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A METHOD FOR DETERMINING CREOSOTE CONTAMINATION OF SEDIMENT FROM THE ELIZABETH RIVER, NORFOLK, VIRGINIA

BY

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B.S. June, 1976 University of Georgia

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ABSTRACT

A METHOD FOR DETERMINING CREOSOTE CONTAMINATION OF SEDIMENT FROM THE ELIZABETH RIVER, NORFOLK, VA

Hydrocarbon input sources to the Elizabeth River were investigated. Carbonized coal products (creosote, coal tar, and roof tar), petroleum products (Kuwait Crude Oil, No. 2 Fuel Oil, and a fuel oil spill sample) and soot (woodstove and diesel engine) have unique hydrocarbon distributions. Elizabeth River sediment hydrocarbon distributions indicate that they are contaminated with both carbonized coal and petroleum products. Using a simple two member mixing model, greater than 65 percent of Elizabeth River sediments' resolved aromatic compounds were determined to originate from carbonized coal products. These aromatic hydrocarbons include the EPA priority pollutant polynuclear aromatic hydrocarbons which are known to be carcinogenic and/or mutagenic. Differences in the hydrocarbon distributions and physical properties between petroleum and carbonized coal products allow the detection of contamination of sediments by carbonized coal products even when the inputs of petroleum products are several times greater. Once incorportated into the sediments, hydrocarbons derived from both sources are dispersed in association with the fine grained materials.

DEDICATION

This Thesis is dedicated to my parents, Bruce B. Merrill and Mary F. Merrill. None of this work would have been possible without their unending support.

AKNOWLEDGEMENTS

I would like to express by sincere appreciation to Dr. Terry L. Wade, my Thesis advisor , for his friendship and intellectual guidance throughout my graduate school years and for providing me with the laboratory equipment and space needed for this work. I would also like to thank Dr. George T. Wong and Dr. Frank F. Scully, Jr., the other members of my committee for their suggestions and guidance during the completion of this research project.

Thanks to Juanita Grabarczyk and Charles Farmer for their help in the collection of my samples and to David Velinsky for his help from the beginning of my graduate school adventure.

A special thank you goes to Paul, who is patiently awaiting early retirement and a new Mercedes.

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INTRODUCTION

Determination of the quantities and types of anthropogenic hydrocarbons in the marine environment are essential in order to understand their fates and long and short-term effects. One of the major fates of released hydrocarbons in the coastal environment is their incorporation into bottom sediments (NAS,1975).

Sediments near large urban areas may contain high concentrations of anthropogenic hydrocarbons due to their proximity to source areas (Wakeham and Farrington, 1980). Resuspension of contaminated sedimentary material by natural (tides,storms, etc.) or by artificial means (dredging, shipping, etc.) can disperse these pollutants to areas much larger than were originally affected. Because of the health hazards associated with anthropogenic hydrocarbons considerable interest has been generated in determining their sources, fates, and effects in the sedimentary environment (NAS, 1975). Of particular interest, are the polynuclear aromatic hydrocarbons (PNAH) because some of these compounds are known carcinogens.

The degree of contamination of Elizabeth River, Norfolk, VA sediments by anthropogenic hydrocarbons and the possibility that this contamination is spreading into

Chesapeake Bay has been a continuing source of debate (Byrd, 1983; Bieri et.al., 1982; Alden and Young, 1982). Management decisions regarding the prevention of hydrocarbon pollution of the Elizabeth River require information on the relative importance of hydrocarbon inputs from various sources.

The Elizabeth River is located in a highly industrialized urban area and empties into lower Chesapeake Bay (Fig. 1 and 2.). The system has low topographic relief, very little freshwater inflow, and flushing of the system is poor and dominated by tidal actions (Cerco and Kuo, 1981; Neilson and Sturm,1978). Lack of flushing tends to trap sediments and associated pollutants within the river system (Neilson and Kuo, 1974). The river is a major shipping channel for the Norfolk area and is regularly dredged to deepen channels or build new docking facilities . The industries along the river that could be considered potential sources of hydrocarbons include marine shipping terminals, ship drydock facilities, sewage treatment plants, wood preserving facilities, a coal-fired electric power plant, dredging operations and a dredge disposal site.

Due to the large number of creosoted docking facilities, the existence of a creosote plant and the occurrence of creosote spills in the past, creosote may be a major contributor of polynuclear aromatic hydrocarbons

Figure 1. Chesapeake Bay. The location of the Elizabeth River is indicated by hatch marks.

FIGURE 1.

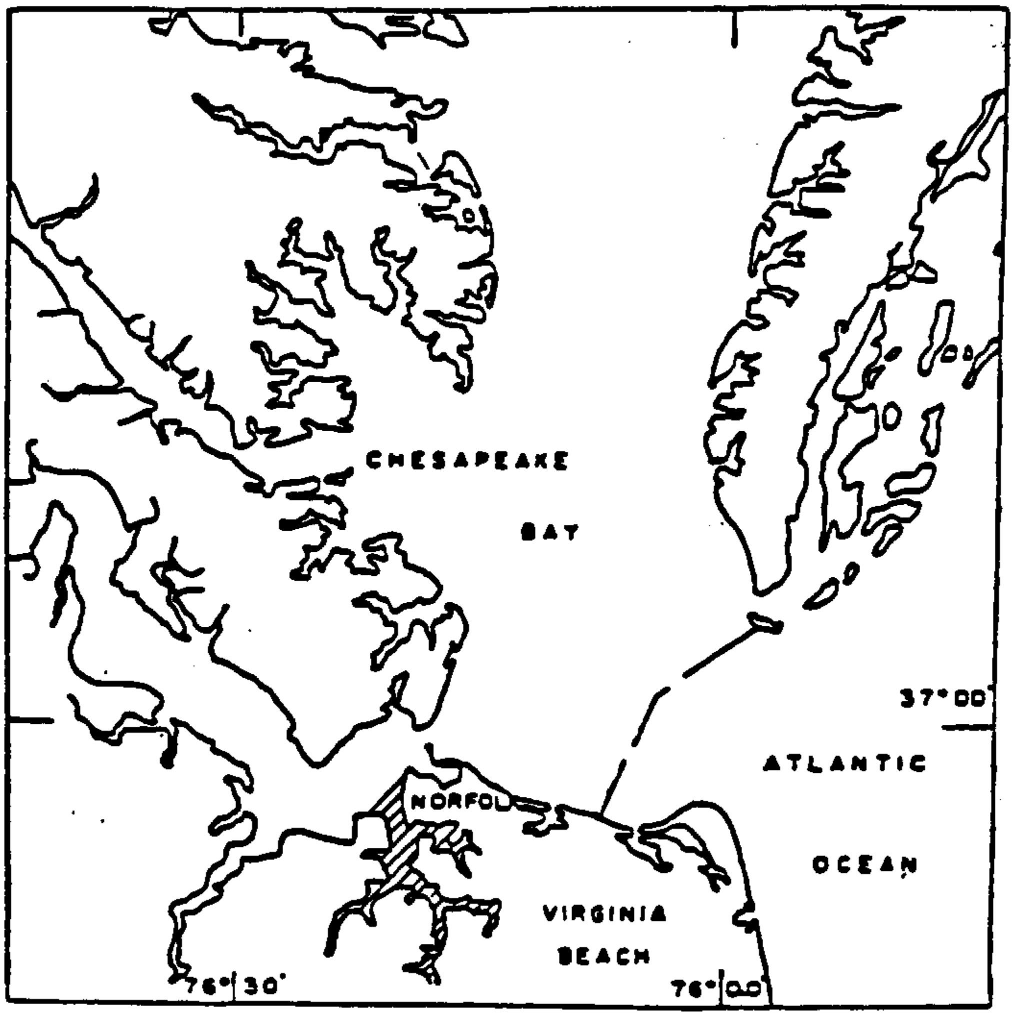
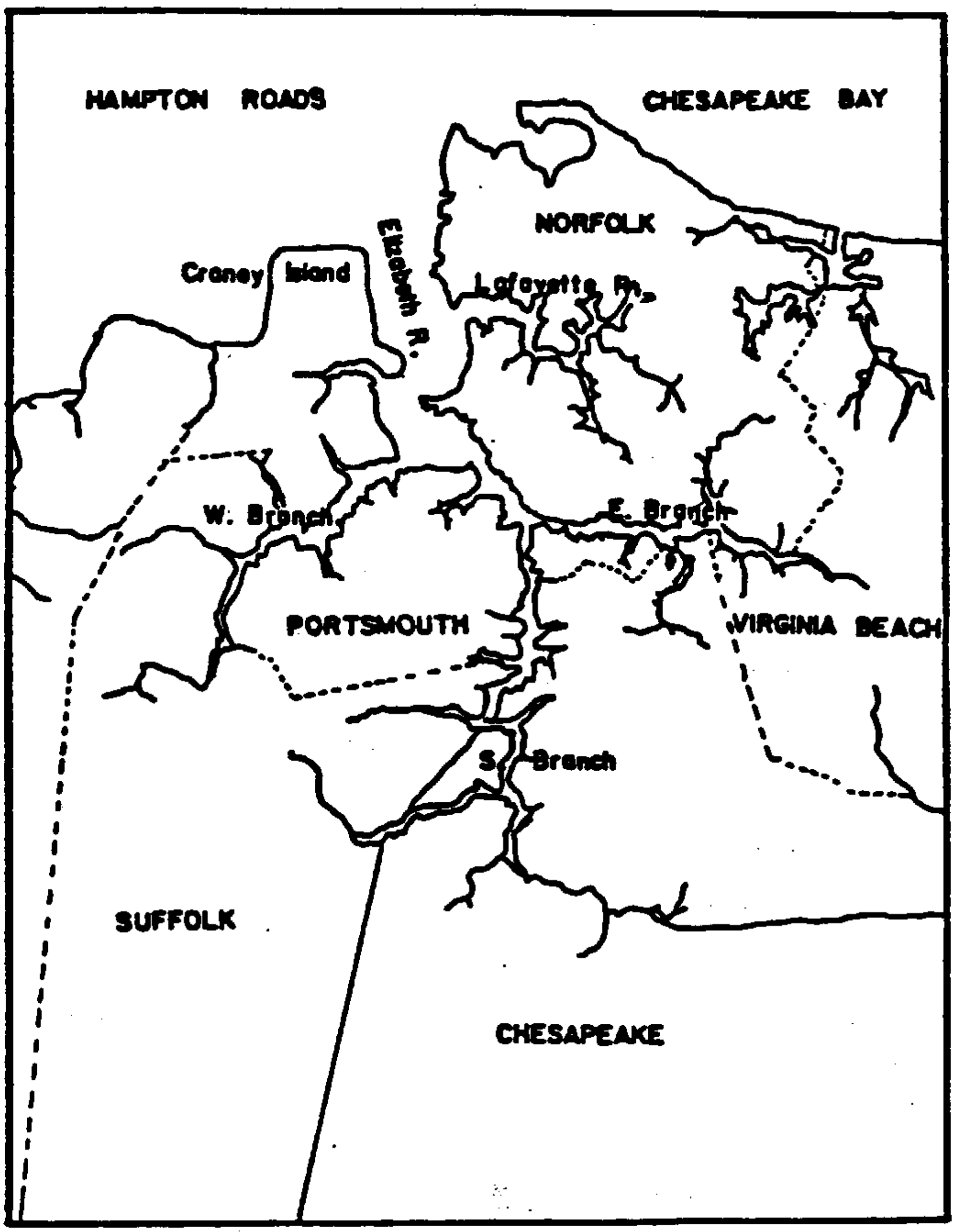

CHESAPEAKE
BAY
37° 00'
ATLANTIC
OCEAN
NORFOLK
VIRGINIA
BEACH
76° 30'
76° 00'

Figure 2. General study area of the Elizabeth River.

FIGURE 2.


HAMPTON ROADS
CHESAPEAKE BAY
NORFOLK
Elizabeth R.
Craney Island
Lafayette R.
W. Branch
E. Branch
PORTSMOUTH
VIRGINIA BEACH
S. Branch
SUFFOLK
CHESAPEAKE

(PNAH) to Elizabeth River sediments. Creosote is defined as a distillate from coal tar made by high-temperature carbonization of bituminous coal (AWPA,1971). Coal tars are fractionally distilled into three cuts, which are customarily designated as (a) light oil, (b) middle oil, and (c) heavy (anthracene) oil. Middle oils are the distillates that boil between approximately 220 and 375°C. After sequential extraction of tar acids, tar bases, and naphthalene, middle oils can be further distilled to meet specifications for creosote, kerosene, or diesel fuels. Heavy oils (450-550°C) are rich in higher hydrocarbons and are fractionally distilled as a source of anthracene, phenanthrene, carbazole, acenaphthene, fluorene, and chrysene. The remaining heavy oils are blended with residual coal tar pitches to meet specifications for various grades of road tar (Berkowitz,1979).

Creosote alone or in combination with coal tar or petroleum is the major preservative used in the wood pressure treating industry. Various creosote treated wood products, their total production and percent of the total product treated with creosote during 1978 are listed in Table 1. (Webb, 1980). For inland uses, such as for railroad crossties, blends of creosote with as much as 50 percent petroleum fuel oils are used (AWPA, 1971). For marine uses, however, the effectiveness of creosote is sharply reduced by the presence of petroleum (Moore

Table 1. Creosote treated wood products with their respective total production and share of the market in 1978. (Webb, 1980)

	Creosote treated Cubic feet (million)	%total treated with creosote
Crossties and Switchties	98.8	99
Pole, Utility and Construction	17.4	28
Piling, Marine and Foundation	8.7	89
Lumber and Timbers	10.7	12
Fence Posts	2.9	26
Cross Arms	0.1	1
Other	3.5	26
TOTAL	142	50

et.al., 1968). Therefore, blends of creosote with coal tar (50:50) are generally used when treating wood for marine use (AWPA, 1971).

Polynuclear aromatic hydrocarbons (PNAHs) generally account for 90 percent of the chemical constituents of creosote, with most of the PNAHs having no substitute groups (McNeil, 1959). Because PNAHs are fluorescent under ultraviolet light, Zitko (1975) used fluorescent fingerprinting techniques to demonstrate creosote contamination of shellfish. Dunn and Stich (1975,1976) showed that creosoted pilings were point sources of PNAHs. The PNAHs isolated from mussels growing near creosoted pilings were similar to those from extracts of creosoted wood. Highly elevated levels of PNAHs have been found in lobsters which were impounded in storage facilities constructed of creosoted timber and extracts of edible lobster meat showed similar PNAH patterns to those seen in commercial creosote and creosoted timber (Dunn and Fee, 1979). Extracts of PNAHs from barnacles growing on creosoted pilings have been shown to be carcinogenic in mice (Shimkin et.al.,1951) and hyperplasia in an esturarine bryozoan growing on creosoted timbers was attributed to coal tar creosote (Powell et.al., 1970). Lake et.al. (1979) showed that the use of creosote in marine construction resulted in the input of PNAHs to marine sediments. It has been demonstrated that coal tar coatings of storage tanks leach PNAHs into potable water supplies (Alben, 1980).

Three wood preserving facilities existed along the Southern Branch of the Elizabeth River in the early 1900's. Their locations are shown in Fig. 5. In 1963, a major portion of Eppinger and Russell Co. was destroyed by a fire, which ruptured a storage tank, causing a large spill. The State Water Control Board regulations initiated in April, 1968 prohibited the direct discharge of industrial process wastewater into rivers. These regulations did not address the problems associated with creosote contaminated stormwater runoff from the plant properties. In the early 1970's several penalities were issued to Eppinger and Russell Co. by the U.S. Coast Guard for unauthorized creosote spills. Details of the spilled amounts were not available from the Coast Guard. Republic Creosote and Eppinger and Russell ceased operations in 1971 and 1981, respectively. The three wood preserving plant sites are still considered as potential sources of pollution through the leaching of creosote from prior waste dump sites, leaking storage tanks, or spill areas (Switzer, State Water Control Board, personal communication). Elevated hydrocarbon concentrations have been found in Elizabeth River sediments sampled from areas adjacent to the three wood preserving plants (Alden, personal communication). Since this highly industrialized area may have other hydrocarbon inputs, elevated levels of hydrocarbons can only give circumstantial evidence pointing to the creosote plants as major contributors of hydrocarbons to the Elizabeth River. Determination of the importance of creosote as a probable source based on a "fingerprinting" approach is necessary.

Land plants, marine organisms, and petroleum have characteristic distributions of n-alkanes. Petroleum typically has an odd/even n-alkane ratio of approximately 1.0 while biogenically produced n-alkanes usually have an odd/even ratio greater than 1.0 (Farrington and Meyers,1975). Terrestrial plants including marsh grasses (Eglington and Hamilton,1963) and pollen (Nilssen et. al.,1957) contain n-C17, n-C19 and n-C31 as their major n-alkanes, while the major n-alkanes found in marine phytoplankton (Blumer et. al.,1971), benthic algae (Youngblood et. al., 1971) and pelagic Sargassum (Burns and Teal,1973) are n-C15 and n-C17. Weathering processes in the marine environment (Erhardt and Blumer, 1972) and industrial processes used in formulating lubricating oils (Zafiriou, 1973) can remove n-alkanes. This removal of n-alkanes diminishes their usefullness as an indicator of petroleum inputs. The presence of an unresolved complex mixture (UCM) indicates a contribution by petrogenic or pyrogenic sources (NAS,1975; Youngblood and Blumer,1975). The presence of an UCM in addition to a homologous series of n-alkanes would indicate a recent petroleum input (Farrington and Quinn,1973; Gearing et. al., 1980). Aromatic compounds are also useful in determining the origin of hydrocarbons. Organisms produce few aromatic hydrocarbons (Meinschein,1969). In contrast, petroleum characteristically contains many members of numerous homologous series of alkylated aromatic hydrocarbons.

