Review

Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by gas chromatography

Zhendi Wang*, Merv Fingas

Emergencies Science Division, ETC, Environment Canada, 3439 River Road, Ottawa, Ontario, Canada, K1A 0H3

Abstract

This review gives a brief survey and comparison of chemical fingerprinting techniques by gas chromatography that are currently used for the characterization of petroleum hydrocarbons, the identification of oil spills and in assessing environmental impacts. This review focuses on new trends and developments in oil analysis methods.

Keywords: Reviews; Petroleum; Environmental analysis; Oils; Polynuclear aromatic hydrocarbons; Volatile organic compounds

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*Corresponding author.

1. Introduction

The contamination of soil and water caused by accidental leakage or chronic release of crude oil and refined products to the environment occurs each year with growing industrialization and demands for energy. In 1995, over 30 accidental large-scale oil spills occurred worldwide, in addition to thousands of small spill accidents [1]. Oils are very complex mixtures of hydrocarbons and substituted derivatives of hydrocarbons, in which the boiling points of components can vary from a few to several hundred degrees. In most cases, after release into the environment, spilled oil is immediately subjected to a variety of weathering processes [2] including evaporation, dissolution, dispersion, photochemical oxidation, water–oil emulsification, microbial degradation, and adsorption onto suspended particulate materials, further complicating the already complex oil mixtures. In order to unambiguously characterize spilled oils, to understand the fate and behaviour and to predict the potential long-term impact of the spilled oil in the environment, accurate and reliable analytical methods are extremely important.

This review gives a brief survey of several analytical methods and techniques currently used for the analysis of crude oils, petroleum products and oil-spill-related environmental samples. In particular, new trends and developments in oil analysis techniques are evaluated. The analytical approach used in our laboratory at Emergencies Science Division of Environment Canada are discussed as an example of current methodologies. High-resolution capillary gas chromatography with flame ionization detectors and capillary gas chromatography–mass spectrometry are used in our laboratory to identify, characterize and quantify various crudes and petroleum products in environmental samples with respect to their composition, nature and source.

2. Methods of petroleum hydrocarbon analysis

2.1. Current analytical methods

In recent years, major advances have been made in the techniques for oil analysis. Various adsorbents (including silica gel, alumina, florisil, combination of silica and alumina and solid-phase extraction) and elution solvents have been used to separate oil into saturated, aromatic and polar groups [3–16]. These fractions are analysed using techniques that include gravimetric methods, gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC), infrared spectroscopy (IR), supercritical fluid chromatography (SFC), ultraviolet (UV) and fluorescence spectroscopy, and nuclear magnetic resonance (NMR). Of all of these techniques, high-resolution capillary GC with flame ionization detection (FID) and combination of capillary GC with other techniques such as GC–MS are the most widely used. Landance and Greibrokk [17] have presented a review with 109 references on employing various analytical techniques for class determination, preparative fractionation of main classes and subgroup determination in fuels, heavy fractions and crude oils. Levy [18] has presented a review with 52 references on application of supercritical fluid extraction and size-exclusion chromatography for sample preparation and analysis in numerous areas of the petroleum industry. Philp [19] reviewed the application of high-temperature GC to the analysis of fossil fuel samples. Due to complexity of oil composition, there is no one method that can "do it all" for the whole spectrum of oils and petroleum products. Based on requirements under different circumstances, many novel methods have been developed to obtain specific information about target or target groups of petroleum hydrocarbons in various matrices [20–74].

Generally speaking, the typical methodologies currently used by most laboratories and regulatory agencies can be categorized into two types: nonspecific methods to determine total petroleum hydrocarbons (TPHs) using gravimetric and IR methods [such as US Environmental Protection Agency (EPA) method 418.1]; and conventional chromatographic target compound methods to determine the concentrations of individual components and/or specific set of petroleum hydrocarbons. Table 1 presents a brief summary of EPA, Americal Petroleum Institute (API), and American Society for Testing and Materials (ASTM)-approved methods for hydrocarbon analysis.

The main objectives in chemical measurements of

Table 1
Summary of the most widely-used analytical methods for oil and petroleum products

Method	Technique	Analyte	Description	Refs.
EPA 418.1	IR	TPHs	For analysis of water sample, and has been modified for soil samples by using the solids extraction procedure from Method 9071	[118] [119]
EPA 9071	Gravimetric	TPHs	Applicable for low levels of oil and grease in sludge samples	
EPA 8015	GC–FID	TPHs	Applicable for nonhalogenated volatile organics, and has been modified for volatile organic compounds (VOCs) and TPHs in soil samples	
EPA 8020 and 8020A[a]	GC–PID	BTEX	Applicable for aromatic volatiles	
EPA 602	Purge and trap GC–MS	VOCs	Analysing a limited number of purgeable aromatics in petroleum products	
EPA 624 and 8240A and 8240B[a]	Purge and trap GC–MS	VOCs	For identification and determination of a number of purgeable volatile hydrocarbons	
EPA 625 and 8270A and 8270B[a]	GC–MS	Semi-VOCs	Determination of a number of base/neutral and acid semivolatile organics, but lacks the sensitivity and specificity for petroleum-related alkylated PAHs	
EPA 610	GC–FID	PAHs	Determination of priority PAHs in municipal and industrial wastes	
API-PHC	GC–FID	PHCs	Determination of petroleum hydrocarbons (PHC)	[120] [121]
API-GRO	GC–FID	GROs	Determination of gasoline range organic (GRO) compounds	[122] [123]
API-DRO	GC–FID	DROs	Determination of diesel range organic (DRO) compounds	
ASTM 3414	IR		Comparison of waterborne petroleum oils	[124] [125]
ASTM 3921	IR	TPHs	Oil and grease and petroleum hydrocarbons in water	
ASTM 3328	GC–FID		Comparison of waterborne petroleum oils by GC	
ASTM test methods	GC, MS, NMR, SFC	Saturated, aromatic hydrocarbons	A series of different methods for the determination of organic hydrocarbons in petroleum products, lubricants, and fossil fuels	

[a] These methods can be found in the proposed SW-846 Update II, November 1992, Revision 2.

spilled oil environmental samples are generally considered [49,65,75] to be: (1) to identify and quantify the major individual components and compound classes which are useful for study of oil fate and behaviour in the environment; (2) to identify and quantify the environmentally hazardous constituents; (3) to characterize "marker compounds" which can be reliably used to indicate source, nature and type of the spilled oils and to differentiate the petroleum products from background pollution sources in the samples.

To achieve these three objectives the analytical methods selected for an oil spill assessment must be

(1) Specific. The methods must be able to provide information on specific target analytes of spilled oil based on the nature of spilled oil. Further, the changes of the oil composition must be determined, especially for key toxic components, because the effects of spilled oil on the environment are strongly related not to just the gross amount of oil, but, more importantly, to the levels of the toxic compounds.

(2) Selective for different oil samples. Each

spilled oil or petroleum product has its own "distinct" component distribution due to different geological source, petroleum type, weathering conditions, and many other factors. For example, different analytes will be selected for crude oil and petroleum products, for short-term spilled oil and long-term weathered oil samples, and for slightly weathered oil and heavily biodegraded oil.

(3) Sensitive. The methods must be able to achieve the detection limit for the target analytes in samples. This is especially important for those trace level of compounds which can be used as "markers" to trace the fate, weathering and environmental partitioning of different fractions of spilled oil.

Non-specific methods, such as gravimetric and IR techniques, require short preparation and analytical time and are inexpensive to use, and are usually used as a screening tool, especially for examining oil degradation. The EPA 418.1 method, based on measuring the absorption of C–H bond in the 3200 to 2700 wavenumber range, was originally intended for use only with liquid waste but had been one of the most widely used methods for the determination of total recoverable petroleum hydrocarbons in soils before its demise because of the use of a chloro-fluoro carbon extractant. For some site assessments, method 418.1 was the sole criterion for verification of site clean-up. However, there were some problems associated with this method [75-79]: (1) inherent inaccuracy in the method (i.e. positive or negative biases caused by various factors); (2) all hydrocarbons do not respond equally to IR; (3) a high degree of variance between laboratories in standard operating procedures; (4) no effective reference standard when working with an unknown; (5) Freon-113 is a banned substance and is difficult to replace.

Other EPA methods such as 602, 610, 624 and some of the SW 846 series methods have been regarded as appropriate for oil spill assessment study and have been used for determining volatile and semivolatile aromatic hydrocarbons presented in spilled oil and petroleum product samples. However, these methods were originally designed for water, industrial water and hazardous waste, and are of limited value for the analysis of oils and petroleum products. The data generated with these methods generally lack petroleum-specific component information. For example, of the more than 160 priority-

pollutant volatile and semivolatile organic compounds determined by these EPA methods, only 20 are petroleum-related hydrocarbons [including the volatile benzene, toluene, ethylbenzene and xylene (BTEX) compounds and some two- to four-ring polycyclic aromatic hydrocarbon (PAH) compounds, see Table 2]. Further, only half of these 20 compounds are found in significant quantities in oil and petroleum products (many of the four- and five-ring PAHs are minor components in most oils). Also, the PAH compounds in oils are dominated almost exclusively by the C_1 to C_4 alkylated homologues of the parent PAHs, in particular, naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene, none of which are measured by the standard EPA methods. Other important classes of petroleum hydrocarbons such as the aliphatics and biomarker species are not measured by these methods at all. The limitations of the standard EPA methods have been discussed in detail by many authors [49,65,75-80].

In response to the need for specific, selective and sensitive oil analytical methods for petroleum-based pollutants, a number of new methods have been developed for the determination of gasoline range (C_6–C_{10}, defined by API), organic and diesel range (C_{10}–C_{28}, defined by API) organic compounds in contaminated soils [73,74,79-86]. Many laboratories have modified the EPA and ASTM methods to improve techniques for measuring spilled oil and petroleum products in soils and waters. A variety of diagnostics, especially ratios of PAH and biomarker compounds, for interpreting chemical data from oil spills have been proposed for oil source identification and monitoring of weathering and biological degradation processes [34-38,48-54,64,67,68,86-88]. These modified methods are a clear advance over standard EPA methods because they can provide far more information directly useful for characterization and quantification of oil hydrocarbons.

