of pyrolytic PAH cannot be discounted. The possibility that the alkylated (petrogenic) aromatic hydrocarbons were depleted is consistent with the low concentration of total hydrocarbons in the HB3 sample (12 months, 0–5 cm), compared with the HB2 (7 months) sample which contains abundant petroleum derived hydrocarbons (see Table I).

The apparent persistence of the combustion derived PAH is contrary to available evidence that suggests non-alkylated aromatic hydrocarbons are biodegraded preferentially to alkylated species.[26,29] One explanation for the recalcitrance of combustion derived parent PAHs is that they are in a form that makes them inaccessible to the bacteria. We have conducted a number of laboratory experiments which examine this hypothesis further.

Laboratory degradation experiments

A sediment containing a high abundance of PAH derived from partially combusted fossil fuels (Figure 5a) was mixed with an aliquot of crude oil (Brent crude, North Sea, U.K.). The resulting mixture of aromatic hydrocarbons was complex (Figure 5b), comprising both non-alkylated and alkylated compounds. Some compounds (such as phenanthrene and 1-,2-,3- and 9-methylphenanthrene) were constituents of both the oil and the sediment, others (such as 4,5-methylenephenanthrene) were contributed only from the sediment.

After 8 days incubation most of the oil-derived aromatic hydrocarbon peaks in the gas chromatogram (Figure 5c) had been depleted relative to the sediment-derived components by the bacteria in the sediment. This conclusion was reached even after taking into account that the sample incubated for 8 days contained more sediment inoculum (and therefore more combustion derived PAH) than the sterilised sample incubated for 135 days. After 28 days incubation, virtually all of the peaks in the gas chromatogram due to the oil-derived aromatics had been removed (Figure 5d), leaving a distribution very similar to the initial distribution of PAH in the sediment (Figure 5a). This is also illustrated by the distribution of methylphenanthrene isomers which, after 28 days, showed a distribution similar to that originally present in the sediment with 4,5-methylenephenanthrene once again abundant relative to these isomers; this indicated that the distribution of oil derived methylphenanthrenes (characterised by a high abundance of 9- and 1-isomers) had been removed by the bacteria. No further major changes were noted after $4\frac{1}{2}$ months incubation.

The oil-derived hydrocarbons may have been rapidly biodegraded because they were present as a thin film on the surface of the water or were dispersed in some way that presented a large surface area to the degrading microorganisms. On the other hand, it has been suggested that the combustion-derived PAH may be sequestered or occluded in particles which makes them unavailable for biodegradation.[33] Further support for this hypothesis comes from studies of the equilibrium partition coefficient of PAH and particle-associated PAH in aqueous systems.[34] These indicated that PAH associated with particulate matter are not in equilibrium with the surrounding aqueous phase (i.e. are unavailable for dynamic exchange with water). This would greatly affect their availability for biodegradation. More quantitative studies in both the laboratory and field will enable much more to be learnt about the relative bioavailability of aromatic hydrocarbons.

CONCLUSIONS

Gas chromatographic "fingerprinting" of oil spills is particularly effective when the spilled oil contains characteristic compounds. In the present study the spilled Nigerian oil contained a distinctive distribution of compounds (e.g. 18α(H)-oleanane, squalane and C_{15} bicyclanes) which were relatively resistant to weathering and these were detectable by GC of the aliphatic or total hydrocarbon fractions in sediments for at least a year after the spill. In sediments where these compounds were in low concentration relative to hydrocarbons from other sources they could still be detected by GC-MS analysis.

The chromatogram of the total hydrocarbons obtained from one sediment revealed several contributing sources of hydrocarbons including those from higher plants, algae, and combustion sources as well as those derived from petroleum.

Measurement of the concentrations of oil-derived hydrocarbons in the sediments and examination of the hydrocarbon distributions by GC revealed the effects of weathering (including biodegradation and water washing) on the spilled oil but it would be easier to interpret such effects if more vapour pressure and solubility data were available.

It appears from the results of both laboratory experiments and analyses of estuarine sediments containing spilled oil, that whilst many oil-derived aromatic hydrocarbons can be rapidly biodegraded in sediments, combustion-derived aromatic hydrocarbons in the same sediments are relatively resistant to degradation. This suggests that the latter are in a form that makes them relatively inaccessible to bacterial action.

Acknowledgements

We are grateful to N.E.R.C. for financial support (D.M.J.) and to Mr. P. Donohoe for assistance with GC-MS. We also wish to acknowledge the considerable help given to us by D. Little (O.P.R.U.) both with collection of samples and access to unpublished data. We thank Drs. J. Taylor and R. J. Parkes (S.M.B.A., Oban) for assistance with some of the initial laboratory degradation experiments. We are grateful to Dr. R. Law (M.A.F.F., Burnham-on-Crouch) for the sample of "Sivand" oil, to Dr. E. Whitehead (B.P. Ltd.) for the sample of the Pentacyclane concentrate and to R. Noble (W.A.I.T., Perth, Australia) for access to unpublished results.

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