Polynuclear aromatic hydrocarbons (PNAH) are generally present in sediments as complex mixtures containing parent and alkylated homolog species, the relative distribution of which can provide information on the probable source of the PNAHs. Natural and anthropogenic combustion is the most common source of PNAHs in nature (NAS,1975). Qualitatively similar PNAH mixtures are produced regardless of the fuel type and the combustion conditions (Hase et. al.,1976; Lindsey,1960). Quantitatively, the distribution of alkyl homologs can be quite different depending on the formation temperature (LaFlame and Hites,1978). At moderate combustion temperatures (burning of wood or coal) the alkyl homologs are relatively abundant. At higher temperatures (combustion of petroleum) lower amounts of alkyl homologs are formed (Lee et. al.,1977). PNAH mixtures in petroleum are deficient in the unsubstituted species with the most abundant alkyl homolog usually containing three or four carbon atoms (Speers and Whitehead,1969).

Distributions for coal tar show relatively low concentrations of alkyl homologs with a predominance of parent compounds (Lake et. al.,1979, Fig. 3). Parent compound distributions and Phenanthrene/Anthracene ratios can also be used to identify sources of input of PNAHs to sediments. Comparisons of parent compound distributions, alkyl homolog distributions and Phenanthrene/Anthracene ratios from sediments near docks with those obtained from the coal tar used to coat the docks showed that PNAHs from coal tar were present in the surrounding sediments (Lake et. al.,1979; see Fig. 4 and Table 2).

Creosote has been shown to contain high concentrations of the Environmental Protection Agency (EPA) priority pollutant PNAHs (Federal Register, 69494; McNeil, 1959) and may be a source of these hydrocarbons to the Elizabeth River. In this study comparisons of the aliphatic and aromatic hydrocarbon distributions in creosote and coal tar were compared to the distributions in creosoted wood and other hydrocarbon sources which included roofing tar, ship stack and woodstove soot, Kuwait Crude Oil, No. 2 Fuel Oil and a fuel oil spill sample collected from Town Beach, Norfolk VA (Hand, 1984). The aliphatic and aromatic distribution characteristics found to be unique to creosote were then compared to the distributions of aliphatic and aromatic hydrocarbons in extracts of sediments from the Elizabeth River. The

Figure 3. PNAH alkyl homolog distributions for (A) petroleum (phenanthrenes) and (B) combustion products (pyrenes). Phenanthrene and pyrene have been shown to have similar homolog distribution patterns for the above processes (Youngblood and Blumer, 1975; LaFlame and Hites, 1980; Pierce et.al., 1982).

FIGURE 3.

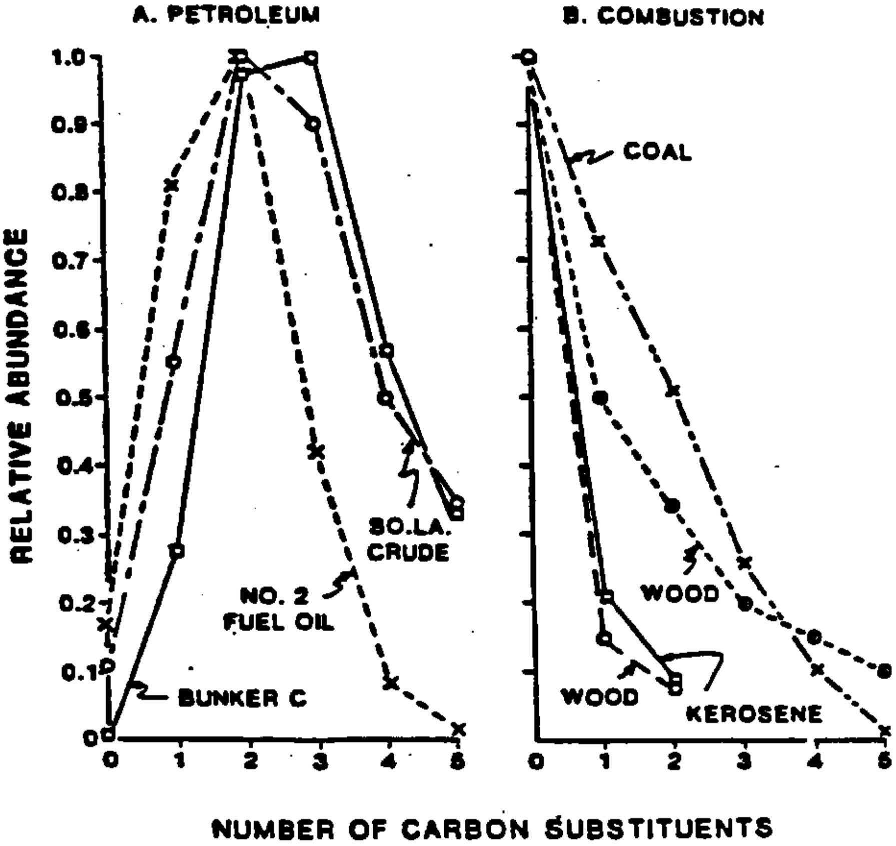

A. PETROLEUM
B. COMBUSTION
RELATIVE ABUNDANCE
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
BUNKER C
NO. 2
FUEL OIL
SO.LA.
CRUDE
COAL
WOOD
WOOD
KEROSENE
0
1
2
3
4
5
NUMBER OF CARBON SUBSTITUENTS

Figure 4. Parent Compound Distributions (PCDs) for sediment samples and for materials representative of possible origins of PNAHs in the marine environment (Data corrected for instrument response; Lake et.al., 1979).

FIGURE 4.

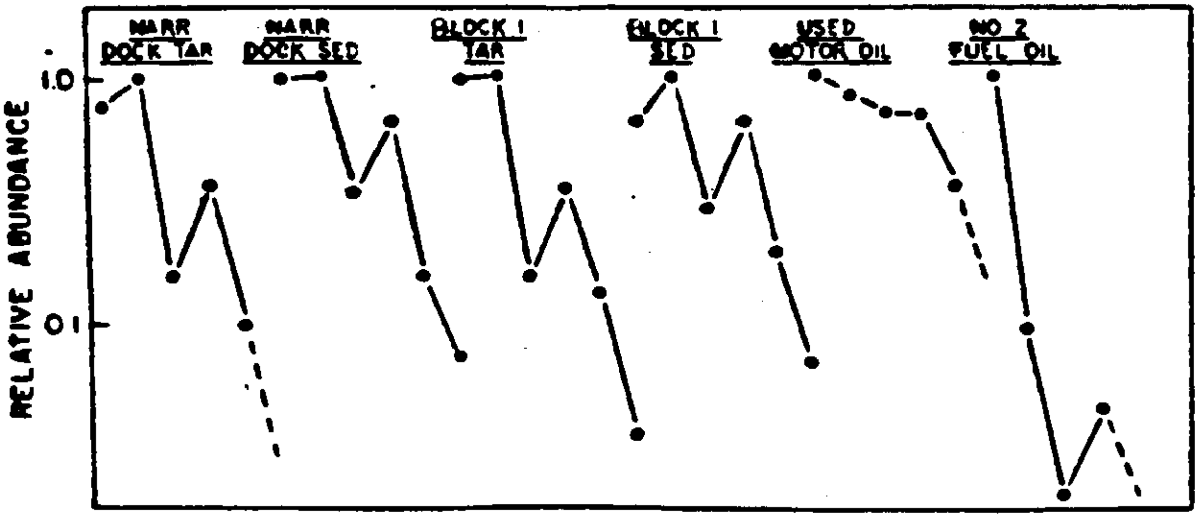

NARR DOCK TAR
NARR DOCK SED
BLOCK I TAR
BLOCK I SED
USED MOTOR OIL
NO 2 FUEL OIL
RELATIVE ABUNDANCE
1.0
0.1

Table 2. Phenanthrene/anthracene ratios (P/As) for sediment samples and for materials representative of possible origins of PNAHs in the marine environment.

P/A ratio	Sample type
50	No. 2 Fuel Oil
17	Woodstove Soot
8	Used Crankcase Oil
23-38	Dock Tar and Sediment

degree of retention of hydrocarbon distribution characteristics unique to creososte by the sediments was used to estimate the influence of creosote as a contaminant of these sediments.

Chapter 2.

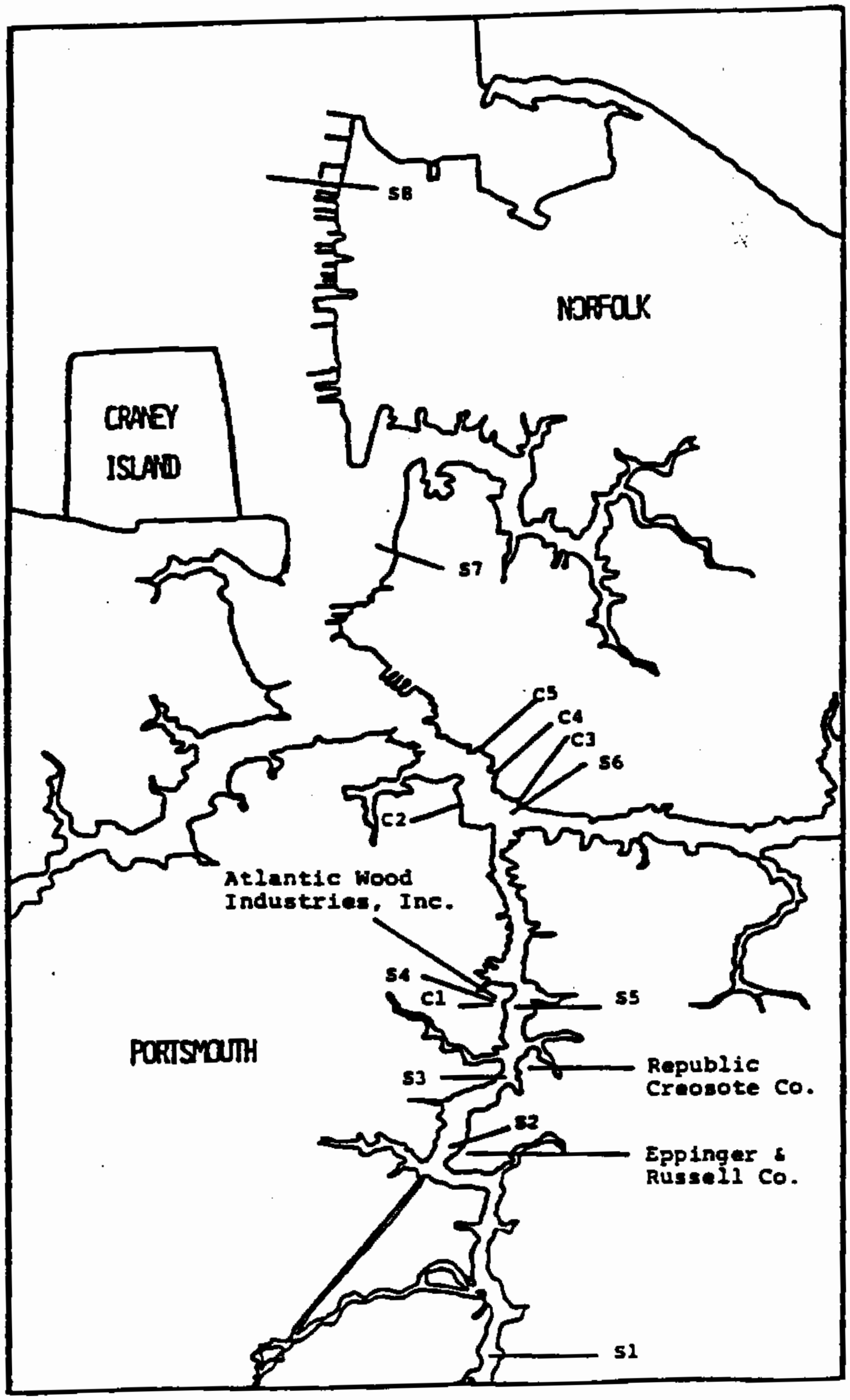
METHODS AND MATERIALS

Sediment samples were collected using a grab sampler, which samples approximately the top 10 centimeters, aboard Old Dominion University's research vessels, ODU-1 and R/V Linwood Holton. The sample locations are shown in Fig. 5. Stations S1, S3 and S5 were sampled on 16 February, 1983; Station S2 was sampled on 28 March, 1983; Stations S7 and S8 were sampled on 9 June, 1983; Station S6 on 7 September, 1983; and Station S4 on 13 January, 1984. The samples were brought aboard ship and transferred to clean, solvent-washed (dichloromethane and methanol) jars, returned to the laboratory, frozen, and stored until analyzed.

In order to determine if the creosote distributions were affected by use in the environment, creosoted wood samples were collected from areas adjacent to the Elizabeth River. The sample locations are shown on Fig. 5. Sample C5 was collected on 11 November, 1983; and samples C1, C2, C3 and C4 were collected on 13 January, 1984. The creosoted wood samples C3, C4 and C5 were collected from pilings within the Elizabeth River. Samples C1 and C2 were collected near the river bank and may not have been intended for use in the marine

Figure 5. Locations on the Elizabeth River for the sediment (S) and creosoted wood (C) samples and the locations of the wood preserving facilities.

FIGURE 5.


S8
NORFOLK
CRANEY ISLAND
S7
C5
C4
C3
S6
C2
Atlantic Wood Industries, Inc.
S4
C1
S5
PORTSMOUTH
Republic Creosote Co.
S3
S2
Eppinger & Russell Co.
S1

environment. Wood samples were wrapped in solvent-washed (dichloromethane and methanol) aluminum foil, returned to the laboratory, and frozen until analyzed. Three samples of refined creosote and one sample of coal tar were also analyzed. Bernuth Lembcke, Inc., a local distributor of creosote, supplied samples of No. 1 creosote (AWPA specifications) and coal tar. The creosote sample is referred to as Creosote A in this paper. Creosote B, obtained from a local hardware store, was labeled as 98.5% refined coal tar creosote, and was packaged by Warner-Graham Co. Creosote C, also obtained at a local hardware store, was labeled as 100% refined creosote oil, and was packaged by Sunnyside Coorporation. Creosote samples from Atlantic Wood Industries, the remaining operative creosoting facility on the Elizabeth River were not available. The company denied permission to collect samples from their property. One sediment sample, S4, was obtained, however, from a public drainage ditch adjacent to Atlantic Wood Industries' property. The woodstove soot sample was obtained from a domestic woodstove in which only hardwoods were burned. The diesel stack soot sample waa taken from Old Dominion University's research vessel R/V Linwood Holton. The No. 2 Fuel Oil sample is of the type used locally for home heating. The Kuwait Crude Oil was kindly supplied by Robert Brown of Mote Marine Lab, Sarasota, FL.

Sediment samples were thawed and mixed to ensure homogeneity. The dry weight and percent water content of the sediment was determined by drying approximately five grams of the sediment at 105-110°C for several hours until a constant weight was reached. Grain size distribution was determined by wet sieving and pipet analysis using the techniques of Folk (1980).

For hydrocarbon analysis approximately two grams of wet sediment or other solid sample (such as creosoted wood, soot, etc.) were placed in a 50 ml centrifuge tube. Internal standards, n-Eicosane (n-C20) and 3-methylfluoranthene, were added to the tube along with five ml of 0.5N methanolic-potassium hydroxide (MeOH-KOH), one ml of toluene, and one ml of distilled water which had been pre-extracted with dichloromethane (CH_2Cl_2). The centrifuge tube was capped tightly and placed in a boiling water bath for two hours. Every 20 minutes the samples were removed from the bath and shaken vigorously. This saponification step converts bound hydrocarbons to free hydrocarbons.

The tubes were cooled to room temperature, ten ml of distilled water which had been pre-extracted with CH_2Cl_2 were added, and the pH was checked to ensure that it was greater than ten. If the pH was less than ten, enough 0.5N MeOH-KOH was added to bring the pH to greater than ten and the tube was heated for an additional 20 minutes.

The sample, still in the centrifuge tube, was extracted three times using ten ml of petroleum ether each time. If an emulsion formed it was broken by centrifugation. Because petroleum ether is less dense than water, the petroleum ether phase was easily removed with a Pasteur pipet. The petroleum ether phases were combined in a 50 ml pear-shaped flask and reduced to dryness on a rotary flash evaporator under a vaccum at a temperature not exceeding 35°C. The aliphatic and aromatic hydrocarbons were separated from the other organics by thin-layer chromatography (Farmer, 1983).

When sample concentrations were low, necessitating the use of a larger sample weight, the following extraction procedure was used. Analysis of selected samples by both extraction techniques showed them to produce similar results (See Appendix A). Approximately 50 grams of wet sediment or other solid sample were placed in a 250 ml round bottom boiling flask. Internal standards, n-C20 and 3-methylfluoranthene, were added along with 100 ml of 0.5N methanolic-potassium hydroxide (MeOH-KOH) and 10 ml of toluene. The samples were saponified/extracted in a fume hood under reflux for two hours. After the samples were cooled, they were filtered through a 4 μm to 8 μm pore size sintered glass filter. The flask and filter were rinsed with 20 ml of methanol (MeOH) and 50 ml CH_2Cl_2 and these solvents were combined with the filtrate. The sediments or other solid samples were discarded. The filtrate was transferred to a 500 ml separatory funnel containing 100 ml of 10% sodium chloride solution. The separatory funnel was shaken vigorously and allowed to settle. The CH_2Cl_2 phase was isolated and the water phase was discarded. The solution was extracted twice with 50 ml portions of CH_2Cl_2. The CH_2Cl_2 fractions were combined and evaporated to dryness on a rotary flash evaporator under vaccum at a temperature not exceeding 35° C. The aliphatic and aromatic hydrocarbons were separated from the other organics by TLC (Farmer, 1983).

For the analysis of liquid samples (such as creosote, oil, etc.), the sample was first dissolved in CH_2Cl_2 . The aliphatic and aromatic hydrocarbons were then separated from the other organics by TLC (Farmer,1983).

