1 Chemical Fingerprinting of Spilled or Discharged Petroleum — Methods and Factors Affecting Petroleum Fingerprints in the Environment

Scott A. Stout[1] and Zhendi Wang[2]

[1] NewFields Environmental Forensics Practice LLC, 100 Ledgewood Place, Suite 302, Rockland, MA 02370.
[2] ESTD, Environment Canada, 335 River Road, Ottawa, ON K1A 0H3.

1.1 Introduction

Oil can enter water by a number of anthropogenic and natural sources. Acute anthropogenic sources of oil can be generally classified as either accidental *oil spills* or intentional *operational discharges*. Despite international antipollution protocols (e.g., Marine Pollution Convention MARPOL 73/78 and its amendments) and improved shipping and handling safeguards (e.g., International Safety Management Code 1998), accidental oil spills and intentional operational discharges from vessels to waterways and the marine environment regularly occur. Table 1-1 shows the estimated masses of petroleum from accidental oil spills and intentional operational discharges in North America and worldwide (NRC, 2003). The primary sources of accidental oil spills are from tanker vessels carrying crude oil or petroleum products, distantly followed by pipeline spills, coastal facility spills, freighter (fuel) spills, and offshore oil production platform spills. The largest sources of intentional operational discharges include discharges from vessels (mostly bilge and other oily discharges), cargo hold washings, and produced water discharges from offshore platforms outside of North America (Table 1-1).

Table 1-1 also shows that chronic anthropogenic sources of oil, such as runoff and atmospheric deposition from terrestrial environments, which are not easily classified as either accidental or intentional, constitute a major source of oil to the marine environment. Since these terrestrial sources are chronic and not easily attributed to a "point source," they collectively constitute a chronic source of anthropogenic "background" hydrocarbons that must be considered in many oil spill investigations. In addition, chronic natural sources of oil (e.g., oil seeps) are thought to exceed all anthropogenic sources combined, contributing up to 2 million tonnes of oil annually (Table 1-1). These naturally occurring oil seeps, as well as other naturally occurring (i.e., biogenic) hydrocarbons, must also be considered in oil spill investigations.

Despite the significant contributions of oil and hydrocarbons to the marine environment from chronic anthropogenic sources, oil seeps, and naturally occurring hydrocarbons, it is the

Table 1-1 Average Estimated Annual Releases (1990–1999) of Petroleum into the Marine Environment in North America and worldwide by Source (in Thousands of Metric Tonnes). Data from National Research Council (2002)

	North America			*Worldwide*		
	Best Est.	*Min.*	*Max.*	*Best Est.*	*Min.*	*Max.*
Accidental Oil Spill Sources						
Tanker/barge vessel spills	5.3	4	6.4	100	93	130
Pipeline spills	1.9	1.7	2.1	12	6.1	37
Coastal facility spills	1.9	1.7	2.2	4.9	2.4	15
Non-tanker (freighter) spills	1.2	1.1	1.4	7.1	6.5	8.8
Oil production platform spills	0.16	0.15	0.18	0.86	0.29	1.4
Intentional Operational Discharge Sources						
Operational discharges (all vessels)	0.22	0.06	0.6	270	90	810
Cargo washings		not allowed		36	18	72
Produced waters from offshore rigs	2.7	2.1	3.7	36	19	58
Recreational marine vessels	5.6	2.2	9		not available	
Atmospheric deposition (offshore rigs)	0.12	0.07	0.45	1.3	0.38	2.6
Atmospheric deposition (vessels)	0.01	trace	0.02	0.4	0.2	1
Jettisoned aircraft fuel	1.5	1	4.4	7.5	5	22
Chronic Terrestrial Sources						
Land-based (river and runoff)	54	2.6	1900	140	6.8	5000
Atmospheric deposition	21	9.1	81	52	23	200
Natural Sources (Seeps)	160	80	240	600	200	2000
Total	**260**	**110**	**2300**	**1300**	**470**	**8300**

acute accidental oil spills and intentional operational discharges that tend to promulgate the greatest need for chemical fingerprinting. These acute releases can require expensive response and cleanup activities and damage marine and terrestrial natural resources; thus, the resulting casualty and punitive financial consequences can be substantial. As such, the source of the spilled oil and the spatial and temporal extent of any damage need to be established confidently so that any resultant liabilities are fairly assessed. Chemical fingerprinting, *def.*, the generation and comparison of diagnostic chemical features among oil samples (i.e., both spill and source oils) and potentially impacted samples (e.g., shorelines, sediments, or biological tissues), can play an important role in assessing this liability and monitoring ecological effects.

The chemical fingerprinting of spilled oils was initiated in the 1970s following an increased environmental awareness and the resulting regulations, such as the Clean Water Act in the U.S. (e.g., Kreider, 1971; Ehrhardt and Blumer, 1972; Duewer et al., 1975; Bentz, 1976, 1978; Albaiges and Albrecht, 1979). Over the past 35 years, the sophistication of the chemical fingerprinting has evolved with the advancement of analytical chemistry methodologies and data interpretation tools — the current state of which is represented in various chapters throughout this book.

The exact role of chemical fingerprinting in an oil spill investigation will vary over time and depending on the circumstances of the release (e.g., Boehm et al., 1997). For example, oil spills or operational discharges that enter surface water can be classified into two basic categories — (1) "mystery" spills and (2) known-source spills. The former typically involves the discovery of a fugitive oil or oily waste at sea, in rivers and harbors, or in other water bodies either in the absence of any known incident or source, or in the presence of multiple source candidates. The latter, as their name implies, involve the release of oil or oily wastes from an identified point source (or at least, a "prime suspect") or a known incident (e.g., accidental discharge during a grounding or collision). In either oil spill scenario there

is an opportunity for chemical fingerprinting to answer important questions, which can be used to determine how any liabilities for any cleanup and resource damage are distributed.

In the case of a "mystery" spill, chemical fingerprinting can be used to compare the spilled oil's "fingerprint" to those of any viable candidate source oils in an attempt to unambiguously identify the lone source — or, at least, limit the population of possible sources. These investigations often involve the collection of waterborne oils (i.e., oil slicks) and their comparison to oils collected from various candidate sources or a particular "prime suspect." If no prime suspect is identifiable, based upon other evidence, then a critical component in the success of a chemical fingerprinting investigation of a "mystery" spill is the recognition of and collection of all available viable candidate source oils. Logically, if the population of possible sources is sufficiently comprehensive, there is a better chance of identifying the source. A positive fingerprinting "match" between a mystery spill and a candidate source can sometimes be used alone, or more powerfully in conjunction with other evidence (e.g., trajectory modeling or remote sensing; see Chapters 13 and 14, respectively), to determine responsibility for the mystery spill. Other evidence can be very important when the same oil was present in multiple sources (e.g., a particular lot of fuel or cargo oil carried by multiple vessels and/or terminals within a port). By their nature, investigations of mystery spills usually occur in the short term (days to weeks) following the discovery of the spill or discharge — and typically either solve the mystery at that point, or the spill's source often remains unsolved. Thus, the effects of short-term weathering (e.g., evaporation) also need to be considered in the investigation of mystery spills. Under most scenarios, once a mystery spill is "solved," the need for chemical fingerprinting shifts toward those of a known-source release, described next.

In the case of a known-source release, for example, a grounded and leaking tanker or a production-well blowout, chemical fingerprinting of the spilled oil can be used to establish the spatial and temporal extent of its impact in the environment over the short and long terms. The matrices most often involved in establishing these impacts involve shoreline or benthic sediments and biological tissues, i.e., sites where oil-derived hydrocarbons might accumulate and reside for longer periods of time. Two critical components of this type of chemical fingerprinting investigation are to (1) establish and allocate the contribution of any pre-existing anthropogenic or naturally occurring "background" hydrocarbons from those that are newly introduced by the spilled oil and (2) monitor the changes in spilled oil composition over time (i.e., weathering and natural recovery). Chemical fingerprinting investigations of this type can occur for decades following the release.

The application of chemical fingerprinting in any oil spill or discharge investigation requires an understanding of the factors that collectively contribute to the chemical character of petroleum in the environment — and thereby, its chemical fingerprint. Figure 1-1 shows some of the factors controlling the chemical fingerprints of oil in the environment. Some of these factors influence the chemical fingerprint of petroleum before it is released to the environment, and other factors influence its chemical fingerprint after a release. In this chapter, we review the analytical methodologies used for chemical fingerprinting of waterborne oil spills and discuss the factors that affect the chemical fingerprints of petroleum that are relevant to oil spill investigations. Examples from various oil spill investigations are used throughout in order to demonstrate various aspects of these factors.

1.2 Methods for Chemical Fingerprinting Petroleum

1.2.1 Historical Perspective

The analytical methods available for chemical fingerprinting of spilled oil in the environ-

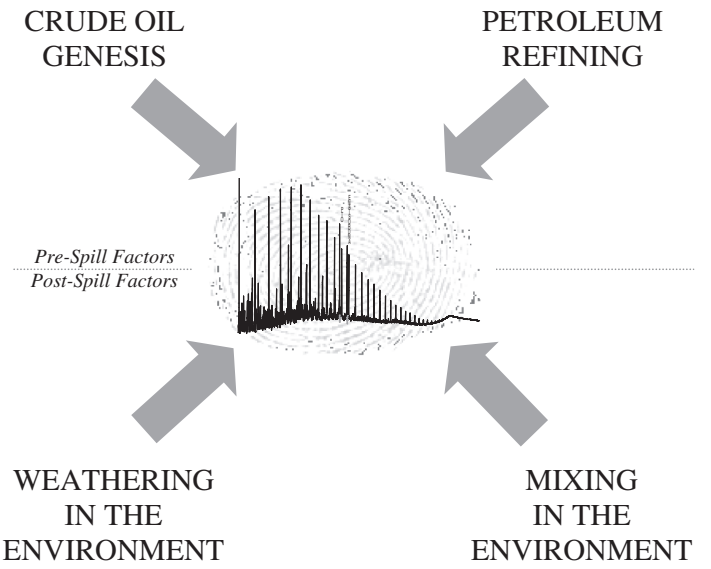

Figure 1-1 Diagram depicting the four factors that affect the chemical fingerprints of petroleum relevant in oil spill investigations.

ment have evolved considerably and basically have paralleled those used by petroleum geochemists in exploration and production applications. In the early 1970s, packed-column gas chromatography and ultraviolet or infrared spectroscopy yielded basic, semiquantitative fingerprints of spilled oils (e.g., Ehrhardt and Blumer, 1972; Bentz, 1976). The application of these methods relied primarily on relatively gross evaluation of the boiling range or *n*-alkane profiles and degree of weathering of spilled oils. These methods were later supplemented by the development of capillary column gas chromatography (e.g., Rasmussen, 1975) often coupled with low-resolution mass spectrometry (GC/MS) for more detailed molecular characterization of spilled oil (e.g., Albaiges and Albrecht, 1979). The increasingly widespread use of low-resolution GC/MS methods provided a means of measuring the more highly specific compounds that occurred at lower concentrations in oils, such as PAH (e.g., Teal et al., 1978; Grahl-Nielsen et al., 1978) and biomarkers (Seifert and Moldowan, 1978; Seifert et al., 1979), which are still targeted analytes in oil spill studies today. (See ahead and in other chapters throughout this book.) However, over the past 25 years the advances in the use of GC/MS in oil spill investigations have relied on (1) increases in the target analytes of interest, including an increasing array of "diagnostic" compounds or compound groups, (2) improved sensitivity of the analyses (due to increasingly higher degrees of instrumental sensitivity and application of selected ion monitoring data acquisition), and (3) stringent quality assurances (Douglas and Uhler, 1993; Wang and Fingas, 1995a, 1997; Boehm et al., 1997).

While spectroscopic methods have improved and continue to be used in some oil spill investigations (e.g., Staniloae et al., 2001), over the last 30 years, capillary gas chromatography (GC) clearly has proven most effective in the chemical fingerprinting of spilled oils. The primary reason for this is that capillary GC, performed using various column types, can resolve many, but clearly not all (e.g., see Chapter 5 and ahead), of the 100s to 1000s of compounds in petroleum permitting their detection and identification by a variety of detectors. Chemical fingerprinting using GC has relied on a variety of detectors, ranging from nonspecific detectors such as flame ionization detectors (GC/FID) to highly selective mass spectrometers (GC/MS). Other compound-specific detectors such as flame

photometric detectors (FPD), chemiluminescence detectors, and atomic emission detectors have been utilized less frequently.

The GC fingerprinting methods most widely used today are based on modifications of the U.S. EPA's codified series of GC techniques intended to measure industrial chemicals (U.S. EPA, 1997). The two modified EPA methods of greatest utility in oil spill fingerprinting studies are (1) method 8015B, *Non-Halogenated Organics Using GC/FID*, and (2) method 8270, *Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*. These standard EPA GC methods are, indeed, excellent base techniques for the chemical fingerprinting of spilled oil, candidate source oils, and potentially impacted environmental media. However, because these methods were developed with the intention of measuring specific chemicals of concern (i.e., the so-called priority pollutant chemicals), fundamental restrictions to the standard EPA methods limit their usefulness in forensic oil spill investigations (Douglas and Uhler, 1993). Of the more than 160 EPA priority pollutant volatile and semivolatile organic compounds, only 20 are petroleum-type hydrocarbons that would potentially be useful in oil spill investigations. This list includes benzene, toluene, ethyl-benzene, xylenes, naphthalene, acenaphthylene, fluorene, anthracene, phenanthrene, fluoranthene, chrysene, pyrene, benzo[a] anthracene, benzo[b]fluoranthene, benzo[a] pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h] anthracene, and benzo[g,h,i]perylene (Sauer and Boehm, 1995). Only half of these compounds are found in significant concentrations in petroleum- or coal-derived products and wastes. Even together, these chemicals alone are of virtually no value in chemical fingerprinting of spilled petroleum because they offer little or no specificity in differentiation between different oils or between oils and other sources of hydrocarbons in the environment. As such, the principal modification to the standard EPA methods involves the expansion of the target analytes to include a greater number of compounds commonly found in petroleums (see ahead).

Modifications of EPA methods 8015B (GC/FID) and 8270C (GC/MS) have been incorporated in multiple oil spill characterization protocols used over the past 30 years. The first of these was 1974's ASTM D3328, *Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography*. This method was based upon GC/FID analysis of spilled oils and their qualitative comparison to potential sources and/or impacted samples. ASTM D3328 has been repeatedly modified, the most current version being updated in 2000 (ASTM, 2000a). The Nordic countries collectively developed a protocol that employed both GC/FID and GC/MS fingerprinting techniques that were first introduced in 1983 (Nordtest, 1983) and subsequently revised in 1991 (Nordtest, 1991). The introduction of the GC/MS fingerprinting component by Nordtest (1991) was, in 1995, followed by the 1995 introduction of ASTM D5739, *Oil Spill Identification by Gas Chromatography and Positive Ion Electron Impact Low-Resolution Mass Spectrometry*. This method was most recently updated in 2000 (ASTM, 2000b). Both the ASTM and Nordtest protocols relied upon qualitative or semiquantitative (i.e., normalized peak areas) comparisons among GC/FID chromatograms and GC/MS extracted ion profiles in comparing a spilled oil to potential sources and to potentially impacted samples (e.g., sediments or biota). Concurrent with the activities of the ASTM and Nordtest organizations, other organizations were developing quantitative fingerprinting protocols in the course of some well-studied oil spill investigations, e.g., *Amoco Cadiz* (e.g., Page et al., 1988), 1991 Gulf War (Michel et al., 1993), or *Exxon Valdez* (e.g., Page et al., 1995). As such, quantitative oil spill fingerprinting protocols in which a large number of target analytes (well beyond those in EPA methods) were quantitatively measured in spilled oils, candidate sources, and in potentially impacted samples, were widely adopted in recent years. Among the analytes most frequently measured in these investigations were *n*-alkanes, acyclic isoprenoids, polycyclic aromatic hydrocarbons

(PAHs), alkylated PAHs and sulfur-containing PAHs, and triterpane and sterane biomarkers (e.g., Douglas and Uhler, 1993; Sauer and Boehm, 1995; Wang et al., 1999a, 2000; Wang and Fingas, 2003; see also Chapters 7 and 8, herein). The success of these studies in fulfilling the roles of chemical fingerprinting in both mystery spills and known-source spills (Section 1.1) has led to the use of quantitative or semiquantitative GC/FID and GC/MS in a logical, "tiered" fashion (Wang et al., 1999a; Stout et al., 2001; Daling et al., 2002; Wang and Fingas, 2003; see also Chapters 7 and 8). An important advantage of these quantitative or semiquantitative chemical fingerprinting methods is the ability to analyze the resulting data using a variety of statistical or numerical methods, rather than rely upon qualitative interpretations of chromatographic patterns (e.g., see Chapters 8 and 9 for more details).

Tier 1 typically is the GC/FID analysis of samples — spilled oils, potential sources, or potentially impacted samples and Tier 2 is the GC/MS analysis of those samples which, after Tier 1, still require additional chemical characterization in order to answer the specific questions at hand. Finally, if necessary, Tier 3 involves the statistical or multivariate analysis of Tiers 1 and 2's data to answer specific questions, e.g., "Is there a positive match to the mystery spill oil" or "what, if any, proportion of hydrocarbons in this sediment is attributable to the spill oil?" Obviously, answers to such questions must consider the precision of the quantitative data, the effects of weathering of any spilled oil, and the potential for mixtures.

1.2.2 Tier 1 — Chemical Fingerprinting via GC/FID

Tier 1 analysis of oil spill-related samples involves a GC/FID based on a modified EPA Method 8015B. The qualitative results available from this tier of analysis include the overall chemical fingerprint of an oil or of extractable hydrocarbons in some matrix (e.g., sediments, soils, or biota). Various methods exist for the extraction, cleanup, and/or fractionation of water, sediment, soil, and tissue extracts so that spilled oil in these matrices can be better characterized either through the removal of external interferences (e.g., biogenic compounds or elemental sulfur) or the concentration of targeted compounds (e.g., compound class or group separation). The reader is directed to sample extraction and preparation procedures described in Sauer and Boehm (1995).

The most appropriate capillary column for oil spill investigations is narrow bore (0.25-mm i.d.) fused silica coated with a 0.25-μm 100% methyl-silicone cross-linked stationary phase. Minimum column length for oil spill investigations is 30 meters, although longer columns, e.g., 60 meters, will afford even better resolution at the expense of longer run times. The keys to the successful application of this method are (1) optimal operation of the GC inlet (McCarthy and Uhler, 1994), which will minimize mass discrimination of heavier hydrocarbons (e.g., $>C_{30}$), and (2) utilization of a very slow GC oven temperature program, to facilitate optimal resolution of close-eluting compounds. GC oven programs for high-quality Tier 1 fingerprints typically have initial temperatures of 30° to 35°C, and oven ramp rates of 6°C/min or less and total run times of about 60 minutes. It is possible to use shorter run times (higher ramp rates) depending upon the specific character of the oil spill under investigation and questions being addressed.

GC/FID fingerprints will reveal the boiling (carbon) range and, hence, the general hydrocarbon composition of a spilled oil or spill-related samples. Even qualitative chromatographic fingerprints are useful because almost all hydrocarbon assemblages — crude oil, petroleum fuels, petroleum lubricant, and their combustion and waste products — have distinctive chromatographic signatures (e.g., Wang and Fingas, 1997; Stout et al., 2002a). These qualitative differences are the basis of the ASTM D3328 oil spill fingerprinting method. Although weathering and/or mixing (described later in this chapter) can greatly influence the appearance of the chromatographic signature of spilled petroleums, more

often than not, distinctive features can be retained in the Tier 1 GC/FID chromatogram. Depending on the extent of weathering, such features may include the ratios between or among resolved compounds that have similar environmental behaviors (e.g., pristane/phytane ratios or carbon preference indices among higher-boiling *n*-alkanes). Even the profile of the unresolved complex mixture (UCM "hump"), a common feature of weathered petroleum, can be distinctive in some circumstances, e.g., perhaps distinguishing an environmentally evaporated petroleum from a refined/distilled petroleum or background hydrocarbons. Despite what can be revealed by qualitative GC/FID analysis (e.g., overall boiling range, the degree of weathering, or likelihood of mixing), Tier 1 analysis can involve quantitation of any individual compounds that can be chromatographically separated and measured, e.g., the *n*-alkanes and selected acyclic isoprenoids (e.g., pristane and phytane). The absolute concentrations of these compounds can be quantitatively measured through the use of internal or external standards and appropriate instrument calibration and quality-control measures (see Section 1.2.4), or relative concentrations measured using peak areas.

Strategically, the results of the Tier 1 GC/FID analysis dictate the next step(s) in an oil spill fingerprinting investigation. If, for example, a mystery crude oil spill is under investigation and a potential source candidate is determined to consist of diesel fuel, there is no obvious need to analyze that diesel fuel further, since GC/FID is sufficient to exclude it as a source of the mystery spill. If, however, the Tier 1 results are equivocal in some way, additional analysis via Tier 2 is likely warranted — again, depending upon the specific question(s) at hand. This type of flexibility is inherent in the tiered chemical fingerprinting approach.

1.2.3 Tier 2 — Chemical Fingerprinting via GC/MS

Although waterborne oil spills can sometimes involve volatile petroleums, such as natural gas condensate or automotive gasoline, the impact of such spills on the aquatic and sedimentary environments generally is short lived due to the propensity for evaporation. Fingerprinting of volatile petroleums generally relies upon GC/MS based on modification of EPA Method 8260, sometimes referred to as "PIANO" analysis (Uhler et al., 2002). Most waterborne oil spills involve petroleums containing semi- to minimally volatile constituents that can persist longer in the environment and are amenable to analysis via GC/MS based on a modified EPA Method 8270C.

The operating procedures and GC/MS conditions for optimal detection, separation, and measurement of these semi- to minimally volatile target compounds are somewhat different from those presented in EPA Method 8270 (Stout et al., 2002; Douglas et al., 2004). First, GC and MS operating conditions need to be optimized for separation and sensitivity. At a minimum, 30-m, 0.25-mm i.d., 0.25-μm film thickness 5% phenyl-95% methyl-silicone (or equivalent) capillary column should be used for separation. Optimal operation of the GC should be established to minimize mass discrimination of heavier hydrocarbons (e.g., $>C_{30}$) during sample injection (McCarthy and Uhler, 1994). A slow GC oven temperature program should be used to ensure adequate resolution of closely eluting compounds. Appropriate GC oven profiles have initial temperatures of 30° to 35°C and oven ramp rates of 6°C/min or less. Total GC run times of 1 to 2 hours are typical for these analyses. The MS is commonly operated in the selected ion monitoring (SIM) mode, which greatly enhances the sensitivity and lower detection limits for quantitative analysis. (See also Chapter 3 for a more detailed discussion of GC/MS analysis in oil spill investigations.)