2.2. Recommended petroleum-specific target analytes and analytical methods

The types and concentrations of specific oil constituents in environmental samples are dictated by the origin and nature of the spilled oil. Each oil has a different "fingerprint" and distribution of hydro-

Table 2
Target analytes for oil studies

Aliphatic hydrocarbons	Target VAHs and PAH (ring numbers)	Target ions	Biomarker compounds	Target ions
	BTEX AND C_3-benzenes	78, 91, 105	*Triterpanes*	
n-C_8	Naphthalene (2)[a]	128	Tricyclic terpanes	191
n-C_9	C_1-naphthalene	142	Tetracyclic terpanes	191
n-C_{10}	C_2-naphthalene	156	Pentacyclic terpanes	191
n-C_{11}	C_3-naphthalene	170		
n-C_{12}	C_4-naphthalene	184	$C_{23}H_{42}$	191
n-C_{13}	Phenanthrene (3)[a]	178	$C_{24}H_{44}$	191
n-C_{14}	C_1-phenanthrene	192	$C_{27}H_{46}$(Ts)	191
n-C_{15}	C_2-phenanthrene	206	$C_{27}H_{46}$(Tm)	191
n-C_{16}	C_3-phenanthrene	220	$C_{29}H_{50}\alpha\beta$-hopane	191
n-C_{17}	C_4-phenanthrene	234	$C_{30}H_{52}\alpha\beta$-hopane	191
Pristane	Dibenzothiophene (3)	184	$C_{31}H_{54}22S/22R$	191
n-C_{18}	C_1-dibenzothiophene	198	$C_{32}H_{56}22S/22R$	191
Phytane	C_2-dibenzothiophene	212	$C_{33}H_{58}22S/22R$	191
n-C_{19}	C_3-dibenzothiophene	226	$C_{34}H_{60}22S/22R$	191
n-C_{20}	Fluorene (3)[a]	166	$C_{35}H_{62}22S/22R$	191
n-C_{21}	C_1-fluorene	180		
n-C_{22}	C_2-fluorene	194	*Steranes*	
n-C_{23}	C_3-fluorene	208	$C_{27}20\ R/S$-cholestanes	217, 218
n-C_{24}	Chrysene (4)[a]	228	$C_{28}20\ R/S$-ergostanes	217, 218
n-C_{25}	C_1-chrysene	242	$C_{29}20\ R/S$-stigmastanes	217, 218
n-C_{26}	C_2-chrysene	256		
n-C_{27}	C_3-chrysene	270	*Surrogates and standards*	
n-C_{28}	Biphenyl (2)	154	1. Surrogates	
n-C_{29}	Acenaphthylene (3)[a]	152	[$^2H_{10}$]Acenaphthene	164
n-C_{30}	Acenaphthene (3)[a]	153	[$^2H_{10}$]Phenabthrene	188
n-C_{31}	Anthracene (3)[a]	178	[$^2H_{12}$]Benz[a]anthracene	240
n-C_{32}	Fluoranthene (4)[a]	202	[$^2H_{12}$]Perylene	264
n-C_{33}	Pyrene (4)[a]	202	o-Terphenyl	(GC–FID)
n-C_{34}	Benz[a]anthracene (4)[a]	228		
n-C_{35}	Benz[b]fluoranthene (5)[a]	252	2. Internal standards	
n-C_{36}	Benzo[k]fluoranthene (5)[a]	252	5-α-Androstane	(GC–FID) Standards
n-C_{37}	Benzo[e]pyrene (5)	252	[$^2H_{14}$]Terphenyl	244
n-C_{38}	Benzo[a]pyrene (5)	252	$C_{30}\beta\beta$-Hopane	191
n-C_{39}	Perylene (5)	252		
n-C_{40}	Dibenz[a,h]anthracene (5)a	278	3. QA/QC standards	
	Indeno[1,2,3-cd]pyrene (6)	276	n-Alkane standards	
	Benzo[ghi]perylene (6)	276	SRM 1491	
			Alkylbenzene standard	
			Triterpane and sterane standards	

[a] 16 EPA priority PAH pollutants.

carbons. In general, the appropriate petroleum-specific target analytes [44,49,70,75,89] should include (Table 2): n-alkanes (C_8–C_{40}) and selected isoprenoids pristane and phytane (in some cases, another three, highly-abundant farnesane, trimethyl-C_{13}, and norpristane, should be also included); the volatile BTEX (benzene, toluene, ethylbenzene and 3

xylene isomers) and alkylated benzenes (C_3–C_5-benzenes); the petroleum-specific PAHs and the alkylated (C_1–C_4) homologues of selected PAHs; and biomarker compounds. Measurements of TPHs should be also included. By contrast, EPA methods do not measure the majority of these important petroleum-specific target analytes. GC is the most

widely used technique for the analysis of these target analytes. Fig. 1 summarises the oil analysis protocol used in our laboratory.

High-resolution GC–FID is used for measuring TPHs in samples, determining the oil product type and the boiling point distribution, and quantifying individual *n*-alkanes and selected isoprenoids [65,66,90]. The method detection limit for most modified GC–FID methods for TPHs is typically 1 to 10 μg/g for soil and sediment samples (dry mass) and 10–50 μg/l for water samples. Individual analytes (such as *n*-alkanes and isoprenoids) may be detected at approximately one order of magnitude lower in concentration. However, because of its nonspecificity, FID may produce erroneous results, due to, for example, analyte coelution and matrix interferences when used for the determination of PAHs. Thus, the compound specific data and in-

formation about PAHs and biomarkers obtained from GC–FID is limited: the separation of aromatic compounds can be only partially achieved, and the identification and quantitation of biomarker compounds is almost impossible.

The combination of chemical separation by GC and spectral resolution by MS allows for specific target compound determination. This is especially important for identification and quantification of individual PAHs and biomarkers (the triterpanes and steranes) at parts per billion (ppb) concentrations. To further enhance the detection of the target compounds, the MS is often run in the selected ion monitoring (SIM) mode. In this mode, the method detection limits for the target analytes are generally lower by almost an order of magnitude than those produced by conventional full-scan GC–MS. The reduction in number of ions per scan in GC–MS-

Weigh Sediment sample

← add surrogates

Serially extract sample with 1:1 CH₂Cl₂/hexane, CH₂Cl₂, CH₂Cl₂ using ultrasonication technique

Filter extract

Concentrate extract

→ Gravimetrically determine TSEM

Silica column cleanup and fractionation

F1 (Hexane fraction)   F2 (50% Benzene fraction)   F3 (1/2F1+1/2F2)   F4 (Methanol fraction)

→ Gravimetrically determine Saturates   → Gravimetrically determine Aromatics   → Gravimetrically determine TPH   → Gravimetrically determine Polars

Add internal standard 5-α-Androstane, C₃₀ ββ-Hopane   Add internal standard d14-Terphenyl   Add internal standard 5-α-Androstane   Polar hydrocarbons

GC/FID   GC/MS (SIM)   GC/MS (SIM)   GC/MS (SIM)   GC/MS (SIM)   GC/FID
n-alkanes analysis   n-alkane distribution   Hopanes & Steranes analysis   23 EPA priority PAHs analysis   C2 -to C5- benzenes, alkylated homologues of Naph, Phen, Diben, Fluo, and Chry.   Total petroleum hydrocarbons (TPH)
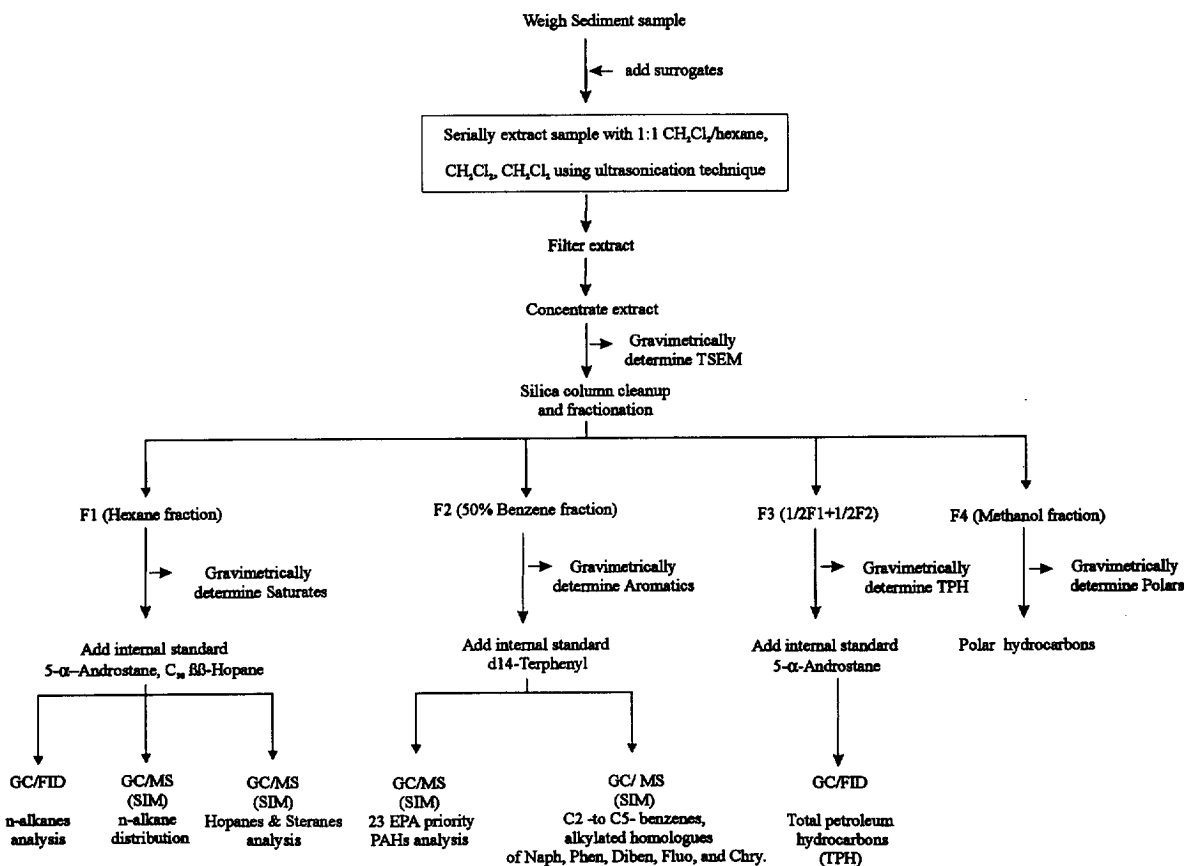
Fig. 1. Oil analysis protocol.

SIM analysis increases the sensitivity of the instrument, thereby lowering the instrument detection limit. Furthermore, the use of GC–MS-SIM method often increases the linear range of the instrument for low-concentration analytes. Over the past several years, new low cost systems have made GC–MS analysis attractive for many analytical laboratories, a trend that will only continue.

The reliability of the GC methods for oil analysis is largely dependent on the quality control procedures used [48,49,65,70]. Quality control charts are used to determine if analyses of a quality control sample are outside statistical limits [91,92]. Recently, Yancey et al. [93] described a quality control scheme to achieve reproducible capillary GC characterization of crude oils and petroleum condensates.

2.3. Definition of petroleum hydrocarbon groups in oil residues

Fig. 1 illustrates the steps used in our laboratory for analysing the oil composition and some important hydrocarbon groups in spilled oil residue samples. In addition to characterization of the key individual hydrocarbons, the following groups are frequently cited and referred to when describing and discussing oil composition changes due to weathering and biodegradation:

TSEMs (total solvent extractable materials): consists of all the hydrocarbons extracted from sediment samples (expressed as mg/g of dry sample).

GTPHs (gravimetrically-determined total petroleum hydrocarbons): is defined as the sum of the saturates and aromatics (after column cleanup of an aliquot of TSEMs) determined by gravimetric method (expressed as mg/g of dry sample). The asphaltene plus polar fraction retained on the clean-up column accounts for the difference between TSEMs and GTPHs.

TPHs (total GC-detectable petroleum hydrocarbons): is defined as the sum of all GC-resolved and unresolved hydrocarbons (expressed as mg/g of dry sample). The resolvable hydrocarbons appear as peaks and the unresolvable complex mixture of hydrocarbons (UCM) appear as an "envelope" or hump area between the lower baseline and the curve defining the base of resolvable peaks.

Total aliphatics: consist of all the resolved and unresolved aliphatic hydrocarbons by GC, including the total n-alkanes, branched alkanes, and cyclic saturates (expressed as mg/g of dry sample).

Total aromatics: is calculated from GC–TPHs minus the total aliphatics (expressed as mg/g of dry sample).

Total n-alkanes: defined as the sum of all the resolved n-alkanes $(C_8–C_{40})$ plus pristane and phytane (expressed as mg/g of dry sample).

Total of 5 PAH homologues: defined as the sum of 5 target alkylated homologues (expressed as μg/g of dry sample) of naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene determined by GC–MS.

Using the TSEM value as a baseline provides a reasonably equal basis for the comparison of the relative composition changes of hydrocarbons between samples [64,67,94]. For highly weathered oil samples in which the volatile hydrocarbons have been largely lost due to weathering, the values of TPHs are always smaller than the corresponding values by gravimetric method. The GC-undefined high-molecular-mass hydrocarbons account for the differences between methods [11,44,64,95]. Fig. 2 shows the relative distribution of hydrocarbon groups in a 22-year-old spilled Arrow oil sample and the weathered source oil, illustrating the effects of weathering on chemical composition of oil. The more weathered the sample, the smaller the percentage of the GC-resolved hydrocarbons and the smaller the ratio of the GC-resolved to GC-unresolved hydrocarbons are, and the larger the percentages of (asphaltenes+polar) fractions and the GC-undefined high-M_r hydrocarbons.