In the TLC procedure employed, TLC plates were coated with 300 µm of Silica Gel G and oven dried for at least two hours at a temperature not exceeding 100° C. To eliminate contamination, the plates were prerun for at least six hours in 80:20 CH_2Cl_2:MeOH. A sample and a PNAH standard were applied to the plates, which were then developed in a tank containing hexane (MCB-OmniSolv). The standard was visualized with ultraviolet light and the sample area corresponding to the PNAH standard area that fluoresced (RF. 0.66 to 0.33) was marked and scraped. This area of the TLC plate contains the aromatic (f2) fraction. The area above the aromatic fraction (RF. 1.00 to 0.66) contains the aliphatic (f1) fraction. The fractions containing aliphatic and aromatic hydrocarbons, after being scraped from the TLC plates, were extracted three times with 10 ml portions of CH_2Cl_2. The CH_2Cl_2 extracts were combined and taken almost to dryness on a rotary flash evaporator under vaccum at a temperature not exceeding 35°C. The volatile lower molecular weight hydrocarbons, such as naphthalene, may not be quantitatively recovered if the sample is allowed to reach dryness on the rotary flash evaporator.

The samples were analyzed on a Hewlett-Packard Model 5830 gas chromatograph equipped with a 25 meter SE-54 fused silica capillary column utilizing a flame ionization detector (FID). The signal from the FID was recorded by a Hewlett-Packard model 18850A reporting integrator. The gas chromatograph was programed from 70°C to 300°C at 10°C per minute.

Quantitative determinations of hydrocarbon concentrations were made by comparing integrator area counts of the internal standard with integrator area counts of the peaks when an unresolved complex mixture (UCM) was not present. When the UCM was present the areas were determined by planimetry. Comparison of peak areas to the area of the internal standard were used to determine concentrations. Qualitative determination of hydrocarbons in the samples was made by comparison of retention times of known compounds, co-injection with known compounds and by gas chromatography combined with mass spectroscopy (GC/MS). Procedural blanks and standards were run systematically throughout the analysis period to determine if contamination had occurred and to ensure the proper functioning of the gas chromatograph (See Appendix A). Maximum values for the procedural blanks were 2.02 µg for the f1 fraction and 0.60 µg for the f2 fraction. The sample values reported are corrected for the presence of these procedural blanks.

Chapter 3

RESULTS AND DISCUSSION

Chromatograms of the aliphatic (f1) and aromatic (f2) fractions of Creosote A, the oil spill sample, sediments from Station S2 and sediments from Station S6 are shown in Fig. 6 through Fig. 9. The aliphatic (f1) fraction was divided into two groups, the resolved peaks, which included the identified n-alkanes and pristane and phytane, and an UCM (Fig. 7).

The resolved aromatic peaks (fraction f2), for comparison purposes were divided into three groupings (Fig. 6). The first group (PP) consists of the 16 Environmental Protection Agency priority pollutant PNAHs (Federal Register, 69494). These PNAHs are listed in Appendix A. The peaks were identified by comparison of peak retention times and coinjection. Seven of the 16 peak identifications were also confirmed by GC/MS run on a sediment sample from Station Six (See Appendix A). The second group consists of 25 other major peaks that were found in most of the creosote samples. These major peaks were identified by their retention times. The compounds they represent were not identified. This group is referred to as Major Resolved Peaks (MRP). The chromatogram of the f2 fraction of Creosote A with the PP

Figure 6. Gas Chromatograms of the f1 and f2 fractions of Creosote A. Lettered peaks in the f2 fraction are identified in Appendix A. Numbered peaks in the f2 fraction are explained in the text.

FIGURE 6.

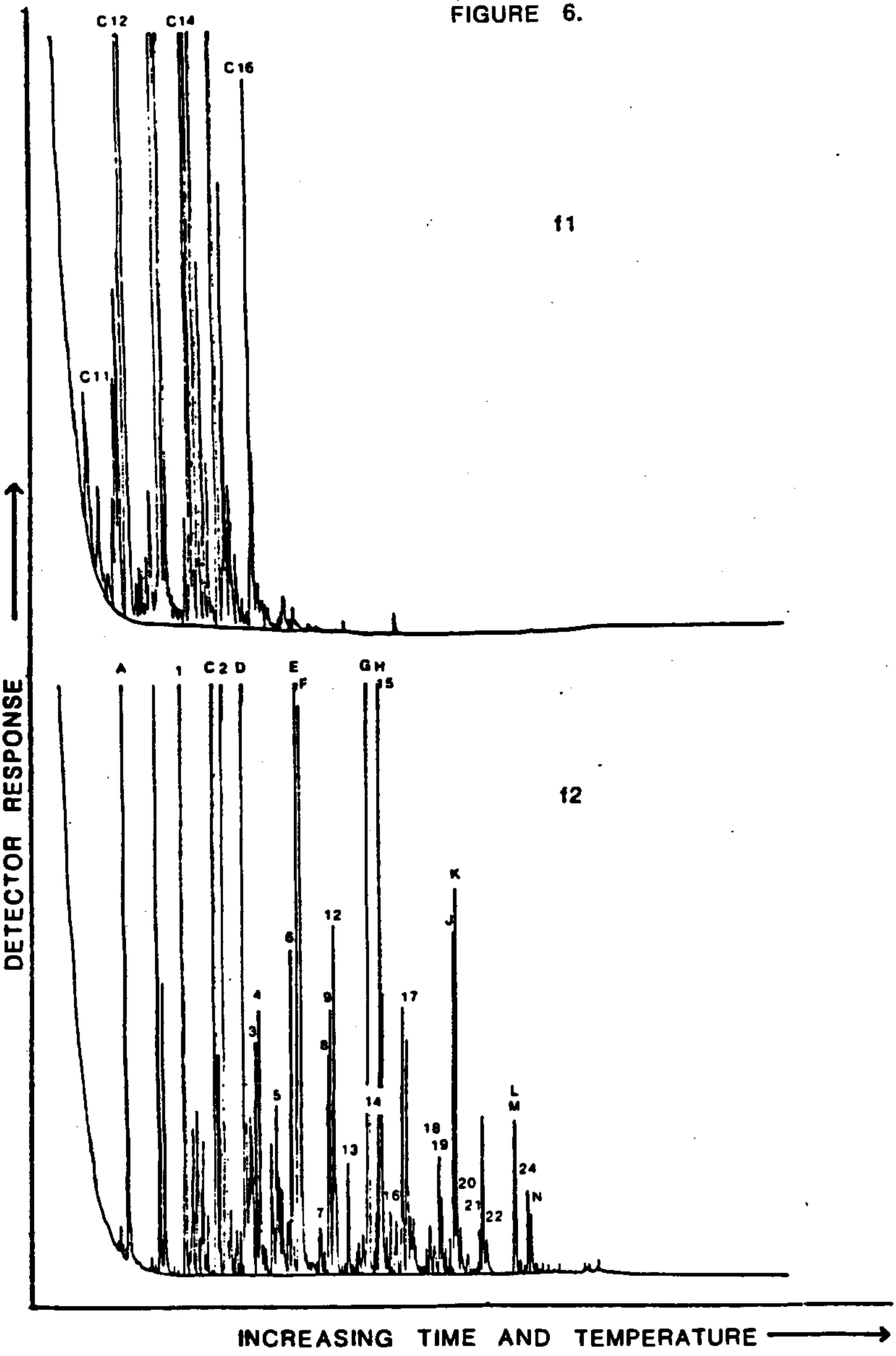

C12
C14
C16
C11
f1
A
1
C
2
D
E
F
G
H
15
f2
K
J
12
6
9
4
3
8
17
5
14
18
19
13
20
21
22
16
7
L
M
24
N
DETECTOR RESPONSE
INCREASING TIME AND TEMPERATURE

Figure 7. Gas Chromatograms of the f1 and f2 fractions of the oil spill sample. Lettered peaks in the f2 fraction are identified in Appendix A. Numbered peaks in the f2 fraction are explained in the text.

FIGURE 7.

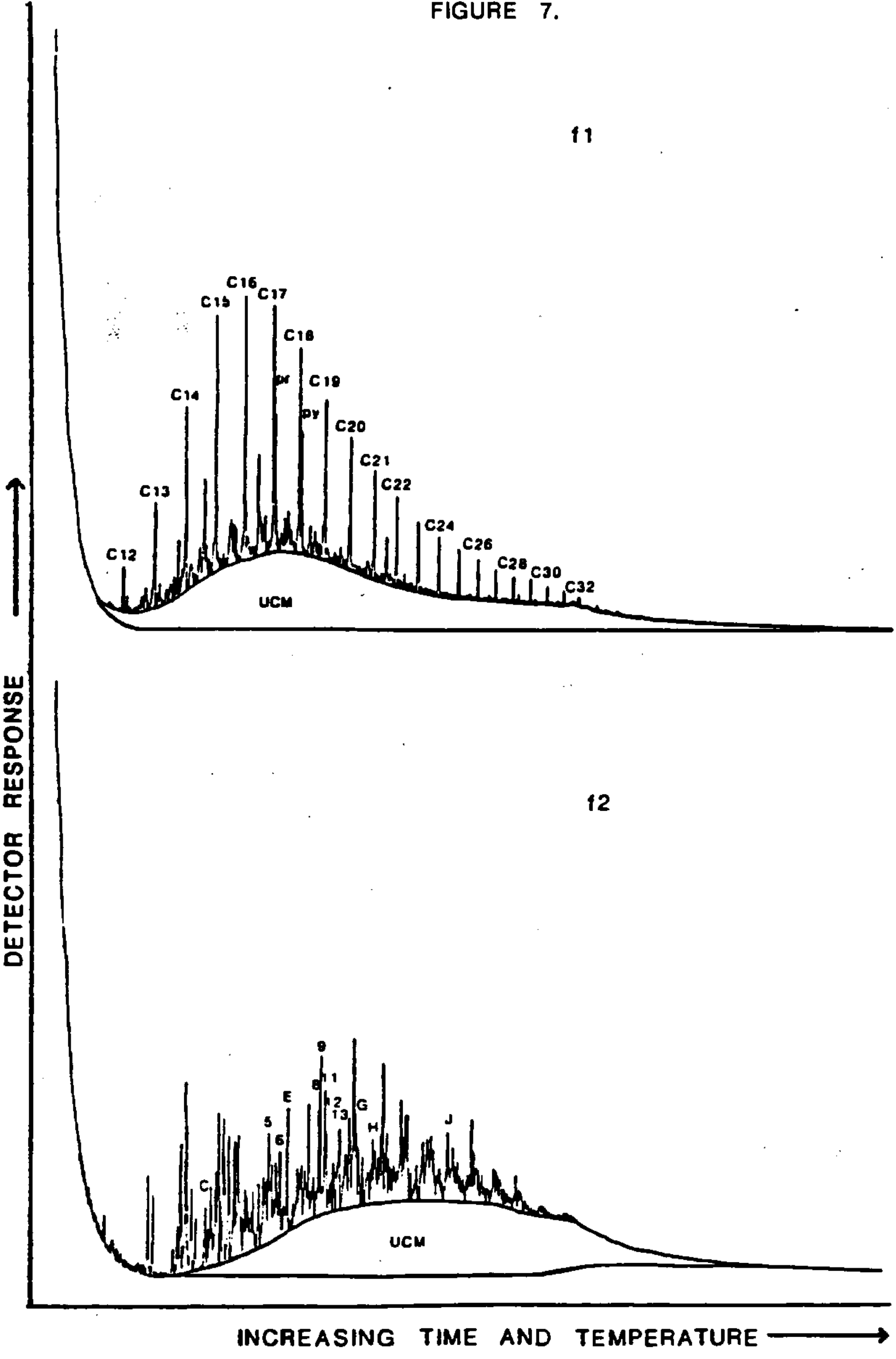

f1
C12
C13
C14
C15
C16
C17
C18
pr
C19
py
C20
C21
C22
C24
C26
C28
C30
C32
UCM
f2
9
8
11
12
13
E
5
6
C
G
H
J
UCM
DETECTOR RESPONSE
INCREASING TIME AND TEMPERATURE

Figure 8. Gas Chromatograms of the f1 and f2 fractions of the sediment sample from Station S2. Lettered peaks in the f2 fraction are identified in Appendix A. Numbered peaks in the f2 fraction are explained in the text.

FIGURE 8.

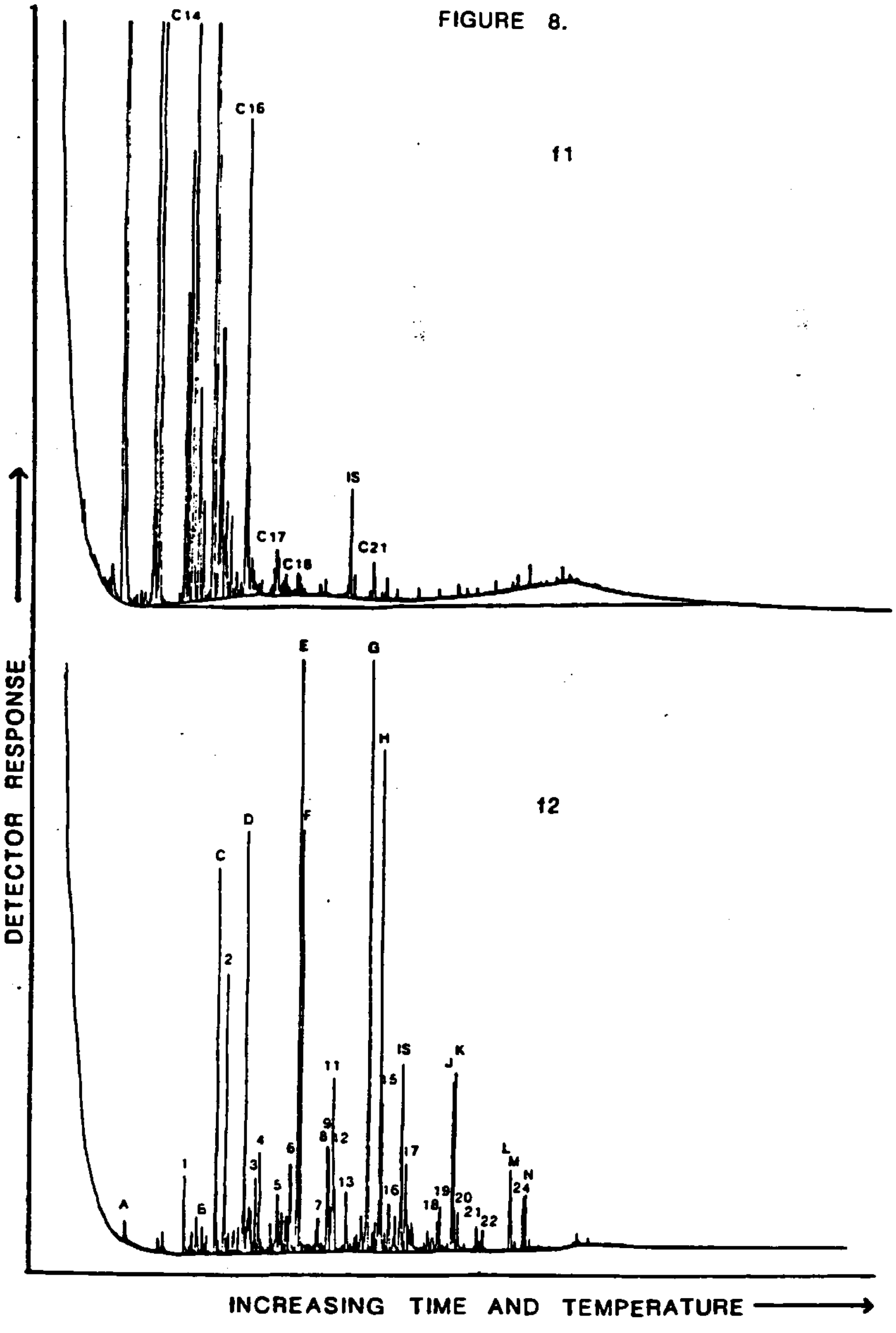
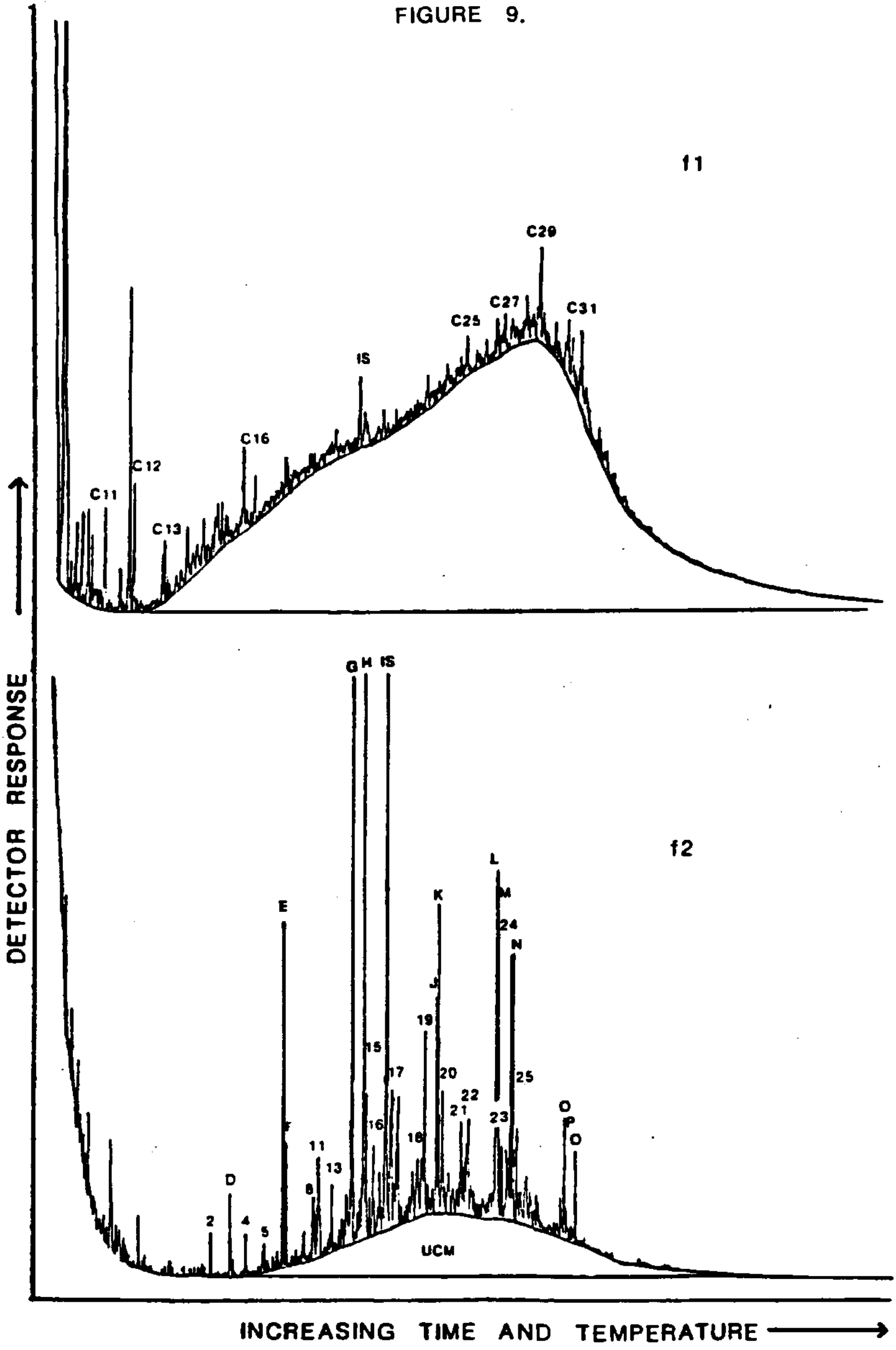

C14
C16
f1
IS
C17
C18
C21
E
G
H
f2
D
F
C
2
11
15
IS
J
K
9
8
12
4
6
3
1
17
L
M
N
13
16
19
20
24
5
7
18
21
22
A
B
DETECTOR RESPONSE
INCREASING TIME AND TEMPERATURE

Figure 9. Gas Chromatograms of the f1 and f2 fractions of the sediment sample from Station S6. Lettered peaks in the f2 fraction are identified in Appendix A. Numbered peaks in the f2 fraction are explained in the text.