The most common groups of targeted analytes via GC/MS analysis of spill oils, candidate sources, and potentially impacted samples are the (1) homo- and hetero-atomic polycyclic aromatic hydrocarbons (PAHs) and (2) petroleum biomarkers. Other compounds of potentially diagnostic value, e.g., diamondoids, *n*-alkylcyclohexanes, macrocyclic alkanes,

etc., can, of course, be included in any oil spill investigation where necessary. The utility of the PAHs and biomarkers lies in the combination of their specificity to different hydrocarbon sources and their generally reduced susceptibility to weathering on environmental time scales (e.g., see Chapter 11). In crude oil and most petroleum fuels and lubricants, the PAHs and biomarkers are present at much lower concentrations than the more abundant normal, branched, and (nonbiomarker) cyclic alkanes that can easily be detected by Tier 1 GC/FID analysis. Once dispersed in environmental media, the concentrations of PAH and biomarkers are often in the parts-per-million to low parts-per-billion range. In order to detect and quantify these hydrocarbons in sediments and biota potentially impacted by spilled oil, these analyses must be conducted under closely monitored analytical and quality-control protocols (Douglas et al., 2004).

1.2.3.1 Polycyclic Aromatic Hydrocarbons

Table 1-2 presents a list of target homo- and hetero-atomic PAHs that are widely used in Tier 2 analysis of oil spill-related samples. This compilation includes parent and alkyl-substituted PAH with long demonstrated utility in environmental forensics investigations (Boehm and Farrington, 1984; Colombo et al., 1989; Sauer and Uhler, 1994/1995). The list also includes the naphthobenzothiophene homologues, which have been less commonly used in oil spill investigations.

The chromatographic retention times for each target compound or compound group

Table 1-2 PAH and Related Compounds or Groups Commonly Targeted in Oil Spill-Related Samples Obtained Using GC/MS-SIM

Target PAH/PAH Groups	*Key*	*Quant. Ion (m/z)*	*RF*	*Target PAH/PAH Groups*	*Key*	*Quant. Ion (m/z)*	*RF*
Naphthalene	N0	128	N0	Pyrene	PY	202	PY
C1-Naphthalenes	N1	142	N0	C1-Fluoranthenes/Pyrenes	FP1	216	FL
C2-Naphthalenes	N2	156	N0	C2-Fluoranthenes/Pyrenes	FP2	230	FL
C3-Naphthalenes	N3	170	N0	C3-Fluoranthenes/Pyrenes	FP3	244	FL
C4-Naphthalenes	N4	184	N0	C4-Fluoranthenes/Pyrenes	FP4	258	FL
Acenaphthene	ACE	154	ACE	Naphthobenzothiophenes	NT0	234	NT0
Acenaphthylene	ACY	152	ACY	C1-Naphthobenzothiophenes	NT1	248	NT0
Biphenyl	BPHN	154	BPHN	C2-Naphthobenzothiophenes	NT2	262	NT0
Dibenzofuran	DBF	168	DBF	C3-Naphthobenzothiophenes	NT3	276	NT0
Fluorene	F0	166	F0	C4-Naphthobenzothiophenes	NT4	290	NT0
C1-Fluorenes	F1	180	F0	Benzo[a]anthracene	BaA	228	BaA
C2-Fluorenes	F2	194	F0	Chrysene	C0	228	C0
C3-Fluorenes	F3	208	F0	C1-Chrysenes/benzanthracenes	C1	242	C0
Dibenzothiophene	D0	184	D0	C2-Chrysenes/benzanthracenes	C2	256	C0
C1-Dibenzothiophenes	D1	198	D	C3-Chrysenes/benzanthracenes	C3	270	C0
C2-Dibenzothiophenes	D2	212	D	C4-Chrysenes/benzanthracenes	C4	284	C0
C3-Dibenzothiophenes	D3	226	D	Benzo[b]fluoranthene	BbF	252	BBF
C4-Dibenzothiophenes	D4	240	D	Benzo[j,k]fluoranthene	BjkF	252	BKJF
Anthracene	AN	178	AN	Benzo[a]fluoranthene	BaF	252	BAF
Phenanthrene	P0	178	P0	Benzo[a]pyrene	BaP	252	BAP
C1-Phenanthrenes/Anthracenes	P1	192	P0	Benzo[e]pyrene	BeP	252	BEP
C2-Phenanthrenes/Anthracenes	P2	206	P0	Perylene	PER	252	PER
C3-Phenanthrenes/Anthracenes	P3	220	P0	Indeno[1,2,3-c,d]pyrene	IND	276	IND
C4-Phenanthrenes/Anthracenes	P4	234	P0	Dibenzo[a,h]anthracene	DA	278	DA
Fluoranthene	FL	202	FL	Benzo[g,h,i]perylene	GHI	276	GHI

RF-response factor.

must be established under the appropriate GC/MS operating conditions. The diagnostic and confirmatory ions for each target analyte must be verified from GC/MS analyses of authentic standards, whenever possible. Since only a handful of authentic standards exists for the literally hundreds of C_1 to C_4 alkylated isomers of PAH, characteristic ions, retention time windows, and homologue group patterns must be constructed based on carefully documented PAH and alkyl PAH chromatographic retention indices (Lee et al., 1979), and then redocumented by the analysis of a well-characterized reference petroleum product such as Alaska North Slope (ANS) crude oil or Alberta Sweet Mix Blend (ASMB) (Wang et al., 1994a). Alkyl homologues of PAH are quantified using the straight baseline integration method versus relative response factors (RRFs) assigned from the parent PAH compound (Madsen, 1991). Although the alkylated PAH homologous groups can be quantified using the RRF of the respective parent PAH compounds, it is preferable to obtain RRFs directly from alkylated PAHs (if they are commercially available) for further improvement of PAH quantitation accuracy. For example, the RRFs obtained from 1-methyl-naphthalene, 2-methyl-naphthalene, 2,6-dimethyl-naphthalene, 2,3,5-trimethyl-naphthalene, and 1-methyl-phenanthrene can be used for quantitation of 1-methyl-naphthalene, 2-methyl-naphthalene, C_2-naphthalenes, C_3-naphthalenes, and C_1-phenanthrenes, respectively; and the RRFs of 2,3,5-trimethyl-naphthalene and 1-methyl-phenanthrene can be used for quantitation of C_4-naphthalenes, and C_2-, C_3-, and C_4-phenanthrenes in oil, respectively (Wang et al., 1994a).

1.2.3.2 Petroleum Biomarkers

In Tier 2 GC/MS analysis, the concentrations and/or relative distribution of biomarkers — e.g., acyclic isoprenoids, regular and rearranged steranes, bicyclic, tricyclic, tetracyclic, and pentacyclic terpanes (Table 1-3) — can be measured by taking advantage of the knowledge of characteristic ion fragments and well-documented retention indices for each class of compounds. The analysis of biomarkers is thoroughly described in Chapter 3 and is

Table 1-3 Inventory of Petroleum Biomarkers Commonly Used in the Characterization of Spilled Oil Obtained Using GC/MS-SIM

Triterpanes		*Steranes*
C_{19} Tricyclic terpane	17α(H),21β(H)-30-norhopane	C_{20} 5α(H),14α(H),17α(H)-sterane
C_{20} Tricyclic terpane	18α(H),21β(H)-30-norneohopane ($C_{29}T_s$)	C_{21} 5α(H),14β(H),17β(H)-sterane
C_{21} Tricyclic terpane	17α(H)-diahopane (X)	C_{22} 5α(H),14β(H),17β(H)-sterane
C_{22} Tricyclic terpane	17β(H),21α(H)-30-normoretane	13β(H),17α(H)-diacholestane (20S)
C_{23} Tricyclic terpane	18α(H) & 18β(H)-oleanane	13β(H),17α(H)-diacholestane (20R)
C_{24} Tricyclic terpane	17α(H),21β(H)-hopane	13β(H),17α(H)-diastigmastane (20S)
C_{25} Tricyclic terpanes (a & b)	17α(H)-30-nor-29-homohopane	13β(H),17α(H)-diastigmastane (20R)
C_{26} Tricyclic terpanes (a & b)	17β(H),21α(H)-moretane	
C_{24} Tetracyclic terpane	22S-17α(H),21β(H)-30-homohopane	5α(H),14α(H),17α(H)-cholestane (20S)
C_{28} Tricyclic terpane (a)	22R-17α(H),21β(H)-30-homohopane	5α(H),14β(H),17β(H)-cholestane (20R)
C_{28} Tricyclic terpane (b)	Gammacerane	5α(H),14β(H),17β(H)-cholestane (20S)
C_{29} Tricyclic terpane (a)	22S-17α(H),21β(H)-30-bishomohopane	5α(H),14α(H),17α(H)-cholestane (20R)
C_{29} Tricyclic terpane (b)	22R-17α(H),21β(H)-30-bishomohopane	5α(H),14β(H),17β(H),24-methylcholestane (20R)
18α(H)-22,29,30-trisnorhopane (T_s)	22S-17α(H),21β(H)-30-trishomohopane	5α(H),14β(H),17β(H),24-methylcholestane (20S)
17α(H)-22,29,30-trisnorhopane (T_m)	22R-17α(H),21β(H)-30-trishomohopane	5α(H),14α(H),17α(H),24-methylcholestane (20R)
C_{30} Tricyclic terpane (a)	22S-17α(H),21β(H)-30-tetrakishomohopane	5α(H),14α(H),17α(H),24-ethylcholestane (20S)
C_{30} Tricyclic terpane (b)	22R-17α(H),21β(H)-30-tetrakishomohopane	5α(H),14βH),17βH),24-ethylcholestane (20R)
17α(H),18α(H),21(β)H-28,30-bisnorhopane	22S-17α(H),21β(H)-30-pentakishomohopane	5α(H),14β(H),17β(H),24-ethylcholestane (20S)
17α(H),21β(H)-25-norhopane	22R-17α(H),21β(H)-30-pentakishomohopane	5α(H),14α(H),17α(H),24-ethylcholestane (20R)

not recounted here. It is notable, however, that the GC/MS analysis of biomarkers can be carried out simultaneously with the analysis of PAH described above. Two types of calibration standards are appropriate for determination of biomarker concentrations. The first are retention time marker compounds [e.g., 5β(H)-cholane], against which measured biomarker retention times can be compared (Sauer and Boehm, 1995). The second are discrete biomarker chemicals, available commercially, that can be used to generate response factors for individual compounds and compounds of similar structure.

In some instances where conventional Tier 1 GC/FID and Tier 2 GC/MS analyses achieve equivocal results, additional chemical detail may be necessary to answer specific questions of some oil spill investigations. In recent years, two such analytical methods have been applied to oil spill investigations, namely, (1) compound-specific stable isotope analysis (CSIA) and (2) two-dimensional GC analysis (GC × GC). Both of these methods are discussed in subsequent chapters in this book and are not discussed further herein.

1.2.4 Quality Assurance and Quality Control

Like any high-quality laboratory work, analytical chemistry measurements carried out in support of oil spill investigations must be conducted within the framework of a robust quality assurance (QA) and quality-control (QC) program. Beyond the obvious, a practical reason a laboratory should operate under a well-defined QA/QC program is the need for the utmost confidence in the quality of the data because of the likelihood that the data will be used in litigious inquiries.

1.2.4.1 Quality Control

The quality of chemical fingerprinting data is an essential component of any environmental forensic investigation. In most litigious situations the data quality must be defended (long) before the interpretations of those data. Different laboratories employ different degrees of quality control (QC) governing the sample handling, sample preparation, sample analysis, and reporting of data. The practicalities of running a commercial laboratory often compete with QC of the data. Fingerprinting data to be used in a given oil spill investigation should be analyzed in exclusive analytical batches, on the same analytical instrument, and, to the extent possible, within the same analytical sequence. Whenever practical the data analyses (peak integrations) for a given batch of samples should be conducted by a single GC/MS analyst with experience in petroleum analysis and hydrocarbon pattern recognition. These steps, combined with the calibrations (initial and continuing), appropriate QC samples (procedural blanks, laboratory control samples, reference oils), and replicates (duplicates or triplicates), each contribute to overall data quality.

1.2.4.2 Quality Assurance

A QA program assures laboratory management and project investigators that documented standards for the quality for facilities, equipment, personnel training, and work performance are being attained, and if not, to identify and report the areas that need improvement to meet those standards. A laboratory's QA program should be described in the laboratory's Quality Management Plan (QMP). The QMP should describe the laboratory's policy for management system reviews, quality-control and data-quality objectives, QA project plans, standard operating procedures, training, procurement of items and services, documentation, computer hardware and software, planning and implementation of project work, assessment and response, and corrective action and continuous improvement. A QA system should consist of a minimum of six components, namely,

1. A formal Work/QA Project Plan that describes all work, QA, and quality-control activities associated with a project is developed for each study.
2. Up-to-date standard operating procedures (SOPs) that describe all technical activities conducted by the laboratory.

3. A program to ensure and document that all project personnel are fully trained and qualified to perform project activities before independent activities may begin. Personnel training records should be maintained by the QA Unit and include records of qualifications, prior experience, professional training, and internal training procedures.
4. A documentation and records system that facilitates full sample and data tracking.
5. A quality assessment program for all projects, conducted through management system reviews, technical system audits, performance evaluation samples, data validation, laboratory inspections, and independent data audits. An independent QA Unit within a laboratory should conduct the latter two activities.
6. A continuous improvement program, facilitated through quality assurance audits, a formal corrective action program, and routine, laboratorywide performance assessments and reviews.

In addition, all laboratory deliverables should receive an independent review that includes a quality assurance (QA) and technical component. The QA review should ensure that the data are (1) complete, (2) in compliance with the procedures defined in the QAPP, (3) in compliance with regulatory statutes, and (4) accurate and technically sound. The technical review should ensure that the results and interpretations are (1) objective, (2) defensible among peers, and (3) presented in a manner that conveys the conclusions clearly, often to nonexpert decision makers.

1.3 Factors Controlling the Chemical Fingerprints of Spilled or Discharged Petroleum

Figure 1-1 depicted the four factors that influence the chemical fingerprints of petroleum in the environment that are relevant to oil spill investigations. In this section, these factors are presented and described.

The term "petroleum" collectively refers to the family of materials, naturally occurring and humanmade, that contain complex mixtures of up to tens of thousands of hydrocarbons and nonhydrocarbons (nitrogen-, sulfhur-, oxygen-, and metal-containing compounds; Speight, 1991). Naturally occurring petroleums include gases (e.g., natural gas), liquids (e.g., gas condensates and crude oils), and solids (e.g., solid bitumens and oil shale/sand). The chemistry of naturally occurring petroleums is the collective result of the geologic processes that led to their formation over millions of years, namely (1) the nature of the ancient, organic-rich, source strata, (2) the thermal history of the source strata, and (3) changes brought about during petroleum's migration to and residence in reservoir strata (Tissot and Welte, 1984; Hunt, 1996; Table 1-4).

Table 1-4 Inventory of the Factors Controlling the Chemical Fingerprints of Spilled or Discharged Petroleum

Controlling Factors in Chemical Fingerprints of Petroleum			*Petroleum Types*
Primary Controls (Geology)	source rock organic matter type	*Naturally Occurring*	natural gas/condensates
	source rock thermal maturity		crude oils
	migration effects		solid bitumens
	in-reservoir alteration		oil sand/shales
Secondary Controls (Refining)	fractionation	*Man-Made*	gasoline
	conversion		distillate/residual fuels
	finishing		lubricants
	blending		waxes/greases/asphalts
Tertiary Controls (Weathering & Mixing)	evaporation		
	water-washing		
	biodegradation		all fugitive petroleums
	photo-oxidation		
	mixing with "background"		

These three "primary controls" impart very specific chemical features to naturally occurring petroleums, which will vary markedly between different oil provinces (e.g., coastal California versus Alaska; Kvenvolden et al., 1995). More subtle differences can even exist between oils produced from individual reservoirs within a single oil field (e.g., Kauffman et al., 1990; Peters and Fowler, 2002). As such, the primary controls impart very specific *genetic* features to petroleums that provide the primary basis for the chemical fingerprinting of naturally occurring petroleums in oil spill investigations (Stout et al., 2002; see Section 1.1.1 ahead).

Manmade petroleums are derivatives of naturally occurring petroleums that are produced in the course of petroleum refining. (Minor changes in chemistry may also occur during the production of natural petroleums from the subsurface, e.g., through phase separation, but these are not considered herein.) Manmade petroleums include various fuels (e.g., liquefied petroleum gas, automotive gasoline, and distillate and residual fuel oils), lubricants, and other products (e.g., waxes, greases, and asphalts) and their wastes (e.g., waste oils, bilge oils). Although some of the genetic chemical features of the naturally occurring *parent* petroleum are passed directly to the *daughter* petroleum products, the refining process can impart its own effects on the chemical composition of the resulting manmade petroleums and can, therefore, be considered as a "secondary control" on their chemical fingerprints. For example, distillation and thermal cracking can affect the distributions of some biomarkers and PAH (e.g., Peters et al., 1992; see also Section 1.3.2 ahead). Thus, in total, the chemical compositions of manmade petroleums are effected by the combined affects of the primary and secondary controls (Table 1-4). The chemical specificity imparted by these combined affects provides the basis for the chemical fingerprinting of manmade petroleums in oil spill investigations.

Both naturally occurring and manmade petroleums are transported from areas of their production to areas of their use. Most often it is in the course of this transportation when oil is accidentally spilled or intentionally discharged (Table 1-1). Once petroleum is released into the environment, it immediately is subjected to various physical, chemical, and biological processes that will affect its chemical composition (Jordan and Payne, 1980). These processes are collectively referred to as *weathering*, which can be considered a "tertiary control" on the chemical fingerprinting of petroleum in the environment (Table 1-4). Weathering will affect the chemical composition of fugitive petroleum at widely different rates. For example, evaporation of volatile constituents will occur much more rapidly than the biodegradation of recalcitrant constituents (see Section 1.3.3), and chemical fingerprinting of samples following an oil spill — sometimes collected decades later (e.g., Wang et al., 1994b, 1998; Reddy et al., 2002; Petkewich, 2002; Prince et al., 2002a; Short et al., 2004; see also Chapters 5 and 15 herein) — must consider these longer-term weathering effects. Because of this, both the shorter-term investigations of mystery oil spills and the longer-term investigations of known-source spills must account for the chemical changes to the spilled oil brought about by weathering and focus instead on those features that are un- or minimally affected by weathering (e.g., Douglas et al., 1996; Wang and Fingas, 1995c; Stout et al., 2001; Daling et al., 2002; see also Chapter 7 herein). In fact, in investigations of known-source spills, the effects of weathering are often what chemical fingerprinting is trying to measure — i.e., how has the spilled oil changed over time (e.g., Wang et al., 1994b, 1998).

Concurrent with the weathering, once petroleum is released into the environment it becomes subject to mixing with pre-existing anthropogenic contaminants or naturally occurring materials already present in the environment. These other sources of "background" hydrocarbons can contribute to the collective fingerprint of any floating oils, sediments or soils, waters, and tissues thought to be impacted by the spilled oil (only) and, there-

fore, need to also be considered as another "tertiary control" on the chemical fingerprint of spilled oil (Table 1-4). If unrecognized, the presence of pre-existing, background hydrocarbons can confound both the identification of a mystery spill's source or the assessment of any long-term effects of a spill on the environment. Even major oil spills from known sources can be confounded by alternative sources of hydrocarbons in the environment. For example, the *Amoco Cadiz* grounding, the Ixtoc-1 blowout, and *Exxon Valdez* groundings each were, in part, confounded by the presence of other anthropogenic and natural hydrocarbons in the spill area (Boehm et al., 1997; Page et al., 1988, 1995). Similarly, smaller oil spills and discharges in ports, which are typically areas with long-term, industrial activities surrounded by urbanized areas, are subject to a multitude of "urban background" hydrocarbons (see Section 1.3.4.4; Stout et al., 2004).

The chemical complexity imparted by the combination of primary, secondary, and tertiary controls on a spilled oil's fingerprint (Table 1-4) provides the oil spill investigator with both the challenges and the means to answer questions surrounding the source and fate of waterborne oil spills or operational discharges in the environment. In the following sections, the bases for these controls on crude oil and petroleum products are described in greater detail (Sections 1.3.1 through 1.3.4).

1.3.1 Primary Control — Crude Oil Genesis

Crude oil is an extremely complex mixture of tens of thousands of individual hydrocarbons and nonhydrocarbons. These compounds range from small, simple, volatile, and distinct compounds (e.g., methane) to extremely large, complex, nonvolatile, colloidally dispersed macromolecules (e.g., asphaltenes). The distribution of these compounds imparts certain physical properties on the oil, and it is these physical properties (e.g., density or viscosity) by which crude oils are generally classified, bought, and sold. These physical properties can be used to grossly classify crude oils as either *conventional* (light or medium) or *heavy*, where conventional oils have an API gravity above 20° or viscosity (at reservoir conditions) below 100 cP (Speight, 1991). Conventional crude oils can be generally classified based upon the predominance of the major hydrocarbon classes — paraffins, naphthenes, and aromatics — as shown in Figure 1-2 and described ahead.

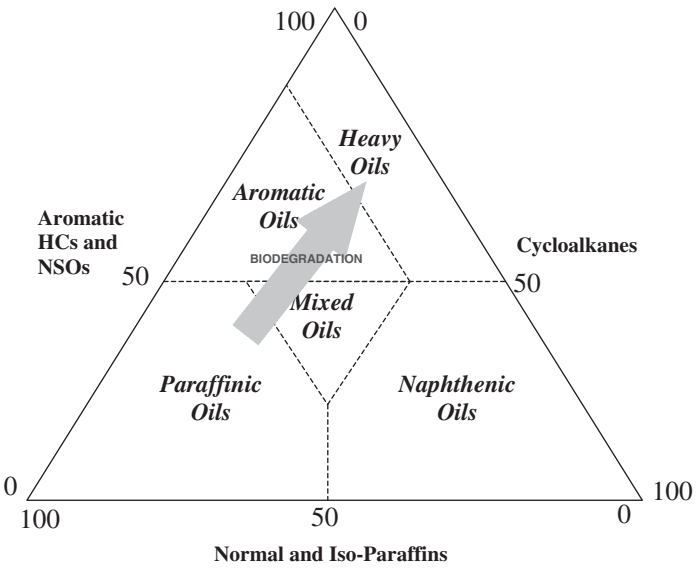

Figure 1-2 Ternary diagram showing the general compositional features of crude oils. After Tissot and Welte (1984). Arrow indicates general compositional change due to biodegradation.