3. Saturated hydrocarbons

3.1. Fingerprinting of n-alkanes

Saturated hydrocarbons are major constituents of petroleum. Although the n-alkanes and isoprenoids are generally not of toxicological concern, analysis of these target compounds using GC–FID and GC–MS $(m/z$ 85, 71 and 57) could be used for many purposes [49,70,96,97]: as a marker of the presence of spilled oil; for the identification of product type; as an indicator of the fate of the spilled oil and for

Weathered Source Arrow Oil

4.8%, GC-resolved hydrocarbons
(among which, 1.2% are 5 alkylated PAHs)

49.7 %, GC - unresolved hydrocarbons

} TPH=54.5%

30.3%, asphaltenes + polars

15.2%, GC - undefined high MW hydrocarbons

22-year-old Arrow Oil sample

0.5%, GC-resolved hydrocarbons
(among wich, 0.16% are 5 alkylated PAHs)

32.8 %, GC - unresolved hydrocarbons

} TPH=33.3%

45%, asphaltenes + polars
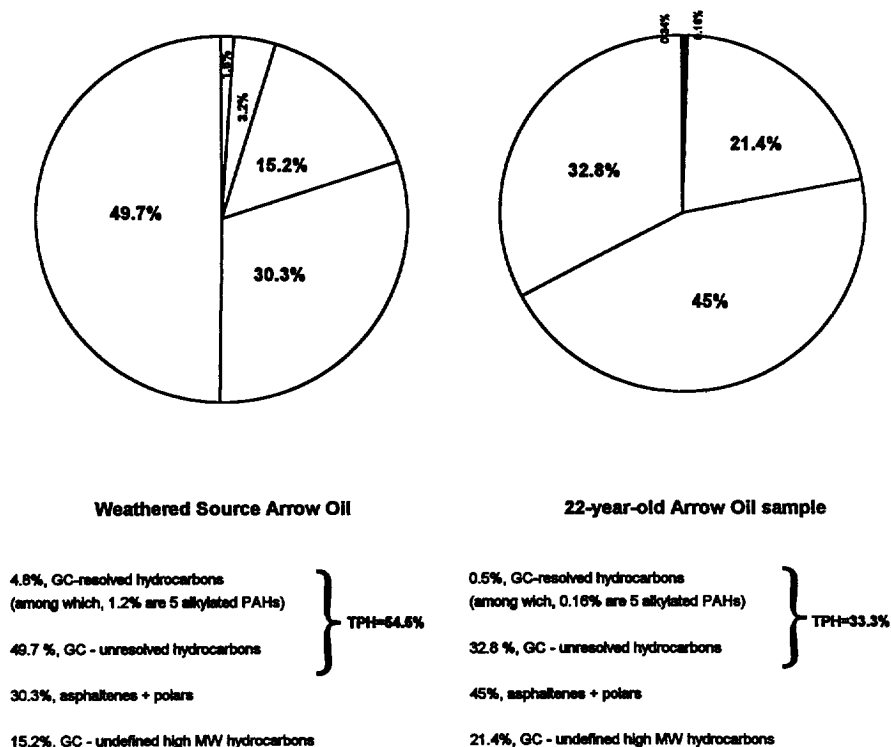
21.4%, GC - undefined high MW hydrocarbons

Fig. 2. Distribution of hydrocarbon groups in a 22-year-old weathered Arrow oil sample and in the reference weathered source oil.

monitoring chemical composition changes of oils due to weathering and/or biodegradation. In addition, determination of the carbon preference index (CPI, defined as the ratio of odd to even n-alkanes) and the relative contribution of the biologic plant wax (in the range of n-C_{21}–n-C_{33}) to the total hydrocarbons in the samples can be used to differentiate the spilled oil from pre-spill background pollution sources in environmental samples [52,67,98]. Comparing biodegradation indicators for the spilled oil (such as n-C_{17}/pristane, n-C_{18}/phytane) with those for the source oil can be used to monitor the effect of microbial biodegradation on the loss of hydrocarbons at a spill site.

Fig. 3 shows GC–FID chromatograms for four different oils. Clearly, these four oils are very different, as not only are there large differences in the n-alkane distributions, but also in relative ratios of isoprenoids to normal alkanes. Note that the

Orimulsion sample [71] has no n-alkanes on its GC–FID chromatogram (Panel C in Fig. 3).

Fig. 4A compares the GC–MS (m/z 85) chromatograms of 4 petroleum products: lightly weathered Jet B fuel, Diesel fuel No. 2, Bunker C 9 and Lube oil. In contrast to the corresponding GC–FID chromatograms, the GC–MS-SIM chromatograms of the four petroleum products have much simpler traces for the saturated hydrocarbons. The unresolved complex mixture "envelope" seen in the GC–FID chromatograms is significantly reduced. Differentiation between samples is significantly simplified by comparing the chromatogram profiles and n-alkane elution range. The Lube oil, eluted late in the 23 to 53 min range, is dominated by a broad hump of unresolved saturated hydrocarbons and can be readily distinguished from the Jet B fuel and Diesel fuel No. 2. The Jet B fuel and Diesel No. 2 can be easily distinguished from the n-alkane dis-
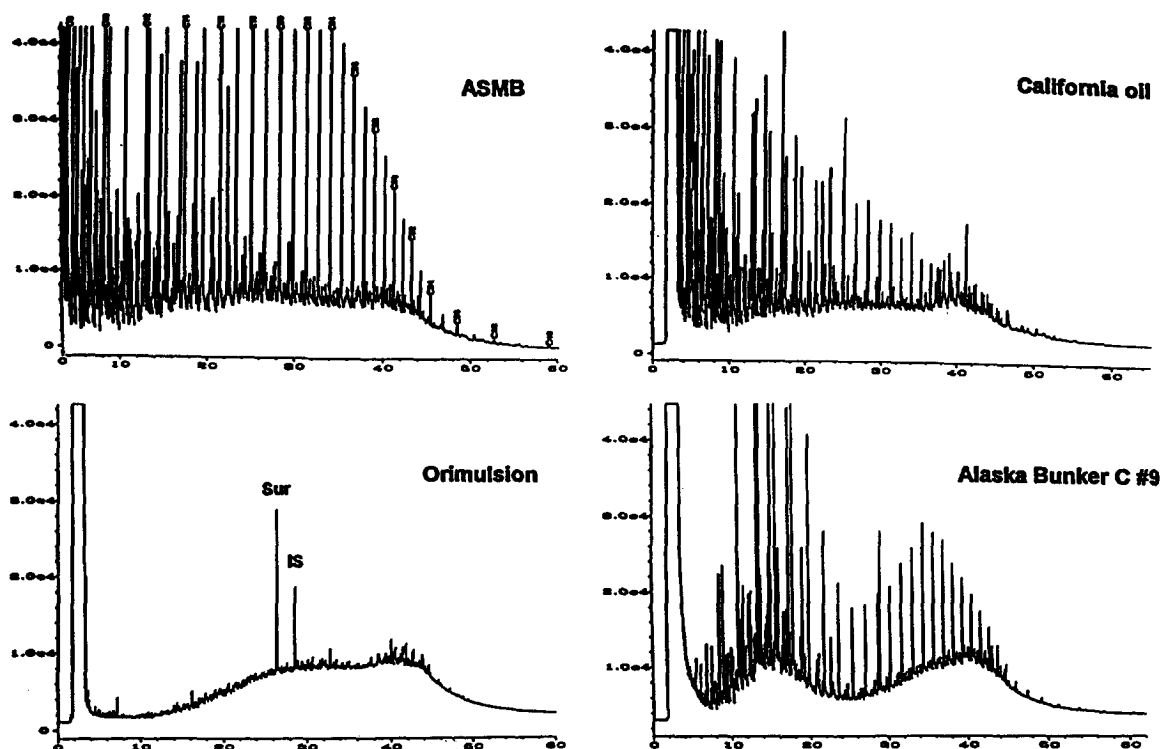
Fig. 3. GC–FID chromatograms of ASMB oil, California oil, Orimulsion, and Alaska Bunker C 9. IS and Sur represent the internal standard and surrogate, respectively.

tribution ranges. Bunker C 9 is shown to be a mixture of heavy residue fuel and lighter diesel fuel. For comparison, Fig. 4B depicts graphically the quantitative distribution of n-alkanes for these four products.

3.2. Changes in the distribution of n-alkanes due to weathering and biodegradation

Weathering causes considerable changes in the chemical and physical properties of spilled oils [99–104]. For lightly weathered oils, significant losses occur in the the low-molecular-mass n-alkanes, however the ratios of n-C_{17}/pristane and n-C_{18}/phytane have been found to be virtually unaltered from those measured for the source oil [68,71]. Therefore, for fresh or mildly weathered oil products, principle component analysis of the alkanes and isoprenoids may be used to assess the degree of weathering in a sample. However, if a spilled oil is