FIGURE 9.


f1
C29
C27
C25
C31
IS
C16
C12
C11
C13
f2
G
H
IS
E
L
K
M
24
N
J
19
15
17
20
25
22
21
23
O
P
Q
16
18
F
11
13
8
D
2
4
5
UCM
DETECTOR RESPONSE
INCREASING TIME AND TEMPERATURE

and MRP groups labeled is shown in Figure 6. The third group consists of all other peaks that did not fit into the PP or MRP groups and is referred to as Other Resolved Peaks (ORP).

The percent contributions made by the UCM and resolved peaks in the aromatic and aliphatic fractions of each sample are given in Table 3a. The f1 fraction is separated into resolved peaks and UCM contributions. The resolved peaks of the f2 fraction are subdivided into PP, MRP and ORP groups. The numbers in parentheses are the percentages contributed by each group to the total resolved peaks.

All creosote, coal tar and creosoted wood samples had similar chromatograms that are typified by Fig. 6. Creosote samples A, B and C, the coal tar sample and creosoted wood samples C3, C4 and C5 had resolved f1 percentages of 81-100 percent and f1 UCM percentages from undetectable to 19 percent. Few n-alkanes larger than n-C16 were detected and n-C15, normally present in unweathered petroleum and biogenic samples (Blumer et.al., 1971) was usually not detected. Creosoted wood samples C2 and C1 were collected from logs that were not directly involved in marine construction and may not have been intended for use in the marine environment. Their f1 chromatograms showed homologous series of n-alkanes indicating a creosote/petroleum mixture was used in the

Table 3a. Percentages for resolved peaks and UCM for aromatic and aliphatic hydrocarbons. The samples are identified in the text. PP-Environmental Protection Agency priority pollutant PNAHs, MRP-major undentified resolved peaks, ORP-other unidentified resolved peaks; these designations are explained in the text. The numbers in parentheses are the percent contribution each category makes to the total resolved aromatic peaks. UD-undetected No.-number of samples

	AROMATICS				ALIPHATICS	
	PP	MRP	ORP	UCM	RESOLVED	UCM
S2	57	28	15	UD	83	17
S4	57	28	15	UD	20	80
S5	28(54)	15(28)	9(18)	48	8	92
S3	49	27	24	UD	9	91
S1	18(46)	7(18)	14(36)	61	20	80
S6	20(58)	10(29)	5(13)	65	8	92
S7	21(58)	10(27)	5(15)	64	8	92
S8	16(38)	8(20)	18(42)	58	9	91
C1	65	22	13	UD	46	54
C2	56	24	20	UD	62	38
C3	68	23	9	UD	81	19
C4	67	23	10	UD	100	UD
C5	68	22	10	UD	85	15
CREOSOTE A	69	18	13	UD	100	UD
CREOSOTE B	60	26	14	UD	84	16
CREOSOTE C	69	26	5	UD	100	UD
COAL TAR	46	29	25	UD	100	UD
ROOF TAR	56	21	23	UD	57	43
WOODSTOVE SOOT	28(44)	17(26)	19(30)	36	85	15
DIESEL STACK SOOT	3(10)	6(21)	20(68)	71	11	89
No 2 FUEL OIL	4(8)	6(11)	40(81)	50	42	58
OIL SPILL	1(3)	2(6)	25(91)	72	20	80
KUWAIT CRUDE	3(8)	4(17)	20(75)	73	100	UD

	No.	PP	MRP	ORP
Mean of all creosotes	8	65±5	23±3	12±4
Mean of all sediments	8	52±7	26±4	22±11
Mean of all oils	3	6±3	11±6	82±8
50:50 creosote:coal tar		58	23	19

wood treatment process (AWPA, 1971). This probable petroleum dilution is reflected in the increased UCM percentages in the f1 fractions. Even in these samples the lower molecular weight peaks (n-C16 and below) were the predominant peaks.

The f2 fraction of all the creosoted wood samples (C1, C2, C3, C4 and C5), all creosote samples (Creosotes A, B and C), the coal tar sample and the roof tar sample contained no detectable UCM and consisted of approximately 100 percent resolved components. The creosote and creosoted wood samples had an average aromatic resolved peak distribution of 65±5 percent PP, 23±3 percent MRP and 12±4 percent ORP. Roof tar, which is a by-product of the coal tar distillation process (Berkowitz, 1979), had a distribution similar to the creosote distributions in the f1 and f2 fractions. The resolved peaks had a greater relative percent in the higher molecular weight compounds than found in creosote.

In sharp contrast to the f1 and f2 fractions of the creosote and creosoted wood samples, are the f1 and f2 fractions of the oil spill sample shown in Fig. 7. The f1 fraction has a homologous series of n-alkanes from n-C12 through n-C31 with the dominant peaks in the n-C15 through n-C18 range. There is also a large UCM. The other source samples varied in their relative percentages of resolved peaks and UCM in the f1 fraction. The Kuwait

Crude Oil had no detectable aliphatic UCM which is unusual for most petroleum products (Farrington and Meyers, 1975). The woodstove soot showed a small UCM (15 percent) with resolved peaks, in contrast to creosote, from n-C16 through n-C31. Woodstove soot, No. 2 Fuel Oil, diesel stack soot, the oil spill sample and Kuwait Crude Oil, all contained a substantial percentage of their aromatic (f2) hydrocarbon in the form of an UCM. The f2 fractions of these samples showed no clearly dominant peaks, with the petroleum derived samples containing 3-10 percent PP, 6-21 percent MRP and 68-91 percent ORP.

Chromatograms of the f1 and f2 fractions of sediments from Station S2 are shown in Fig. 8. Chromatograms of the f1 and f2 fractions from sediment Station S6 which are similar to those from Stations S1, S3, S5, S7 and S8 are shown in Fig. 9. Because aliphatic compounds are present as less than one percent of creosote (Nestler, 1974) they are not as indicative of creosote contamination as PNAHs which make up greater than 90 percent of creosote (McNeil, 1959). Station S2, from the area of the creosote spill, shows a resolved f1 contribution of 83 percent and an UCM of 17 percent, which falls within the range of the percentages of the creosote and most creosoted wood samples. The f1 fraction is dominated by the lower molecular weight (n-C16 and below) aliphatics. Few n-alkanes greater than n-C16 are seen and n-C15 was not detected. Station S4, from the drainage ditch adjacent to Atlantic Wood Industries, (20 percent resolved and 80 percent UCM) appears to be influenced by a combination of creosote and petroleum inputs. Stations S5, S3, S6, S7 and S8 show very few resolved peaks (8-9 percent) and very large UCMs (91-92 percent) indicative of weathered petroleum inputs for the aliphatic hydrocarbons (Ehrhardt and Blumer, 1972). A terrestrial influence can be seen by the presence of n-alkanes n-C27, n-C29 and n-C31. The presence of n-C16 and other lower molecular weight aliphatics may represent the influence of creosote as well as other sources.

Sediment samples from Stations S2, S4 and S3 have no detectable UCM in the aromatic fraction. These stations are located near the wood preserving facility sites. Sediment samples S2, S4, S5, S6 and S7 show similar resolved f2 peak distributions to creosote ranging from 58-54 percent PP, 27-29 percent MRP and 15-18 percent ORP. The presence of an UCM in the f2 fraction of sediments from Stations S5, S6 and S7 may indicate contamination from other sources such as petroleum, in addition to creosote. Sediments from Station S3 contain a distribution of 49 percent PP, 27 percent MRP and 24 percent ORP. Because of the lack of UCM in the f2 fraction and the location of Station S3, it may reflect an input by coal tar which has 46 percent PP, 25 percent MRP, 25 percent ORP and no detectable UCM. Stations S8 and S1 are the stations most distant from the creosoting facility sites and have percentage distributions different from creosote, coal tar or petroleum derived samples. Their percentages are intermediate between creosote and petroleum and may reflect combined creosote and petroleum sources.

If we assume that the resolved peaks in the f2 fraction of the sediments are solely derived from a mixture of petroleum and creosote, a simplistic mixing model can be developed which shows the percentage of the resolved f2 peaks that are derived from each source. The mean percentages for the resolved f2 peak groups for the creosote and creosoted wood samples, the sediments and the oil samples are shown in Table 3a. Due to differences in the percent contribution of the PP and ORP groups to the total resolved f2 peaks in the oils and creosotes, the mean percent contribution of these groups can be used to calculate the relative proportions of creosote and oil derived resolved aromatic compounds in the sediments. The similarity of the mean percentages for the MRP group compounds in the creosotes and oils makes them less valuable as a diagnostic tool for a mixing model.

If we assume that creosote and petroleum are the only contributors of resolved aromatic peaks, Equations 1a and 1b give a mixing model which can be used to predict the contribution of resolved f2 peaks by creosote.

1a. $$XCpp + (1-X)Opp = Spp$$

1b. $$XCorp + (1-X)Oorp = Sorp$$

X(100)--the percent contribution of resolved f2 peaks by creosote

Cpp--the percent of the crosote resolved f2 peaks that is found in group PP

Opp--the percent of the oil resolved f2 peaks that is found in group PP

Corp--the percent of the creosote resolved f2 peaks that is found in group ORP

Oorp--the percent of the oil resolved f2 peaks that is found in group ORP

Spp--the percent of the sediment resolved f2 peaks that is found in group PP

Sorp--the percent of the sediment resolved f2 peaks that is found in group ORP

Oil has been shown to be rapidly affected by weathering processes before reaching the sediments (NAS, 1975). Therefore, it is expected that hydrocarbon distributions in sediments removed from a spill site would more likely reflect the distribution remaining in the spill site sediments rather than the distributions seen in the unspilled oil. The percent PP and ORP contributions in the sediments from Station S2 (creosote spill area) are probably the most reflective distributions to use for the PP and ORP percent contribution due to creosote. They are within the percentage range seen in the creosote and coal tar samples and may reflect differences due to weathering or creosote/coal tar formulations which would affect the

PP or ORP distributions of the initial creosote source. The PP and ORP distributions found in the creosote spill site sample (S2) and in the oil spill sample can be applied to Eq. 1a and 1b. The equations them become:

2a.
$$X(57) + (1-X)(3) = Spp$$
$$X = \frac{Spp - 3}{54}$$

2b.
$$X(15) + (1-X)(91) = Sorp$$
$$X = \frac{91 - Sorp}{76}$$

Standard deviations for the mixing model were calculated using the standard deviations for both the creosotes' and oil sample mean PP and ORP group percentages (Table 3a).

The percent contribution of creosote resolved aromatic peaks to the total resolved aromatic peaks at each of the sediment stations is shown in Table 3b. These numbers are calculated using the percent PP and the percent ORP groups respectively.

Table 3b. The percent contribution by creosote to the resolved f2 peaks of the sediment samples.

	PP	ORP
S2	100±10	100±6
S4	100±10	100±6
S5	94± 9	96±6
S3	85± 9	88±5
S1	85± 9	72±4
S6	102±10	103±6
S7	102±10	100±6
S8	65± 6	65±4

The results of the percent contribution calculations for the mixing model (Table 3b) indicate that 65 to 100 percent of the resolved aromatic peaks in the sediments can be attributed to contamination from carbonized coal products (creosote, coal tar etc.). The very high concentrations of PP group compounds in creosote, and the very high concentrations of ORP compounds in petroleum enabled percent contributions to be calculated using unrelated aromatic parameters. The close agreement of the percent contribution calculated when using the PP group compounds with the percent contribution calculated when using the ORP group compounds indicates that the contribution of PP or ORP compounds by sources other than petroleum or carbonized coal products is probably insignificant.

The coal tar sample (Table 3a) shows the lowest percentage of PP PNAHs and the highest percentage of ORP PNAHs of the samples derived from the carbonization of coal. Any PP percent distributions in sediments of less than 46 percent would be expected to show an input by petroleum. Correspondingly, any percentage of ORP greater than 25 percent would reflect an input by petroleum. A sediment with 45 percent PP and 26 percent ORP would have a creosote resolved f2 peak contribution of 78±8 percent and 85±5 percent for the PP and ORP groups respectively. Because of the inherant variability in the PP percentages of products derived from coal carbonization, the minimum level of oil detectable would need to contribute 22 8 percent to the total resolvable aromatic peaks. If we assume that creosote is approximately 90 percent aromatic (McNeil, 1959) and that fuel oil is approximately 25 percent aromatic (Gearing et.al., 1980), the ratio of the amount of whole oil to whole creosote that must be combined to derive the aromatic distribution calculated for a sediment with a minimum detectable oil level (22 8 percent) can be calculated. If 90 percent of creosote is aromatic and 100 percent of the aromatic fraction is resolved (Table 3a) then 90 percent of whole creosote is resolved aromatic compounds. If 25 percent of oil is aromatic and 28 percent of the aromatic fraction is resolved compounds (Table 3a) then seven percent of the whole oil is resolved aromatic compounds. A sediment which has a minimum of 22±8 percent of the resolved aromatic peaks derived from oil would contain approximately 3.5 times more oil than creosote.

When management decisions are made regarding the control of aromatic hydrocarbon inputs into the environment it is important to remember that if equal amounts of creosote and oil enter the environment, that creosote because of its higher aromatic content, could have a far greater deleterious effect on the environment. The aromatic peak contribution derived from a creosote spill of less than one third the amount of a corresponding oil spill would effectively mask any contribution of aromatic peaks derived from the oil.

When sediments from Narragansett Bay, which is primarily impacted by petroleum pollution, were analyzed the aromatic fraction showed a maximum of 10 percent resolved peaks (Wade and Quinn, 1979). Assuming that these resolved peaks were contributed entirely by petroleum, on the basis of UCM percentages (Table 3a), Elizabeth River sediments should have a maximum of 7 percent of the total resolved aromatic peaks contributed by petroleum (eleven percent of a maximum of 65 percent UCM seen in Elizabeth River sediments). Using the PP and ORP distributions for the oil spill sample (Table 3a), that would mean a petroleum contribution of 0.2 percent PP and six percent ORP. These percentages are within the limits of uncertainty when the percent contributions by creosote to the resolved aromatic peaks were calculated.

It appears that in most Elizabeth River sediments the majority (greater than 85 percent) of the resolved aromatic peaks (which include the hazardous EPA priority pollutant PNAHs) can be attributed to contamination by products derived from the carbonization of coal. The UCM in the aromatic fraction of these sediments appears to be attributable to petroleum and can amount to as much as 65 percent of the total aromatics. Because of the lack of knowledge about the hazards associated with the compounds which comprise the UCM, these compounds should not be dismissed as environmentally safe.