All crude oils contain aliphatic and aromatic hydrocarbons and nonhydrocarbons. The proportions of these three major classes of compounds, and the specific distributions of individual compounds within each class, vary widely among crude oils (Tissot and Welte, 1984). The aliphatic hydrocarbons (sometimes called paraffins or saturates) include multiple compound types, such as normal alkanes (sometimes called normal paraffins), acyclic isoprenoids (sometimes called iso-paraffins), and monocyclic and polycyclic alkanes (collectively called naphthenes), the latter of which include sesquit-, di-, tri-, tetra-, and pentacyclic terpanes and sterane biomarkers (Figure 1-3). The aliphatic hydrocarbons com-

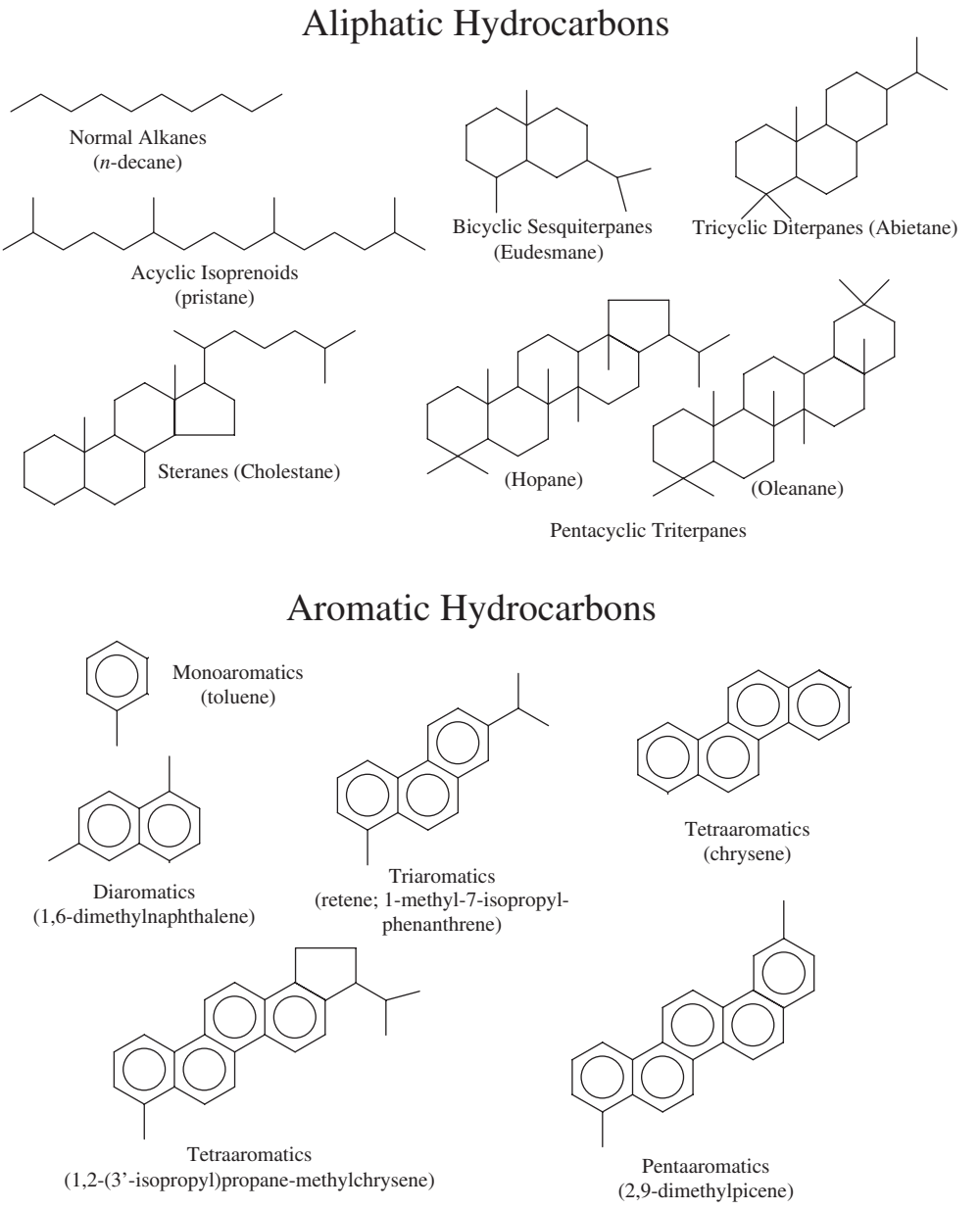

Figure 1-3 Examples of aliphatic and aromatic hydrocarbons in crude oils.

prise the largest weight percentage of most conventional crude oils, and are markedly reduced due to biodegradation in heavy crude oils (Figure 1-2; Speight, 1991; Hunt, 1996). Aromatic hydrocarbons include mono-aromatic (BTEX) and polycyclic aromatic hydrocarbons (PAH), the latter of which include various aromatic biomarkers (e.g., PAH with terpane or sterane skeletons; Figure 1-3). Nonhydrocarbons include polars, resins, and asphaltenes. Polars include compounds containing one or more nitrogen, sulfhur, or oxygen atoms (NSOs) that impart a "polarity" to the compounds. Nitrogen-containing compounds include benzocarbazoles, quinolines, and porphyrins, sulfhur-containing compounds include benzo-, dibenzo-, and polynuclear thiophenes, and oxygen-containing compounds include furans, phenols, and acids. Heavy crude oils contain higher percentages of aromatic hydrocarbons, predominantly PAH, and nonhydrocarbons (NSOs) than conventional crude oils (Figure 1-2; Speight, 1991; Hunt, 1996).

Many excellent reviews of crude oil composition are already available (Kinghorn, 1983; Tissot and Welte, 1984; Speight, 1991; Hunt, 1996), which allows this section to focus on those primary molecular features of crude oils that are most useful in oil spill fingerprinting. (Isotopic features of crude oils that are useful in oil spill fingerprinting are discussed in Chapter 6 herein.)

On a molecular level, it can be safely stated that no two crude oils are identical due to the variability in the primary controlling factors leading to their formation (Table 1-4). First, the nature of a crude oil's source rock organic matter type(s) varies widely with geologic age, lithology, and the particular conditions of the ancient depositional environment (e.g., lake, ocean, delta, etc.) in which these source strata accumulated (Tissot and Welte, 1984). Second, the variable kinetic conditions during the generation and expulsion of crude oil from the source strata will impart certain maturity-based features driven by various cracking, isomerization, and aromatization reactions on a crude oil. Third, migration can impart additional changes on the composition of an oil due to geochromatographic or "contamination" effects. Exploration geochemists have long understood the effect that the source rock organic matter type has on the molecular and isotopic composition of crude oil and have used this knowledge to improve crude oil exploration and production (Moldowan et al., 1985). The environmental applications of this knowledge have been increasingly applied to oil spill investigations over the past 35 years or so (see Section 1.3.1 below).

Primary chemical features imparted by the source, maturity, and migration of crude oil are of great value in chemical fingerprinting of both mystery and known-source oil spills. In particular, a variety of petroleum biomarkers offer a very high degree of specificity among crude oils (Table 1-5). Petroleum biomarkers are organic compounds in crude oil whose carbon skeletons can be unequivocally linked to those found in the naturally occurring biochemicals from which they are derived, i.e., biomarkers are "chemical fossils" (Eglinton and Calvin, 1967). The biochemicals that accumulated in ancient sediments are converted into biomarkers during the diagenesis and thermal maturation of the sediments over geologic time, i.e., during their conversion into petroleum source rocks (e.g., Seifert and Moldowan, 1978; Simoneit, 1986). Crude oil expelled from a given source rock sequence will contain biomarkers whose character testifies to the ancient biomass that had originally accumulated in the ancient sediments that later formed the source rock (Didyk et al., 1978; Moldowan et al., 1985; Peters et al., 1986; Volkman, 1988) and its lithology (Rubinstein and Albrecht, 1975). The relative abundances of more and less thermally stable biomarker isomers, or their degree of aromatization, will testify to the thermal maturity of the source rock strata when the oil was expelled (e.g., Seifert and Moldowan, 1978; Mackenzie et al., 1980; Radke, 1988; Farrimond et al., 1998). The migration of crude after its expulsion from the source strata can introduce new compounds "extracted" from carrier beds or reservoir rocks (Curiale, 2002) or experience subtle molecular fractionation (Larter et al., 1996; Matyasik et al., 2000). Finally, after reaching

Table 1-5 Inventory of Common Biomarker Compound Classes Available for Chemical Fingerprinting of Petroleum in the Environment. The Table Includes the Carbon Boiling Range over Which Each Class Occurs and the Dominant Mass/Charge (m/z) Ratio upon Which They Can Be Identified Using Gas Chromatography-Mass Spectrometry

Biomarker Compound Class	*Approximate Carbon Boiling Range*	*Mass Spectral Fragment Ions*
n-alkanes	C1 to C45*	*m/z* 85
acyclic isoprenoids	C12 to C19	*m/z* 113
bicyclic sesquiterpanes	C13 to C17	*m/z* 123
diterpanes	C19 to C24	*m/z* 191
extended tricyclic terpanes	C18 to C26	*m/z* 191
tetracyclic terpanes	C22 to C23	*m/z* 191
25-norhopanes (10-desmethylhopanes)	C25 to C33	*m/z* 177
pentacyclic triterpanes	C26 to C34	*m/z* 191
diasteranes	C23 to C26	*m/z* 217
regular steranes	C25 to C29	*m/z* 217 and 218
C-ring monoaromatic steranes	C23 to C26	*m/z* 253
triaromatic steranes	C26 to C29	*m/z* 231

* As measured by conventional (low temperature) gas chromatography.

a reservoir (but prior to its discovery and production) crude oil composition can further change due to water-washing by meteoric water, deasphaltening, or biodegradation in the reservoir (Connan, 1984; Seifert et al., 1984; Palmer, 1993; Cassani and Eglinton, 1991. The latter process, biodegradation, is generally responsible for the vast majority of heavy crude oil deposits worldwide (Tissot and Welte, 1984).

Thus, collectively these primary controls on crude oil (Table 1-4) invoke tremendous variability in the molecular compositions, including the biomarker "fingerprints," of conventional and heavy crude oils (Peters et al., 2005, and refs. therein; see also Chapter 3 herein). Because of this inherent variability, and their relative resistance to biodegradation on environmental time scales (see Chapter 11 herein), petroleum biomarkers have proven particularly useful in crude oil spill investigations (e.g., Kvenvolden et al., 1995; Daling et al., 2002; Page et al., 1995; Volkman et al., 1997; Kaplan et al., 1997, 2001; Stout et al., 2001; Wang and Fingas, 2003; Stout, 2003; Wang et al., 1999b, 2006). The reader is directed to Chapter 3 (herein) to see multiple examples of the biomarker variability among crude oils.

Figure 1-4 demonstrates some disparate primary features for two conventional crude oils. Figures 1-4a and b show the gas chromatography-flame ionization detection (GC/FID) chromatograms for a North Slope crude (NSC) and a Nigerian Bonnie Light crude oil blend, respectively. Both oils contain abundant normal alkanes, but each exhibits a different *n*-alkane profile and the Nigerian crude exhibits a slight odd-over-even predominance in the C_{25}+ normal alkanes. The NSC has a higher nC_{17}/Pr and lower Pr/Ph ratio than the Nigerian crude. Figures 1-4c and d show the partial *m/z* 191 mass chromatograms in each oil, which reveals a relative abundance of extended tricyclic triterpanes and homohopanes in the NSC, and a relative abundance of oleanane in the Nigerian crude (all versus hopane). The ratios of T_s/T_m vary between the oils, being lower in the NSC. Finally, Figures 1-4e and f show the distributions of dia- (rearranged) and regular steranes, which show a higher proportion of diasteranes and C_{27} regular steranes and a higher C29S/(C29S + C29R) ratio in the NSC than in the Nigerian crude. These differences collectively indicate that these oils' source rocks had varying proportions of marine and terrestrial organic matter and had expelled oil at different heating conditions. These differences in the biomarker distributions are more fully explained in the geochemical literature of these two oil

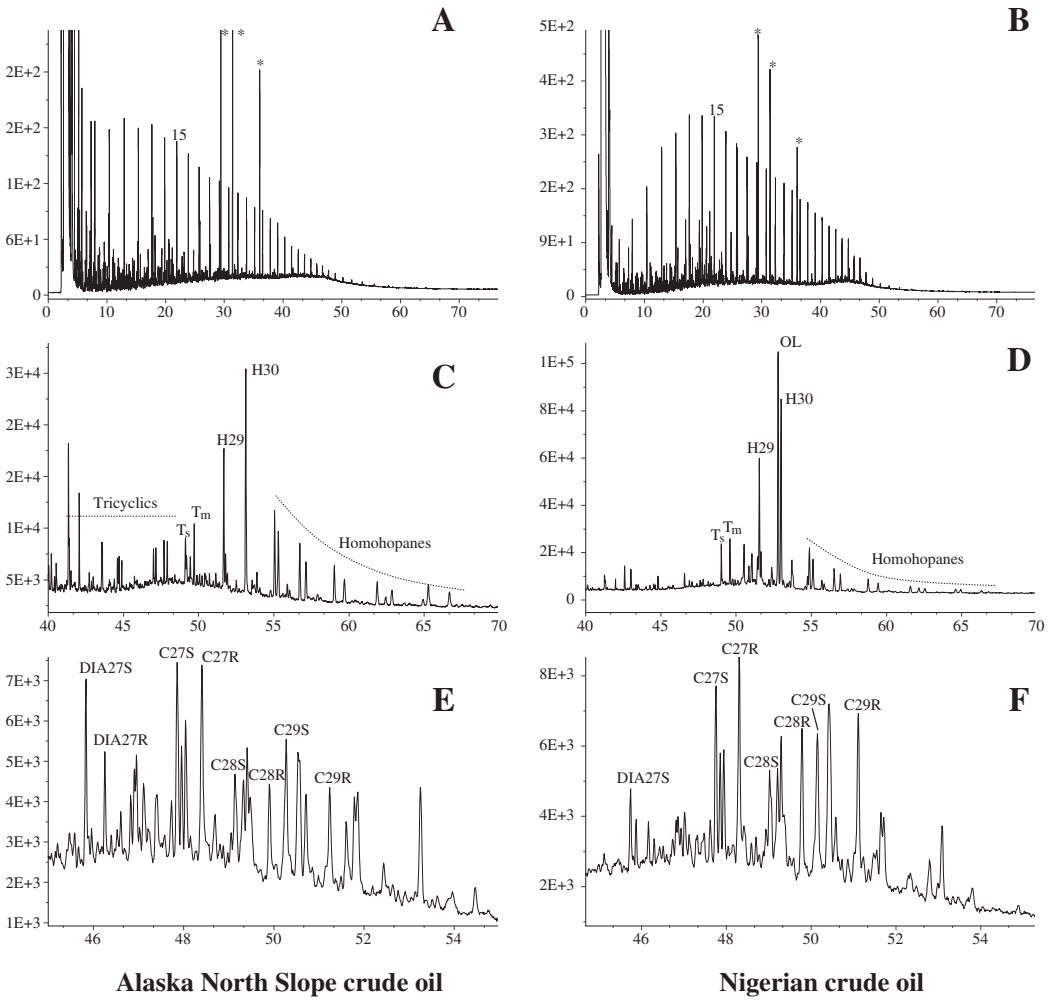

Figure 1-4 Example of the disparate primary chemical fingerprinting features in crude oils from the North Slope of Alaska and the Niger Delta, Nigeria. (a–b) GC/FID chromatograms, (c–d) partial *m/z* 191 mass chromatograms, and (e–f) partial *m/z* 217 mass chromatograms. * = internal standards, left to right: *o*-terphenyl, 5α-androstane and tetracosane-d_{50}.

provinces (e.g., Mackenzie et al., 1985; Ekweozor and Udo, 1988; Ukpabio et al., 1994). However, it should be clear that such differences will provide a strong basis to positively or negatively correlate a spilled crude oil to its candidate sources and to recognize any contribution to potentially impacted sediments or biota. This high degree of chemical disparity between crude oils parallels those recognized in crude oil spill investigations in California and Alaska, where significant primary chemical differences are known to exist between crude oils produced from the Miocene, coastal California basins, the Mesozoic North Slope of Alaska, and natural oil seeps east of Prince William Sound (e.g., Kvenvolden et al., 1995; Bence et al., 1996; and Chapter 15 herein).

The primary chemical differences demonstrated in Figure 1-4 are relatively obvious, given the significant geologic differences between the Mesozoic petroleum system in the North Slope of Alaska versus the Tertiary petroleum system in the Niger Delta. A simple

qualitative comparison of these oils' fingerprints (Figure 1-4) can reveal these marked differences. However, crude oils produced from a single petroleum system within a single petroleum province will exhibit far more subtle primary differences than are evident in Figure 1-4. Petroleum geochemists working within a petroleum province recognize these subtle differences, often recognizing "oil families," frequently using multivariate techniques (e.g., Telnaes and Dahl, 1986; Osadetz et al., 1995). Similarly, oil spill investigations in some areas may require precise quantitative (or semiquantitative) comparisons among oils with similar chemical fingerprints in order to facilitate their distinction (see Chapter 8 herein). This situation, for example, as might exist for a mystery oil spill in an offshore producing area where genetically similar crude oils are being produced from different production platforms, has led to the development of numerically or statistically based analysis of crude oils' primary (*genetic*) fingerprinting data in efforts to more quantitatively determine the degree of correlation between spill oils and candidate sources (e.g., Urdal et al., 1986; Stout et al., 2001; Daling et al., 2002; and Chapters 7 and 9 herein). In such cases, the subtle differences between oils produced from individual reservoirs or production zones may reveal important differences.

An example of this type of oil spill investigation is shown in Figure 1-5, which shows the GC/FID chromatograms and partial triterpane (*m/z* 191) distributions in a mystery spill oil found in an offshore operating area and in two (of the many studied) candidate source oils from nearby crude oil production platforms. All the crude oils produced in the area are "genetically" similar due to the overall consistency in the primary factors described above — source organic matter type, thermal maturity, and migration — within the local petroleum system. The overall similarity of the oils is evident in the highly comparable GC/FID fingerprints of the whole oils. For example, while the spilled oil obviously has been affected by evaporation, each oil is dominated by *n*-alkanes that exhibit a slight odd-over-even predominance in the C_{25}+ range (Figure 1-5). While there is no obvious difference among the oils based upon the GC/FID chromatograms, subtle differences in the primary factors lead to subtle differences in the triterpane distributions in the oils. Close inspection reveals that the relative abundance of gammacerane, a pentacyclic triterpane with a bacterial origin (ten Haven et al., 1989), varies among the oils. This variation eliminated Platform B as a source for the spilled oil (Figure 1-5). In this investigation, all other candidate crude oil sources were similarly eliminated on some subtle basis and Platform A was confirmed to be the likely source of the mystery oil spill.

1.3.2 Secondary Controls — Petroleum Refining

Crude oil is converted into marketable petroleum products through refining. Refined petroleum products are then transported from the refinery to market via trucks, pipelines, and product tankers and barges. The most common petroleum products transported generally reflect their economic value, with automotive gasoline, distillate fuel oils, and residual fuel oils being the most common petroleum products in use. For example, Figure 1-6 shows the approximate volumes of different petroleum products transported as cargo by product tankers and barges in U.S. waterways in 2003 (the last year data are available; WCUS, 2003). These data show that gasoline, distillate fuels, and residual fuels are the most commonly transported petroleum products in U.S. waters. Accidental releases of petroleum product cargo or fuel from vessels, pipelines, and coastal facilities, or intentional discharges of cargo washings or wastes (oily water, slops, and sludges) from vessels can produce both mystery spills and known-source spills. In addition, other sources of fugitive petroleum products in the environment can require investigation as to their source or impact (e.g., jettisoned aircraft fuel; Table 1-1). Thus, although crude oil is the most voluminous petroleum cargo (see above), refined

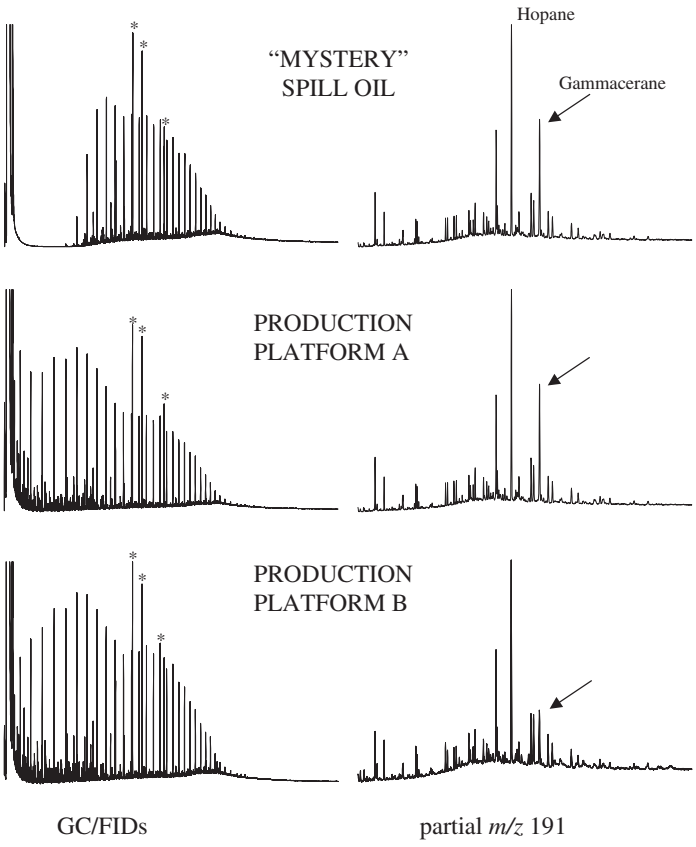

Figure 1-5 GC/FID chromatograms and partial *m/z* 191 mass chromatograms for a mystery oil spill and produced crude oil from two nearby production platforms. Differences in the relative abundance of gammacerane were sufficient to distinguish these (and other) genetically related oils from one another. * = internal standards.

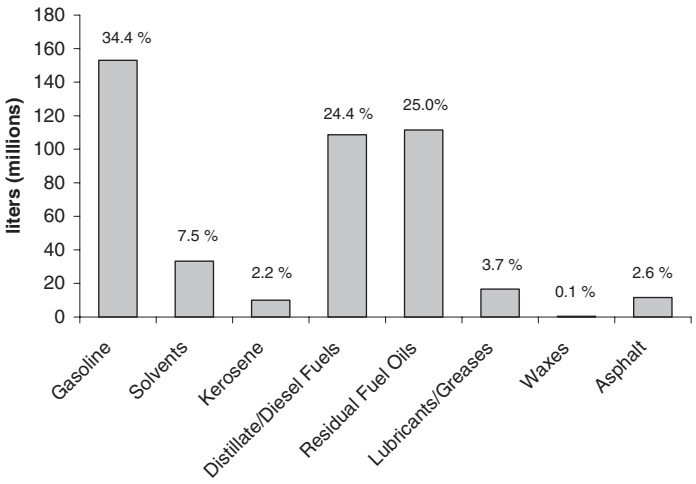

Figure 1-6 Summary of foreign and domestic petroleum products transported as cargo in U.S. waterways and ports in 2003. Volume calculated from short ton using average density. Data from WCUS (2003).

product spills and discharges regularly are the focus of chemical fingerprinting investigations. As such, it is important to recognize the effects of refining on the chemical fingerprints of different petroleum product types.

Refinery chemical engineers concern themselves with the bulk chemical and physical properties of the crude oil feedstock, without specific regard for the molecular details that are of interest in oil spill fingerprinting. The

crude oil feedstock processed at any given refinery can include a single "local" crude oil commingled from genetically similar crude oils from within a single basin or a dynamic blend of multiple and genetically dissimilar crude oils produced from different basins, often obtained from different continents. In either case, the commingled production of similar crude oils or the blending of disparate crude oils will result in a crude oil feedstock that exhibits the collective and mass-balanced "primary" chemical (elemental, molecular, and isotopic) features of the individual parent crude oils in the feedstock. As such, the crude oil feedstock at any given refinery at any given time will still exhibit a unique set of primary features (Table 1-4). These features still offer a high degree of chemical specificity that is, at least in part, passed along to the daughter petroleum products or altered to reflect the refining process.