moderately weathered and/or biodegraded, these traditional diagnostic ratios have been found to be less reliable as an indicator of degree of weathering because bacteria degrade the n-alkanes faster than the isoprenoids, resulting in a decrease in ratios of n-C_{17}/pristane and n-C_{18}/phytane [38,45,49,94,96]. In heavily weathered oils, the n-alkanes, and even the isoprenoids in some cases, may be completely lost [64,67]. Under such circumstances, GC–FID analysis is of little value for suspect source identification (Fig. 5), and additional GC–MS analysis of more degradation-resistant PAHs and biomarker compounds is required for accurate product characterization. As Fig. 5 shows, the n-alkanes including the five most abundant isoprenoids, have been completely depleted in the 22-year-old Arrow oil sample, and the UCM dominates the total peak area. Fingerprinting based on n-alkane or isoprenoid distribution patterns cannot therefore provide much information on the source of highly degraded spilled oils.
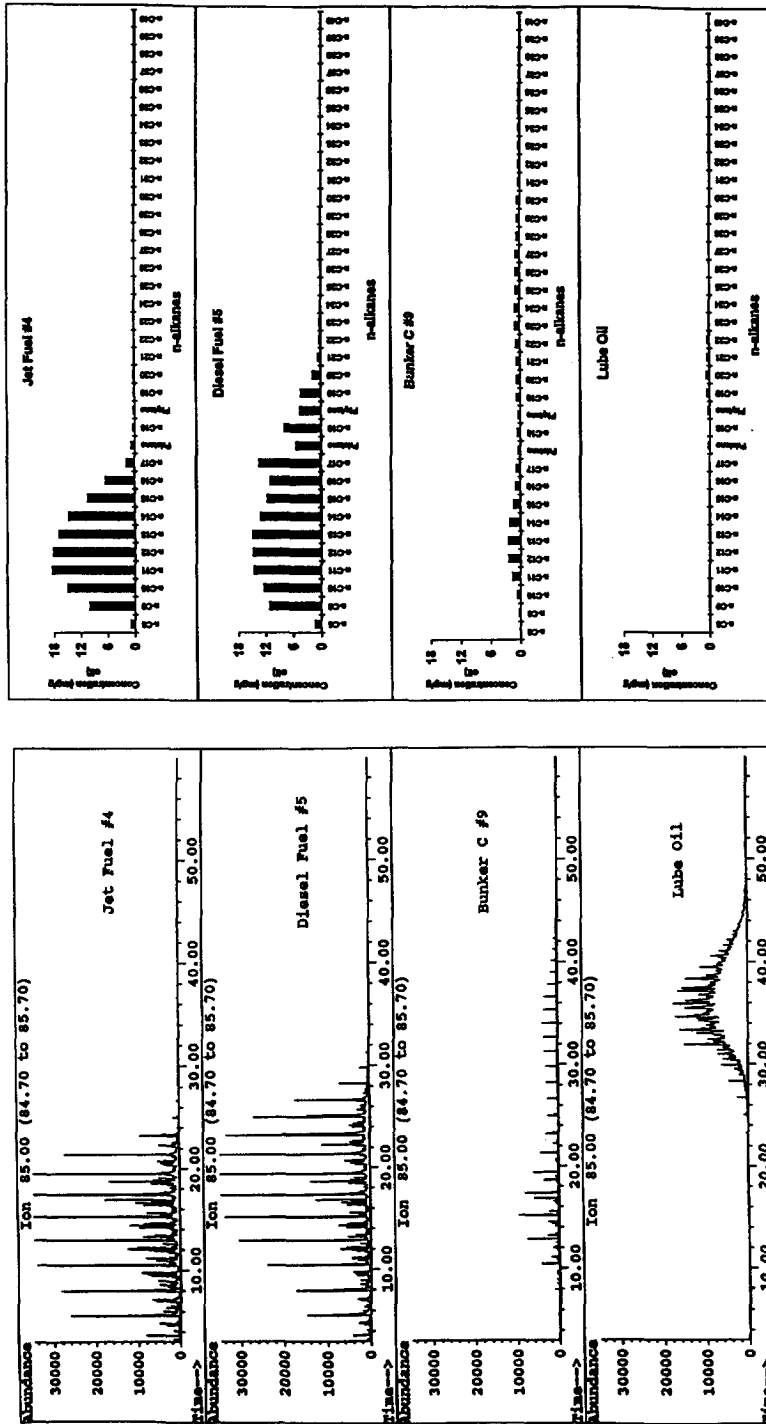
Fig. 4. GC–MS chromatograms (m/z 85, left side) and n-alkane distributions (right side) of Jet B fuel, Diesel No. 2, Bunker C 9, and Lube oil.
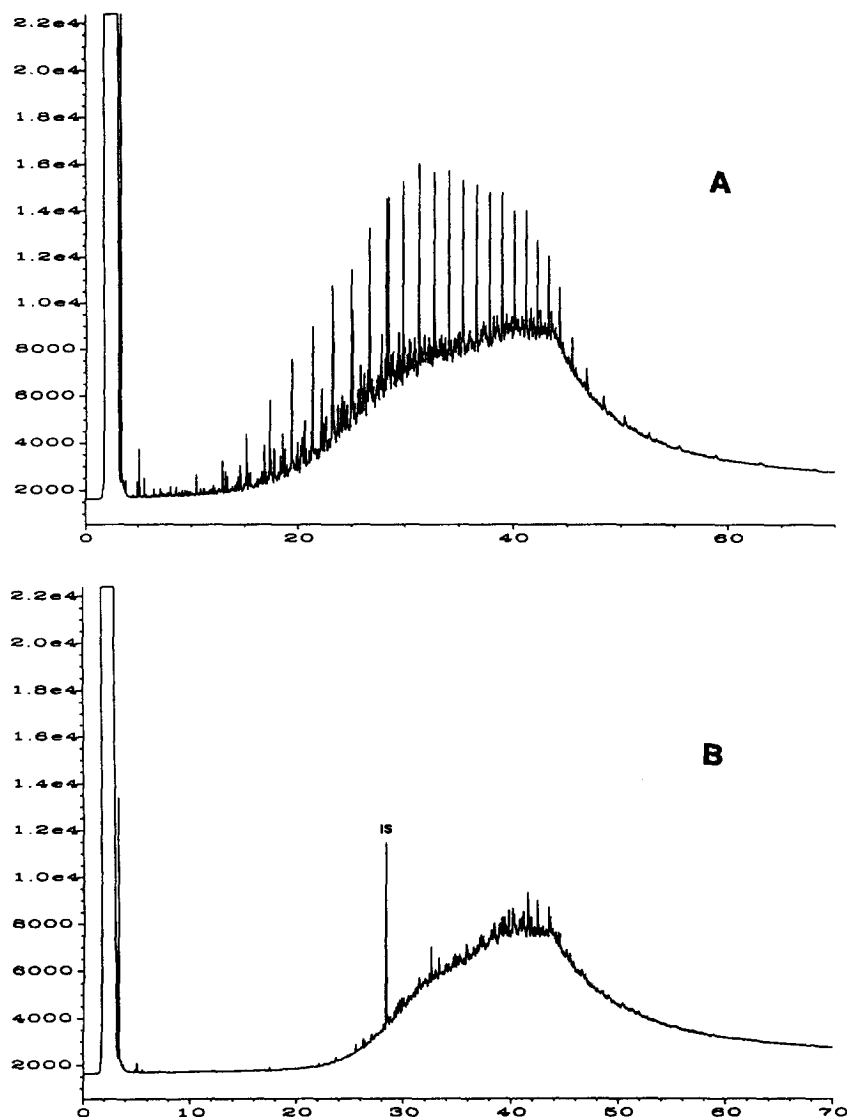
Fig. 5. GC–FID traces for the weathered Arrow oil samples S-6 (A) and S-2 (B), illustrating weathering effect on the chemical composition of weathered samples. Note that the n-alkanes including the five most abundant isoprenoids have been completely depleted on the sample S-2, and the UCM dominates the total peak area.

4. Petroleum-specific BTEX, PAHs and their alkylated homologues

4.1. Fingerprinting of BTEX and PAH compounds

Because of their environmental impact and toxicity, the levels of volatile aromatic hydrocarbon (VAH) and PAH compounds in oils and petroleum products are considered to be very important parameters [69,105]. Williams and co-workers [106] identified 85 aromatic hydrocarbons in diesel fuel by capillary GC coupled with ion-trap detection. Bundt [107] reported the identification of 121 aromatic compounds in a diesel fuel using capillary gas GC–MS. Very recently, Wang et al. [65,66,69] identified and characterized 58 alkyl- substituted benzene

components and 126 PAH components in light ASMB crude oil. Structural identification of the individual and alkylated VAH and PAH homologues in oil samples is based on the mass spectra (both scan and SIM data), the comparison of GC retention data with reference standards and calculation of retention index (RI) values and subsequent verification of the values with literature RI values. Quantitation of the important VAH and PAH components is performed with relative response factors (RRFs) for each compound or alkyl group determined using an internal standard method during instrumental calibration. Quantitation of the BTEX and C_3-benzenes in over 200 different oils has shown that these compounds can make up as much as a few percent of the total mass of some crude oils [69]. The total of the 5 target alkylated PAH homologous families can compose less than 50 ppm for Lube oil but can be as much as several percent by mass of diesel and jet fuels.

Petroleum from different fields can have very different PAH distributions. Fig. 6 shows the alkylated PAH homologue distributions in representative light ASMB oil, medium Maya oil, and heavy Bunker C, and the Shell diesel. In this example, the character of each oil is apparent in the distinct distributions of the alkylated PAH homologues (Fig. 6B). By contrast, if only the 16 EPA defined priority PAH compounds are used as the target analytes, the compositional differences between oils would not be evident. As Fig. 6B shows, there are much higher abundances of alkylnaphthalenes and alkylphenanthrenes in the Shell diesel and Bunker C relative to other alkylated PAH homologous series. Also, compared to the three oils, the diesel sample was found to have extremely low concentrations of the high-molecular-mass alkylated chrysene series and sulfur-containing alkylated dibenzothiophene series (2.4 and 125 µg/g oil, respectively) [108]. This depletion of high-M_r fractions is a common feature of diesel fuels. When crude oil is distilled to manufacture diesel fuel, the higher boiling fractions including the chrysene family are almost entirely removed.

The distribution fingerprints of BTEX and alkylbenzenes can be used to further distinguish different oils. As seen in Fig. 6A, the distributions of alkylbenzenes in the oils are significantly different, not only because of their different distribution patterns and profiles of BTEX compounds, but also because of the strikingly higher relative abundances of C_3- and C_4-substituted benzenes in the Shell diesel. The use of higher-substituted benzenes, especially C_3-benzenes [69], can greatly enhance the utility of BTEX fingerprinting.

Aromatic species have been found to be very useful target compounds for petroleum residue analysis. Studies have been reported using distributions of the alkylated PAH homologues as environmental fate indicators and source-specific markers of oil in sediments [47,64,67,100], tissue [50] and water samples [49].

4.2. Weathering trends of alkylated benzenes and PAHs

Fig. 7 shows GC–SIM-MS distribution chromatograms of alkylated benzenes and alkylated PAHs for a set of artificially evaporatively-weathered ASMB oils with percentage mass losses of 0, 29.8 and 44.5%. These chromatograms clearly demonstrate the effects of weathering on chemical composition changes of the aromatic fraction of the ASMB oil. In the highest weathered sample (44.5%), not only were the lighter BTEX, naphthalene and C_3-benzene fractions completely removed, the alkyl substituted C_1- and C_2-naphthalene series were also greatly reduced in abundance.

Fig. 8 shows the GC–SIM-MS distribution chromatograms of alkylated benzenes and alkylated PAHs for samples of weathered Nipisi oil. The compositional changes in alkylbenzenes and alkylated PAHs can be seen by comparing the GC traces of the weathered reference oil (8A) with the four 25-year-old spilled Nipisi oil samples N2-1A (8B), P-1 (8C), and N2-1C (8D) and N2-1B (8E) [109]. The majority of the Nipisi sediment samples were classified into three groups, based on the level of oil contamination and the degree and extent of weathering and degradation. The samples N2-1A, P-1, and N2-1C and N2-1B are typical representatives of highly contaminated and highly weathered/degraded samples (Group 3, sampling depth: 0–2 cm), highly contaminated and moderately weathered/degraded samples (Group 4, sampling depth: 4–6 cm), and highly contaminated but lightly weathered/
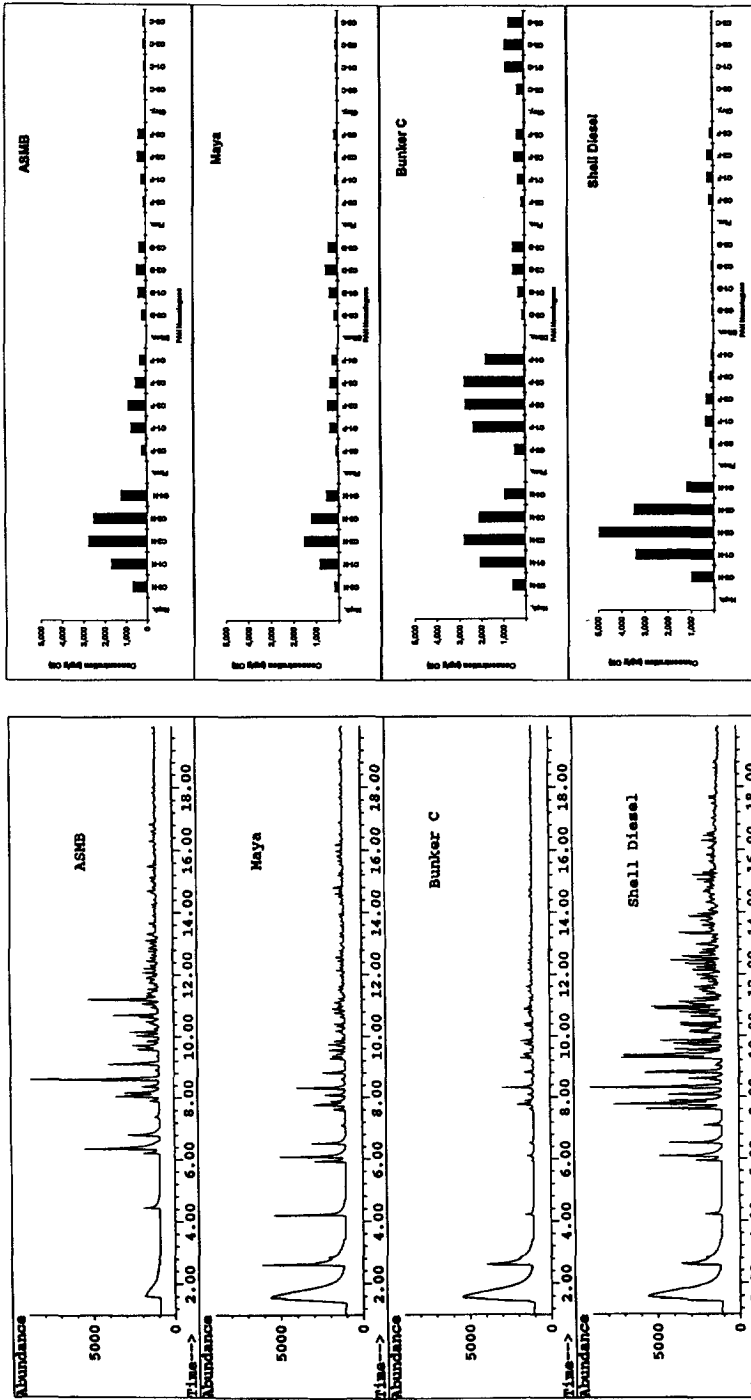
Fig. 6. Alkylated PAH homologue distributions (right side) and the corresponding GC–MS total ion chromatograms of alkylbenzene compounds (left side) in representative light ASMB oil (density=0.839), medium Maya oil (density=0.923), and heavy Bunker C oil (density=0.974), and a petroleum product-Shell diesel. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene, respectively; 0, 1, 2, 3 and 4 represent carbon numbers of alkyk groups in alkylated PAH homologues.