Hydrocarbon concentrations for the sediment stations are given in Table 4. The concentrations are within the range of those reported in the literature for the Elizabeth River (Bieri et.al., 1982; VA SWCB, 1983). The total hydrocarbon concentrations range from 2855 µg/g dry weight at Station S2 to 141 µg/g dry weight at Station S1. Hydrocarbons have been shown to preferentially associate with the fine grained sediments (Meyers and Quinn, 1973; Wade and Quinn, 1979). The presence of sand in the sediment would act as a dilutent when concentrations on a dry weight basis are considered. Because the fine grained sediments are easily transported, a more realistic portrayal of hydrocarbon concentrations is given by dividing the hydrocarbon concentration by the sediment's percent silt and clay concentrations in order to normalize the hydrocarbon concentrations for the percent fines (Brown and Wade, 1984). The hydrocarbon concentrations for the sediment stations normalized for fines are also given in Table 4. The highest normalized f2 concentrations are in the vicinity of the creosote facility sites at Stations S2, S4 and S5. A different distribution would be seen if only total hydrocarbon concentrations had been determined. The highest normalized hydrocarbon concentrations are at Stations S2, S1 and S3. At Stations S1 and S3 the low f2

TABLE 4. Total hydrocarbon concentrations and percent f1 and f2 for the sediment stations in µg/g dry weight. TOTALN=total hydrocarbons normalized for fines F1N=total f1 hydrocarbons normalized for fines F2N=total f2 hydrocarbons normalized for fines

	S2	S4	S5	S3	S1	S6	S7	S8
F1N	2775	847	1881	3159	4615	1091	567	926
F2N	2935	766	506	245	79	65	16	8
TOTAL	2856	822	2101	681	141	1063	437	430
TOTALN	5710	1613	2387	3404	4694	1156	583	934
%F1	49	54	79	93	98	94	97	99
%F2	51	46	21	7	2	6	3	1

concentrations are masked by the higher relative concentrations of the f1 fractions. The high f2 percentages at Stations S2, S4 and S5 indicate higher inputs of aromatic hydrocarbons at these stations. The f1 and f2 percentages at Stations S1, S3, S6, S7 and S8 are similar to those reported in areas primarily impacted by petroleum pollution (Wade, 1978; Wade and Quinn, 1979). The composition of the f2 fractions in these petroleum impacted areas however, was primarily an UCM and showed few resolved peaks. The f2 normalized fractions show decreasing aromatic hydrocarbon concentrations with increasing distance from the area of the creosoting facilities, indicating the possibility of an aromatic hydrocarbon source in this area. The f1 normalized fraction does not show a similar decreasing concentration pattern but instead shows varied concentrations along the length of the Elizabeth River. This variation indicates multiple sources for aliphatic hydrocarbons (f1) which do not add sufficient quantites of aromatic hydrocarbons (f2) to influence the decreasing concentration pattern of f2 fraction.

Aromatic compounds constitute a very high percentage of creosote (McNeil, 1959), and therefore these compounds may provide a unique fingerprint for creosote. The peaks were separated into two groups, the PP and MRP groups, which have previously been discussed. The weight percent

Figure 10. PP PNAH plots of the Creosotes, Coal tar and Creosoted wood samples.

(a) Creosote A

(b) Creosote B

(c) Creosote C

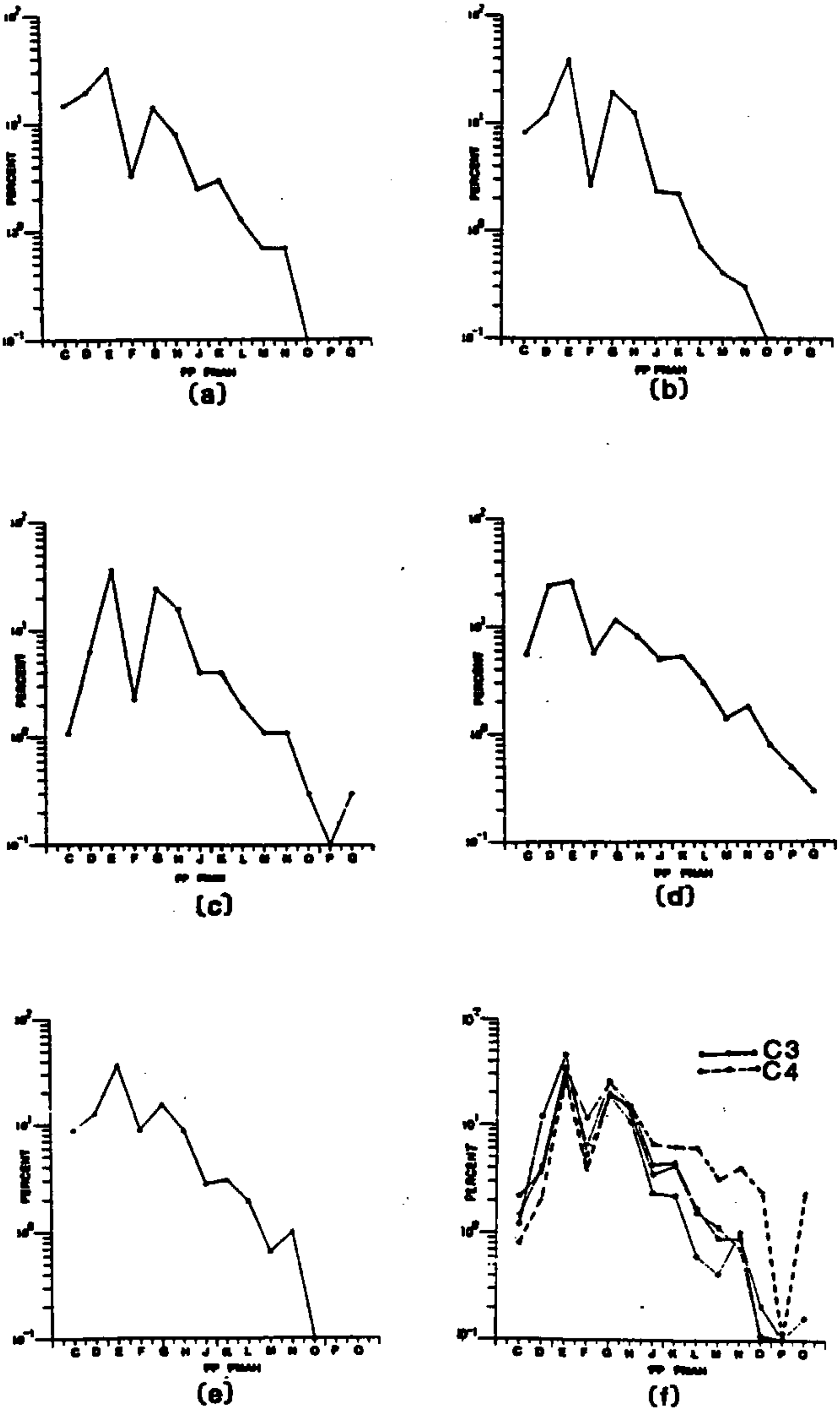
(d) Coal tar

(e) C2

(f) C1, C3, C4 and C5

PNAHs are identified in Appendix A.

FIGURE 10.



(a) (b) (c) (d) (e) (f)

each peak made to the total concentration of its group was calculated. These percentages for each sample are given in Appendix B. Because few samples contained Naphthalene (A) or Acenaphthylene (B) these peaks were eliminated when calculating percentages for the PP group. The PNAHs in order of increasing GC retention time, were plotted on the X-axis and the log of the percent contribution (in semi-log fashion) was plotted on the Y-axis. These plots describe relative PNAH distributions and permit comparison between samples from various sources and with widely varying PNAH concentrations.

The plots of the PP group of PNAHs for the creosote, coal tar and creosoted wood samples are found in Fig. 10. The error bars in Fig. 12a indicate the maximum analytical variability encountered with multiple injections of the same sample. Plots of Creosotes A, B and C appear in Figs. 10a, 10b and 10c. The plots are quite similar with the percentages of most PNAHs varying only slightly. The lower molecular weight PNAHs (Acenaphthene (C) and Fluorene (D)) have the greatest variation. The higher molecular weight PNAHs (Indeno(1,2,3-c,d)pyrene (O), Dibenz(a,h)anthracene (P) and Benzo(g,h,i)perylene (Q)) are at low concentrations and close to detection limits (approximately 0.1 percent). Plots for samples C2, C1 and C5 (Figs. 10e and 10f) are similar to the plots of Creosotes A, B and C. Sample C3 appeared to be the oldest sample and weathering processes including evaporation, photochemical oxidation, dissolution and microbial degradation (NAS,1975) may have removed the PNAHs with molecular weights less than Fluoranthene (G) causing the higher molecular weight peaks (Benz(a)anthracene (J) and greater) to have a larger relative percent (Lee and Ryan, 1983). Sample C4 appeared to be the youngest sample. In sample C4 the lower molecular weight PNAHs have a relatively higher percent while the higher molecular weight PNAHs have relatively lower percentages indicating it had not undergone as much weathering as Sample C3. The relative percentages of the higher molecular weight PNAHs in coal tar (Fig. 10d) are slightly higher than in the creosote samples. Since most creosote formulations for marine use are 50:50 creosote:coal tar mixtures (AWPA,1971) it appears that the larger relative percentages of the higher molecular weight compounds, especially Dibenz(a,h)anthracene (P) and Benzo(g,h,i)perylene (Q), in some creosoted wood samples may be attributable to the use of creosote-coal tar mixtures and/or to the removal of the lower molecular weight PNAHs by weathering processes. The PP plot for the woodstove sample (Fig. 11a) has lower percentages of the lower molecular weight PNAHs than found in creosote. Acenaphthene (C) and Fluorene (D) were not detected. Conversely, it shows higher relative percentages of the higher molecular weight compounds (especially

Figure 11. PP PNAH plots of the other hydrocarbon source samples.

(a) Woodstove soot

(b) Roof tar

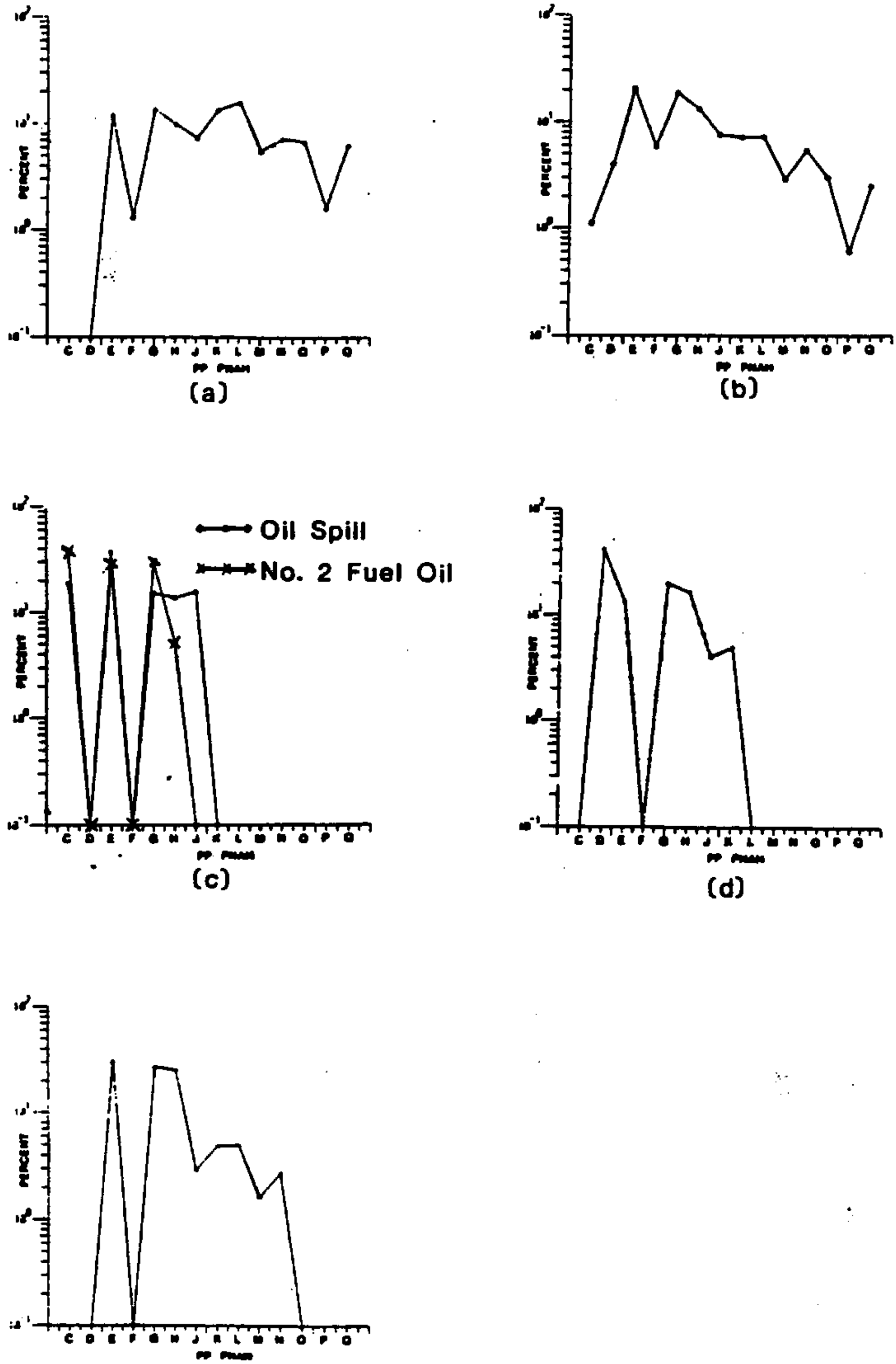
(c) Oil spill sample and No. 2 Fuel Oil

(d) Kuwait Crude Oil

(e) Diesel stack soot

PNAHs are identified in Appendix A.

FIGURE 11.



(a)

(b)

(c)

(d)

(e)

Benzo(k)fluoranthene (L), Indeno(1,2,3-c,d)pyrene (O) and Benzo(g,h,i)perylene (Q). Roof tar contains the components of coal tar which remain after the fractional distillation of the light, middle (creosote) and heavy oils (Berkowitz, 1959). Its PNAH distribution (Fig. 11b) reflects its coal tar origins with the lower molecular weight components of lower relative percent and the higher molecular weight components with a higher relative percent distribution.

The oil spill, No. 2 Fuel Oil (Fig. 11c) and Kuwait Crude Oil (Fig. 11d) plots have clearly different patterns from the creosote related sample plots, containing no detectable quantities of many of the PNAHs. The diesel stack soot sample (Fig. 11e) has more of the higher molecular weight PNAHs than the other petroleum derived samples. The PNAH distribution is still quite different from the creosote distributions, as concentrations of Acenaphthene (C), Fluorene (D), Anthracene (F), Indeno(1,2,3-c,d)pyrene (O), Dibenz(a,h)anthracene (P) and Benzo(g,h,i)perylene (Q) are below the detection limit.

The percent PP distribution patterns for the sediment stations are plotted in Fig. 12. The error bars (Fig. 12a) show the variation produced when this sample was injected on the GC six times, and shows the expected analytical variability. The plot for Station S2 (Fig.

Figure 12. PP PNAH plots of the sediment samples.

(a) S2

(b) S4

(c) S5

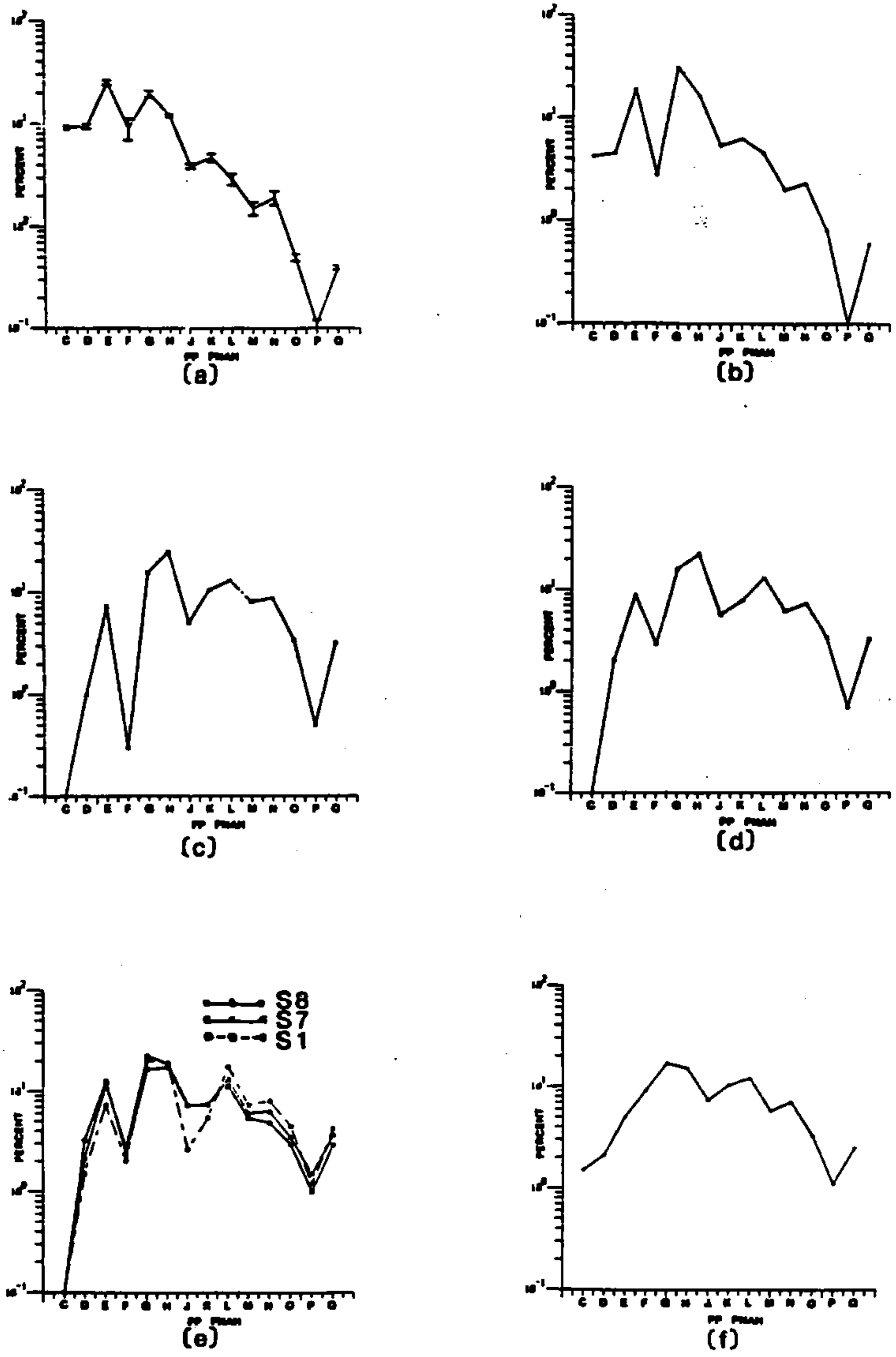
(d) S6

(e) S1, S8 and S7

(f) S3

PNAHs are identified in Appendix A.