The modern petroleum refinery has evolved from a simple turn-of-the-century facility whose goal was to produce fuel oils for heating and lighting (while discarding then uneconomical gasoline-range hydrocarbons) to modern operations of varying complexity focused on squeezing as much automotive gasoline (the most economically valuable product) out of a barrel of crude oil as feasible. Modern refineries are complex industrial plants where various crude oil feedstocks are utilized to produce not only gasoline, but other economically valuable distillate and residual products. Figure 1-7 shows the complexity that can exist at a modern refinery. For an in-depth understanding of refinery operations, we recommend one of several excellent reference texts on the subject (Gary and Handwerk, 1984; Speight, 1991; Leffler, 2000).

The dominant three processes at any refinery are (1) fractionation, (2) conversion, and (3) finishing (Speight, 1991). Fractionation involves the separation of a crude oil feedstock into various "cuts" that are defined by their boiling points. These cuts, obtained by both atmospheric and vacuum distillation (Figure 1-7), traditionally include light gases (C_1 to C_4 hydrocarbons), straight run naphthas, kerosene, light and heavy gas oils, vacuum distillates, and residual material (bottoms). The approximate boiling and carbon ranges of these distillate cuts are shown in Table 1-6. Few of these distillation cuts are used directly in products (anymore), but rather they are fed to other units in the refinery, either for conversion or for blending into commercial products. Conversion, as the name implies, changes the molecular composition of a distillation cut by cracking larger molecules into smaller ones (thermal or catalytic cracking), sometimes in the presence of excess hydrogen (hydrocracking), stripping hydrogen to convert naphthenes into aromatics or normal paraffins into branched paraffins (catalytic reforming), combining two lower-octane molecules into one higher-octane molecule (alkylation), or converting the chemical structure from one configuration to another (isomerization; Figure 1-7). The finishing process typically involves sweetening and blending of multiple straight-run and converted intermediates into finished petroleum products that meet the required performance and regulatory specifications.

The petroleum products at the right of Figure 1-7 have a range of boiling distributions, which generally increase from top to bottom in the figure. Examples of the chemical fingerprints obtained via Tier 1 GC/FID (Section 1.2.2) of representatives of these different products are shown in Figure 1-8. The carbon (boiling) ranges of these products vary widely and chemical fingerprinting can rely upon these gross differences to distinguish one petroleum product from another.

The detailed chemistry of these various petroleum products depends in part upon the nature of the crude oil feedstock, which, as described above, is highly variable. Furthermore, the detailed product chemistry is a function of the specific operational conditions within a given refinery. Since no two refineries operate in an identical manner, and even a single refinery can change operations daily, the chemical composition of petroleum products on a molecular level is expected to widely vary, while still meeting any required product specifications. This is indeed the case and is why chemical fingerprinting of petroleum

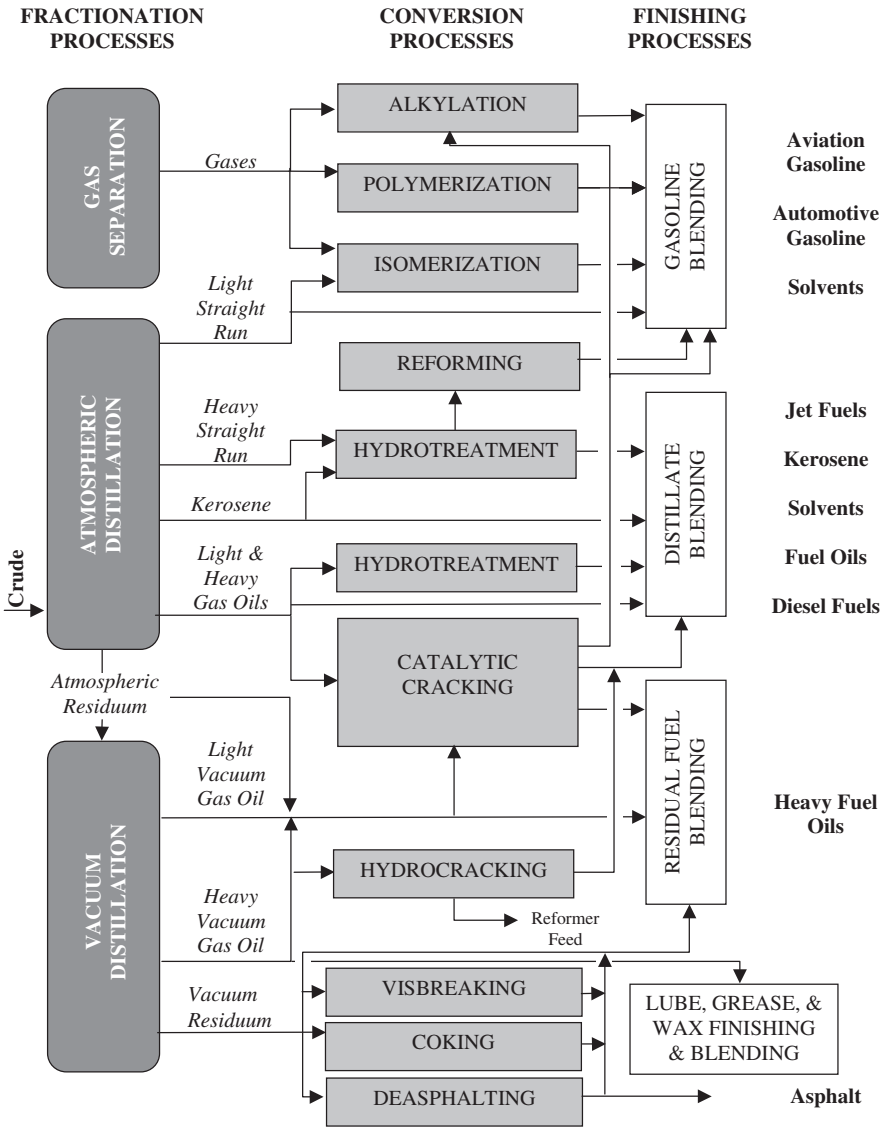

Figure 1-7 Schematic flowchart of a modern complex refinery highlighting the distillation, conversion, and finishing processes used in the production of petroleum products.

products has proven a useful tool in all types of environmental forensic investigations (e.g., Kaplan et al., 1997; Stout et al., 2002a), not just waterborne oil spills.

1.3.2.1 Gasoline

Although automotive gasoline is the most voluminous petroleum product produced and transported, the sources of waterborne gasoline spills and discharges are rarely a "mystery" and their persistence in the surface water environment is relatively short-lived due to their volatility and solubility. As such, the chemical fingerprinting investigations of gasoline spilled onto open water are rare. Occasionally, gasoline spilled onshore into storm water drains can enter waterways through

Table 1-6 Typical Distillation Fractions and Petroleum Products Produced from Crude Oil. (Boiling and Carbon Ranges Are Approximate and Can Vary Slightly with Refiner)

	Boiling Point at 1 atm (°C)	*Carbon Range (as n-alkane)*
Distillation Fractions		
Gases	−160–0	C1–C4
Light Straight Run	25–90	C5–C6
Heavy Straight Run	85–190	C6–C10
Kerosene	160–275	C9–C15
Atmospheric Gas Oils	250–425	C13–C27
Vacuum Gas Oils	370–575	C22–C45
Vacuum Residuum	>540	>C40
Petroleum Products		
Aviation Gasoline	25–175	C4–C10
Automotive Gasoline	25–215	C4–C12
Volatile Solvents	70–250	C6–C14
Commercial Jet Fuel	80–290	C7–C16
Kerosene (Fuel Oil #1)	200–290	C11–C16
Fuel Oil #2	150–400	C9–C25
Diesel Fuel #2	150–425	C9–C27
Heavy (Residual) Fuel Oils	150–575	C9–C45
Lubricating Oils	270–525	C15–C40

outfalls and require chemical fingerprinting to determine the source. Similarly, small spills during fueling or boat repairs at marinas may have a cumulative effect in some environments and therefore can be investigated using chemical fingerprinting.

Modern automotive gasoline contains hundreds of hydrocarbons and nonhydrocarbons boiling in the C_4 to C_{14} range (Figure 1-8A). The exact number and distribution of these compounds depend on refining processes employed in the production. For example, gasolines blended to contain a high percentage of alkylate or reformate can contain less than half the number of detectable hydrocarbons than in gasolines containing mostly cracked naphthas (Hamilton and Falkiner, 2003). The complexity and composition of automotive gasoline and its chemical fingerprinting in the environment have been recently reviewed (Stout et al., 2006a). This review has shown that modern gasolines are a complex mix of highly refined intermediate blending stocks — such as polymer gas, alkylate, straight-run naphtha, reformate, and cracked naphtha (Figure 1-7) — and various additives (e.g., oxygenates). Historically, a significant proportion of gasoline included a straight-run naphtha blending stock that might retain certain primary features of the crude oil feedstock (e.g., adamantane or C_7 isoparaffin distributions; Stout and Douglas, 2004). However, due to the complicated blending of multiple refinery intermediates in the production of modern gasoline (Figure 1-7), different gasoline grades and brands can exhibit markedly different chemical fingerprints reflecting the blending practice of a particular refiner. Some features in gasoline are more useful than others in distinguishing different gasoline sources. For example, most modern gasolines are blended to include an alkylate blending stock produced during alkylation. The alkylate blending stock is enriched in high-octane trimethylpentane isomers, the abundance and proportions of which can vary depending on the specific nature of the alkylation process and blending practice (Beall et al., 2002). As such, the relatively rare oil spill investigations involving gasolines can still benefit from detailed chemical fingerprinting in an attempt to distinguish the source of waterborne gasoline or to trace its impact in the environment. However, the effects of weathering on waterborne gasoline, which due to its relatively low boiling range (Figure 1-8A), is subject to rapid evaporation that can quickly remove many potentially diagnostic features. In such instances, chemical fingerprinting of the highest boiling fractions of any gasoline residues, e.g., in the C_9+ range may still yield useful results.

1.3.2.2 Distillate Fuels

Distillate fuels, on the other hand, are commonly the focus of waterborne oil spills due to the frequency by which they are transported as cargo (Figure 1-6) and their widespread use as fuels in marine diesel engines. Middle distillate fuel refers to a category of fuels, largely

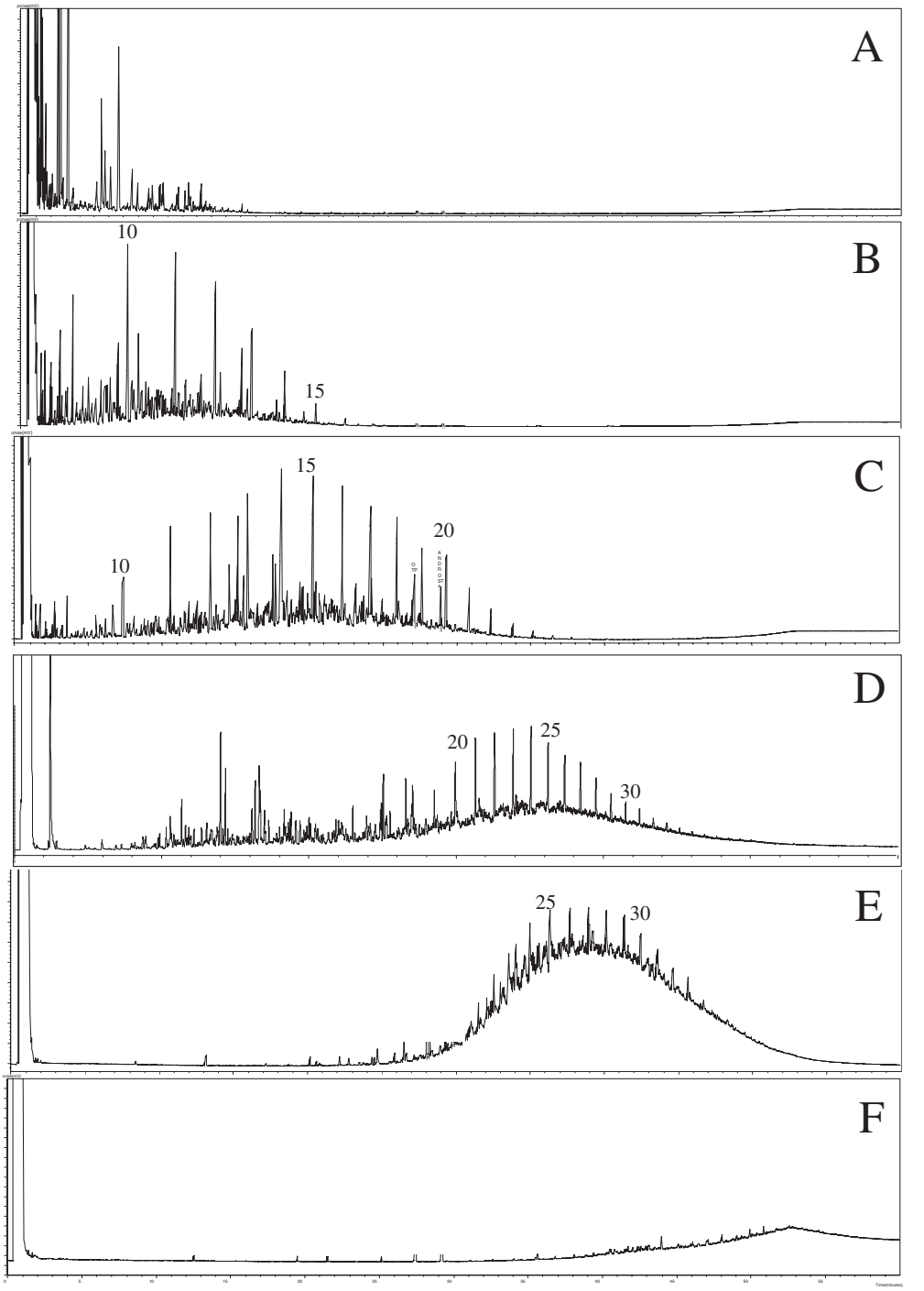

Figure 1-8 Gas chromatography-flame ionization detection (GC/FID) chromatograms of distinct petroleum products. (A) automotive gasoline, (B) jet fuel A, (C) diesel fuel #2, (D) heavy fuel oil #6, (E) lubricating oil, and (F) petroleum asphalt. # = *n*-alkane carbon number.

classified depending on their intended use. They include civilian and military jet engine fuels, on-road diesel (truck and bus), off-road diesel (diesel-electric locomotives, heavy equipment, and farm machinery), marine diesel engine fuels, nonaviation gas turbine fuels, and domestic and commercial heating fuels. Although each distillate fuel type's specifications are defined by various ASTM standards, the primary distinguishing features of relevance to chemical fingerprinting of the different distillate fuel types relate to their boiling distributions and sulfur contents. In addition, the specific molecular characteristics of a distillate fuel type will depend, in part, on the primary characteristics inherited from the crude oil feedstock.

As their name implies, the production of distillate fuels primarily involves fractionation by distillation. The primary effect of distillation on the different distillation cuts (Table 1-6) is to alter the distributions of compounds depending upon their volatility. An example of this effect appears in Figure 1-9, which shows the distributions of tricyclic triterpane biomarkers in a parent crude oil feedstock and in a middle distillate cut of the feedstock. These tricyclic triterpanes occur in the C_{20} to C_{26} range, i.e., near the higher boiling range of most distillate fuels. As can be seen, there is a gradual reduction in the abundance of tricyclic triterpanes with increasing molecular weight (decreasing volatility) in the distillate cut (Figure 1-9). This type of distillation effect can alter any ratios between compounds with varying volatility (e.g., Peters et al., 1992), particularly those that boil nearer to the end points of the distillate fuel.

Oppositely, molecular features that exist nearer to the middle of any distillate cuts and fuels often are inherited directly from the crude oil feedstock without modification. For the more broad-boiling distillate fuels, these features can include ratios between comparably boiling isoprenoids (pristane/phytane), proportions of methyl-phenanthrene isomers, or distillate range biomarkers such as sesqui- or diterpanes (see Table 1-5 and Chapter 3 herein). Proportions of *n*-alkanes-to-isoprenoids (nC$_{17}$/Pr or nC$_{18}$/Ph) can be altered from the feedstock during blending of distillate blending stock to produce higher cetane fuels, which typically contain a high proportion of *n*-alkanes (see Figure 1-11 below, in which the nC$_{17}$/Pr ratio is increased in the cracked distillate relative to the straight-run distillate).

The five methyl-phenanthrene isomers all boil in the C_{20} range and as such can be passed unchanged from the crude oil feedstock into a straight-run distillate. The proportion of these isomers is a primary feature related to the thermal maturity of the source strata, which can be expressed by ratios involving the less stable α-type and more stable β-type isomers (Radke et al., 1982; Radke, 1988). However, conversion refinery processes can alter the distribution of the methyl-phenanthrene isomers — and create new compounds typically absent in the feedstock. Specifically, catalytic cracking can reduce the proportion of the less stable α-type (9-, 4-, and 1-) methyl-phenanthrene isomers and produce methyl-anthracene isomers that are not typically present in crude oil. (An example of this is shown in Chapter 10 herein.)

The sesquiterpanes with a drimane skeleton are "low-boiling" biomarkers that occur in the C_{13} to C_{16} range (Peters et al., 2005). These compounds can provide diagnostic information about the parent crude oil feedstock used in the production of distillate fuels. Under some oil spill circumstances, these biomarkers can distinguish and correlate distillate fuel sources from spilled fuel (Stout et al., 2005, Wang et al., 2005). For example, Figure 1-10 shows the distributions of sesquiterpanes in a spilled jet fuel and a candidate source jet fuel from a nearby storage facility. The patterns of sesquiterpanes were distinct between these fuels, indicating that the candidate source from the storage facility was not the source of the spilled jet fuel.

Another group of compounds that can be useful in the characterization distillate fuels are normal alkylcyclohexanes (as revealed in *m/z* 83 mass chromatograms). *N*-alkylcyclohexanes are 6-carbon cyclic hydrocarbons

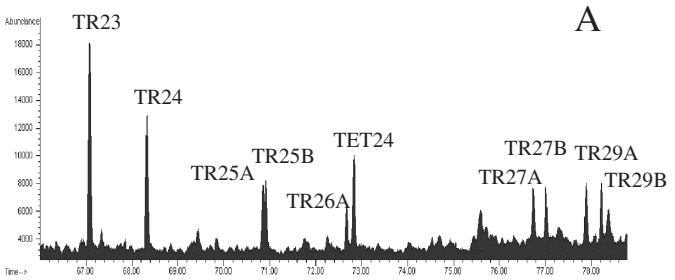

Figure 1-9 Partial *m/z* 191 mass chromatograms for a (A) parent crude oil feedstock and (B) daughter distillate cut showing the progressive loss of tricyclic triterpanes due to distillation effects.

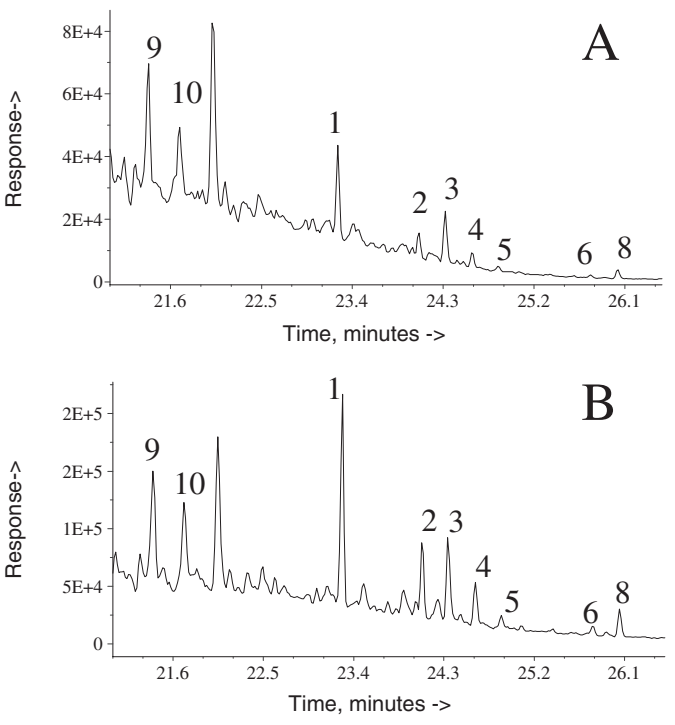

Figure 1-10 Partial *m/z* 123 mass chromatograms showing the distributions of sesquiterpanes in (A) a spilled jet fuel and (B) a candidate source oil. Peak numbers correspond to compounds described by Alexander et al. (1984). The large peak between peaks 10 and 1 is unidentified.

with different numbers of straight-chained or normal "alkyl" side chains — for example, CH-1 (cyclohexane with one methyl group attached), CH-2 (cyclohexane with an ethyl group attached), etc. The distribution of the various CH-1 to CH-18 alkyl-cyclohexanes is indicative of both a petroleum product's nature and type under most weathering states (Kaplan and Galperin, 1997). Thus, as the refinery blends various middle distillate fuels to meet

its customer specifications using distinct blending stocks, it will produce distillate fuels with distinctive *n*-alkylcyclohexane distributions (Song, 2000; Stout et al., 2004, 2006).

Under most circumstances the production of finished distillate fuels that meet modern specifications from a straight-run crude oil distillate(s) is noneconomical. This fact, combined with the availability of many refining intermediate streams (Figure 1-7). Most modern refineries blend cracked intermediated products (e.g., light- and mid-cut cycle oils, visbreaker or coker gas oil, or hydrocrackate) with straight-run distillate products [e.g., light and heavy straight-run (virgin) distillates] in order to produce their distillate fuels (Jewitt et al., 1993). Cracked products can exhibit distinct *secondary* chemical fingerprinting features (Table 1-4) produced during various refinery conversion processes. For example, Figure 1-11 shows the GC/MS total ion chromatograms for a straight-run distillate (Figure 1-11A) and a cracked intermediate distillate (Figure 1-11B) produced from a single crude oil feedstock from the Williston Basin. The straight-run gas oil represents a "slice" of the Williston Basin parent crude oil feedstock and, as such, retains any primary chemical features of the feedstock unaffected by the distillation process (e.g., pristane/phytane ratios, sesquiterpane distributions, and relative abundance of alkylated dibenzothiophenes to alkylated phenanthrenes). The cracked intermediate, however, contains lower relative abundances of isoprenoids (e.g., pristane and phytane relative to *n*-alkanes) and a three-times higher concentration of PAHs than the straight-run distillate. These differences indicate that excess *n*-alkanes and PAH apparently were formed, or released from asphaltenes, due to the thermal stresses of the catalytic cracking process. In addition, the distribution of individual PAH groups, as reflected by the relative abundance of alkylated dibenzothiophenes to alkylated phenanthrenes, also has been significantly decreased by the cracking process (Figure 1-11C and D).