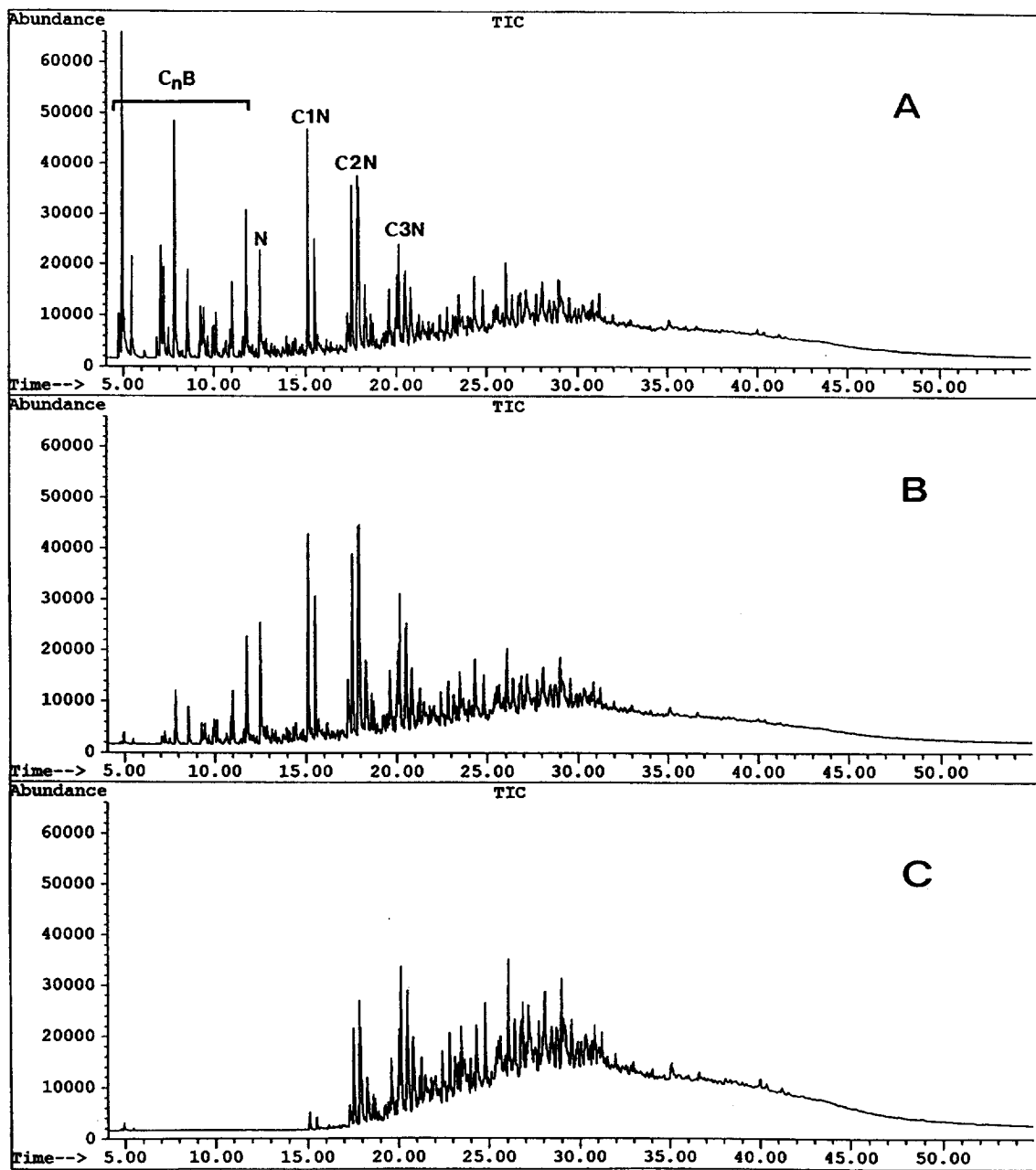Fig. 7. GC–SIM-MS distribution chromatograms of alkylated benzenes and alkylated PAHs for a set of artificially evaporatively-weathered ASMB oils with percentage mass losses of 0% (A), 29.8% (B) and 44.5% (C). CnB, N, C1N, C2N, and C3N represent alkyl benzenes, naphthalene and alkylated naphthalenes, respectively.
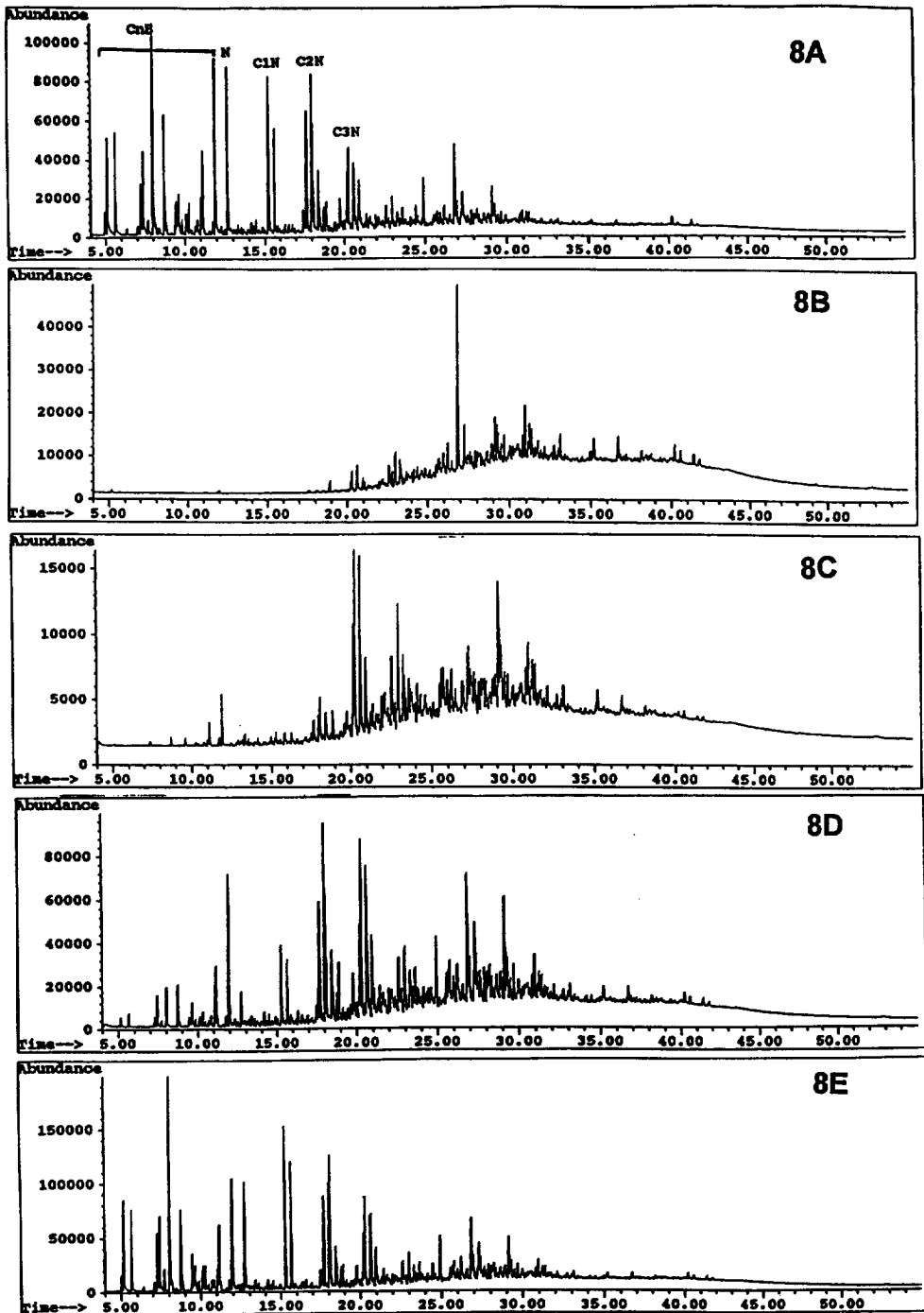
Fig. 8. GC–SIM-MS distibution chromatograms of alkylated benzenes and alkylated PAHs for the reference weathered Nipisi oil (A), and four 25-year-old spilled Nipisi oil sediment samples N2-1A (B), P-1 (C), and N2-1B (D) and N2-1C (E), illustrating the effect of field weathering conditions and sample depths on composition changes of alkylbenzenes and PAHs. The samples N2-1A, P-1, and N2-1C and N2-1B are typical samples representing Group 3 (sampling depth: 0–2 cm), Group 4 (sampling depth: 4–6 cm), and Group 5 (sampling depth: 10–40 cm), respectively.

degraded samples (Group 5, sampling depth: 10–40 cm), respectively. Compared to the reference weathered Nipisi oil, it is evident that there was a greater loss of alkylated benzenes and lighter PAHs in 25-year-old spilled Nipisi oil samples nearer to the surface.

The weathering of spilled oil in the environment has been the subject of much research in recent years [38,48,50,52,64,67,110]. The major compositional changes of aromatics in oils caused by weathering can be generally summarized as follows:

(1) The degradation rates are correlated to the molecular mass, boiling points and degree of alkylation of the aromatic compounds. The low-M_r and the volatile BTEX compounds are preferentially depleted during weathering. The BTEX and C_3-benzene fractions are nearly completely depleted for many oils with weathering losses of 25% or more.

(2) The degradation rates of PAHs are proportional to the number of aromatic rings. There is a pronounced decrease in the abundances of naphthalene and its alkylated homologues relative to other PAHs as weathering percentages increase.

(3) Degradation rates are inversely proportional to the degree of alkylation of the benzene and PAH homologues: $C_0 \rightarrow C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$; (Fig. 9B).

(4) Of the 5 alkylated PAH homologous families, the alkylated chrysene series is the least susceptible to weathering as indicated by the increase of their percentages in the total of the alkylated PAHs and the relative decrease in the ratios of the sum of naphthalenes, phenanthrenes, dibenzothiophenes and fluorenes to the sum of chrysenes.

4.3. Differentiation of compositional changes of PAHs due to weathering and biodegradation

The chemical composition of spilled petroleum products can be greatly affected by both biodegradation and weathering, particularly for those products which have undergone for a prolonged period of weathering. Identification of the characteristic oil composition changes due to biodegradation and/or due to physical weathering is very important when planning clean-up strategy, especially when evaluating the efficacy of bioremediation products and conventional clean-up techniques.