FIGURE 12.



(a) (b) (c) (d) (e) (f)

12a) resembles the distribution pattern for creosote (Fig. 10) with each peak percentage within the percentage ranges found for the creosote samples. Station S4's plot (Fig. 12b) also has a distribution similar to the creosote samples, only differing by having slightly smaller concentrations of the lower molecular weight PNAHs and slightly greater concentrations of the higher molecular weight PNAHs. Possible creosote contamination of Stations S2 (spill area) and S4 (drainage ditch) seems clearly reflected in their percentage distribution plots of the PP PNAH group. The greater concentrations of the higher molecular weight compounds may indicate an additional input by coal tar or removal of the lower molecular weight compounds by weathering. Stations S5, S6, S1, S8 and S7 (Figs. 12c,d,e) have very similar distributions with the percentages varying only slightly with the exception of Anthracene (F) at Station S5 (Fig. 12c) which is anomalously low. Sediments from Station S3 (Fig. 12f) have similar distributions in the higher molecular weight region but have relatively high percentages of Fluorene (D) and especially Anthracene (F). The PP group PNAH distributions of the S5, S6, S1, S8 S7 stations do not resemble the PNAH distributions of the petroleum derived samples and could not result from them unless the petroleum PNAHs had undergone extensive modification in their transportation to the sediments.

The characteristic PNAH distribution in creosote is probably altered by environmental processes. PNAHs introduced into the marine environment may experience biological uptake, microbial degradation, volitalization, dissolution and dilution, photo-oxidation and sedimentation (Wade and Quinn, 1979; Lee and Ryan, 1983; Farrington and Quinn, 1973). Lee et.al. (1981) showed in enclosed ecosystems, that for the lower molecular weight aromatics, such as naphthalenes, anthracenes and phenanthrenes microbial degradation in the water column and evaporation maybe the primary removal processes. For the higher molecular weight aromatics, such as crysenes, benzanthracenes and benzpyrenes, the removal process was dominated by sedimentation and photo-oxidation. From mesocosm experiments, Lee and Ryan (1983) reported that once reaching the sediments, the PNAHs including Benz(a)anthracene, Crysene, Fluorene and Anthracene were readily degraded at the sediment/water interface, whereas, the higher molecular weight PNAHs including Benz(a)pyrene and Dibenz(a,h)anthracene showed only slight degradation at the sediment/water interface. When PNAHs are added to a natural aqueous environment the removal processes may be dominated by a process such as dissolution and dilution with ultimate sedimentation (Farrington and Quinn, 1973). Regardless of the process, degradation and removal is less important once the PNAHs reach the subsurface sediment where they can remain unaltered for years (Lee and Ryan, 1983; Gschwend and Hites, 1981). Preferential removal processes for the lower molecular weight PNAHs in creosote, before reaching the subsurface sediments, could lead to the PNAH distributions seen in Stations S5, S6, S1, S8 and S7. The fact that high concentrations of PNAHs remain in these sediments may also be due to large inputs, or to other materials contained in creosote (such as phenols) and not in petroleum that lower the microbial activity in the sediments. Differences in the physical states of creosote and oils may also affect the PNAH distributions seen. When creosote was mixed with seawater in the laboratory, three phases were formed; one more dense than seawater, one as dense as seawater and one less dense than seawater. The phase more dense than seawater was indistinguishable from intact creosote. At a spill site, the dense phase may be rapidly removed to the sediments with only slight alteration. The water soluble compounds may then be slowly leached into the water column and act as a chronic PNAH source. Petroleum, conversely, is less dense than seawater, and would be subjected to more weathering and dispersal processes than creosote before reaching the sediments.

In addition to the PP group PNAHs, the MRP group of 25 unidentified compounds was also plotted. The 25 MRP PNAHs were plotted on the X-axis, in order of increasing GC retention times, and the log of the percent plotted, in a semi-log fashion, on the Y-axis. The MRP peaks for Creosotes A and C are plotted in Fig. 13a. The Creosote B plot had a similar pattern. In each, peaks 1 through 18 follow the same pattern, with peaks 1,2,6,9,11,15 and 17 showing the highest concentrations. Peaks 7 and 10 have low to undetectable concentrations in both samples. The higher molecular weight peaks (peaks 19 and greater) do not follow similar distribution patterns. Creosote C has slightly lower concentrations of the lower molecular weight compounds (peaks 1-7) and correspondingly higher percentages of the other peaks. The basic pattern of rises and falls is still the same in both samples regardless of differences in actual percentages. The MRP distribution for coal tar is plotted in Fig. 13b. As in the creosote samples, peaks 1,2,11,15 and 17 have highest concentrations. Peaks 6 and 9, high in creosote, show mid-range percentages in coal tar. Peak 7, similar to creosote, is at a low level. Peaks 12 and 14 are at undetectable levels in coal tar even though they are present at mid-range percentages in the creosote samples. The higher molecular weight region (peaks 19 and larger) has higher concentrations than those generally seen in the creosote samples. Because creosote/coal tar formulations are commonly used in the wood preserving industry (AWPA, 1971), a more realistic approach when patterning the MRP peaks, which occur in much smaller concentrations than most of the PP peaks, is to develop a creosote/coal tar

Figure 13. MRP PNAH plots of the Creosotes, Coal tar and Creosoted Wood samples.

(a) Creosote A and Creosote C

(b) Coal tar

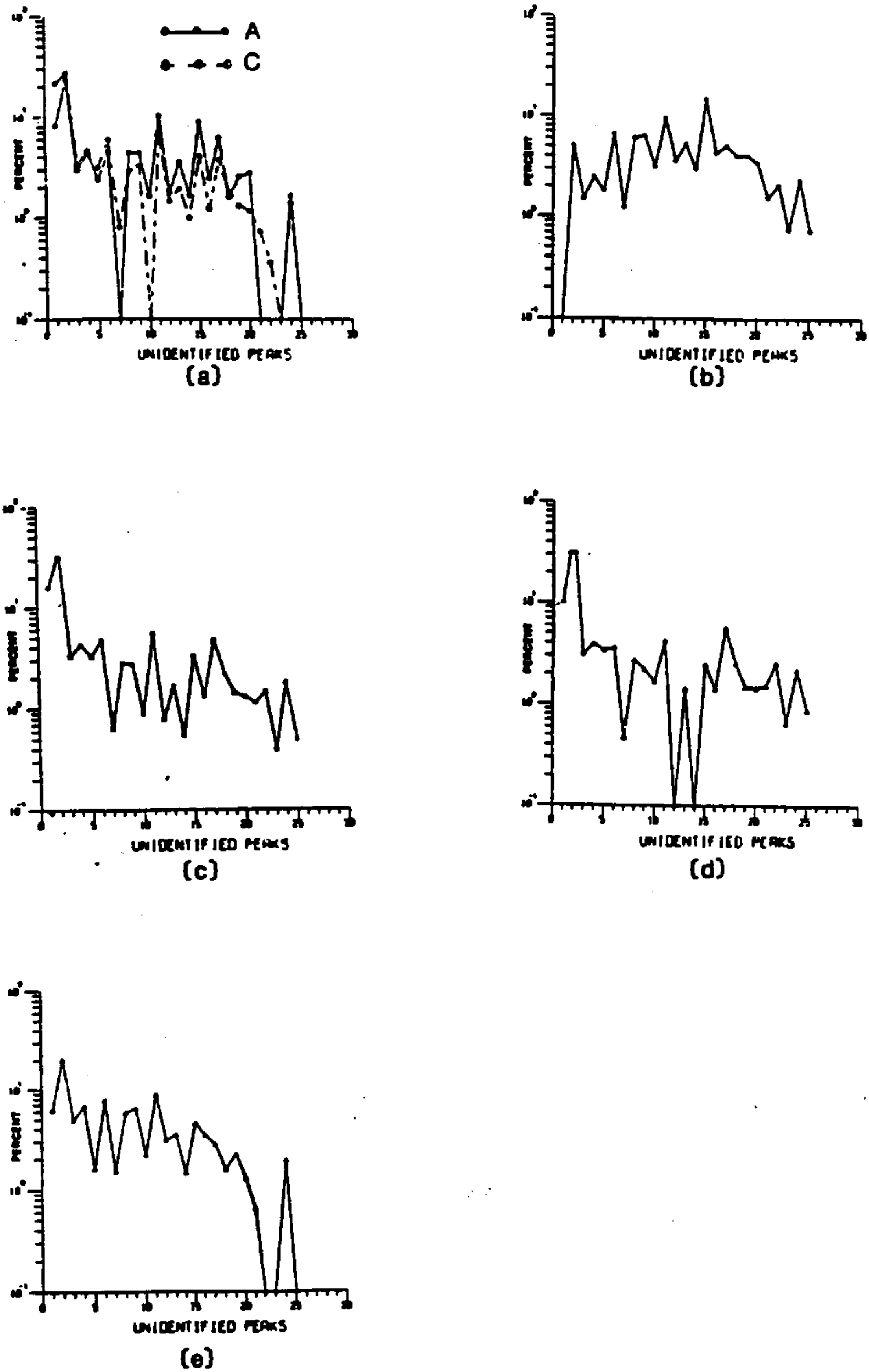
(c) Creosote A/Coal tar

(d) C1

(e) C2

MRP PNAH designation is explained in the text.

FIGURE 13.



(a) (b) (c) (d) (e)

mixture pattern. A pattern for a 50/50 Creosote A/coal tar mixture is plotted in Fig. 13c. A 50/50 mixture was chosen because that is the mixture of choice when treating lumber for marine use (AWPA, 1971).

MRP group PNAHs for creosoted wood samples C1 and C2 are plotted in Fig. 13d and 13e. Wood sample C1 (Fig. 13d) follows closely the rise and fall pattern seen in the 50/50 creosote/coal tar mixture. The low molecular weight peaks (peaks 1-5) are lower than in the creosote/coal tar mixture and the other peaks correspondingly higher. Wood sample C2 (Fig. 13e) matches the creosote/coal tar pattern in peak region 1 through 15. The higher molecular weight peaks have a pattern more similar to the creosote samples. These slight peak variations can probably best be explained by the use of different creosote brands or creosote/coal tar mixtures than shown here.

Other source samples, woodstove soot and roof tar, are shown in Fig. 14a and 14b. The petroleum derived samples (diesel stack soot, Kuwait Crude Oil, the oil spill sample and No. 2 Fuel Oil) all contained no more than seven of the 25 MRP peaks above detectable levels, all of which eluted before peak 14. The actual percentages are given in Appendix B. The petroleum samples' MRP plots did not resemble the creosote plots and therefore were not included.

Figure 14. MRP PNAH plots of the other hydrocarbon source samples and the sediment samples.

(a) Woodstove soot

(b) Roof tar

(c) S2

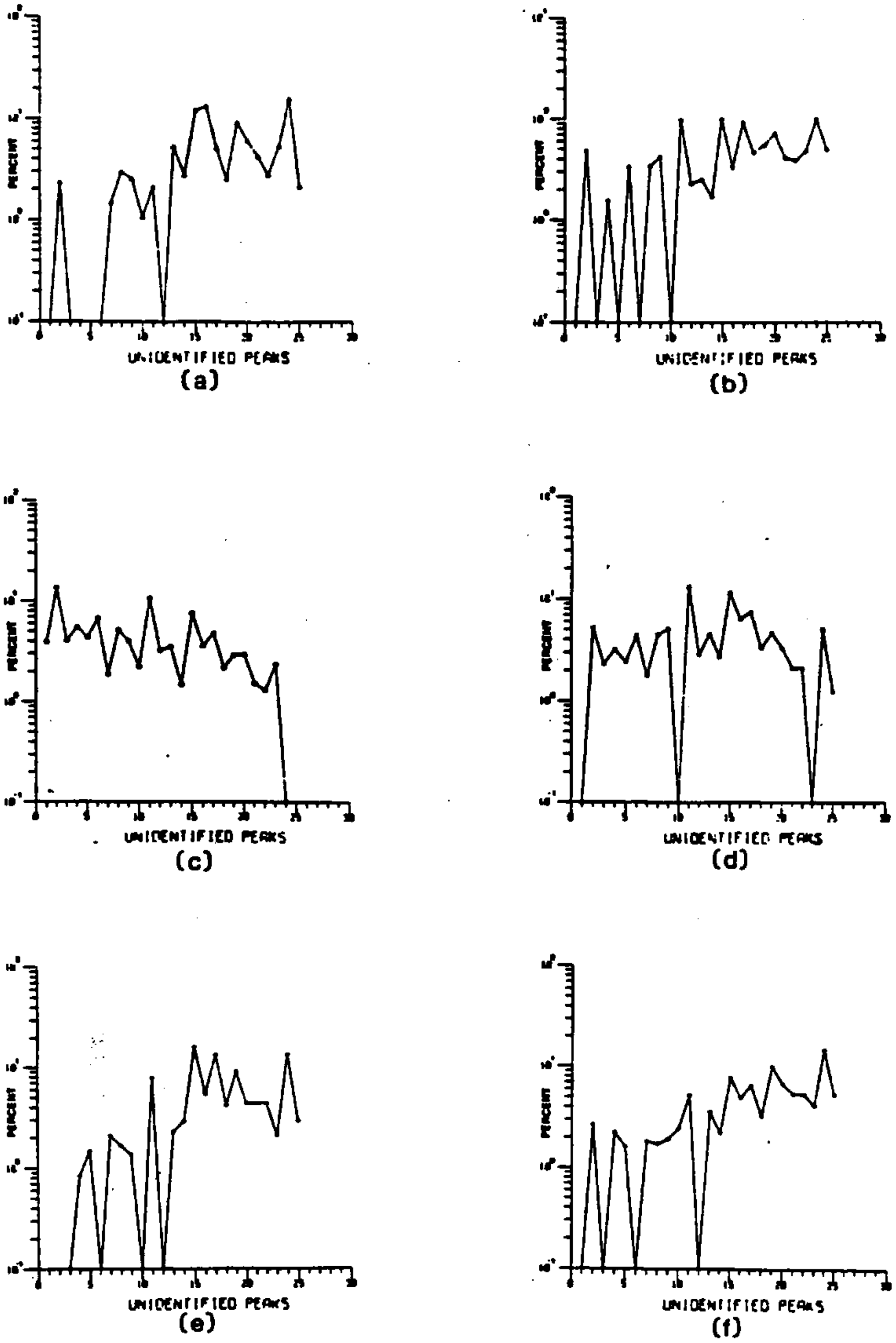
(d) S4

(e) S5

(f) S6

MRP PNAH designation is explained in the text.

FIGURE 14.



(a) (b) (c) (d) (e) (f)

The woodstove soot sample plot (Fig. 14a) has a pattern quite different from the creosote/coal tar pattern. The lower molecular weight peaks (less than peak 7) are at low or undetectable levels. The rise and fall pattern of peaks 8 through 15 follows the pattern seen in the creosote samples but the variability in the actual percentages is large. The higher molecular weight peaks (greater than peak 16) are at higher concentrations and have different rise and fall patterns than seen in the creosote samples. The roof tar sample plotted in Fig. 14b has low to undetectable levels of many of the lower molecular weight peaks (less than peak 7) in contrast to the creosote samples. The midrange peaks (peaks 7-18) have a pattern similar to the pattern seen in creosote. The higher molecular weight range peaks (greater than peak 18) have the highest concentrations and a pattern quite different from the creosote/coal tar pattern.

Selected sediment stations MRP peaks are plotted in Figs. 14c through 14f. The plot for Station S2 (Fig. 14c) matches the creosote/coal tar MRP plot (Fig. 13c) closely, reflecting the same rise and fall pattern and relative percent variations. Peaks 1 and 2 are at lower percentages which causes a correspondingly higher percentage in the peak 3 through 18 range. The higher molecular weight peaks (peak 19 and higher) have a pattern similar to the pattern seen in the roof tar sample.

The MRP plot for Station S4 is given in Fig. 14d. Its PNAH pattern resembles the pattern seen in Creosote A (Fig. 13a), differing only in the lower relative percentages of the peaks eluting before peak 5 and in the higher relative percentages of the PNAHs with higher molecular weights. At Station S5, (Fig. 14e) most of the peaks less than 14 are at low or undetectable concentrations. The peaks 14 and greater have a pattern, with the exception of peak 20, like that of the creosote/coal tar mixture (Fig. 13c). The plot for Station S6 is given in Fig. 14f and displays the same pattern in the peak 14 and greater range as Station S5 and the creosote/coal tar. The peaks in the lower molecular weight range have higher concentrations and more diversity than the corresponding range seen in Station S5.

CONCLUSIONS

Creosote has been shown to contaminate sediments adjacent to creosoted timbers (Dunn and Stich, 1975,1976; Lake et.al., 1979) but it has not been considered as a hydrocarbon source which can affect large areas. This study has shown that, in the Elizabeth River, creosote, coal tar and related products from the carbonization of coal effect the aromatic hydrocarbon distribution in the sediments. Because of the higher PNAH content of these sources, they may be more important than petroleum sources in their impact on the River's environment.

This study has also shown that, when differentiating sources, more diagnostic information is obtained when both the f1 and f2 hydrocarbon fractions are fully characterized. The distribution of the PP group PNAHs in the creosote and oil samples show overlapping PNAH percentages and differ absolutely only in the lack of detectable quantities of Anthracene (F), Benzo(k)fluoranthene (L), Benzo(b)fluoranthene (M) and Benzo(a)pyrene (N) in the oil samples. Yet, when the PP distribution in conjunction with other characteristics of the hydrocarbon constituents are employed the ability to differentiate between oil sources and creosote sources increases. Creosote has no UCM in the f1 fraction with few compounds larger than N-C16. Most petroleum derived materials have a large UCM in the f1 fraction with homologous series of n-alkanes from n-C11 through n-C32. In creosote the f2 fraction has approximately 65 percent of the PNAHs in the Priority Pollutant (PP) category whereas, the oil samples have an average of six percent in the PP category. The oil samples had a large UCM in the f2 fraction and the creosote samples had low to undetectable quantities of UCM. The distribution patterns of the PP and MRP group compounds in the oil and creosote samples were different, with the oil samples having a maximum of seven of the 25 peaks characterized in creosote.