Because the sulfur content is an important specification of distillate fuels, the distribution and proportions of sulfur-containing com-

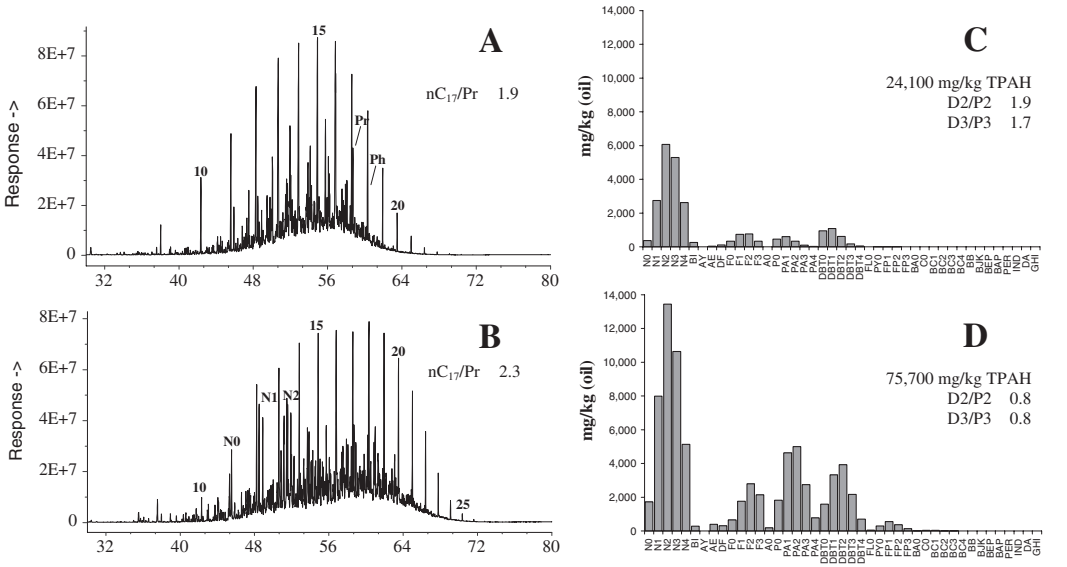

Figure 1-11 Chemical fingerprints for two distillate fuel blending stocks. (A) GC/MS TIC for straight-run (virgin) gas oil, (B) GC/MS TIC for light cracked distillate (cycle oil), (C) PAH histogram for straight-run gas oil, and (D) PAH histogram for light cracked distillate. # = *n*-alkane carbon number, Pr = pristane, Ph = phytane; for PAH analytes, see Table 1-2.

pounds in middle distillate fuels can prove useful in oil spill investigations of these fuels. The lower sulfur requirements of modern on-road diesel fuel #2 (<50 or 500 ppm) require that refineries employ some form of distillate desulfurization in order to produce low or ultralow sulfur diesel fuels. Most commonly, this requires the deep hydrodesulfurization (HDS) of distillate blending stocks, which reduce sulfur-containing compounds by replacing sulfur with hydrogen (and producing H_2S). Many sulfur-containing compounds, e.g., benzothiophene and sterically hindered alkyl-benzothiophenes like 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, and 4-ethyl-6-methyldibenzothiophene, are resistant to HDS (Song, 2000), and therefore the distribution of individual dibenzothiophene isomers can be altered during HDS, which could be useful in some oil spill investigations. (See Chapter 4 herein.)

The sulfur content in distillate fuels is expressed by the relative concentration of alkylated naphthothiophenes, benzothiophenes, or dibenzothiophenes, which are the predominant forms of organic sulfhur within the distillate boiling range (Mossner and Wise, 1999). Most commonly, the relative concentration of the dibenzothiophenes is reflected in the ratio of alkylated dibenzothiophenes to the comparably boiling alkylated phenanthrenes. Both groups of compounds respond similarly in the environment and thereby retain their proportions during environmental weathering (Douglas et al., 1996). Ratios between the two-carbon (C_2) and three-carbon (C_3) alkylated derivatives of dibenzothiophenes and phenanthrenes — D2/P2 and D3/P3 — can help distinguish distillate fuels refined from sweet and sour crude oil feedstocks and/or fuels subject to different degrees of desulfurization (e.g., see Figure 1-11). For example, the relative abundance of alkyl-dibenzothiophenes was a distinguishing feature in identifying the source of a "mystery" diesel fuel spill in the Lachine Canal, Quebec, Canada (Wang et al., 2000). Among other features, including comparable methyl-phenanthrene ratios, these authors showed that the ratios of D2/P2 and D3/P3 were virtually identical between the mystery spill samples and one of the two candidate sources.

As noted above, distillate fuels refined to contain predominantly or exclusively a straight-run distillate component, a difference in the relative abundance of alkyl-dibenzothiophenes to alkyl-phenanthrenes may be identical to that of the crude oil feedstock. This was apparently the case for marine diesel fuels refined from Alaska North Slope (ANS) crude oil versus the *Exxon Valdez* cargo oil, both of which exhibited comparable D2/P2 and D3/ P3 ratios (Page et al., 1995). However, the ANS diesel could be distinguished from the cargo oil on the basis of the absence of higher boiling chrysenes in the ANS diesel.

1.3.2.3 Residual Fuels

Residual fuels, as their name implies, are predominantly comprised of the less valuable residues from the various fractionation and conversion processes at a refinery. These fuels are used in marine diesel engines and boilers and in industrial power generation. They require preheating prior to their use due to their high viscosity, relative to distillate fuels, and are often transported by heated barges. As the need for gasoline in distillate fuels increases and refining operations "squeeze" more of these products from crude oil, the nature of the residual hydrocarbon mixtures has become increasingly "heavier" in character. This practice, and the resulting effect on the chemistry residual fuels, is described thoroughly in Chapter 10.

The molecular composition of residual fuels derives, in part, from the molecular composition in the crude oil feedstock. The highest boiling distillation residuum of the feedstock is the primary blending stocks used in the production of residual fuels (Figure 1-7). Molecular features contained within these highest boiling residues largely will be inherited by the residual fuel. These would include the features of most higher-boiling biomarkers such as pentacyclic triterpanes, steranes, aromatic steranes, and porphyrins. However, the effects of heating during distillation, particularly vacuum distillation, can alter various bio-

marker thermal parameters in residual fuels containing vacuum distillation residuum, i.e., flasher bottoms (Peters et al., 1992; Pieri et al., 1996). Peters et al. (1992) showed that biomarkers with comparable boiling points in a parent crude oil feedstock were variously depleted or enriched compared to daughter refinery streams; e.g., vacuum gas oil or vacuum residuum. Such changes were attributed to either (1) a preferential preservation (i.e., a greater thermal stability) of certain biomarkers or (2) preferential formation (cracking from bound precursors in the oil) of certain biomarkers during heating. Such changes do not preclude the use of biomarker-based ratios in characterizing a spilled residual fuel to its source, but they can confound any attempt to determine the crude oil parent of the spilled fuel. See Chapter 10 for additional information on the compositions of residual fuel oils.

1.3.2.4 Lubricating Oils

Lubricating oils are produced from the finishing (deasphaltening, hydrotreatment, solvent extraction, and dewaxing) of heavy vacuum gas oils (Figure 1-7). The resulting family of base oils is blended to yield different types of lubricating and hydraulic oils that meet various physical- and performance-based properties. Figure 1-12 shows a series of GC/FIDs for different types of base oils. The chemical compositions of the base oils are complex and poorly understood due to the overwhelming predominance of hydrocarbons (straight, branched, cyclic, and aromatic) that cannot be resolved by conventional GC methods. As such, the predominant feature of the GC/FID chemical fingerprints of lubricating oils is the shape of the UCM. Figure 1-12 shows, however, that some base oils contain *n*-alkanes and biomarkers, the latter of which sometimes can appear as the only resolved peaks in some lubricating oils (e.g., Figure 1-12D). The biomarker distributions in lubricating oils will largely reflect those inherited from the crude oil feedstock and thereby provide a high degree of specificity in the characterization of spilled lubricating oils.

1.3.2.5 Oily Waste/Bilge Water Discharges

Bilge water consists of drippings of various liquids that accumulate in the bottom of a boat. Although bilge water is not comprised of any particular petroleum product, it is worth mentioning here since it most often contains a mixture of petroleum products found onboard a given vessel. As such, the chemical fingerprint of any oily waste contained within the bilge water will reflect the collective features of the fuels, lubricants, and solvents in use on a given vessel. The discharge of oil in bilge water is prohibited in navigable waters of many countries. In order to satisfy the prevailing regulations, most vessels pass bilge water through an oil–water separator to isolate oils until they can be off-loaded at the dock or burned on-board. In addition, large ships install sensors that trigger alarms and the need for immediate corrective actions if the bilge water effluent contains more than 15 parts per million (ppm) of oil and grease. Despite these precautions, poor engine and oil–water separator maintenance are suspected causes of significant chronic petroleum discharges above regulatory concentration limits in coastal waters (Costa, 2001). In addition, the intentional and illegal bypass of the bilge water oil–water separator, unfortunately, is not an uncommon practice.

The chemical fingerprint of oily waste will vary based on the type of materials and waste management practices on-board. Consequently, the chemical composition of hydrocarbons and other chemicals within the waste stream is expected to be highly variable and often reflect the presence of multiple petroleums. Figure 1-13 shows the GC/FID for a bilge oil that exhibits multiple *n*-alkane and UCM maxima suggesting the presence of middle distillate fuel oil (MFO), heavy fuel oil (HFO), and lubricating oil. Characterization of the oily wastes on-board vessels would employ the same chemical fingerprinting as for the fuels and lubricants used on vessels (described above). Specifically, the distributions of PAHs and biomarkers can be used to characterize oily wastes and their associated discharges.

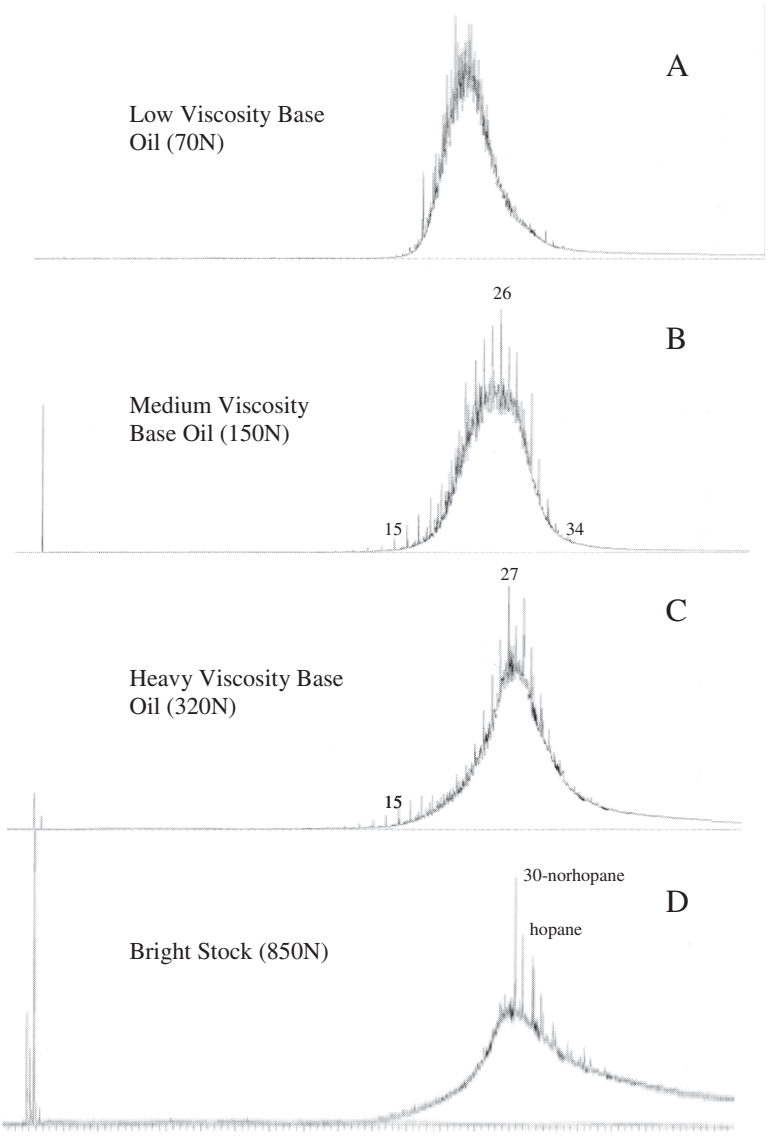

Figure 1-12 GC/FID chromatograms for four base oils used in the manufacture of lubricating oils. (A) low-viscosity base oil (70N), (B) mediumviscosity base oil (150N), (C) heavy-viscosity base oil (320N), and (D) bright stock (850N).

1.3.3 Tertiary Controls — Weathering

In addition to primary and secondary controls on the chemical fingerprints petroleum imposed during petroleum's generation and refining (Sections 1.3.1 and 1.3.2), petroleum released into or onto water immediately is subjected to the collective effects of multiple, naturally occurring chemical, physical, and biological processes, collectively referred to as *weathering*. Weathering will alter the chemical fingerprint of spilled or discharged oil so that its fingerprint may not "match" the original oil.

The most important weathering processes following a release of oil to fresh or marine waters include processes such as spreading, evaporation, dissolution, dispersion into the

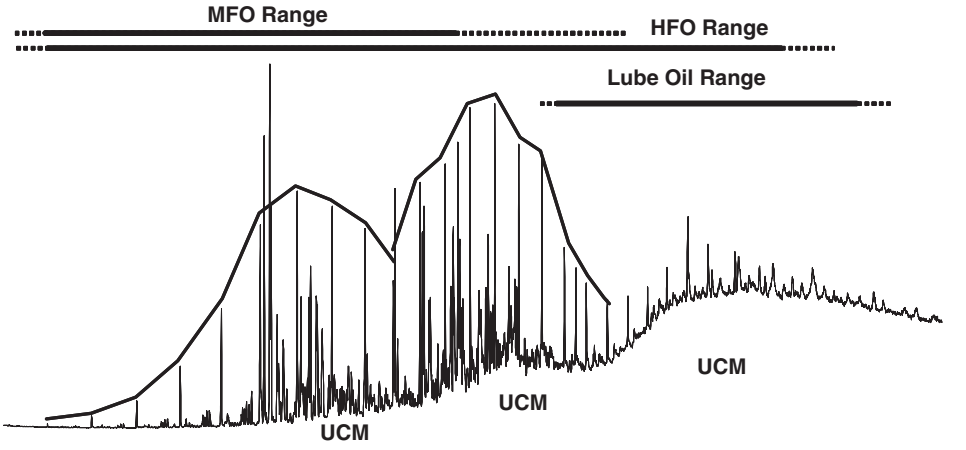

Figure 1-13 GC/FID of a bilge oil containing a mixture of different petroleums. (Modified from Emsbo-Mattingly, 2006.)

water column, formation of water-in-oil emulsions, photochemical oxidation, microbial degradation, adsorption to suspended particulate matter, and stranding on the shore or sedimentation to bottom sediments (Payne and McNabb, 1985; Payne et al., 1987; Mackay and McAuliffe, 1988; Neff, 1990; Wolfe et al., 1994; Wang and Fingas, 1995b). Generally, the mostly physical processes (e.g., dispersion, spreading, emulsification, tar ball formation) do not alone substantially alter the chemical fingerprint of spilled oil. However, these processes largely will affect the rates by which and degrees to which an oil will evaporate, dissolve, or biodegrade — i.e., all processes that will alter a spilled oil's chemical fingerprint. For example, as an oil spreads, the rates of evaporation and dissolution will increase as a greater mass of oil becomes exposed to air and water, respectively, thereby increasing the rates of evaporation and dissolution, respectively. As volatile and soluble constituents preferentially are lost, the physical properties and consequent spreading of the spilled oil are further altered. Thus, the physical behavior and chemical composition of a spilled oil are interrelated and dynamic (Fingas, 1995; Michel et al., 1995).

Extensive reviews on the effects of weathering on spilled oil are found elsewhere (Mackay and McAuliffe, 1988; NRC, 2003). In this section, the effects of weathering on the chemical composition of spilled oils generally are described in terms of their effect on the "chemical fingerprint" of the oil. As such, we focus on the effects of evaporation, dissolution, biodegradation; however, other processes are also considered.

1.3.3.1 Evaporation

Evaporation and dissolution are the primary weathering processes affecting the chemical composition/fingerprint of spilled oil in the hours or days following an oil spill. Although spill-specific conditions (e.g., thickness, mousse formation, wind speed, ambient water/air temperature) will affect the rate of evaporation, under all conditions the propensity for evaporation is ultimately governed by the vapor pressure of individual constituents.

Compounds in petroleum that boil at temperatures below about 270°C, or have vapor pressures greater than about 0.1 mm Hg, tend to evaporate rapidly from the surface of spilled crude oil (Stiver and Mackay, 1984; Fingas, 1995). Included in this category are alkanes from methane to *n*-C_{15} and one- and two-ring aromatics ranging from benzene through alkylnaphthalenes (Bobra et al., 1979; Wolfe et al., 1994). The rate of evaporative loss depends on multiple factors, but in general, compounds with boiling points below about 200°C (~C_{12}) will evaporate within a 24-hour

period of a spill (Stiver and Mackay, 1984). The mass reduction attributable to evaporative loss will depend on the composition of the spilled oil, with the percent mass reduction being inversely proportional to the density of the petroleum (e.g., Mackay and McAuliffe, 1988). Under some rare circumstances — e.g., high altitude, 22°C, and turbulent water — evaporative losses can reduce compounds up to C_{36} (Prince et al., 2002b).

The effect of evaporation on the fingerprint of a spilled oil will depend on the oil's original composition. Obviously, spilled gasoline may evaporate completely within a few hours, effectively eliminating its fingerprint, whereas a heavy crude oil will experience minimal losses or change to its fingerprint due to evaporation.

Figure 1-14 shows the effects of evaporation on a 34°API crude oil spilled following the structural failure of an aboveground storage tank (AST) during Hurricane Katrina (Stout et al., 2006b). Figure 1-14A shows the slightly evaporated crude recovered from inside the failed AST two weeks after the failure. It shows a mild loss of hydrocarbons boiling below *n*-C_{14}. Figure 1-14B shows the residual crude oil recovered from a surface soil

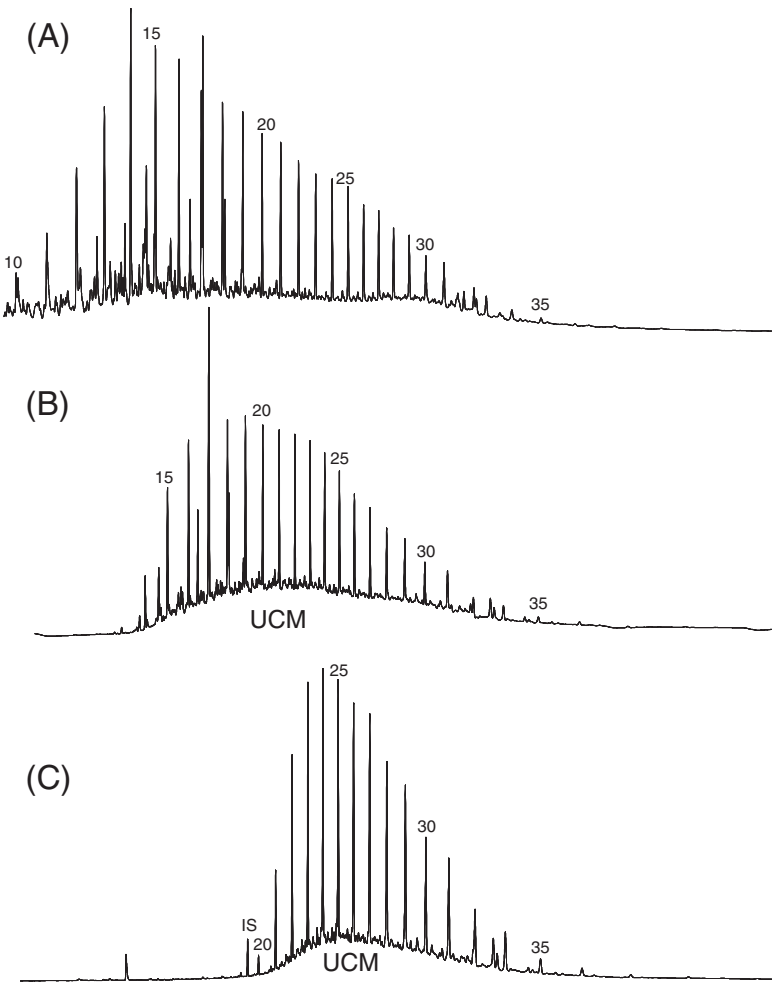

Figure 1-14 GC/FID chromatograms showing the progressive loss of compounds from a 34°API crude oil spilled following Hurricane Katrina. (A) slightly evaporated crude oil, (B) moderately evaporated crude oil, and (C) severely evaporated crude oil.

impacted by the crude oil approximately two weeks after the spill. In this sample, the crude oil has experienced evaporative loss of compounds below *n*-C_{19} resulting in an increase in the relative mass of the UCM. Figure 1-14C shows the residual crude oil recovered from an oily "bathtub ring" on the side of a building, also about two weeks after the spill. This oily residue has experienced evaporative loss of most all compounds boiling below *n*-C_{20}.

As demonstrated by the crude oil shown in Figure 1-14, some spilled fuels (e.g., gasoline or kerosene) or high-API gravity crude oils may evaporate completely. Most light- and midweight crude oils will lose between 10 and 50% of their mass to evaporation in the first few days of a spill. Emulsification, the process wherein small water droplets are incorporated into the spilled oil, can substantially retard the rate of evaporation allowing the retention of otherwise volatile compounds in some light- and midweight oils (Fingas, 1995). In the case of heavy crude oils and residual fuel oils, which are already depleted of volatile hydrocarbons, the effects of evaporation generally are lower (Mackay and McAuliffe, 1988). However, evaporation may have a greater effect on certain residual fuel oils that have been blended using a lower-boiling (lower-viscosity) petroleum. In such instances the preferential evaporation of the "diluent" may alter the chemical fingerprinting.

Under most conditions, the effects of evaporation are generally restricted to compounds having vapor pressures above that of approximately *n*-C_{15}, or to be conservative (and as evident in Figure 1-14), above that of approximately *n*-C_{20}. As such, chemical fingerprinting of spilled oil residues often must focus on diagnostic features expressed in constituents with vapor pressures lower than about *n*-C_{20}. In such instances, the effects of evaporation on any diagnostic features (e.g., biomarkers) must be carefully examined.

In general, the effects of evaporative weathering on the oil chemical compositions generally are predictable. Studies of the effects of evaporation on chemical composition changes of a number of oils (Wang et al., 1995b, 2003) at various weathering degrees (from 0 to ~40% loss by mass) reveal that (1) ratios of *n*-C_{17}/pristane, *n*-C_{18}/phytane, and pristane/phytane were virtually unaltered, (2) isomeric distributions within C_1-phenanthrenes (4 isomers), C_1-dibenzothiophenes (3 isomers), C_1-fluorenes (3 isomers), and C_1-naphthalenes (2-methyl- and 1-methyl-naphthalene) exhibited great consistency in their relative ratios as the weathering percentages increased, (3) biomarker compounds were concentrated in proportion with the increase of the weathering percentages, and (4) the weathering degree can be readily checked by integration of *n*-alkanes in the GC-FID chromatograms, as Figure 1-14 shows.

1.3.3.2 Dissolution

Although occurring simultaneously with evaporation, the effects of dissolution are less obvious—and difficult to separate from evaporation. For example, the most soluble constituents in most spilled oils are the monoaromatic hydrocarbons, which are also among the more volatile. Studies have shown that evaporation clearly dominates the losses—for example, as reflected in the lack of preferential removal of benzene over cyclohexane (i.e., compounds with comparable vapor pressures and dissimilar aqueous solubilities; Harrison et al., 1975). It is estimated that dissolution will reduce the mass of a crude oil by 1 to 3 wt% (as opposed to 10 to 50 wt% due to evaporation; Mackay and McAuliffe, 1988). Thus, dissolution is relatively insignificant compared to evaporation (McAuliffe, 1977; Payne et al., 1987; Neff, 1990) and will have little effect on a spilled oil's chemical fingerprint. Understanding the dissolution process, however, may be important in recognizing the impact of spilled oil on biota, which can uptake dissolved hydrocarbons more readily.