Biodegradation rates of hydrocarbons are dependent on the type of bacteria, presence of nutrients, temperature and the nature and amount of the oil or hydrocarbons present. Many laboratory studies and field investigations [38,64,67–69,88,89,94,111,112] have demonstrated that biodegradation causes a number of characteristic composition changes in the spilled oil, which are significantly different from those changes caused by physical weathering. These changes are summarized as follows:

(1) For aliphatic hydrocarbons, GC-resolved aliphatics degrade faster than the unresolved hydrocarbon complex mixture, and n-alkanes degrade much faster than branched alkanes. This leads to a significant decrease of n-C_{17}/pristane and n-C_{18}/phytane ratios.

(2) Aromatics with fewer rings degrade faster. For example, the alkyl homologues of naphthalene are the most quickly biodegraded family of the 5 target alkylated PAH homologues.

(3) The degradation order of alkylated PAHs is $C_0 > C_1 > C_2 > C_3 > C_4$ in each alkylated PAH family. This effect is especially evident for the naphthalenes. Table 3 lists changes of the relative distributions of PAHs in each alkylated PAH homologous family of ASMB and North Slope oil due to biodegradation [86]. Within each homologous series, the relative ratios of parent and C_1-substituted PAHs (and also for the C_2-naphthalenes) decreases strikingly as degradation proceeds. In contrast, the C_2 and C_3-alkylated homologues are much less effected, as seen by the increase in ratios relative to the parent and C_1-substituted compounds. For the purposes of comparison, the corresponding distribution changes in ASMB oil due to physical weathering are also listed in Table 3 [71]. Clearly, there are pronounced differences in relative distribution changes caused by biodegradation and physical weathering.

(4) Microbial degradation is isomer specific for alkylated PAHs, as shown in Fig. 10. The circled regions in Fig. 10 highlight the characteristic preferential depletion of certain isomers with respect to others. In particular there are characteristic changes in the ratios of 2-/3-methyldibenzothiophene/4-methyldibenzothiophene, (3-methyl-phen + 2-methyl-phen)/(9-methyl-phen + 1-methyl-phen), (1,3-methyl-naph + 1,6-dimethyl-naph)/total of C_2–N, and methyl-fluorene/total of C_1–F. In contrast, no such
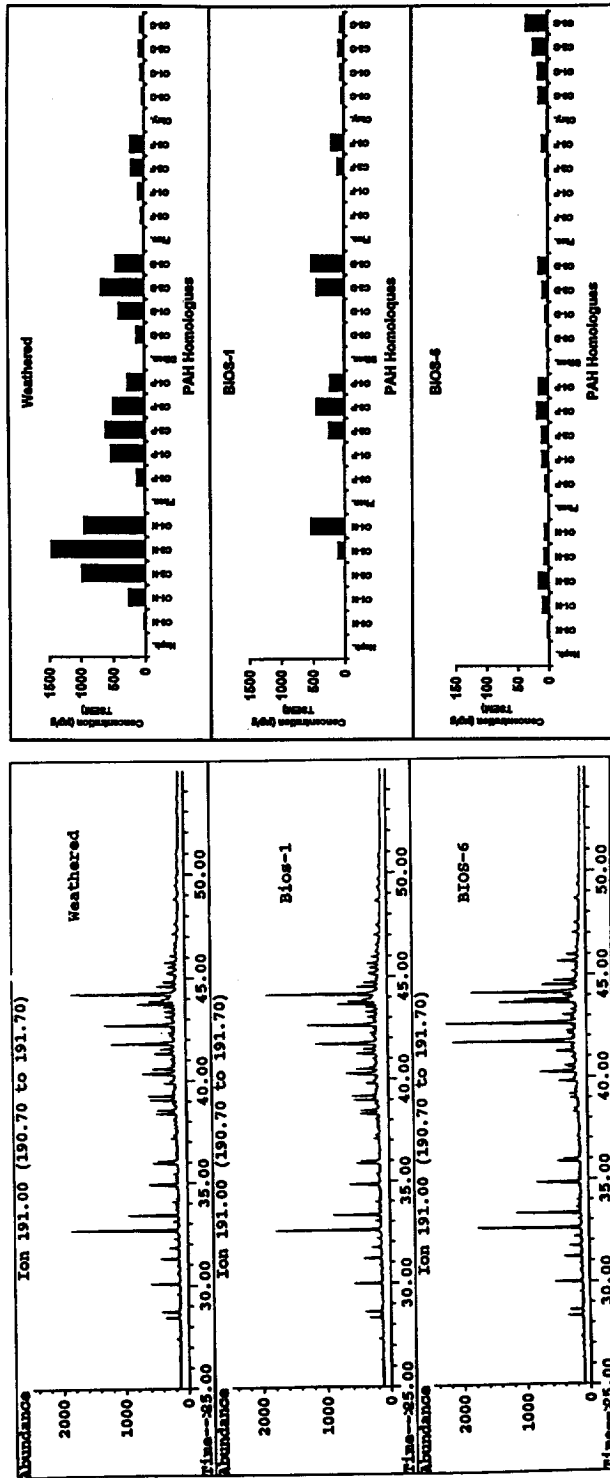
Fig. 9. Distribution of target PAH homologues (right side) and GC–MS fragmentograms (m/z 191) of trepane compounds (left side) for the weathered source BIOS oil, and field samples 1 and 6 from the BIOS spill.

Table 3

Relative distribution changes of PAHs in each alkylated PAH homologous family and within isomeric group of ASMB and North Slope (NS) oil due to biodegradation (1995) and due to weathering (1993)[a]

	NS (Biodegradation)				ASMB (Biodegradation)				ASMB (Weathering)					
	W	SC	PC	NC	W	SC	PC	NC	0%	9.8%	19.5%	29.8%	34.5%	44.5%
Within alkylated homologous family														
Naphthalene														
C_0-N	0.06	0.03	0.00	0.00	0.06	0.03	0.00	0.00	0.08	0.08	0.08	0.07	0.04	0.00
C_1-N	0.21	0.18	0.00	0.00	0.21	0.17	0.00	0.00	0.19	0.19	0.19	0.19	0.17	0.02
C_2-N	0.33	0.34	0.02	0.03	0.33	0.35	0.03	0.07	0.32	0.31	0.31	0.32	0.34	0.25
C_3-N	0.27	0.30	0.57	0.51	0.28	0.31	0.61	0.56	0.29	0.29	0.29	0.29	0.31	0.47
C_4-N	0.13	0.15	0.42	0.46	0.12	0.14	0.35	0.37	0.13	0.13	0.13	0.14	0.15	0.26
Sum	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Phenanthrene														
C_0-P	0.10	0.10	0.00	0.00	0.09	0.08	0.00	0.00	0.09	0.08	0.08	0.08	0.08	0.08
C_1-P	0.30	0.30	0.19	0.12	0.31	0.31	0.26	0.19	0.28	0.28	0.28	0.28	0.28	0.28
C_2-P	0.28	0.27	0.36	0.39	0.27	0.27	0.34	0.35	0.34	0.34	0.34	0.34	0.34	0.34
C_3-P	0.21	0.22	0.29	0.32	0.21	0.22	0.25	0.29	0.19	0.20	0.20	0.20	0.19	0.20
C_4-P	0.12	0.12	0.15	0.17	0.12	0.12	0.15	0.17	0.11	0.11	0.11	0.11	0.11	0.11
Sum	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dibenzothiophene														
C_0-D	0.15	0.14	0.00	0.00	0.15	0.15	0.00	0.00	0.15	0.15	0.15	0.15	0.15	0.14
C_1-D	0.27	0.26	0.18	0.13	0.27	0.27	0.24	0.18	0.28	0.28	0.28	0.28	0.28	0.28
C_2-D	0.31	0.31	0.43	0.45	0.34	0.34	0.44	0.48	0.34	0.34	0.34	0.35	0.34	0.35
C_3-D	0.27	0.28	0.39	0.42	0.24	0.25	0.31	0.34	0.23	0.23	0.23	0.23	0.23	0.23
Sum	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fluorene														
C_0-F	0.13	0.13	0.01	0.01	0.10	0.10	0.00	0.00	0.09	0.09	0.09	0.09	0.09	0.08
C_1-F	0.26	0.28	0.21	0.15	0.22	0.22	0.18	0.14	0.22	0.22	0.22	0.22	0.22	0.21
C_2-F	0.31	0.32	0.40	0.43	0.34	0.34	0.41	0.41	0.36	0.36	0.36	0.36	0.36	0.36
C_3-F	0.30	0.27	0.38	0.41	0.34	0.35	0.41	0.44	0.33	0.33	0.34	0.34	0.34	0.36
Sum	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Chrysene														
C_0-C	0.23	0.23	0.23	0.23	0.16	0.16	0.16	0.16	0.14	0.15	0.15	0.15	0.15	0.15
C_1-C	0.29	0.29	0.29	0.29	0.24	0.24	0.24	0.25	0.22	0.22	0.22	0.22	0.22	0.22
C_2-C	0.29	0.27	0.28	0.28	0.34	0.33	0.33	0.34	0.32	0.32	0.33	0.32	0.33	0.33
C_3-C	0.19	0.21	0.21	0.21	0.27	0.27	0.27	0.26	0.32	0.31	0.31	0.31	0.30	0.30
Sum	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Within given alkylation isomeric series														
(1,3+1,6-dimethyl-N)/total of C_2-N	0.49	0.49	0.07	0.03	0.50	0.51	0.10	0.08	0.49	0.49	0.49	0.49	0.49	0.52
(3+2-methyl-P)/(4-/9+1-methyl-P)	0.74	0.73	0.25	0.16	0.94	0.94	0.63	0.37	0.96	0.95	0.96	0.95	0.96	0.96
2-/3-methyl-D/4-methyl-D	0.66	0.66	0.17	0.10	0.75	0.75	0.47	0.36	0.76	0.75	0.76	0.75	0.75	0.76
methyl-F/total of C_1-F	0.27	0.26	0.20	0.21	0.34	0.33	0.27	0.29	0.36	0.35	0.35	0.36	0.35	0.36

[a] W: weathered oil; SC: Sterile Control; PC: Positive Control; and NC: Negative Control. The values given in above are mean values ($n = 2$ for SC, $n = 3$ for PC and NC).