The existance of a creosote spill site (Station S2) on the Elizabeth River provided a site for determination if the hydrocarbon distribution unique to creosote was retained in a spill area. The close match of the various characteristics and hydrocarbon distributions found at Station S2 with the characteristics and distributions found in creosote show that this information can be used to determine hydrocarbon sources. When sediments from stations near the site of Atlantic Wood Industries Inc. were analyzed they showed evidence in the f1 and f2 fractions of a hydrocarbon source primarily from creosote or related coal tar compounds. The remaining stations on the river appear to have both a creosote and petroleum hydrocarbon input for hydrocarbons. The f1 fractions of these sediments reflect imputs consistent with a predominantly weathered petroleum source (NAS, 1975). The f2 fractions however, have many characteristics similar to those seen in the creosote/coal tar samples.

Mixing model calculations showed that creosote, coal tar and related products contribute greater amounts (on a weight basis) of the PP PNAHs to the environment than petroleum because of their high aromatic hydrocarbon content. In Elizabeth River sediments, it appears that greater than 65 percent of the resolved aromatic hydrocarbon components can be attributed to products derived from the carbonization of coal. The resolved aromatic peaks contributed by petroleum products are not at detectable levels in the sediments at concentrations of petroleum less than 3.5 times the concentration of creosote or related products. Due to physical differences between petroleum and creosote, petroleum is probably subjected to more weathering and dispersal processes at a spill site than creosote. The aromatic hydrocarbons derived from creosote appear to be dispersed throughout the Elizabeth River in association with the fine grained sediments. The aliphatic hydrocarbon compliment appears to come from petroleum sources found at various locations on the River. It was necessary to examine the total information on the hydrocarbon distributions in order to establish a distinctive fingerprint. This method is superior to comparing only one characteristic such as total hydrocarbons or parent compound distributions. Identification of the major resolved peaks (MRP) could add a further refinement to the creosote fingerprint.

Brown and Wade (1984), in their investigation of the lower Chesapeake Bay, found an increase in hydrocarbon content of the sediments in the vicinity of the Chesapeake Bay Bridge Tunnel and attributed it to road runoff. Asphalt, a coal tar by-product, has been considered a major source of PNAHs in road runoff contamination of lake sediments (Wakeham et.al., 1979). An examination of the hydrocarbon inputs from road runoff is needed in order to establish the degree of contamination of the Elizabeth River sediments from this source.

Before rational mamagement of environmental problems can be instituted, understanding of the source, fate and impact of pollutants must be established. The chemical "fingerprinting" techniques used in this study show that carbonized coal products (creosote, coal tar, etc.), which contain high concentrations of known environmental carcinogens (PNAHs) are a unique and important contaminant of Elizabeth River sediments. The mixing model developed shows that for the best management decisions it is necessary to know the concentrations of the various hydrocarbon classes which are being added to the environment as well as the total hydrocarbon concentration. This information can give a better estimate of the input sources of hazardous compounds (such as PNAHs) when determining maximum allowable discharge amounts of a specific pollutant. Further studies of the fates and effects of the compounds derived from the carbonization of coal and the fate and effects of the petroleum derived resolved aromatic compounds and petroleum derived aromatic UCM should be undertaken.

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Fig. A1. Gas chromatograms of aliphatic and aromatic (PNAH) reference standards. Chromatographic conditions: 70 to 300°C at 10°/min.

Note: 12-34, n-alkanes
A-P, polynuclear aromatic hydrocarbons (PNAH)

A. Naphthalene
B. Acenaphthylene
C. Acenaphthlene
D. Fluorene
E. Phananthrene
F. Anthracene
G. Fluoranthene
H. Pyrene
I. 3-Methyfluoranthene
J. Benz(a)anthracene
K. Chrysene
L. Benzo(k)fluoranthene
M. Benzo(b)fluoranthene
N. Benzo(a)pyrene
O. Indeno(1,2,3-cd)pyrene
P. Dibenz (a,h)anthracene
Q. Benzo(ghi)perylene

FIGURE 1A.

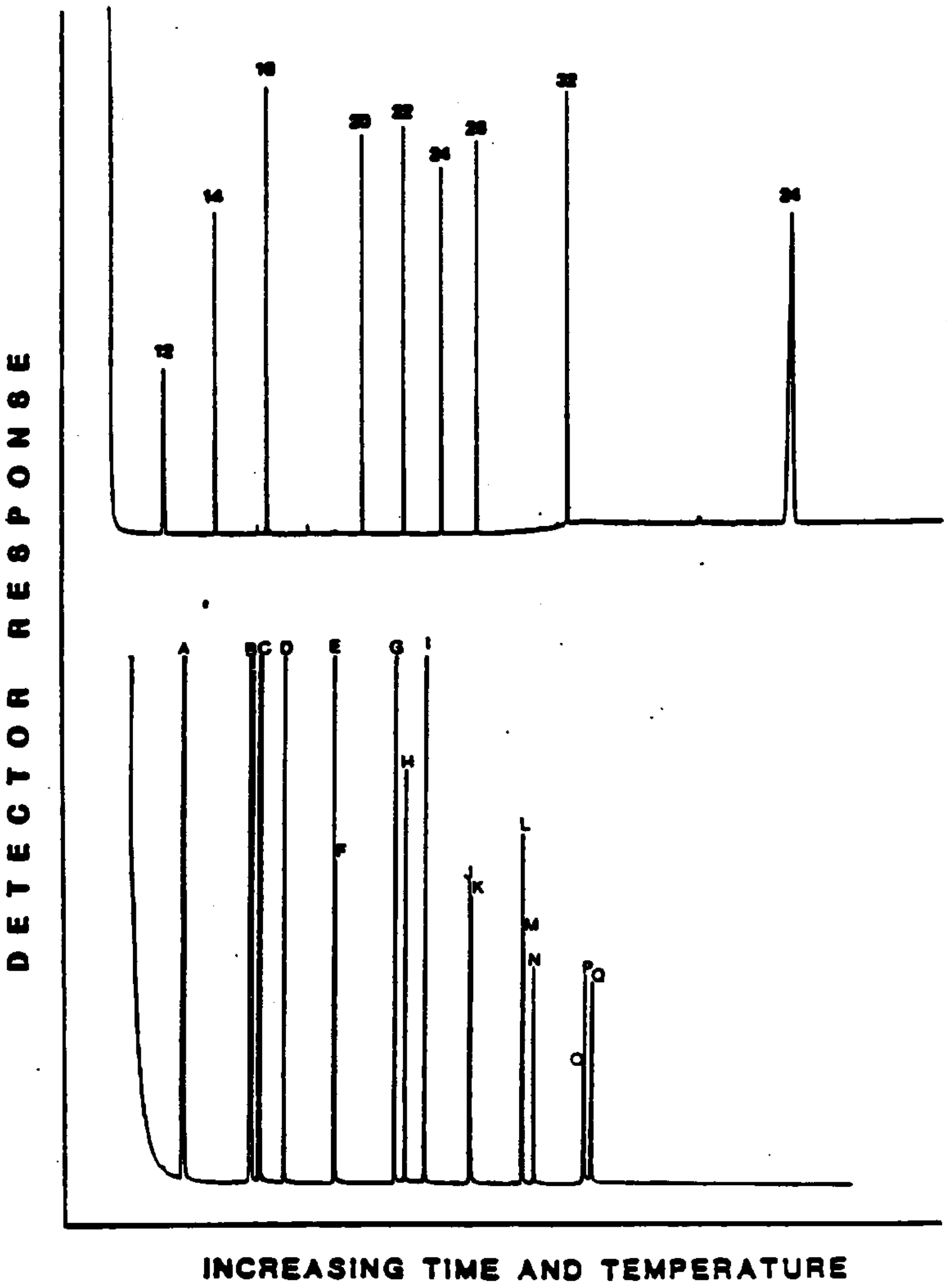
12
14
16
20
22
24
28
32
34
A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Q
DETECTOR RESPONSE
INCREASING TIME AND TEMPERATURE

Figure 2A. Gas chromatograms of typical blanks.
Note: IS-internal standard
f1 maximum blank 2.02 µg
f2 maximum blank 0.60 µg

FIGURE 2A.

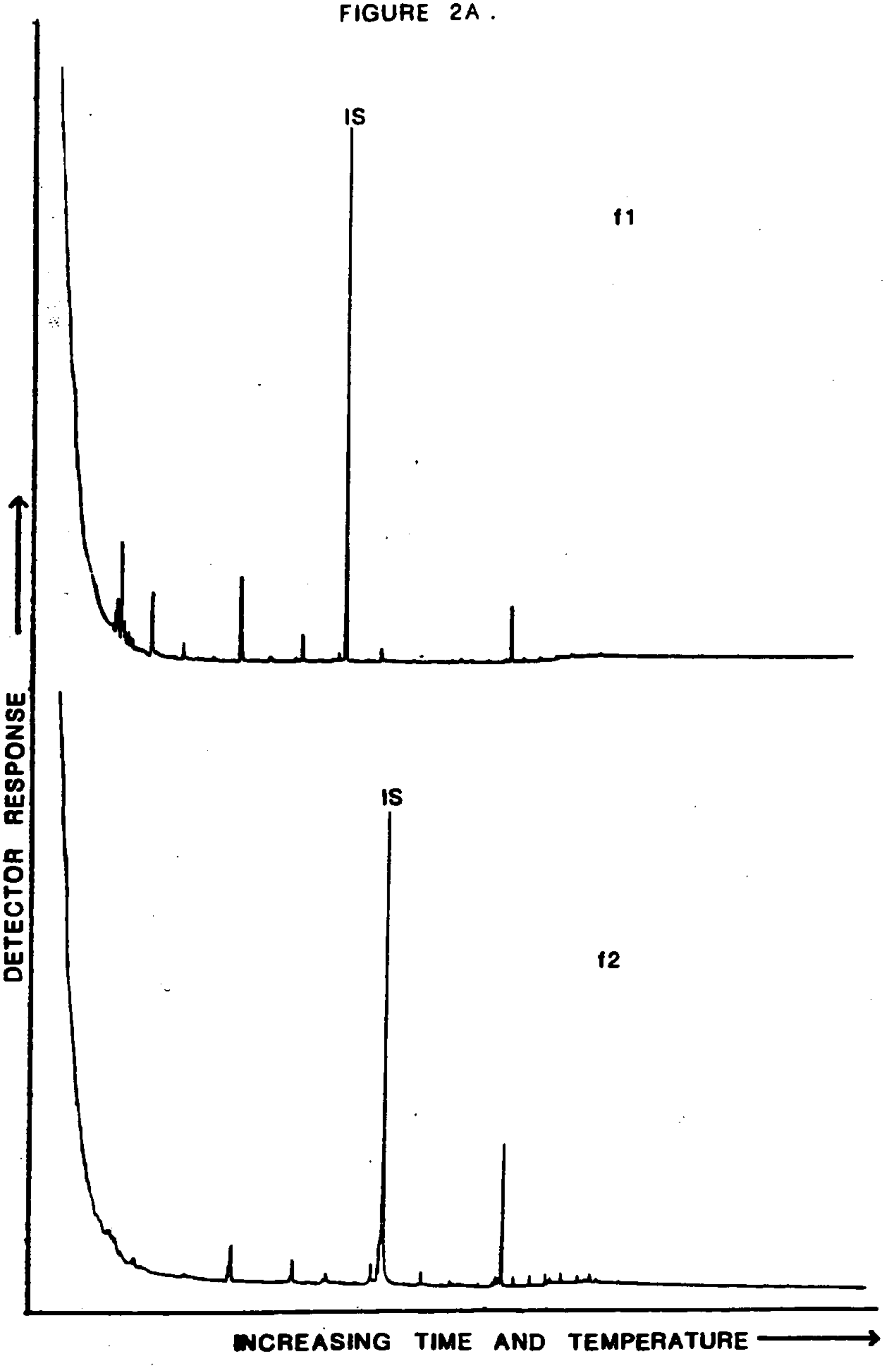
IS
f1
IS
f2
DETECTOR RESPONSE
INCREASING TIME AND TEMPERATURE

TABLE 1A. PNAH concentrations (µg/g dry weight) by soxlet, reflux and the test tube reflux method used in this study. Soxlet and corresponding test tube reflux sediments are from a core taken upstream from Station S2 and were not included in this study. The reflux and corresponding test tube reflux sediments were from a core taken at Station S6 and were not included in this study. UD-undetected

PNAH	SOXLET	TTUBE	REFLUX	TTUBE
A	UD	UD	0.14	0.20
B	UD	UD	0.07	0.09
C	0.07X	0.06	0.24	0.12
D	0.08X	0.10	0.22X	0.19
E	0.68X	0.39	0.65X	0.56
F	0.32X	0.38	0.16	0.20
G	1.99X	1.37	1.76X	1.37
H	1.40X	0.97	2.47X	2.62
J	0.53X	0.45	0.94X	0.72
K	0.78X	0.76	1.27X	0.91
L	0.79X	0.72	3.02	2.38
M	0.46	0.44	1.54X	1.34
N	0.50X	0.48	1.62	1.72
O	0.22	0.25	1.15	0.89
P	0.07	0.08	0.32	0.20
Q	0.21	0.25	1.36	1.23

X-confirmed by GC/MS

TABLE 1B. Percentages for the PP PNAHs in creosote and coal tar. PNAHs are identified in Appendix A. UD-undetected, CREO A-Creosote A, CREO B-Creosote B, CREO C-Creosote C

PNAH	CREO A	CREO B	CREO B	COAL TAR
C	14.7	8.1	1.1	5.7
D	19.4	12.4	6.3	24.2
E	32.2	38.9	36.7	26.4
F	3.3	2.6	2.3	5.8
G	14.2	19.6	24.7	11.6
H	8.0	12.5	16.1	8.2
J	2.5	2.3	4.1	5.0
K	3.0	2.2	4.0	5.3
L	1.3	0.7	1.9	3.0
M	0.7	0.4	1.1	1.4
N	0.7	0.3	1.1	1.8
O	UD	UD	0.3	0.8
P	UD	UD	UD	0.5
Q	UD	UD	0.3	0.3

TABLE 2B. Percentage PP PNAHs for the creosoted wood samples. The PNAHs are identified in Appendix A.

PNAH	C1	C2	C3	C4	C5
C	1.4	8.9	0.8	1.2	2.2
D	4.0	12.8	2.1	12.1	3.7
E	34.5	36.3	27.3	46.0	33.1
F	6.3	8.9	3.9	5.2	11.7
G	25.9	15.2	19.9	19.0	25.2
H	15.2	8.7	14.7	10.7	12.8
J	4.3	2.7	6.7	2.3	3.5
K	4.5	3.0	6.3	2.2	4.2
L	1.7	1.9	6.2	0.6	1.6
M	0.9	0.6	3.2	0.4	1.2
N	0.9	1.0	4.1	1.0	0.7
O	0.2	UD	2.4	UD	0.1
P	UD	UD	UD	UD	UD
Q	0.2	UD	2.4	UD	UD

TABLE 3B. Percentages for the PP PNAHs in other source samples. PNAHs are identified in Appendix A. RT-roof tar WS-woodstove soot SS-diesel stack soot KC-Kuwait Crude Oil OS-oil spill sample FO-No. 2 Fuel Oil UD-undetected

PNAH	RT	WS	SS	KC	OS	FO
C	1.0	UD	UD	UD	18.6	37.0
D	4.0	UD	UD	41.4	UD	UD
E	20.5	11.9	30.4	13.2	37.0	27.7
F	5.9	1.3	UD	UD	UD	UD
G	18.8	13.4	27.4	19.8	15.1	30.1
H	13.4	9.8	25.2	16.5	13.7	5.2
J	7.6	7.3	2.9	4.1	15.6	UD
K	7.2	13.4	4.9	5.0	UD	UD
L	7.2	15.8	4.9	UD	UD	UD
M	2.9	5.5	1.6	UD	UD	UD
N	5.4	7.1	2.7	UD	UD	UD
O	3.0	6.7	UD	UD	UD	UD
P	0.6	1.6	UD	UD	UD	UD
Q	2.5	6.2	UD	UD	UD	UD

TABLE 4B. Percentage composition of the PP PNAHs for the sediment samples. See Appendix A for the identification of the PNAHs. UD-undetected

	S2	24	S5	S3	S1	S6	S7	S8
C	9.2	4.2	UD	1.5	UD	UD	UD	UD
D	9.4	4.5	1.0	2.1	1.5	2.0	2.1	3.2
E	25.1	19.2	7.2	5.0	7.2	8.9	11.7	12.6
F	9.0	2.8	0.3	9.2	2.0	2.9	2.7	2.4
G	19.4	31.0	15.4	17.1	20.2	16.0	22.2	16.5
H	12.0	16.5	24.3	15.2	18.8	22.4	18.6	17.0
J	3.9	5.4	5.0	7.4	2.6	5.7	7.1	7.1
K	4.7	6.3	10.3	10.5	5.4	7.9	7.4	7.3
L	2.9	4.6	12.8	12.2	17.4	13.2	11.3	13.2
M	1.5	2.0	8.0	5.8	7.2	6.2	5.3	6.0
N	1.9	2.3	8.6	7.1	7.9	7.4	4.8	6.2
O	0.5	0.8	3.4	3.3	4.4	3.4	2.9	3.4
P	0.1	UD	0.5	1.1	1.2	0.7	1.0	1.5
Q	0.4	0.6	3.2	2.5	4.2	3.3	2.9	3.6

TABLE 5B. Percentages for the MRP PNAHs in the creosotes, coal tar and 50/50 Creosote A/coal tar mixture. UD-undetected