1.3.3.3 Biodegradation

The rate of mass loss due to biodegradation is slower than that of evaporation or dissolution.

As such, the effects of biodegradation on a spilled oil's chemical fingerprint are not obvious in the short term following a release. As with the other weathering processes, the effect of biodegradation will depend upon the nature of the spilled oil and the spill conditions.

Following a spill of crude oil or refined petroleum to soils, sediments, or open water, different hydrocarbon classes are degraded simultaneously, but at widely different rates by indigenous microbiota (Atlas et al., 1981; Oudot, 1984; Gough et al., 1992; Prince et al., 2003; see also Chapter 11 herein). Low-molecular-weight *n*-alkanes with chain lengths of 10 to 22 carbons are biodegraded most rapidly, followed by isoalkanes and higher-molecular-weight *n*-alkanes, olefins, monoaromatics, PAHs, and, finally, highly condensed cycloalkanes, resins, and asphaltenes. Some sulfur heterocyclics, such as dibenzothiophene and its alkyl homologues, seem to be more resistant than PAHs of similar molecular weight to aerobic microbial degradation (Fedorak and Westlake, 1984; Wang and Fingas, 1995c). However, some strains of aerobic and anaerobic bacteria are able to efficiently degrade dibenzothiophenes (Wu et al., 2002). Compounds that are degraded are typically converted into oxidized compounds that can be further degraded, dissolved, or retained within the oil. Few studies have been directed at understanding that chemical fingerprinting tends to focus mostly on compounds considered resistant to the effects of biodegradation over environmental timescales, namely, PAH and petroleum biomarkers. Though relatively resistant, not all PAH or biomarkers are recalcitrant. Notably, parent PAHs often are biodegraded more rapidly than their alkyl homologues; the rate of biodegradation decreases as the number of alkyl groups on the PAH nucleus increases (Prince et al., 2002a). This is opposite the pattern for photooxidation of PAH (see below); the rate of photooxidation often increases with increasing PAH alkylation (Prince et al., 2003).

Recognizing and monitoring the effects of biodegradation on conventional crude oils and most fuels (kerosene, diesel fuels, fuel oils) are readily reflected in the relative depletion of *n*-alkanes which is relative to comparably volatile isoprenoids (e.g., *n*-C_{17}/Pr and *n*-C_{18}/Ph). However, in the case of heavy crude oil or residual fuels, which can contain little or no *n*-alkanes by virtue of their formation or refining, the effects of biodegradation are less obvious. For example, heavy crude oils, which (in most cases) have already been biodegraded in an oil reservoir for millions of years, in most cases, are likely to be largely unaffected by microbial biodegradation on environmental timescales. Similarly, residual fuel oils that can be blended using vacuum distillation residuum (Figure 1-7) can contain little or no *n*-alkanes (see Chapter 10 herein). Nonetheless, given sufficient time, biodegradation can alter even heavy oils and residual fuels, in generally predictable ways. For example, the PAHs in a Bunker C oil, stranded for 22 years on a shoreline in Nova Scotia, Canada (following the 1970 *Arrow* spill), were highly depleted in naphthalene and alkyl-naphthalenes, enriched in C_2- through C_4-phenanthrenes and dibenzothiophenes, and strongly enriched in C_1- through C_3-chrysenes due to weathering, probably primarily by a combination of biodegradation and water-washing (Wang et al., 1994b).

Prince et al. (2003) provide several examples of the effects of biodegradation (and photooxidation) of crude and refined oils following release to the environment. In December 1999, the *Erika* broke up in a storm off the French coast and released about 19,000 tons of a heavy fuel oil, which emulsified and subsequently came ashore (Oudot, 2000). A sample of the cargo oil was collected from the shore at Le Croisic less than four months after the spill and evaluated for loss of hydrocarbons by comparison of analyte concentrations with the concentration of a conservative natural internal marker in the oil, 17α(H)21β(H)-hopane. Almost 20% of the hydrocarbons in the heavy oil had been lost in less than four months (Prince et al., 2003).

Petroleum biomarkers, such as steranes and triterpanes (Table 1-3) are considered to be

extremely resistant to microbial degradation (Hughes and Holba, 1987). Because of the persistence of most petroleum-derived steranes and triterpanes, they are used frequently to fingerprint and identify the sources of complex hydrocarbon mixtures in soils and sediments and to quantify rates of biodegradation (Atlas, 1995; Page et al., 1995; Prince et al., 2002a, 2003).

1.3.3.4 Photooxidation

Exposure of spilled crude oil and petroleum products to solar radiation leads to several free radical, photooxygenation reactions that produce a variety of oxygen-containing compounds, including peroxides, aldehydes, ketones, alcohols, carbonyls, sulfoxides, epoxides, and fatty acids (Larson et al., 1977; Thominette and Verdu, 1984a, 1984b; Nicodem et al., 1997). Since these compounds are polar, they are more soluble in water than the parent compounds (Payne and McNabb, 1985; Ehrhardt and Douabul, 1989; Ehrhardt and Burns, 1990; Ehrhardt et al., 1992) and therefore can be preferentially dissolved from the spilled oil. However, photo-sensitive higher-molecular-weight compounds can form cross-links upon photooxidation, thereby becoming increasingly large and insoluble — and the spilled oil increasingly viscous (Thominette and Verdu, 1984a; Daling and Brandvik, 1988). The rate of photooxidation of crude oil is directly related to the intensity of ultraviolet radiation from sunlight, but is not sensitive to ambient temperature (Syndes et al., 2001; Prince et al., 2003).

Photooxidation and biodegradation are the only two natural processes that actually destroy petroleum hydrocarbons and remove them from the environment — in many cases forming the same classes of oxygen-containing products. In many cases the target oil ingredients of the two degradative processes are different. Under suitable conditions, they act together to degrade oil more rapidly than either process working alone (Dutta and Harayama, 2000; Prince et al., 2003).

1.3.3.5 Mousse Formation

Among the various weathering processes, the formation of emulsions (mousse) is the only one that promotes the persistence of oil on the surface of water and on the shore — and concurrently retards the weathering processes. The formation and stability of mousses have been well studied in both the laboratory and field for some time (Payne and Phillips, 1985; Daling and Brandvik, 1988; Durell et al., 1993; Strom-Kristiansen et al., 1993; Ronningsen et al., 1995; Fingas and Fieldhouse, 2003). A stable oil mousse no longer behaves as a well-mixed phase. Emulsions often form a crust of oxidized asphaltene materials that inhibit dissolution, evaporation, photooxidation, and biodegradation of hydrocarbons in the bulk oil phase. As such, the chemical fingerprint of the emulsified oil is preserved relative to a non-emulsified oil. Thus, weathered deposits of mousse, tar, and asphalt pavement on the shore may retain some volatile hydrocarbons and biodegradable compounds for long periods of time (Boehm and Fiest, 1982; Payne and Phillips, 1985; Irvine et al., 1999). If the mousse is exposed to air and sunlight, weathering continues at a slow rate, converting the oil deposit to a tar mat or asphalt pavement that may be extremely persistent and retain many of the primary and secondary features of the spilled oil for long periods of time. Some tar mats and asphalt pavements become brittle with time and wave action may erode tarry particles from the surface, forming tar balls. The "centers" of tar balls can contain virtually unweathered oils, weeks or months after the initial oil spill, thereby providing the potential to generate chemical fingerprints with little effect of biodegradation.

1.3.3.6 De-Waxing and Wax Enrichment

Some oils containing prominent *n*-alkanes (waxes) are prone to precipitation of the wax when spilled, especially at low temperatures (Strom-Kristiansen et al., 1997). This phenomenon can impart a heterogeneity in the

chemical fingerprint of the spilled oil by reducing the relative abundance of *n*-alkanes in the C_{20}+ range in the wax-depleted fraction and increasing their relative abundance in the wax-enriched fraction. An example of this phenomenon is shown in Figure 1-15. In this example, a paraffinic North Sea crude oil (Figure 1-15A) becomes depleted (Figure 1-15B) and enriched (Figure 1-15C) in *n*-alkanes above *n*-C_{20} after being spilled under controlled conditions at 3°C for 71 hours (Daling et al., 2002). The effect on the GC/FID fingerprints of the spilled oils is marked and would need to be considered in an oil spill investigation in which the source and spilled oils are compared.

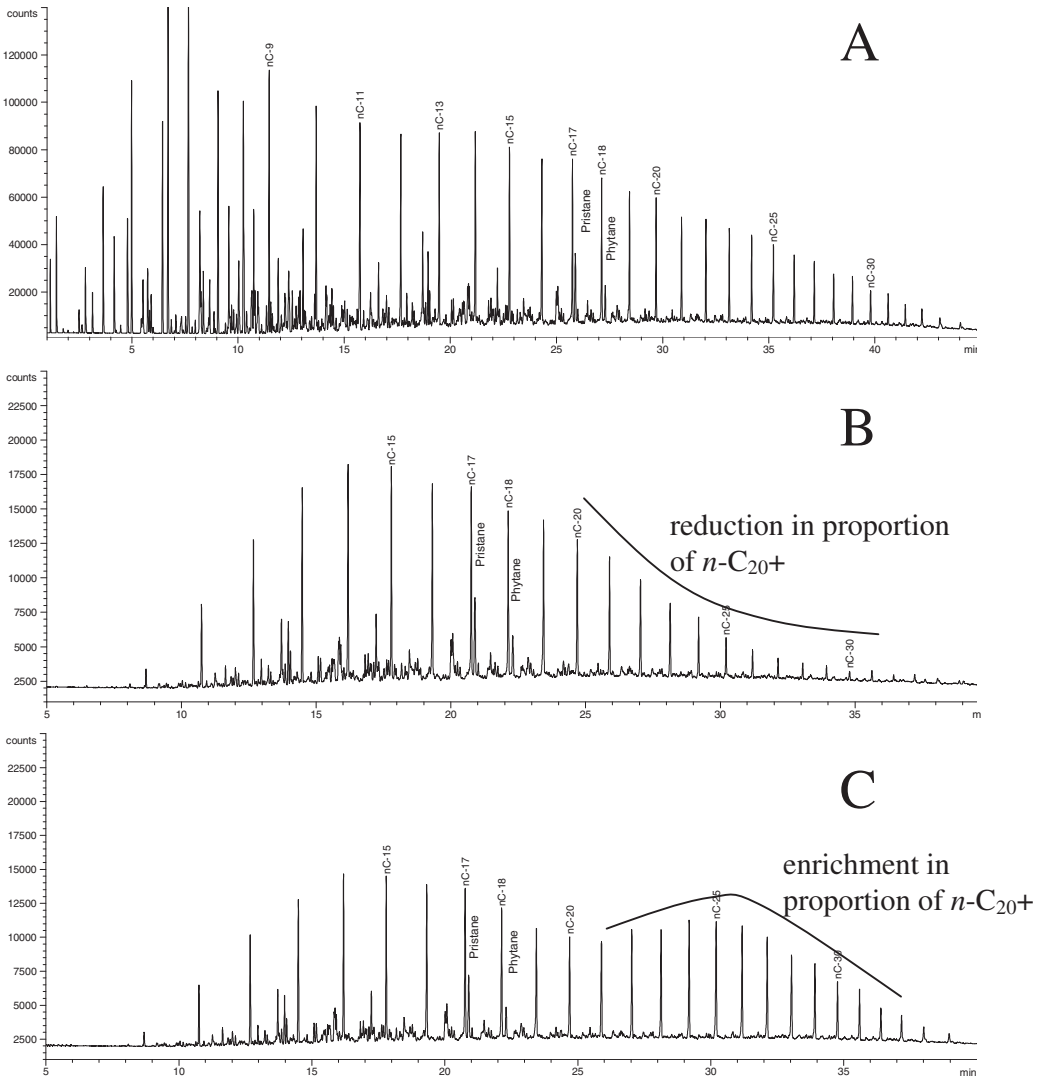

Figure 1-15 GC/FID chromatograms showing the effect of wax precipitation on the chemical fingerprint of a paraffinic oil. (A) starting oil, (B) wax-depleted fraction within spilled oil 71 hours after the spill, and (C) wax-enriched fraction within the spilled oil 71 hours after the controlled spill experiment. Data from Daling et al. (2002).

1.3.4 Tertiary Controls—Mixing with "Background"

Although accidental oil spills or intentional discharges of oil can draw particular attention due to their acute nature, "background" hydrocarbons derived from chronic anthropogenic and natural sources are ubiquitous in modern environments (Table 1-1). The chemical fingerprint of contamination authentically resulting from an accidental oil spill or intentional discharge is often superimposed upon the chemical fingerprint of any pre-existing or "background" chemicals that may have been present before the impact. Recognizing and distinguishing this "background" from any authentic contamination is, therefore, an important component of oil spill investigations. In this section, we review the potential sources of background hydrocarbons in the environment and their potential effect on the chemical fingerprints of spilled or discharged petroleum.

1.3.4.1 What Is "Background"?

"Background" chemicals can take the form of either naturally occurring or anthropogenic chemicals (U.S. EPA, 1989), either of which can be confused with authentic contamination resulting from an oil spill. These two types of background can be defined as follows:

- Naturally occurring background chemicals are inorganic or organic chemicals in the environment that are attributable to natural geological or hydrological characteristics of the area. These chemicals have not been altered by human activity, e.g., natural oil seeps, metals or plant-derived organic matter in soils, forest fire debris, etc.
- Anthropogenic background chemicals are ubiquitous (mostly) synthetic or natural substances that have been released due to human activities but are unrelated to a specific oil spill or discharge. Examples may include agricultural and urban runoff or direct deposition of air pollution particulates.

As implied by these definitions, the issue surrounding background chemicals in oil spill investigations is most often faced in the characterization of soils/sediments and tissues, although water and air can be similarly influenced. In any case, if the contribution of "background" contamination remains unrecognized, the nature and extent of any impact (or even if any impact has occurred at all) can be overestimated. As a result, any environmental risk associated with an oil spill can be overestimated, or unreasonably low cleanup levels may be established. Therefore, every effort should be made to recognize and establish the specific character(s) of the background chemicals and conditions.

The U.S. EPA acknowledges the issue of background contamination in various laws and guidance documents. For example, the Comprehensive Environmental Response, Compensation, and Liability Act includes a provision [CERCLA; 42 USC 9604(a)(3)(A)] that recognizes that elevated background chemicals can render cleanup impractical or impossible and therefore must be assessed. The EPA's *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA* (U.S. EPA, 1988) includes the requirement that background or reference samples be collected for comparison to impacts associated with site-specific or incident-specific releases. These samples are usually collected in areas where chemicals only attributable to anthropogenic or natural background are expected to occur. Of course, where background conditions exclusively occur is not always apparent ahead of time. Chapter 2 describes the importance of collecting "background" samples in the course of oil spill investigations.

Most of the EPA's guidance for recognizing and distinguishing background contamination arises with respect to inorganic contaminants such as toxic metals. The Office of Solid Waste and Emergency Response has published a forum issue paper that specifically addresses this issue with respect to background metals (U.S. EPA, 1995). The reason for the emphasis on background metals is that they are nat-

urally occurring in all soils and sediments and therefore must always be considered in site assessments involving metal contaminants. However, the issue of background contamination also is crucial in oil spill investigations due to the ubiquitous distribution of anthropogenic and naturally occurring hydrocarbons in nature (Table 1-1).

In this section, the fingerprinting characteristics of some commonly encountered *organic* background chemicals are presented and discussed. The objective is to review the effects these background chemicals can have on the chemical fingerprint of spilled oil.

1.3.4.2 Recognizing and Establishing Background

Two methods are commonly used to assess background contamination, i.e., statistical analysis and chemical fingerprinting. The statistical analysis approach is thoroughly described in the U.S. EPA's issue paper on this topic, which emphasizes the issue with respect to toxic metals (U.S. EPA, 1992). The approach generally relies upon various comparative population statistical methods that are used to establish the range of a chemical's background concentrations (anthropogenic and natural) for a study area, and thereby permit recognition of any impacts above this range. This approach obviously requires a sufficient number of samples from both the background area(s) and the impacted area(s) than can be analyzed statistically. As the number of samples increases, the accuracy and precision of each population's probability density function can be established and compared. However, in most oil spill investigations, the statistical approach is often difficult to achieve since studies can rarely afford a sufficient number of background samples to yield reliable population statistics, and furthermore (as mentioned above), the locations of true background impacts are seldom known *a priori.*

Whereas statistical approaches may be more suited to datasets of toxic metals, which may or may not co-occur with one another, chemical fingerprinting is well suited for datasets involving petroleum. This is because (as described in Section 1.3.1) crude oil and petroleum products are complex mixtures of hundreds of hydrocarbons and nonhydrocarbons, which, while they may all (or mostly) be present in different sources of contamination, are typically assembled in a specific distribution. This allows for their distinction from each other, and from the equally complex mixtures of hydrocarbons and nonhydrocarbons in natural and anthropogenic background materials. This allows for the chemical fingerprinting approach to recognizing and establishing background benefits from the complexity of organic materials and organic-based contaminants. Thus, in most oil spill investigations chemical fingerprinting is the best means of establishing "background" hydrocarbon fingerprints and concentrations.

The chemical fingerprinting approach to recognizing the influence of background chemicals involves either a qualitative visual comparison or a quantitative comparison of diagnostic ratios or distributions within known forms of contamination (e.g., fuels, lubricants, or crude oil) and various types of background (see ahead). Such comparisons can allow an investigator to recognize and thereby account for the influence of "background" hydrocarbons in potentially impacted soils, sediments, and tissues. These influences can then be reconciled with respect to the absolute concentrations attributable to the background to assess the magnitude of any influence attributable to the spilled oil. In the sections that follow, various examples of different forms of natural and anthropogenic organic "background" contamination encountered in oil spill investigations are presented and discussed.

1.3.4.3 Naturally Occurring Background Hydrocarbons

Naturally occurring hydrocarbons can take many forms, including modern plant debris, forest fire debris, bacteria-derived compounds (e.g., sulfur species), crude oil seeps, or sedimentary organic particles (e.g., eroded coal).

The influence of these types of materials typically is greatest in investigations involving the chemical fingerprinting of soils and sediments. For example, most soils and sediments contain some fraction of naturally occurring organic matter. Upon solvent extraction by typical methods (e.g., EPA Method Series 3500), the naturally occurring organic matter in most soils or sediments yields hydrocarbons and nonhydrocarbons within the same boiling range as petroleum. In addition, some individual naturally occurring hydrocarbons also occur within oil (see ahead). Thus, the presence of naturally occurring hydrocarbons can be confused with, or contribute to the concentration of, hydrocarbons derived from spilled or discharged oil. This can result in an overestimate of the concentration of total petroleum hydrocarbons (TPH) or PAH, both of which can erroneously increase the liability for the incident.

During solvent extraction of a soil or sediment in the laboratory (EPA Method Series 3500), any naturally occurring organic matter (OM) that may be present is co-extracted along with any authentic organic contamination present. Thus, the resulting extract contains a combination of soluble natural background and the authentic contamination. Some forms of extractable background contamination can be removed from an extract prior to chemical analysis through various extract "cleanup" procedures (e.g., EPA Method Series 3600). When properly performed, these procedures can eliminate the complications due to the presence of sulfur (EPA 3660), polar compounds (EPA 3610 or 3630), or humic acids, proteins, etc. (EPA 3640). And while such cleanup procedures should routinely be employed in assessing the impacts to soils and sediments, they sometimes are not. Even when they are performed, some background contaminants, e.g., naturally occurring background *hydrocarbons* cannot be separated from authentic *hydrocarbon* contamination. In these instances, chemical fingerprinting is required to recognize the presence of the background hydrocarbons and account for them appropriately. In the following sections, some descriptions of examples of naturally occurring hydrocarbons are discussed.

1.3.4.3.1 Vascular Plant and Algal Debris. The most common naturally occurring organic background material encountered in soils and sediments is due to the presence of vascular (land) plant debris, which is pervasive in most soils and coastal sediments. The extractable component within soils and sediments containing plant debris can be significant, particularly in moist, highly vegetated environments where peat or other organic-rich soil accumulate (or had in the past). For example, Dworian (1997) reported that the concentration of total petroleum hydrocarbons (TPH) as diesel range organics (DRO) in some Alaskan soils was as high as 3600 mg/kg. In such environments, modern plant debris can significantly increase the measured concentrations of total petroleum hydrocarbons (TPH).

The types of compounds extracted from vascular plant debris include various polar compounds (e.g., organic acids and alcohols, sulfur compounds, phenols, tannins) and their diagenetic products. Fortunately, if not removed during cleanup of the extract (e.g., EPA Methods 3610 or 3630) these materials produce "unusual" chemical fingerprints (via gas chromatographic methods such as EPA Method 8015) that can be distinguished from crude oil or petroleum products. However, in some studies these unusual fingerprints are not inspected, and the inflated TPH concentrations reported by the laboratory are accepted blindly. This, of course, can greatly increase what is accepted to be the authentic TPH concentration and aerial extent of any spilled oil.

Even after cleanup of soil/sediment extracts, any plant-derived hydrocarbons (e.g., waxes, terpenes, fats, oils) will persist and potentially contribute to the chemical fingerprint of any spilled oil. Their presence will increase measured TPH concentrations and have a dramatic influence on the appearance and, thus, (mis)interpretation of a potentially impacted sample's chromatographic fingerprint. This circumstance was common in a recent investigation of a crude oil spill following Hurricane

Katrina in Chalmette, Louisiana (Stout et al., 2006b). The massive floodwaters associated with Katrina carried and deposited large masses of peaty debris into the area that, even after alumina cleanup of soil extracts, yielded measurable TPH in surface soils. This TPH could have been mistaken for crude oil spilled during Katrina if not for the inspection of the associated chromatograms. Figure 1-16 shows the GC/FID chromatogram for an alumina-cleaned extract from a peaty soil from a coastal Louisiana bayou. The peat is dominated by a series of odd numbered *n*-alkanes ranging from *n*-C_{25} to *n*-C_{33}. This odd-over-even pattern is typical of *n*-alkanes derived from leaf (epicuticular) waxes (Bray and Evans, 1961). GC/MS-SIM analysis of the peat also revealed the presence of anteiso-alkanes in the same carbon ranges. Also present are numerous late-eluting peaks consistent with various plant- and microbial-derived terpenes, including a prominent C_{31} hopene (Figure 1-16). Pristane is absent in this peat, although this isoprenoid is a significant component of some plankton (Blumer et al., 1963), and consequently its presence in coastal sediments is not necessarily due to petroleum. A small UCM hump in the C_{29}–C_{35} range is also evident in this sample. These chromatographic features cannot reasonably be confused with crude oil, even highly weathered crude oil, and thereby demonstrate the importance of fingerprinting in distinguishing low levels of spilled crude oil from allochthonous peat following Hurricane Katrina.

1.3.4.3.2 Particulate Coal and Wood Charcoal. In many coastal environments, coal is eroded from sedimentary rock outcrops, and minute coal particles are transported and deposited in coastal sediments by rivers. In such areas, coal would be considered a naturally occurring source of background hydrocarbons. Alternatively, many ports formerly hosted industries that utilized coal delivered by vessel or barge. Over the decades of operation particulate coal and coal dust can become widely distributed in sediments. In such areas, coal would be considered as an anthropogenic background material. In either case, particulate coal can occur as a background contaminant that must be distinguished from authentic contamination arising from spilled oil.