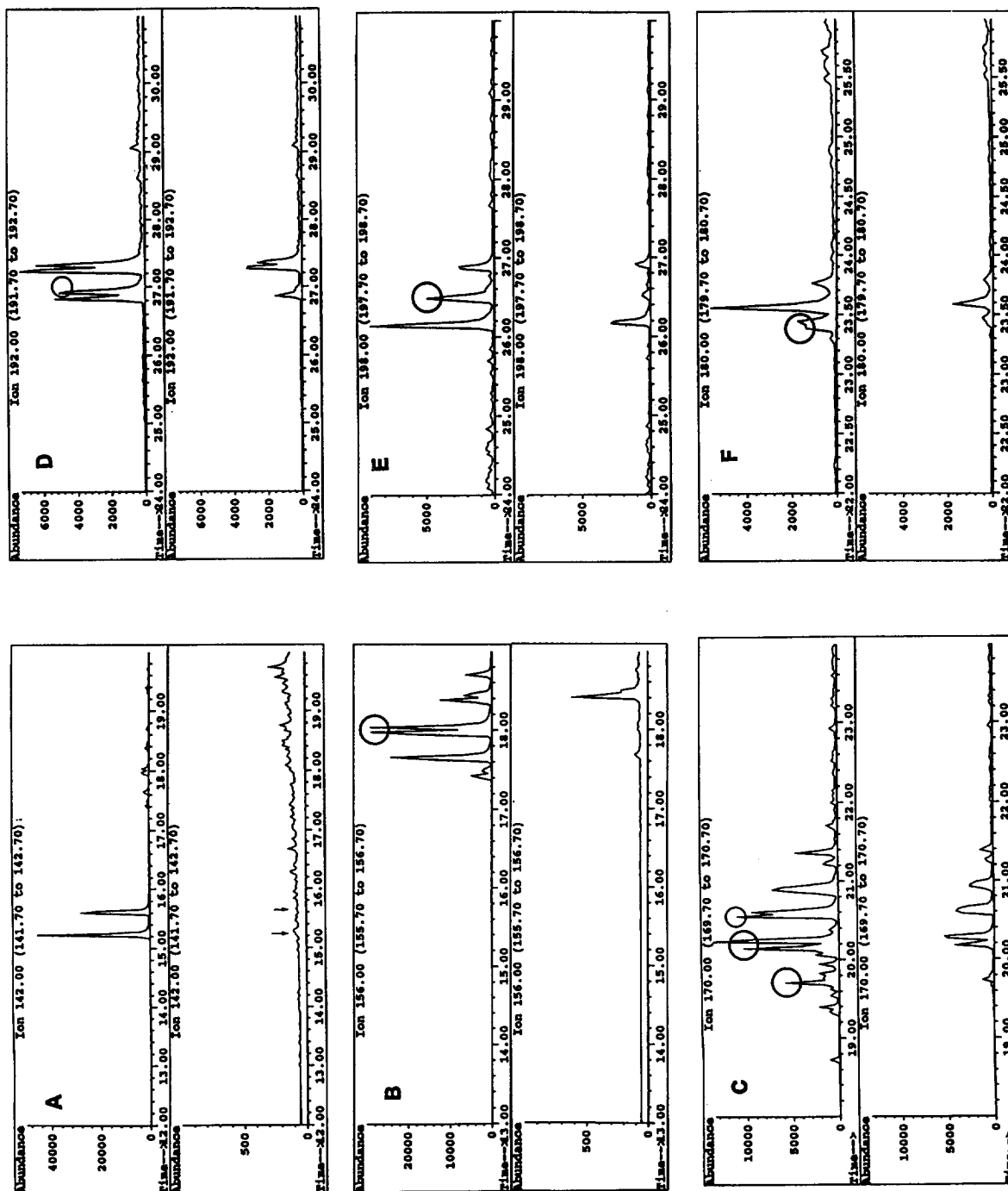[b] See Ref. [71] for detailed weathering results.

Fig. 10. Extracted ion chromatograms for C_1-naphthalenes (ion 142, A), C_2-naphthalenes (ion 156, B), C_3-naphthalenes (ion 170, C), C_1-phenanthrenes (ion 192, D), C_1-dibenzothiophenes (ion 198, E), C_1-fluorenes (ion 180, F), in the source ASMB oil and corresponding biodegradation ASMB oil samples, illustrating characteristic composition changes of target PAHs due to biodegradation. The circled regions highlight the preferential depletion of certain isomers by bacteria with respect to others.

characteristic preferential depletion have been found in physically or short-term weathered oils [71,86].

4.4. Diagnostic ratios of target PAHs for weathering and biodegradation studies

A number of diagnostic ratios of target PAHs (and some n-alkanes and total hydrocarbons) have been successfully used for weathering and biodegradation indicators. These are summarized in Table 4.

A method developed by Boehm, Page and co-

workers [48,52,89], using the double ratio plots (C_2D/C_2P versus C_3D/C_3P) of alkylated PAH homologues for differentiation of petroleum product sources, was successfully used in the study of the 1989 Exxon Valdez oil spill to distinguish Alaska North Slope (ANS) crude, its weathering products and diesel refined from ANS feed stock from other petrogenic hydrocarbons.

Recently, Wang and Fingas [68] developed a GC–MS method for the differentiation and source identification of crude, weathered and biodegraded oils

Table 4
Diagnostic ratios used for weathering and biodegradation indicators

Target group	Diagnostic ratio	Application	Ref.
PAHs	(C_2-C_4)-Naphs/TPAH[a]	–Weathering index for the 1989 EXXON VALDEZ oil spill	[48,50] [89]
	Double ratios: C_2D/C_2P versus C_3D/C_3P	–Used to correlate the 1989 EXXON VALDEZ spill oil samples to the source oil –Used to differentiate hydrocarbon sources from the Gulf war oil spills	[48,50] [52,87] [89]
	Naphs/Chrys Phens/Chrys Dibens/Chrys Fluos/Chrys	–Weathering index for Arrow and BIOS oil spills	[64,67]
	Relative ratios of PAH in each homologous family (e.g. C_0-: C_1-: C_2-: C_3-)	–Weathering indicator –Differentiation between composition changes due to weathering & biodegradation –Used for source identification	[71,86] [94,109]
	C_2-Naphs/total Naphs C_1-Phens/total Phens C_1-Dibens/total Dibens	–Biodegradation index	[86,111]
	2-/3-M-DBT/4-M-DB T[b] (or ratios of 3 M-DBT isomers) (3- +2-M-Phen)/(9-/4- +1-M-Phen) (1,3+1,6-dimethyl-N)/total C_2-Naphs	–Used for oil source identification –Marker of biodegradation extent –Used for oil discrimination	[68,70] [86,94] [109] [111,127]
n-Alkanes and and isoprenoids	n-C_{17}/pristane n-C_{18}/phytane WI $(n$-$C_{8+10+12+14}/n$-$C_{22+24+26+28})$[c] Alk/Iso[d] SHWR[e]	–Weathering and biodegradation indicator –Used for determination of weathered percentages of lightly or short-term weathered oils –Used for weathering index in BIOS spill	[38,64] [67,70] [71,86] [94,109] [111,126–131]
TPH	GC-resolved peaks/TPH (or UCM) TPHs/TSEM	–Weathering index	[64,67,86] [109,111] [132]

[a] TPAH: total PAHs.
[b] M-DBT: methyldibenzothiophene.
[c] WI: weathering index.
[d] Alk/Iso: defined as the ratios of the sum of n-C_{14}–n-C_{18} over the sum of farnesane, trimethyl-C_{13}, norpristane, pristane, and phytane.
[e] SHWR: defined as the ratio of the sum of n-C_{10}–n-C_{25} over the sum of n-C_{17}–n-C_{25}.

using the relative abundances of three isomeric methyldibenzothiophene (C_1-DBT) compounds. A database of the ratios of the three isomers of C_1-DBT for several hundred crude, weathered and biodegraded oils, and petroleum products has been developed. The use of these ratios complements existing methods of oil characterization, but has its own distinct advantages. The ratios of the C_1-DBT compounds have been used to successfully discriminate different oil samples [68,109,111], to identify the source of oil on contaminated birds [94] and on tarball samples collected along the west coast of British Columbia (Canada) and California (USA) [113]. This selectivity has been found to be a very powerful fingerprinting technique for the differentiation of oils and petroleum products.

5. Biomarker hydrocarbons

Biological markers (biomarkers) are complex "molecular fossils" derived from once living organisms [51]. For decades, petroleum geochemists have used biomarker compounds such as terpanes and steranes (which are common in crude oils) to identify petroleum deposits. In the past decade these biomarkers have become increasingly important as oil fingerprints for the purposes of tracing the source of spilled oil, differentiating oils and monitoring the weathering and degradation process in oils under a wide variety of conditions. A significant number of studies using biomarker technology to study oil-spill-related environmental problems have been published [33–43,46,54–56,64–72,94,109,111,114,115], and biomarker parameters are beginning to play a prominent role in almost all oil spill work. A recently published book, "The Biomarker Guide" by Peters and Moldowan [51], provides a comprehensive discussion of the basic principles of biomarkers, their relationship with other parameters, and the interpretation of biomarker data. Peters and Moldowan [51] describe the uses of biomarkers for applications such as the maturation, correlation, source input and deposition of oil in the environment.

Prior to widespread use of biomarkers, non-biomarker analyses were used to study the weathering of oil. As described in Section 3 and Section 4, a lightly weathered oil is usually indicated by partial depletion of n-alkanes, a moderately-degraded sample often exhibits a heavy loss of n-alkanes and a partial loss of lighter PAHs. These samples can be source-traced by conventional fingerprinting techniques. However, in highly degraded oil, the n-alkanes and branched alkanes are usually completely depleted, the PAHs and their alkyl homologues highly degraded, and diagnostic ratios of target PAHs dramatically changed from the source oil. It is very difficult and sometimes impossible to identify highly degraded oil samples through n-alkane and PAH distribution patterns. For such samples, the analysis of biomarker compounds is the only method that can be used to determine the origin of a spill with confidence. Biomarkers are uniquely valuable because they are highly degradation-resistant and are essentially unaffected by long-term weathering and biodegradation. Therefore, their use can provide the detailed information needed to answer questions such as the oil source, its characteristics, the degree of weathering, and can be used to trace the fate of spilled oils in the environment.

5.1. Differentiation of oils using biomarkers

The common features of the mass spectra of biomarkers are that they have a relatively large parent ion, an important fragment ion from the parent missing a methyl group, and basepeaks at m/z 191 and 217 (or 218) for terpanes and steranes, respectively. The distribution patterns of biomarker compounds are, in general, different from oil to oil. For example, Fig. 11A–D show the distribution chromatograms of triterpane compounds at m/z 191 and sterane compounds at m/z 217 and 218 for two crude oils: ASMB and Newfoundland Offshore Burn Experiment (NOBE) oil (the NOBE blend was used for the burn experiments on 13 August 1993 [115]). The ASMB and NOBE oil are both light oils originating from western Canada, but they exhibit significantly different distribution profiles of biomarkers.

Analyses of numerous oil samples from many sources have demonstrated that the terpanes include a wide range of compounds, ranging from C_{19} to C_{35} with various pentacyclic hopanes (e.g., C_{29} $\alpha\beta$- and C_{30} $\alpha\beta$-hopane) predominating. In the sterane distributions, the C_{27}, C_{28} and C_{29} steranes have the
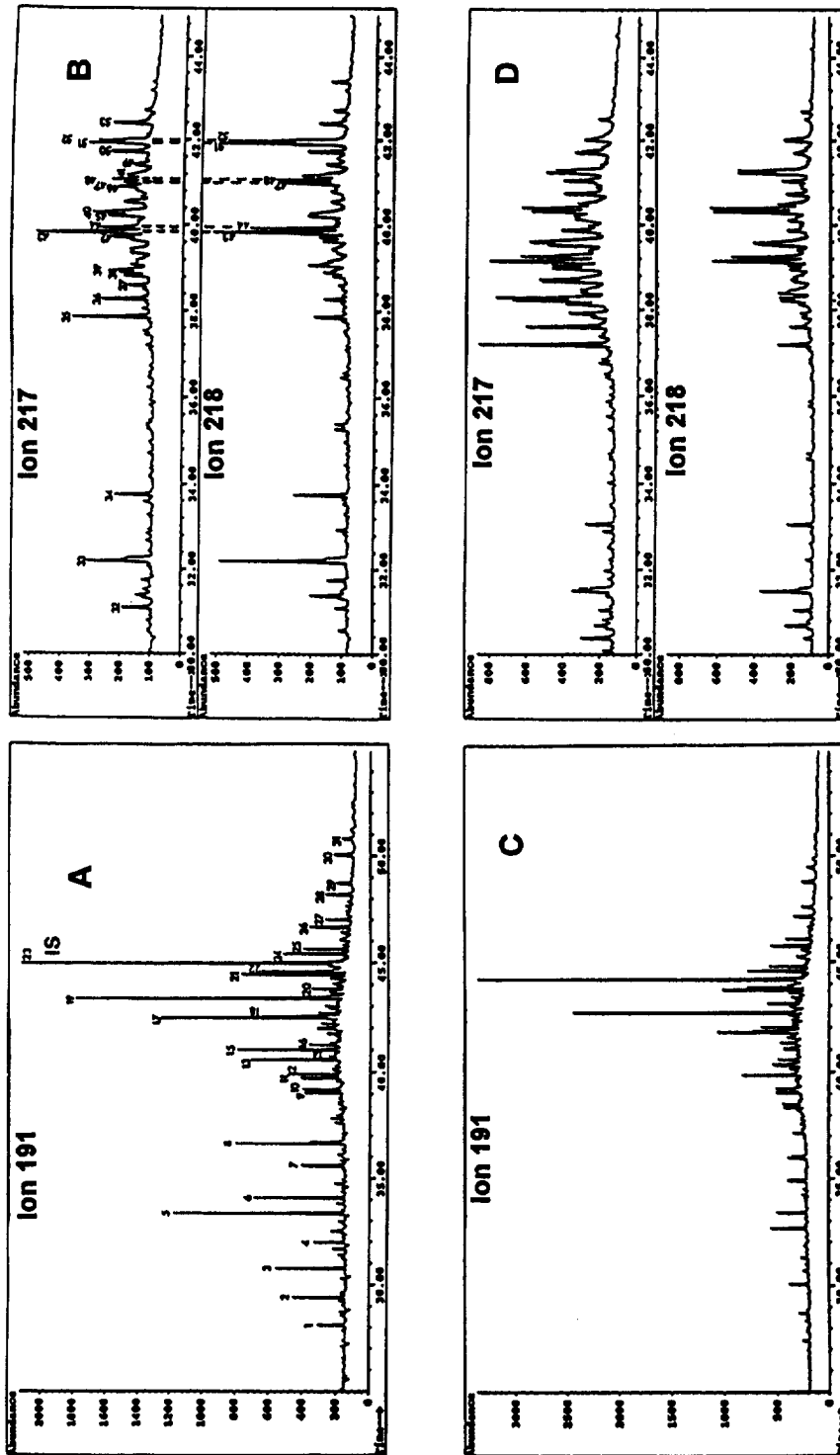
Fig. 11. Distribution of terpanes (ion 191) and steranes (ions 217 and 218) in ASMB oil (A and B) and NOBE oil (C and D).