MRP	A	B	C	COAL TAR	A/COAL TAR
1	21.54	8.36	8.22	10.23	15.58
2	27.10	20.94	23.47	39.93	33.52
3	3.40	2.88	3.01	3.11	3.26
4	4.64	4.41	4.41	3.93	4.28
5	3.14	3.40	2.38	3.38	3.26
6	5.99	6.64	4.53	3.59	4.79
7	0.79	1.21	UD	0.47	0.63
8	2.93	5.80	4.44	2.72	2.82
9	3.29	5.24	4.42	2.22	2.76
10	UD	UD	1.62	1.68	0.89
11	7.01	13.51	10.32	4.74	5.62
12	1.45	2.35	1.76	UD	0.78
13	1.94	3.46	3.58	1.44	1.69
14	0.98	1.81	1.66	UD	0.54
15	4.10	7.56	8.94	2.51	3.30
16	1.21	1.92	2.44	1.43	1.32
17	3.77	4.36	6.22	5.75	4.75
18	1.79	1.00	1.57	2.56	2.18
19	1.30	1.80	2.57	1.49	1.40
20	1.16	1.92	2.79	1.45	1.31
21	0.73	0.76	UD	1.54	1.14
22	0.36	UD	UD	2.57	1.46
23	UD	UD	UD	0.67	0.38
24	1.38	0.67	1.65	2.21	1.79
25	UD	UD	UD	0.88	0.49

TABLE 6B. Percent contributions for the MRP PNAHs in the creosoted wood samples. UD-undetected

	C1	C2	C3	C4	C5
1	UD	UD	2.90	2.93	UD
2	5.10	20.37	15.52	20.50	5.11
3	1.51	4.89	UD	2.44	1.81
4	2.51	6.77	3.60	7.01	2.80
5	1.81	1.60	UD	3.58	2.02
6	6.66	7.83	2.87	8.37	6.86
7	1.26	1.52	UD	1.38	1.79
8	6.14	5.84	5.69	6.45	5.48
9	6.49	6.49	4.94	6.92	6.14
10	3.20	2.24	7.27	1.72	2.27
11	9.73	9.01	1.91	9.26	9.10
12	3.68	3.14	UD	2.91	3.85
13	5.39	3.59	3.91	4.24	7.44
14	3.02	1.49	1.29	1.77	3.08
15	14.95	4.69	6.81	7.21	17.94
16	4.33	3.55	3.63	2.72	3.99
17	5.13	2.89	3.77	2.67	2.79
18	4.07	1.61	3.23	2.17	3.41
19	4.10	2.30	5.39	2.00	4.09
20	3.47	1.31	2.21	1.40	3.36
21	1.56	0.67	2.98	0.65	1.48
22	2.07	UD	1.73	0.83	1.71
23	0.77	UD	3.25	UD	0.94
24	2.32	2.03	13.46	0.87	2.59
25	0.77	UD	3.64	UD	UD

TABLE 7B. Percent contributions for 25 Major Unidentified Peaks (MRP) in the other source samples. UD-undetected RF-roof tar WS-woodstove soot SS-diesel stack soot KC-Kuwait Crude Oil OS-oil spill sample FO-No. 2 Fuel Oil

MRP	RF	WS	SS	KC	OS	FO
1	UD	UD	UD	UD	UD	UD
2	4.75	2.35	UD	46.92	UD	UD
3	UD	UD	UD	UD	UD	UD
4	1.48	UD	UD	UD	UD	UD
5	UD	UD	UD	UD	12.09	28.32
6	3.24	UD	UD	10.72	15.93	UD
7	UD	1.50	UD	UD	UD	UD
8	3.29	2.99	21.76	12.33	15.93	21.39
9	4.15	2.56	26.49	UD	17.59	22.16
10	UD	1.07	UD	UD	UD	UD
11	9.74	2.14	20.64	11.80	15.93	12.33
12	2.20	UD	16.74	UD	10.99	10.02
13	2.44	5.34	UD	18.23	11.54	5.78
14	1.62	2.78	UD	UD	UD	UD
15	10.00	12.29	UD	UD	UD	UD
16	3.24	13.46	UD	UD	UD	UD
17	9.27	5.13	7.53	UD	UD	UD
18	4.57	2.56	3.35	UD	UD	UD
19	5.45	9.40	UD	UD	UD	UD
20	7.13	6.09	UD	UD	UD	UD
21	4.04	4.27	UD	UD	UD	UD
22	3.77	2.78	UD	UD	UD	UD
23	4.72	5.34	UD	UD	UD	UD
24	10.00	15.81	3.49	UD	UD	UD
25	4.90	2.41	UD	UD	UD	UD

TABLE 8B. Percentages for the MRP PNAHs for the sediment stations. UD-undetected

MRP	S2	S4	S5	S3	S1	S6	S7	S8
1	3.92	UD	UD	UD	UD	UD	UD	UD
2	13.64	5.21	UD	2.48	UD	2.65	4.79	3.05
3	4.04	2.32	UD	UD	UD	UD	UD	UD
4	5.54	3.19	0.83	1.74	UD	2.23	3.59	2.54
5	4.38	2.41	1.46	UD	UD	1.59	3.59	3.05
6	6.76	4.42	UD	1.96	UD	UD	UD	UD
7	1.87	1.78	2.09	UD	UD	1.80	UD	UD
8	5.18	4.44	1.67	UD	UD	1.70	5.99	5.08
9	4.04	5.12	1.36	UD	9.63	1.91	5.59	5.58
10	2.22	UD	UD	UD	2.63	2.44	UD	UD
11	10.77	13.32	7.82	5.78	2.19	5.19	6.59	9.14
12	3.26	2.85	UD	UD	UD	UD	7.78	4.57
13	3.54	4.58	2.29	2.68	UD	3.60	4.59	4.06
14	1.49	2.72	2.92	2.32	5.25	2.23	3.59	3.30
15	7.64	11.70	16.06	8.17	8.75	7.85	5.99	7.61
16	3.63	6.43	5.42	4.46	6.13	4.98	5.19	5.58
17	4.81	7.53	13.35	10.94	6.56	6.69	6.39	4.57
18	2.18	3.34	4.17	6.88	UD	3.28	UD	2.54
19	2.93	4.66	9.07	7.55	UD	10.16	UD	3.55
20	2.97	3.34	4.38	8.22	UD	6.78	3.19	3.55
21	1.53	2.12	4.38	6.83	UD	5.40	UD	4.57
22	1.30	2.14	4.38	8.57	20.79	5.40	4.79	3.30
23	2.63	UD	2.09	2.71	3.50	4.13	UD	4.06
24	UD	5.12	13.34	12.50	23.19	14.71	12.38	12.18
25	UD	1.26	2.92	6.21	11.38	5.30	15.97	8.12

TABLE 9B. Percent contributions by the identified n-alkanes and pristane (Prist) and phytane (Phyt) in the f1 fractions of the creosote samples (A,B,C), creosoted wood samples and the coal tar sample. UD-undetected

	A	B	C	C1	C2	C3	C4	C5	COAL TAR
n-C15	UD	UD	UD	1.0	UD	UD	UD	UD	UD
n-C16	100	63.3	85.8	6.1	42.1	61.1	42.1	72.5	100
n-C17	UD	10.8	4.5	0.8	2.4	6.7	2.4	9.2	UD
n-C18	UD	7.0	1.2	0.7	UD	UD	UD	9.2	UD
n-C19	UD	3.8	1.5	1.4	1.4	UD	1.4	3.4	UD
n-C20	UD	1.6	UD	2.5	1.7	UD	1.7	UD	UD
n-C21	UD	2.2	UD	5.6	1.9	12.9	1.9	UD	UD
n-C22	UD	UD	UD	8.5	4.0	UD	4.0	UD	UD
n-C23	UD	UD	UD	11.2	5.2	UD	5.2	UD	UD
n-C24	UD	UD	UD	13.5	5.9	10.5	5.9	UD	UD
n-C25	UD	UD	UD	12.7	6.1	UD	6.1	UD	UD
n-C26	UD	UD	UD	10.8	5.2	UD	5.2	UD	UD
n-C27	UD	UD	UD	7.7	4.5	UD	4.5	UD	UD
n-C28	UD	UD	UD	5.8	4.0	UD	4.0	UD	UD
n-C29	UD	UD	UD	4.2	3.7	UD	3.7	UD	UD
n-C30	UD	UD	UD	2.9	2.8	UD	2.8	UD	UD
n-C31	UD	UD	UD	1.9	2.3	UD	2.3	UD	UD
n-C32	UD	UD	UD	1.0	1.4	UD	1.4	UD	UD
n-C33	UD	UD	UD	0.4	0.9	UD	0.9	UD	UD
n-C34	UD	UD	UD	0.3	0.3	UD	0.3	UD	UD
Prist	UD	8.6	4.5	0.6	4.2	9.0	4.2	4.6	UD
Phyt	UD	2.7	2.5	0.4	UD	UD	UD	1.1	UD

TABLE 10B. Percent contribution of n-alkanes and pristane (Prist) and phytane (Phyt) in roof tar (RT), woodstove soot (WS), diesel stack soot (SS), Kuwait Crude Oil (KC), the oil spill sample (OS) and No. 2 Fuel Oil (FO). UD-undetected

	RT	WS	SS	KC	OS	FO
n-C15	UD	3.5	1.0	16.5	12.3	20.5
n-C16	44.0	9.9	3.1	14.0	12.7	17.7
n-C17	2.5	6.2	6.4	11.9	12.0	14.7
n-C18	13.0	4.3	10.6	9.5	9.9	12.5
n-C19	1.4	3.7	16.4	7.8	7.9	8.8
n-C20	6.9	4.0	17.2	6.6	6.4	6.3
n-C21	2.3	5.2	14.6	5.5	5.2	4.1
n-C22	2.3	6.9	9.3	4.7	4.4	2.6
n-C23	8.1	9.9	4.8	3.6	3.6	1.2
n-C24	0.9	8.2	2.9	3.5	3.2	0.6
n-C25	0.9	10.8	2.9	2.9	2.4	UD
n-C26	1.2	8.6	2.0	2.4	1.9	UD
n-C27	1.2	2.8	UD	1.8	1.5	UD
n-C28	1.6	2.6	UD	1.4	1.3	UD
n-C29	1.8	0.8	UD	1.3	1.1	UD
n-C30	1.6	UD	UD	0.8	0.9	UD
n-C31	1.6	8.6	UD	0.6	0.7	UD
n-C32	1.6	UD	UD	UD	UD	UD
n-C33	0.9	UD	UD	UD	UD	UD
n-C34	UD	UD	UD	UD	UD	UD
Prist	2.3	2.5	4.5	2.1	6.6	6.9
Phyt	3.9	1.5	4.3	3.1	6.0	4.1

TABLE 11B. Aliphatic concentrations (μg/g dry weight) for sediment stations. Prist.=Pristane Phyt.=Phytane IS=Internal Standard UD=undetected

ALKANES	S2	S4	S5	S3	S1	S6	S7	S8
n-C15	UD	29.43	UD	0.20	0.10	0.29	0.37	UD
n-C16	46.36	17.31	0.74	0.20	0.13	0.49	0.63	0.28
n-C17	3.39	22.51	1.09	0.23	0.17	0.40	0.43	0.11
n-C18	2.33	12.70	0.69	0.13	0.18	0.27	0.29	0.06
n-C19	1.59	14.43	0.74	0.13	0.14	0.31	0.34	UD
n-C20	IS	11.54	IS	IS	0.13	IS	IS	IS
n-C21	3.76	8.66	0.59	0.11	0.12	0.31	0.19	0.20
n-C22	1.16	6.92	0.84	0.10	0.12	UD	0.19	0.19
n-C23	1.43	4.62	0.40	0.20	0.14	0.38	0.29	0.36
n-C24	1.06	3.42	0.59	0.26	0.18	0.31	0.43	0.40
n-C25	1.27	4.04	0.64	0.23	0.22	0.44	0.48	0.64
n-C26	0.74	1.62	0.40	0.12	0.10	0.27	0.29	0.38
n-C27	1.16	4.62	0.79	0.28	0.20	0.49	0.63	0.45
n-C28	0.74	1.73	0.44	0.13	0.09	UD	0.48	0.25
n-C29	1.80	6.92	1.38	0.78	0.41	1.07	1.06	UD
n-C30	0.48	1.73	0.35	0.20	0.08	0.44	0.29	0.15
n-C31	1.38	UD	0.99	0.66	0.17	0.88	0.51	0.39
n-C32	UD	UD	UD	0.16	UD	UD	UD	0.09
n-C33	UD	UD	UD	UD	UD	UD	UD	0.13
Prist.	4.50	31.16	1.19	0.16	0.08	0.31	0.34	0.07
Phyt.	1.91	25.97	0.99	0.10	0.08	0.27	0.34	0.06

TABLE 12B. Aliphatic concentrations (µg/g dry weight) for sediment stations normalized for fines. Prist.=Pristane Phyt.=Phytane UD=undetected

ALKANES	S2	S4	S5	S3	S1	S6	S7	S8
n-C15	UD	57.71	UD	1.00	3.33	0.32	0.49	UD
n-C16	92.72	33.94	0.84	1.00	4.33	0.53	0.84	0.61
n-C17	6.78	44.14	1.24	1.15	5.67	0.43	0.57	0.24
n-C18	4.66	24.90	0.78	0.65	6.00	0.29	0.39	0.13
n-C19	3.18	28.29	0.84	0.65	4.67	0.34	0.45	UD
n-C20	IS	22.62	IS	IS	4.33	IS	IS	IS
n-C21	7.52	16.98	0.67	0.55	4.00	0.34	0.25	0.43
n-C22	2.32	13.57	0.95	0.50	4.00	UD	0.25	0.41
n-C23	2.86	9.06	0.45	1.00	4.67	0.41	0.39	0.78
n-C24	2.12	6.70	0.67	1.30	6.00	0.34	0.57	0.87
n-C25	2.54	7.92	0.72	1.15	7.33	0.48	0.64	1.39
n-C26	1.48	3.18	0.45	0.60	3.33	0.29	0.39	0.82
n-C27	2.32	9.06	0.89	1.40	6.67	0.53	0.84	0.98
n-C28	1.48	3.39	0.50	0.65	3.00	UD	0.64	0.54
n-C29	3.20	13.57	1.57	3.90	13.67	1.16	1.41	UD
n-C30	0.96	3.39	0.40	1.00	2.67	0.48	0.39	0.33
n-C31	2.76	UD	1.12	3.30	5.67	0.96	0.68	0.85
n-C32	UD	UD	UD	0.80	UD	UD	UD	0.20
n-C33	UD	UD	UD	UD	UD	UD	UD	0.28
Prist.	9.50	61.09	1.35	0.80	2.67	0.34	0.85	0.15
Phyt.	3.82	50.92	1.12	0.50	2.67	0.29	0.45	0.13

TABLE 13B. PNAH concentrations in µg/g (dry weight basis) and grain size distributions for sediment stations. PNAHs are identified in Appendix A. UD=undetected

PNAH	S2	S4	S5	S3	S1	S6	S7	S8
A	9.12	UD	UD	0.50	UD	UD	0.179	0.124
B	7.60	UD	UD	0.11	UD	UD	UD	0.013
C	75.74	8.99	0.96	0.38	UD	UD	UD	UD
D	77.26	8.81	1.69	0.53	0.006	0.14	0.048	0.015
E	205.02	49.63	7.28	1.40	0.031	0.62	0.270	0.059
F	73.65	4.71	1.46	2.29	0.009	0.20	0.062	0.011
G	159.38	63.68	24.09	4.33	0.087	1.12	0.516	0.077
H	98.61	33.87	33.45	3.49	0.081	1.56	0.429	0.080
J	31.88	12.92	5.27	1.63	0.011	0.40	0.164	0.033
K	38.29	14.42	10.44	2.26	0.023	0.55	0.170	0.034
L	23.90	12.22	14.87	2.50	0.075	0.92	0.262	0.062
M	12.29	5.39	8.09	1.34	0.031	0.43	0.122	0.028
N	15.98	4.51	10.24	1.69	0.034	0.52	0.141	0.029
O	3.72	1.82	2.97	0.69	0.019	0.24	0.067	0.016
P	0.79	UD	0.62	0.18	0.005	0.05	0.022	0.007
Q	3.19	1.61	3.19	0.71	0.017	0.23	0.068	0.017
%SAND	50	49	12	80	97	8	25	54
%SILT	27	28	39	12	1	42	37	29
%CLAY	23	23	49	8	2	50	38	17

Table 14B. PNAH concentrations in μg/g (dry weight basis) normalized for the percentage of fines. The PNAHs are identified in Appendix A. UD=undetected

	S2	S4	S5	S3	S6	S7	S8	S1
A	18.24	UD	UD	2.50	UD	0.24	0.27	UD
B	15.20	UD	UD	0.55	UD	UD	0.03	UD
C	151.48	17.63	1.09	1.90	UD	UD	UD	UD
D	154.52	17.27	1.92	2.65	0.15	0.06	0.03	0.21
E	410.04	97.31	8.27	7.00	0.67	0.36	0.13	1.02
F	147.30	9.24	1.66	11.45	0.22	0.08	0.02	0.29
G	318.76	124.86	27.38	21.65	1.22	0.69	0.17	2.90
H	197.22	66.41	38.01	17.45	1.70	0.57	0.17	2.70
J	63.76	25.33	5.99	8.15	0.43	0.22	0.07	0.37
K	76.56	28.27	11.86	11.20	0.60	0.23	0.07	0.77
L	47.80	23.96	16.90	12.50	1.00	0.35	0.13	2.50
M	24.58	10.39	9.19	6.70	0.47	0.16	0.16	1.03
N	31.96	8.84	11.64	8.45	0.57	0.19	0.06	1.13
O	7.44	3.57	3.38	3.45	0.26	0.07	0.03	0.63
P	1.58	UD	0.70	0.90	0.05	0.03	0.02	0.17
Q	6.38	3.16	3.63	3.55	0.25	0.09	0.04	0.57