The contribution of background hydrocarbons that particulate coal may impart is largely a function of the precursor plant material (e.g., Mesozoic gynmosperm versus Tertiary angiosperm dominant) and the coal's rank (Chaffee et al., 1986). Lower-rank coals (lignite and sub-bituminous) typically yield higher concentrations of nonhydrocarbons during solvent extraction while bituminous coals yield more hydrocarbons (Radke et al., 1980; White and Lee, 1980) with the highest yields resulting from high volatile bituminous coals (Stout et al., 2002b).

The occurrence of coal particles in sediment could confound interpretations surrounding TPH, PAH, and biomarkers in the sample. Figure 1-17 shows the distributions of PAH in three coals of varying rank (obtained from

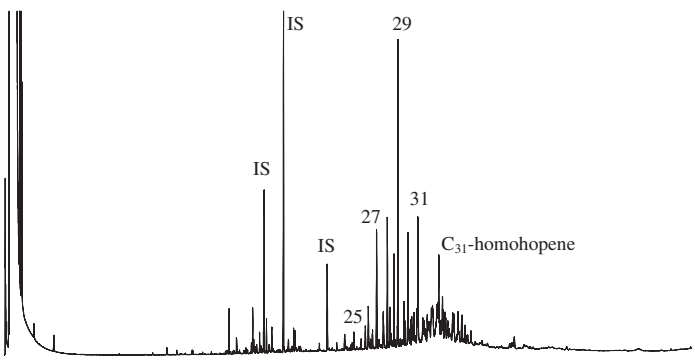

Figure 1-16 GC/FID chromatogram of the TPH extracted from a Louisiana peat containing 2000 mg/kg (dry).

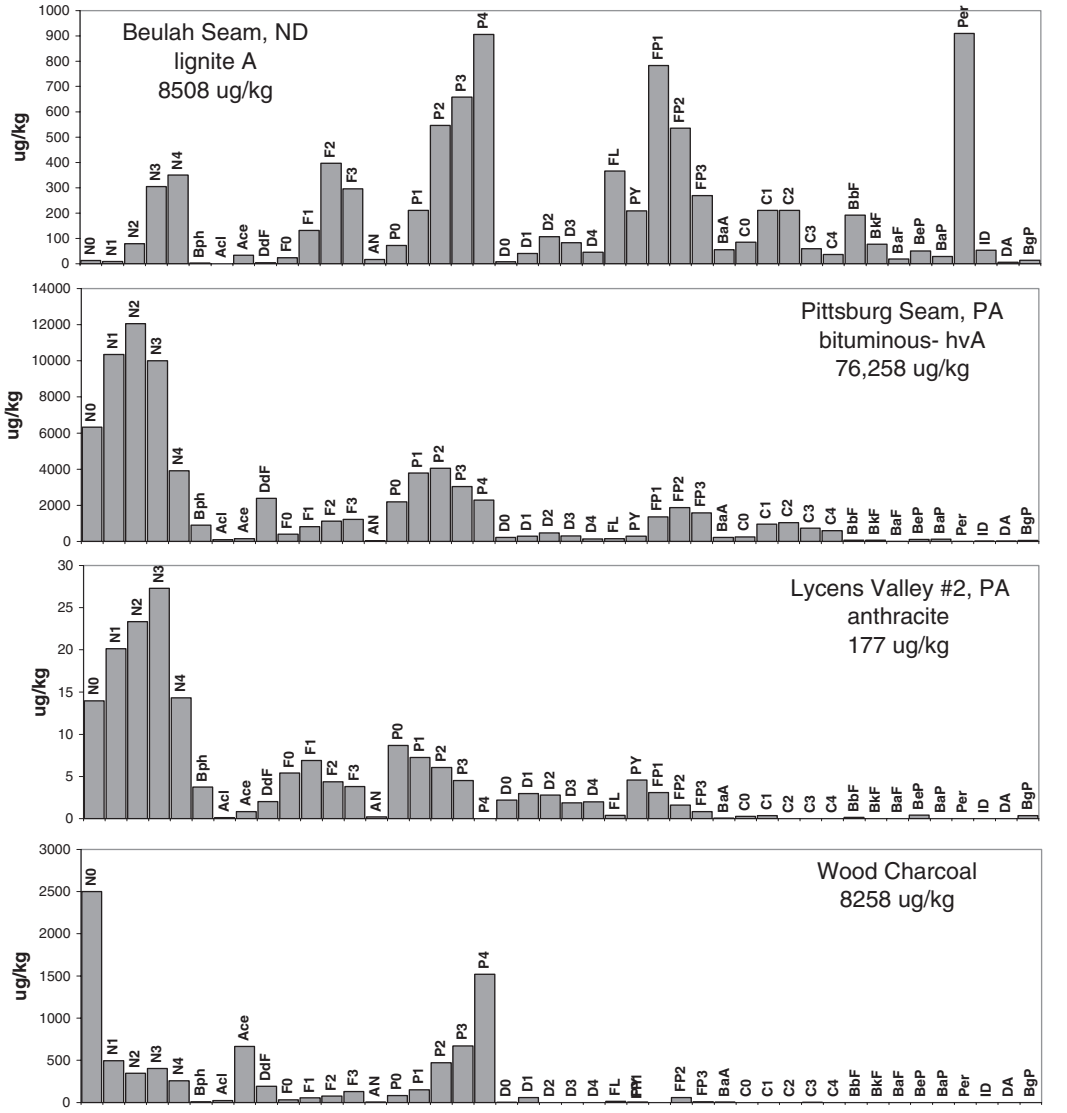

Figure 1-17 Histograms showing the distribution of PAH in three U.S. coals of varying rank and in modern wood-derived charcoal. For PAH compound abbreviations, see Table 1-2.

different U.S. coal fields). The PAH concentrations and distributions vary widely among the coals. The distribution of PAH in the lower-rank coals is dominated by 3- and 4-ring PAH (phenanthrenes P0–P4 and fluoranthene/pyrenes FP1–FP3). Perylene, a commonly recognized naturally occurring PAH (e.g., Silliman et al., 2001), is also abundant. The highly volatile bituminous A coal and the anthracite are both dominated by 2-ring PAH (naphthalenes N0–N4). However, the anthracite, a much higher-rank coal, contains these at far lower concentrations than the bituminous coal. Obviously, the presence of dispersed coal particles in sediments and soils will increase the concentrations of PAH (and TPH), which could be mistakenly identified as spilled oil if the chemical fingerprints were not considered.

In some instances, organic petrographic inspection of the sediment may be necessary to recognize the presence of coal. In fact, the presence of sedimentary coal in Prince William Sound sediments has been argued to have confounded the allocation of the different PAH sources in Prince William Sound following the *Exxon Valdez* oil spill (Short et al., 1999; Boehm et al., 2000a, 2000b; see also Chapter 15 herein).

Finally, debris from forest fires can also occur naturally in many sediments. This debris contains various PAH derived from the combustion/pyrolysis of vegetation (e.g., Laflamme and Hites, 1979; Simoneit and Elias, 2000). This material can also contribute hydrocarbons that, if unrecognized, can affect interpretations and decisions surrounding the potential impact of spilled oil. Figure 1-17 also shows the distribution and concentration of PAH in wood charcoal collected from a recently burned area. The charcoal contained 8258 µg/kg of PAH, which were dominantly comprised of 2- and 3-ring PAH. These occurred in a very different distribution than was observed in the coal samples.

1.3.4.3.3 Natural Oil Seeps. In some oil spill investigations, the occurrence and influence of natural oil seeps must be considered. The reason for this is obvious — *is there any "real" contamination or only background contamination*? Natural oil seeps are a worldwide phenomenon that contributes more petroleum to the environment than all other sources combined (Table 1-1). In coastal southern California the phenomenon is particularly prolific (e.g., Mikolaj et al., 1972; Straughan, 1979) and must always be considered when investigating the origin of forms of coastal contamination, e.g., tar balls (Wang et al., 1993). Chemical fingerprinting studies have shown that some of the hydrocarbons in Prince William Sound sediments also are attributable to long-persistent oil seeps that exist east of Prince William Sound (see Chapter 15 herein). The character of this seeped oil was established through the analysis of radiogenically age-dated sediment cores, which revealed the distinctive fingerprint of the naturally seeped oil in sediments deposited centuries prior to the *Exxon Valdez* oil spill (Burns et al., 1997; Boehm et al., 1997, 2000a).

Of course, in some instances when the suspected spill oil is from the same geologic province as the naturally occurring seeped oil (and therefore shares identical or nearly identical primary chemical features (Section 1.3.1), the ability of chemical fingerprinting to distinguish any spilled oil from any seeped oil is vastly reduced.

There is some expectation that seeped crude oil may exhibit features of a more highly weathered equivalent of locally produced (and typically obtained from deeper production zones) oil. The basis for this is that natural oil seeps often occur when shallower and cooler reservoirs, i.e., those most prone to in-reservoir weathering, are connected to the surface via faults. Alternatively, it is possible that produced (and possibly spilled) oils are derived primarily from deeper reservoir zones where in-reservoir weathering is reduced relative to the natural seeps. In such cases where the naturally seeped oils are already weathered, it may be possible to distinguish spilled crude oil from seeped crude oil — at least in the earlier stages of weathering of the spilled oil. When genetically related seeped and spilled oils from the same petroleum system co-occur in the environment, chemical fingerprinting may be unable to distinguish these two sources unless subtle though measurable variations are present (e.g., as in Figure 1-5). In such instances other forensic tools such as spill trajectory modeling (Chapter 13) or remote sensing (Chapter 14) may prove useful.

1.3.4.4 Anthropogenic Background Hydrocarbons

In port sediments and near urban areas, the anthropogenic background contains PAH and other hydrocarbons that are collectively called "urban background." Urban background consists of hydrocarbons derived from a variety of nonpoint sources such as (1) stormwater

runoff, (2) direct deposition (atmospheric fallout) of combustion particles (soot) from vehicle exhaust and factories, (3) surface runoff from proximal roadways, parking lots, and bridges, or (4) discharges from recreational, commercial, and military boat/ship traffic. In many environments, stormwater and river runoff are probably the largest chronic contributors of anthropogenic background PAH to urban and coastal sediments (Eganhouse et al., 1982; Table 1-1). These PAH source materials, which often have been entering a waterway for decades, can impart obvious and recognizable profiles of anthropogenic background PAH to the sediments (e.g., Daskalakis and O'Connor, 1995).

1.3.4.4.1 Urban and River Runoff. Runoff is the most important source of anthropogenic background hydrocarbons to urban and coastal sediments. It consists of a mixture of organic materials — dust, dirt, particulate matter, soot, solid wastes — that are transported to urban waterways, ports, rivers, or coastal waters and sediments via nonpoint (general runoff) and point (end-of-pipe) sources, often during storm events. In many oil spill investigations involving urban or coastal sediments, the presence of anthropogenic background hydrocarbons derived from runoff must be established in order to assess the potential impact from any authentic contamination derived from spilled or discharged oil.

The presence and composition of the hydrocarbons within runoff have been long recognized (Wade and Quinn, 1979; Eganhouse et al., 1982; Hoffman and Quinn, 1987). Lubricating and other heavy oils contained within urban runoff can be an important source of anthropogenic background hydrocarbons, which must be distinguished from any authentic petroleum contamination. The presence of these (mostly) residual range background hydrocarbons can be generally recognized in GC/FID fingerprints by the presence of an unresolved complex mixture (UCM) that appears as a broad "hump" in the baseline of the fingerprint. The prominence of the UCM is typical of biodegraded petroleum, uncombusted petroleum, lubricating oils, and asphalts, all of which may be components of urban runoff (Gogou et al., 2000). The specific shape of the UCM "hump" can vary in different study areas, but these can generally be distinguished from specific petroleum types. Figure 1-18 shows an example of the UCM hump for an urban runoff-impacted sediment from the Thea Foss Waterway, Tacoma, Washington (Stout et al., 2003). The fingerprints for a motor oil and a hydraulic oil are shown for comparison. Each of these is dominated by a UCM hump, and it is easy to envi-

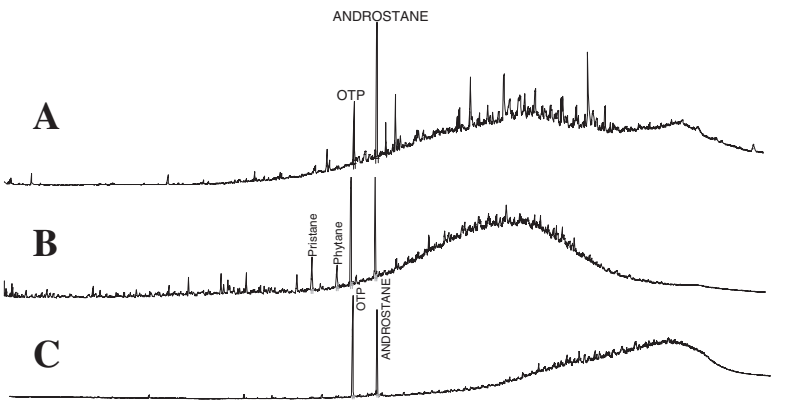

Figure 1-18 GC/FID fingerprints showing the chromatographic character of the UCM "humps" in (A) urban sediment impacted by urban runoff, (B) motor oil, and (C) hydraulic oil. OTP (*o*-terphenyl) and 5α-androstane are internal standards.

sion how these heavy petroleum products, dripped from vehicles and washed from urban road surfaces during storm events, could eventually enter the sediment and produce a broad UCM hump (as appears in Figure 1-17A).

PAHs are also well-known components of urban runoff (Stout et al., 2004). The sources of PAH in urban runoff vary, but the most common sources are (1) soot particles containing combustion-related PAH (principally arising from internal combustion engines, especially diesel based (e.g., Harrison et al., 1996; Marr et al., 1999), (2) street runoff containing traces of used lubricating/hydraulic oils, and (3) illegal or unintentional discharging of waste oil and petroleum products into storm drain systems. The PAHs associated with urban runoff are complex mixtures that tend to be dominated by higher-molecular-weight 4- to 6-ring PAHs (Stout et al., 2004). The prominence of 4- to 6-ring, nonalkylated PAH is indicative of a combustion (pyrolysis) product (Laflamme and Hites, 1978), as is typical in motor exhaust (Westerholm et al., 1988) or wood smoke (Oahn et al., 1999; Simoneit and Elias, 2000). Thus, the PAHs associated with combustion-derived soot particles are likely to contribute the majority of background anthropogenic PAH to urban and coastal sediments.

Figure 1-19 shows the distributions and concentrations of PAH in an urban runoff-influenced sediment from a tributary to the southern branch of the Elizabeth River in Norfolk, Virginia. For comparison, the PAHs in selected components that may be contained within urban runoff are also shown. These include the PAH found in urban dust (SRM 1649a), diesel exhaust soot (SRM 1650), used motor oil (Restek, Inc. Standard), used hydraulic oil, and road asphalt. A strong pyrogenic signature of the PAH is evident in the urban dust and tends to most closely resemble that found in the Elizabeth River sediment. The diesel soot, used motor oil, used hydraulic oil, and road asphalt all exhibit strong petrogenic PAH signatures, although each of these exhibits a distinct distribution. The greater resemblance between the distribution of the PAH in the sediment and in urban dust suggests that the latter (i.e., its equivalent in the Elizabeth River area) is the predominant source of background PAH to the area's sediments. This appears to be the case in spite of the generally low concentration of PAH in urban dust compared to the other contributing sources.

1.4 Summary

Accidental *oil spills* or intentional *operational discharges* of crude oil and petroleum products and wastes are frequent occurrences. Determining the liable source and environmental impact, both spatially and temporally, of these releases relies largely upon chemical fingerprinting. Chemical fingerprinting of petroleum in the environment can be defined as the generation and comparison of diagnostic chemical features among oil samples (i.e., both spill and source oils) and potentially impacted samples (e.g., shorelines, sediments, or biological tissues). The analytical methods available for chemical fingerprinting have evolved over time, with advances in analytical methods generally providing an increasing degree of molecular specificity. Most chemical fingerprinting of oils relies upon gas chromatography (GC) or gas chromatography-mass spectrometry (GC/MS) that can target specific molecular features within petroleum. Because of the chemical complexity of petroleum, which contains hundreds to many thousands of individual compounds, this specificity attainable by GC and GC/MS analysis provides the ability to determine the source and impact of petroleum in the environment. These analyses most often target compounds affording a high degree of specificity between oils, namely, biomarkers and PAHs.

Any determination of the source or impact necessarily relies upon a comparison of the chemical fingerprints of the spilled or discharged petroleum versus those of the candidate source(s) or the potentially impacted samples. Such comparisons, be they qualitative or quantitative, need to consider and account for the factors that collectively affect the chemical fingerprints of petroleum spilled or discharged in the environment. These

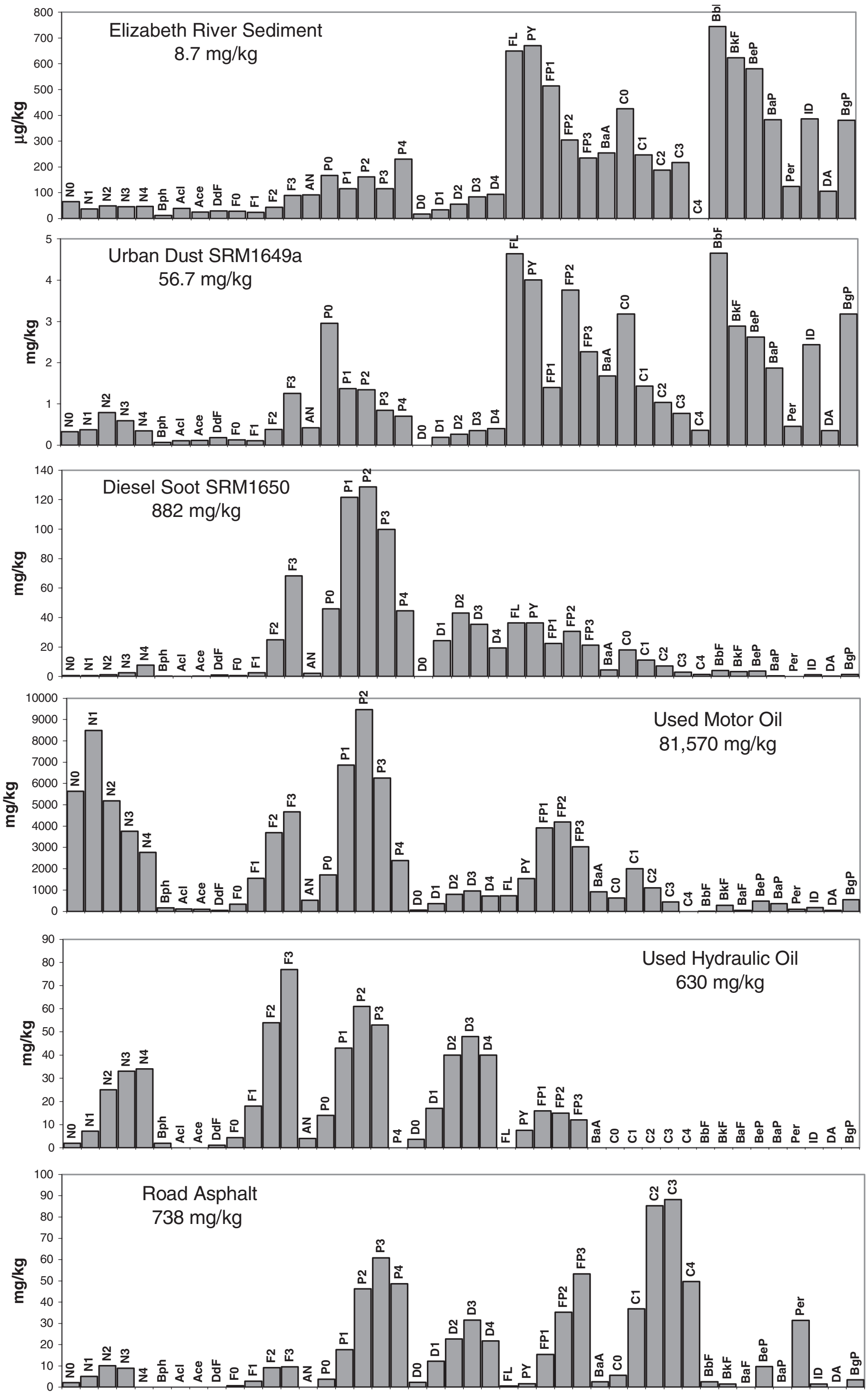

Figure 1-19 Histograms showing the distributions and concentrations of PAH in an urban sediment from the Elizabeth River (Virginia) containing anthropogenic background PAH and in various urban runoff candidate source components. For compound abbreviations, see Table 1-2. Concentrations refer to mg of PAH per kg of sediment (dry), urban dust (dry), soot (dry), oil, and asphalt (dry).

factors can be classified as (1) primary, (2) secondary, and (3) tertiary.

Primary factors include those processes at work during the original generation and accumulation of crude oil over geologic time, and include the (1) character of the ancient organic matter in the source rock strata, (2) the thermal history of the source rock strata, and (3) the processes active during migration and within the crude oil reservoir. Because of these primary factors, crude oils from different geologic provinces and even from different reservoirs in a single oil field can exhibit distinguishable chemical fingerprints, thereby allowing their distinction in oil spill investigations involving crude oil(s).

Secondary factors include those processes used in the refining of crude oil to produce various petroleum products, mostly fuels and lubricants. The modern refining process relies upon various fractionation, conversion, and finishing steps that collectively will determine the chemical fingerprint of the petroleum products produced. Some primary features of the parent crude oil feedstock will be inherited by the daughter petroleum products and other features will be modified by the refining process. The combined effects of primary and secondary processes (i.e., different crude oil feedstocks and different refining processes) can impart different chemical fingerprints for the same petroleum product types, thereby allowing their distinction in oil spill investigations involving a petroleum product(s).

Tertiary factors include the processes that affect the chemical fingerprint of petroleum after it is released into the environment. The two most important tertiary factors are (1) weathering and (2) mixing. It is well established that the processes of weathering will alter the chemical fingerprint of petroleum. For petroleum spilled or discharged to water, the weathering processes of evaporation and biodegradation can have a significant effect on the petroleum's chemical fingerprint, though the effects of other processes on both the chemical fingerprint and the rates of evaporation and biodegradation — dissolution, photooxidation, mousse formation, and dewaxing/wax-enrichment — must also be considered. Another tertiary factor is the effect of mixing of a spilled or discharged oil with any pre-existing, "background" petroleum or other hydrocarbon sources in the environment. "Background" hydrocarbons may be naturally occurring (e.g., modern organic matter, coal or ash, or seeped oil) or anthropogenic (e.g., runoff or atmospheric particulates). The effect of mixing can alter the chemical fingerprint of a petroleum spilled or discharged into the environment, emphasizing the importance of recognizing and characterizing the contribution of "background" when attempting to determine the source or potential impact of spilled petroleum.

Collectively, the effects of these primary, secondary, and tertiary factors must be considered and accounted for in any comparison of chemical fingerprints before any determination as to the source or impact of spilled or discharged petroleum can be established.