highest abundances in most oils. However, some oil samples also exhibit significant contributions of diasterane compounds.

5.2. Tracking spill sources using biomarker distributions and ratios

In recent years the relative distributions and ratios of selected biomarkers have become increasingly important for tracking spilled oils and identifying unknown oils. Peters and Moldowan [51] describe a series of ratios of certain biomarker compounds which can be applied as thermal maturity indicators for both oils and bitumens. Kvenvolden et al. [54] report a method using carbon-isotopic and biomarker composition (especially the characteristic triplet, C_{24}-tetracyclic terpane, C_{26}-tricyclic terpane $(R?)$ and C_{26}-tricyclic terpane $(S?)$, and their ratios) to characterize and distinguish the oil-like residues found throughout the northern and western parts of Prince William Sound. Of the 90 samples of shoreline residues examined, 27 samples were traced to the Exxon Valdez oil spill and 61 residues came from spills of California-derived products. Only two samples could not be identified. Bieger et al. [116] used tricyclic and pentacyclic terpanes, which are trace constituents in most lubricating oils, as indicators of the origin of diffuse lubricating oil contamination in plankton and sediments around St. John's, Newfoundland, Canada. The ratios of the abundance of the pentacyclic terpanes to the size of the unresolved complex mixture were used to indicate the degree of weathering for the lubricating oils. Wang et al. [86] describe a detailed systematic analytical approach by which an unknown oil on contaminated birds was identified, and the chemical compositions characterized. The unknown oil was characterized by key individual component analyses,

and also by determination of the diagnostic ratios of a variety of target source-specific-markers (including the C_{23} and C_{24} tricyclic terpanes, Ts and Tm, the C_{29} and C_{30} hopanes, and the S and R isomers of the C_{32} and C_{33} hopanes).

Fig. 9 shows the PAH distribution diagrams and GC–MS chromatograms of terpanes for the weathered source BIOS oil, and field samples 1 and 6 from the BIOS spill. It can be seen from Fig. 9 that there has been a significant loss of PAHs and their alkylated homologues in the field BIOS samples when compared with the weathered source oil. In contrast, however, the terpanes fingerprint provides us with a clear indication of the source of these highly weathered and biodegraded oil samples. The GC–MS measurements demonstrate that the distribution patterns of the m/z 191 and 217 ion chromatograms are nearly identical for all samples. More importantly, the relative ratios of target pairs of terpanes and steranes (Table 5) are apparently independent of weathering and consistent for all of the BIOS samples.

5.3. Determination of the weathered percentages of oils

Wang et al. [71] introduced the weathering index (WI) to describe the weathering behaviour for evaporation-dominated short-term weathered oils. The value of the WI is estimated from the relative abundances of eight n-alkanes in a GC–FID chromatogram using the equation:

$$WI = (n - C_8 + n - C_{10} + n - C_{12} + n - C_{14})/(n - C_{22} + n - C_{24} + n - C_{26} + n - C_{28}). \quad (1)$$

If the weathering indices obtained from the source

Table 5
Comparison of diagnostic ratios of biomarker compounds for BIOS samples

Sample	Weathered	BIOS-1	BIOS-2	BIOS-3	BIOS-4	BIOS-5	BIOS-6	BIOS-7	BIOS-8	BIOS-9	BIOS-10	BIOS-11
C_{23}/C_{24}	2.17	2.28	2.15	1.53	2.14	1.94	1.61	2.02	2.12	2.14	2.16	2.16
Ts/Tm	0.22	0.24	0.23	0.22	0.24	0.28	0.33	0.27	0.23	0.24	0.24	0.23
C_{29}/C_{30}	0.95	0.95	0.93	0.94	0.95	0.95	0.94	0.95	0.95	0.95	0.96	0.94
$C_{32}(S)/C_{32}(R)$	1.57	1.56	1.58	1.57	1.59	1.57	1.59	1.61	1.56	1.60	1.57	1.58
$C_{33}(S)/C_{33}(R)$	1.53	1.54	1.56	[a]	1.57	1.59	1.60	1.57	1.60	1.61	1.56	1.62

[a] The peaks are too small to be accurately integrated.

oil are drawn against the weathered percentages, a straight line is obtained [71].

An advantage to using this equation is that all of the eight n-alkanes are well resolved in the GC spectrum and have relatively high abundances. The weathering index of a sample is thus easily determined, and the weathered percentage of the sample can be then estimated from the working line. It has been demonstrated from the laboratory tests [71] and analyses of oil spill remote sensing samples and spilled oil burn samples [68] that the value of WI is sensitive to the changes of weathering degree, and as the weathering percentages increase, the value of the numerator significantly decrease and the denominator, in contrast, grows larger. However, for samples in which the low-boiling n-alkanes n-C_8 to n-C_{14} are completely lost, the WI approaches zero. Thus the weathered percentages become difficult or impossible to measure.

For long-term weathered and biodegraded oil samples, the estimation of oil depletion has, in the past, relied on ratios of biodegradable to less degradable compounds such as the n-C_{17}/pristane and n-C_{18}/phytane ratios. It has been demonstrated, however, that changes in these ratios may substantially underestimate the extent of biodegradation because isoprenoids also biodegrade to a significant degree [37,38,64,67]. Components which are selected to serve as conserved "internal standards" for assessing biodegradation of oils should meet the following criteria: firstly, they should be highly resistant to weathering and biodegradation on long time scales; secondly, they should not be created during the weathering and biodegradation process itself; and finally, they should be relatively abundant and easily quantified. Based on these criteria, a new method using the highly biodegradation-resistant compound, C_{30} 17α(H), 21β(H)-hopane, as an internal reference to estimate the depletion of crude oil in oiled sediment samples, has been proposed [37,114] and successfully used to quantify weathered percentages of oil residual samples [67,71]. The weathered percentage of an oil based on this compound is calculated using:

$$P(\%) = (1 - C_s/C_w) \times 100\%, \qquad (2)$$

where P is the total weathered percentage of the oil

in degraded oil samples and C_s and C_w are the concentrations of C_{30} $\alpha\beta$-hopane in the source oil and degraded samples, respectively. The advantages of using this method include a more accurate representation of the degree of biodegradation than the traditional aliphatic/isoprenoid hydrocarbon ratios, and a reduced spatial variability, which, in turn, reduces the number of samples required [49].

For distilled oil products which may not contain significant quantities of biomarker compounds such as diesel and jet fuel samples, less "conservative" PAHs with a high degree of alkylation such as C_4 or C_3-phenanthrenes are selected and used as alternative internal standards. If the source is known, then the weathered percentage of the oil can be estimated using Eq. (2) with C_s and C_w representing the concentrations of C_4 or C_3-phenanthrenes in the source oil and degraded samples respectively. Douglas et al. [49] has successfully determined the total weathered percentage of diesel samples by the use of C_4-phenanthrenes as the internal standards.

5.4. Statistical analysis for oil identification

Recently, PAH and biomaker analyses have been coupled with statistical methods, in order to characterize samples among a wide range of possible petroleum sources, both for natural resource damage assessments and for legal or regulatory purposes.

Page and co-workers [48,52,89,117] have used both the double ratios plots and a principal component analysis (PCA) to successfully discriminate between petroleum origins including petrogenic, biogenic and pyrogenic hydrocarbon sources. The statistical methods they used are based on normal and non-normal theory (determined by the structure of the data) including generalized linear models and multivariate correspondence analysis. Bragg et al. [44,45] used a first-order model and multiple-regression models to interpret the effectiveness of bioremediation for the Exxon Valdez spill. The simple first order model provides the most straightforward way to compare changes with time in the amounts of key hydrocarbon species in adjacent fertilized and control plots, while the multiple-regression models allow data from one or more test

sites, subsurface and surface, to be combined. These new interpretive techniques show clearly that fertilizer applications significantly increase the rates of oil biodegradation. The results also suggest avenues to improve the effectiveness of biodegradation measures in future.

Aboul-Kassim and Simoneit [55,56] have used a variety of statistical techniques for source oil identification. In their analysis of the aliphatic and aromatic compositions in particulate fallout samples (PFS) in Alexandria [55], multivariate statistical analyses, including extended Q-mode factor analysis and linear programming, were performed in order to reduce the hydrocarbon data set into a meaningful number of end members (sources). Their analysis indicated that there are two significant end members explaining 90% of the total variation among the samples and confirming petrochemical (79.6%) and thermogenic/pyrolytic (10.4%) sources in the PFS model. In a study of sediment samples in the Eastern Harbour (EH) of Alexandria [56], a similar multivariate statistical approach, including both factor analysis and linear programming techniques, was used to determine the end member compositions and evaluate sediment partitioning and transport in the EH area. In this study, Aboul-Kassim and Simoneit determined that the untreated sewage was the main source of petroleum hydrocarbons in the EH area rather than direct inputs from boating activities or urban run-off.

Lavine et al. [53] made use of pattern recognition methods (PCA and statistical discriminant analysis) to classify high-speed GC chromatograms of weathered and unweathered jet fuels. Following the characterization of a total of 228 neat jet fuel samples of common US aviation fuels, discriminants were developed by parametric and nonparametric pattern recognition procedures to classify the GC chromatograms of jet fuels according to fuel type (JP-4, Jet-A, JP-&, JPTS, or JP-5). These discriminant functions were then used to successfully classify GC chromatograms of jet fuels which had undergone weathering in a subsurface environment.

The application of sophisticated statistical techniques to oil analysis is a new and dynamic area of research which promises to greatly improve the identification of oil spill sources.

6. Conclusions

Analytical methodologies using the state-of-the-art in fingerprinting aspects of oil spill chemistry have made major advances in recent years. Analytical techniques currently focus on specific target petroleum hydrocarbons and classes of hydrocarbons, coupled with the use of diagnostic ratios. These diagnostics are source specific, selective and, in general, sensitive for a wide range of oil spills. Using these techniques, the source of a spill and its degree of weathering and biodegradation can quickly be determined. Very recently, improved data treatments such as principal component analysis and multivariate statistical analyses have shown even greater ability to determine the origin of an oil.

Acknowledgments

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