References

Albaiges, J. and P. Albrecht. Fingerprinting marine pollutant hydrocarbons by computerized gas chromatography-mass spectrometry. *Int'l. J. Environ. Anal. Chem.*; 1979, **6**, 171–190.

Alexander, R., R.I. Kagi, R.A. Noble, and J.K. Volkman. Identification of some bicyclic alkanes in petroleum. *Org. Geochem.*; 1984, **6**, 63–70.

American Society for Testing and Materials (ASTM). Standard Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography. *ASTM 3328D-00*; 2000a; ASTM International, W. Conshohocken, PA.

American Society for Testing and Materials (ASTM). Oil spill identification by gas chromatography and positive ion electron impact low resolution mass spectrometry. *ASTM D5739–00*; 2000b; ASTM International, W. Conshohocken, PA.

Atlas, R.M. Petroleum biodegradation and oil spill bioremediation. *Mar. Pollut. Bull.*; 1995, **31**, 178–182.

Atlas, R.M., P.D. Boehm, and J.A. Calder. Chemical and biological weathering of oil from the *Amoco Cadiz* spillage within the littoral zone. *Estuar. Coast. and Shelf Sci.*; 1981, **12**, 589–608.

Beall, P.W., S.A. Stout, G.S. Douglas, and A.D. Uhler. On the role of process forensics in the characterization of fugitive gasoline. *Env. Claims J.*; 2002, **14**, 487–506.

Bence, A.E., K.A. Kvenvolden, and M.C. Kennicutt II. Organic geochemistry applied to environmental assessments of Prince William Sound, Alaska, after the *Exxon Valdez* oil spill — a review. *Org. Geochem.*; 1996, **24**, 7–42.

Bentz, A.P. Oil spill identification. *Anal. Chem.*; 1976, **48**, 454A–472A.

Bentz, A.P. Who spilled the oil? *Anal. Chem.*; 1978, **48**, 655A–658A.

Blumer, M., M.M. Mullin, and D.W. Thomas. Pristane in zooplankton. *Science*; 1963, **140**, 974.

Bobra, A.M., D. Mackay, and W.Y. Shiu. Distribution of hydrocarbons among oil, water and vapor phases during oil dispersant toxicity tests. *Bull. Environ. Contam. Toxicol.*; 1979, **23**, 558–565.

Boehm, P.D. and J.W. Farrington. Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank region. *Environ. Sci. Technol.*; 1984, **18**, 840–845.

Boehm, P.D., G.S. Douglas, J.S. Brown, D.S. Page, A.E. Bence, W.A. Burns, and P.J. Mankiewicz. Comment on "Natural hydrocarbon background in benthic sediments of Prince William Sound, Alaska: Oil vs. coal." *Environ. Sci. Technol.*; 2000b, **34**, 2064–2065.

Boehm, P.D., G.S. Douglas, W.A. Burns, P.J. Mankiewicz, D.S. Page, and A.E. Bence. Application of petroleum hydrocarbon chemical fingerprinting and allocation techniques after the *Exxon Valdez* oil spill. *Mar. Pollut. Bull.*; 1997, **34**, 599–613.

Boehm, P.D. and D.L. Fiest. Subsurface distributions of petroleum from an offshore well blowout. The Ixtoc I Blowout, Bay of Campeche. *Environ. Sci. Technol.*; 1982, **16**, 67–74.

Boehm, P.D., D.S. Page, W.A. Burns, A.E. Bence, P.J. Mankiewicz, and J.S. Brown. Resolving the origin of the petrogenic hydrocarbon background in Prince William Sound, Alaska. *Environ. Sci. Technol.*; 2000a, **35**, 471–479.

Bray, E.E. and E.D. Evans. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta*; 1961, **22**, 2–15.

Burns, W.A., P.J. Mankiewicz, A.E. Bence, D.S. Page, and K.R. Parker. A principal component and least squares method for allocating polycyclic aromatic hydrocarbons in sediment to multiple sources. *Environ. Tox. Chem.*; 1997, **16**, 1119–1131.

Cassani, F. and G. Eglinton. Organic geochemistry of Venezuelan extra-heavy crude oils. 2. Molecular assessment of biodegradation. *Chem. Geol.*; 1991, **91**, 315–333.

Chaffee, A.L., D.S. Hoover, R.B. Johns, and F.K. Schweighardt. Biological markers extractable from coal. In: *Biological Markers in the Sedimentary Record*; Elsevier, Amsterdam, The Netherlands; 1986, 311–345.

Colombo, J.C., E. Pelletier, C. Brochu, and M. Khalil. Determination of hydrocarbon sources using *n*-alkane and polyaromatic hydrocarbon distribution indexes: Case Study — Rio de La Plata Estuary, Argentina. *Environ. Sci. Technol.*; 1989, **23**, 888–894.

Connan J. Biodegradation of crude oils in reservoirs. *Adv. Petrol. Geochem.*; 1984, **1**, 299–333.

Curiale, J.A. A review of the occurrences and causes of migration-contamination in crude oil. *Org. Geochem.*; 2002, **33**, 1389–1400.

Daling, P.S. and P.J. Brandvik. A study of the formation and stability of water-in-oil emulsions. In: *Proc. 11th AMOP Technical Seminar, Vancouver, BC, Canada.* Environment Canada, Ottawa, Canada; 1988, 488–499.

Daling, P.S., L.-G. Faksness, A.B. Hansen, and S.A. Stout. Improved and standardized methodology for oil spill fingerprinting. *Environ. Forensics*; 2002, **3**, 263–278.

Daskalakis, K.D. and T.P. O'Connor. Distribution of chemical concentrations in US coastal and estuarine sediment. *Mar. Environ. Res.*; 1995, **40**, 381–398.

Didyk, B.M., B.R.T. Simoneit, S.C. Brassell, and G. Eglinton. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature*; 1978, **272**, 216–222.

Douglas, G.S., W.A. Burns, A.E. Bence, D.S. Page, and P.D. Boehm. Optimizing detection limits for the analysis of petroleum hydrocarbons in complex environmental samples. *Environ. Sci. Technol.*; 2004, **38**, 3958–3964.

Douglas, G.S. and A.D. Uhler. Optimizing EPA methods for petroleum-contaminated site assessments. *Environ. Testing and Analysis*; 1993, **5**, 46–53.

Douglas, G.S., A.E. Bence, R.C. Prince, S.J. McMillen, and E.L. Butler. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technol.*; 1996, **30**, 2332–2339.

Duewer, D.L., B.R. Kowalski, and T.F. Schatzki. Source identification of oil spills by pattern

recognition analysis of natural element composition. *Anal. Chem.*; 1975, **47**, 1573–1783.

Durell, G.S., S.A. Ostazeski, A.D. Uhler, and A.B. Nordvik. Transfer of crude oil weathering technology. Technical Report No. 93–027; Marine Spill Response Corporation, Washington, D.C.; 1993.

Dutta, T.K. and S. Harayama. Fate of crude oil by the combination of photooxidation and biodegradation. *Environ. Sci. Technol.*; 2000, **34**, 1500–1505.

Dworian, P. Interferences by natural organics in diesel analyses. *J. Cold Regions Eng.*; 1997, **1**(2), 71–81.

Eganhouse, R.P., D.L. Blumfield, and I.R. Kaplan. Petroleum hydrocarbons in stormwater runoff and municipal wastes: Input to coastal waters and fate in marine sediments. *Thalassia Jugoslavica.*; 1982, **18**, 411–431.

Eglinton, G. and M. Calvin. Chemical fossils. *Sci. Am.*; 1967, **261**, 32–43.

Ehrhardt, M. and M. Blumer. The source identification of marine hydrocarbons by gas chromatography. *Environ. Pollut.*; 1972, **3**, 179–194.

Ehrhardt, M. and A. Douabul. Dissolved petroleum residues and alkylbenzene photo-oxidation products in the upper Arabian Gulf. *Mar. Chem.*; 1989, **26**, 363–370.

Ehrhardt, M.G. and K.A. Burns. Petroleum-derived dissolved organic compounds concentrated from inshore waters in Bermuda. *J. Exper. Mar. Biol. Ecol.*; 1990, **138**, 35–47.

Ehrhardt, M.G., K.A. Burns, and M.C. Bicego. Sunlight-induced compositional alterations in the seawater-soluble fraction of a crude oil. *Mar. Chem.*; 1992, **37**, 53–64.

Ekweozor, C.M. and O.T. Udo. The oleananes: Origin, maturation and limits of occurrence in Southern Nigeria sedimentary basins. *Org. Geochem.*; 1988, **13**, 131–140.

Emsbo-Mattingly, S.D. Hydrocarbon composition of vessel discharges: Potential sources of petroleum in coastal environments. *Remed. Profess.*; 2005, Dec.

Farrimond, P., A. Taylor, and N. Telnæs. Biomarker maturity parameters: The role of generation and thermal degradation. *Org. Geochem.*; 1998, **29**, 1181–1197.

Fedorak, P.M. and D.W.S. Westlake. Degradation of sulfur heterocycles in Prudhoe Bay crude oil by soil enrichments. *Water, Air, Soil Pollut.*; 1984, **21**, 225–230.

Fingas, M. A literature review of the physics and predictive modeling of oil spill evaporation. *J. Hazard. Mat.*; 1995, **42**, 157–175.

Fingas, M. and B. Fieldhouse. Studies on the formation process of water-in-oil emulsions. *Mar. Pollut. Bull.*; 2003, **47**, 369–396.

Gary, J.H. and G.E. Handwerk. *Petroleum Refining*; Marcel Dekker, New York, NY; 1984.

Gogou, A., I. Bouloubassi, and E.G. Stephanou. Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. *Mar. Chem.*; 2000, **68**, 265–282.

Gough, M.A., M.M. Rhead, and S.J. Rowland. Biodegradation studies of unresolved complex mixtures of hydrocarbons: Model UCM hydrocarbons and the aliphatic UCM. *Org. Geochem.*; 1992, **18**, 17–22.

Grahl-Nielsen, O., J.T. Staveland, and S. Wilhelmsen. Aromatic hydrocarbons in benthic organisms from coastal areas polluted by Iranian crude oil. *J. Fisheries Res. Board of Canada*; 1978, **35**, 615–623.

Hamilton, B. and R.J. Falkiner. Motor Gasoline. In: G.E. Totten (ed.), *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*; ASTM Manual Series, MNL37WCD; 2003, ASTM International, W. Conshohocken, PA; 61–88.

Harrison, R.M., D.J.T. Smith, and L. Luhana. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environ. Sci. Technol.*; 1996, **30**, 825–832.

Harrison, W., M.A. Winnik, P.T.Y. Kwong, and D. Mackay. Disappearance of aromatic and aliphatic components from small sea-surface slicks. *Environ. Sci. Technol.*; 1975, **9**, 231–234.

Hoffman, E.J. and J.G. Quinn. Chronic hydrocarbon discharges into aquatic environments: II — Urban runoff and combined sewer overflows. In: J.H. Vandermeulen and S.E. Hurley (eds.), *Oil in Freshwater: Chemistry, Biology, Countermeasure Technology*; Pergamon Press, New York; 1987, 114–137.

Hughes, W.B. and A.G. Holba. Relationship between crude oil quality and biomarker patterns. *Org. Geochem.*; 1987, **13**, 15–30.

Hunt, J.M. *Petroleum Geochemistry and Geology*, 2nd ed. Freeman Press, USA; 1996.

Irvine, G.V., D.H. Mann, and J.W. Short. Multi-year persistance of oil mousse on high energy beaches distant from *Exxon Valdez* oil source. *Mar. Pollut. Bull.*; 1999, **38**, 572–584.

Jewitt, C.H., S.R. Westbrook, D.L. Ripley, and R.H. Thornton. Fuels for land and marine diesel engines and for nonaviation gas turbines. In: G.V.

Dyroff (ed.), *ASTM Manual on Significance of Tests for Petroleum Products, 6th ed.* Am. Soc. Testing Materials; Phil., PA; 1993.

Jordan, R.E. and J.R. Payne. *Fate and Weathering of Petroleum Spills in the Marine Environment*; Ann Arbor Science Press, Ann Arbor, Michigan; 1980.

Kaplan, I.R. and Y. Galperin. Application of alkylcyclohexane distribution patterns for hydrocarbon fuel identification in environmental samples. In: P.T. Kostecki, E.J. Calabrese, and M. Bonazountas (eds.), *Contaminated Soils*; Amherst Scientific Publishers, Amherst, MA; 1997, **2**, 65–78.

Kaplan, I.R., Y. Galperin, S.-T. Lu, and R.-P. Lee. Forensic environmental geochemistry: Differentiation of fuel-types, their sources and release time. *Org. Geochem.*; 1997, **27**, 289–317.

Kaplan, I.R., S.-T. Lu, H.M. Alimi, and J. MacMurphey. Fingerprinting of high boiling hydrocarbon fuels, asphalts and lubricants. *Environ. Forensics*; 2001, **2**, 231–248.

Kauffman, R.L., A.S. Ahmed, and R.J. Elsinger. Gas chromatography as a development and production tool for fingerprinting oils from individual reservoirs: Applications in the Gulf of Mexico. In: D. Schumaker and B.F. Perkins (eds.), *Proc. 9th Annual Research Conf. of the Soc. Econ. Paleont. Mineral*; New Orleans; 1990, 263–282.

Kinghorn, R.R.F. *An Introduction to the Physics and Chemistry of Petroleum*. J. Wiley & Sons, New York, NY; 1983.

Kreider, R.E. Identification of oil leaks and spills. In: *Proc. 1971 Oil Spill Conf.* API-USEPA-US Coast Guard, Washington, D.C.; 1971, 119–124.

Kvenvolden, K.A., F.D. Hostettler, P.R. Carlson, J.B. Rapp, C.N. Threlkeld, and A. Warden. Ubiquitous tar balls with a California-source signature on the shorelines of Prince William Sound, Alaska. *Environ. Sci. Technol.*; 1995, **29**, 2684–2694.

Laflamme, R.E. and R.A. Hites. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochim. Cosmochim. Acta*; 1978, **42**, 289–303.

Laflamme, R.E. and R.A. Hites. Tetra- and pentacyclic, naturally occurring, aromatic hydrocarbons in recent sediments. *Geochim. Cosmochim. Acta*; 1979, **42**, 1687–1691.

Larson, R.A., L.L. Hunt, and D.W. Blankenship. Formation of toxic products from a #2 fuel oil by photooxidation. *Environ. Sci. Technol.*; 1977, **11**, 492–496.

Larter, S.R., B.F.J. Bowler, M. Li, M. Chen, D. Brincat, B. Bennett, K. Noke, P. Donohoe, D. Simmons, M. Kohnen, J. Allan, N. Telaes, and I. Horstad. Molecular indicators of secondary oil migration distances. *Nature*; 1996, **383**, 593–597.

Lee, M.L., D.L. Vassilaros, C.M. White, and M. Novotny. Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. *Anal. Chem.*; 1979, **51**, 768–773.

Leffler, W.L. *Petroleum Refining*, 3rd ed. PennWell Corp., Tulsa, OK; 2000.

Mackay, D. and C.D. McAuliffe. Fate of hydrocarbons discharged at sea. *Oil Chem. Pollut.*; 1988, **5**, 1–20.

Mackenzie, A.S., R.L. Patience, and J.R. Maxwell. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France — I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta*; 1980, **44**, 1709–1721.

Mackenzie, A.S., J. Rullkotter, D.H. Welte, and P. Mankiewicz. Reconstruction of oil formation and accumulation in North Slope, Alaska, using quantitative gas chromatography-mass spectrometry. In: L.B. Magoon and G. Claypool (eds.), *Alaska North Slope Oil/Rock Correlation Study, AAPG Studies in Geology #20*; AAPG, Tulsa, OK; 1985, 319–377.

Madsen, E.L. Determining in situ biodegradation. Facts and challenges. *Environ. Sci. Technol.*; 1991, **25**, 1663–1673.

Marr, L.C., T.W. Kirchstetter, R.A. Harley, A.H. Miguel, S.V. Hering, and S.K. Hammond. Characterization of PAH in motor vehicle fuels and exhaust emissions. *Environ. Sci. Technol.*; 1999, **33**, 3091–3099.

Matyasik, I., A. Steczko, and R.P. Philp. Biodegradation and migrational fractionation of oils from the Eastern Carpathians, Poland. *Org. Geochem.*; 2000, **31**, 1509–1523.

McAuliffe, C.D. Evaporation and solution of C2 to C10 hydrocarbons from crude oils on the sea surface. In: D.Wolfe (ed.), *Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems*; Pergamon Press, NY; 1977, 19–35.

McCarthy, K.J. and R.M. Uhler. Optimizing gas chromatography conditions for improved hydrocarbon analysis; *Proc. 9th Annual Conf. on Contaminated Soils*; Amherst Scientific Publishers, Amherst, MA; 1994.

Michel, J., C.B. Sholz, and B.L. Benggio. Group V fuel oils: Source, behavior, and response issues. In: *Proc. 1995 Oil Spill Conf.* U.S. Coast Guard, American Petroleum Institute, U.S. Environmental Protection Agency, Washington, D.C.; 1995, 559–564.

Michel, J., M.O. Hayes, R.S. Keenan, T.C. Sauer, J.R. Jensen, and S. Narumalani. Contamination of nearshore subtidal sediments of Saudi Arabia from the Gulf War oil spill. *Mar. Pollut. Bull.*; 1993, **27**, 109–116.

Mikolaj, P.G., A.A. Allen, and R.S. Schlueter. Investigation of the nature, extent and fate of natural oil seepage off Southern California. In: *Proc. 4th Annual Offshore Technology Conference*; Dallas, TX; Rpt. No. 1549; 1972.

Moldowan, J.M., W.K. Seifert, and E.J. Gallegos. Relationship between petroleum composition and depositional environment of petroleum source rocks. *Am. Assoc. Petrol. Geol. Bul.*; 1985, **69**, 1255–1268.

Mossner, S.G. and S.A. Wise. Determination of polycyclic aromatic sulfur heterocycles in fossil fuel-related samples. *Anal. Chem.*; 1999, **71**, 58–69.

National Research Council (NRC). *Oil in the Sea III: Inputs, Fates, and Effects.* The National Academy of Science, The National Academies Press, Washington, D.C.; 2003.

Neff, J.M. Composition and fate of petroleum and spill-treating agents in the marine environment. In: J. Geraci and D. St. Aubin (eds.), *Sea Mammals and Oil: Confronting the Risks*; Academic Press, New York; 1990, 1–33.

Nicodem, D.E., M.C.Z. Fernandes, C.L.B. Guedes, and R.J. Correa. Photochemical processes and the environmental impact of petroleum spills. *Biogeochem.*; 1997, **39**, 121–138.

Nordtest. Oil Spill at Sea: Identification, NT Chem 001; Nordtest, Esbo, Finland; 1983.

Nordtest. Oil Spill Identification, NT Chem 001, 2nd ed.; Nordtest, Esbo, Finland; 1991.

Oahn, N.T.K., L.B. Reutergardh, and N.T. Dung. Emission of PAH and particulate matter from domestic combustion of selected fuels. *Environ. Sci. Technol.*; 1999, **33**, 2703–2709.

Osadetz, K.G., L.R. Snowdon, and P.W. Brooks. Oil families in Canadian Williston Basin southwestern Sadkatchewan. *Bull. Can. Petrol. Geol.*; 1995, **42**, 155–177.

Oudot J. Biodegradability of the Erika fuel oil. *Comptes Rendus de l'Academie des Sciences, Serie III, Sci. de la Vie (Life Sciences)*; 2000, **323**, 945–950.

Oudot, J. Rates of microbial degradation of petroleum components as determined by computerized capillary gas chromatography and computerized mass spectrometry. *Mar. Environ. Res.*; 1984, **13**, 277–302.

Page, D.S., J.C. Foster, P.M. Fickett, and E.S. Gilfillan. Identification of petroleum sources in an area impacted by the Amoco *Cadiz* oil spill. *Mar. Pollut. Bull.*; 1988, **19**, 107–115.

Page, D.S., P.D. Boehm, G.S. Douglas, and A.E. Bence. Identification of hydrocarbon sources in the benthic sediments of Prince William Sound and the Gulf of Alaska following the *Exxon Valdez* oil spill. In: P.G. Wells, J.N. Butler, and J.S. Hughes (eds.), *Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters*; ASTM STP 1219; Am. Soc. Testing Materials, Phil., PA; 1995, 41–83.

Palmer, S.E. Effects of biodegradation and water washing on crude oil composition. In: M.H. Engel and S.A. Macko (eds.), *Advances in Organic Geochemistry — 1993*; Plenum Press, New York; 1993, 511–533.

Payne, J.R. and G.D. McNabb. Weathering of petroleum in the marine environment. *Mar. Technol. Soc.*; 1985, **18**, 1–19.

Payne, J.R. and C.R. Phillips. *Petroleum Spills in the Marine Environment: The Chemistry and Formation of Water-in-Oil Emulsions and Tar Balls*; Lewis Publ., Chelsea, MI; 1985.

Payne, J.R., C.R. Phillips, and W. Hom. Transport and transformations: Water column processes. In: D.F. Bosch and N.N. Rabalais (eds.), *Long Term Environmental Effects of Offshore Oil and Gas Development*; Elsevier Applied Science Publ., London; 1987, 175–231.

Peters, K.E., J.M. Moldowan, M. Schoell, and W.B. Hempkins. Petroleum isotopic and biomarker composition related to source rock organic matter and depositional environment. *Org. Geochem.*; 1986, **10**, 17–27.

Peters, K.E., G.L. Scheuerman, C.Y. Lee, J.M. Moldowan, R.N. Reynolds, and M.M. Pena. Effects of refinery processes on biological markers. *Energy & Fuels*; 1992, **6**, 560–577.

Peters, K.E., C.C. Walters, and J.M. Moldowan. *The Biomarker Guide, 2nd ed*. Cambridge University Press, Cambridge, UK; 2005.

Peters, K.E. and M.G. Fowler. Applications of petroleum geochemistry to exploration and reservoir management. *Org. Geochem.*; 2002, **33**, 5–36.

Petkewich, R. Spilled oil persists after 30 years. *Environ. Sci. Technol.*; 2002, 446.

Pieri, N., F. Jacquot, G. Mille, J.P. Planche, and J. Kister. GC-MS identification of biomarkers in road asphalts and in their parent crude oils. Relationships between crude oil maturity and asphalt reactivity towards weathering. *Org. Geochem.*; 1996, **25**, 51–68.

Prince, R.C., R.M. Garrett, R.E. Bare, M.J. Grossman, T. Townsend, J.M. Suflita, K. Lee, E.H. Owens, G.A. Sergy, J.F. Braddock, J.E. Lindstrom, and R.R. Lessard. The roles of photooxidation and biodegradation in long-term weathering of crude oil and heavy fuel oils. *Spill Sci. Technol. Bull.*; 2003, **8**, 145–156.

Prince, R.C., E.H. Owens, and G.A. Sergy. Weathering of an arctic oil spill after 20 years: The BIOS experiment revisited. *Mar. Pollut. Bull.*; 2002a, **44**, 1236–1242.

Prince, R.C., R.T. Stibrany, J. Hardenstine, G.S. Douglas, and E.H. Owens. Aqueous vapor extraction: A previously unrecognized weathering process affecting oil spills in vigorously aerated water. *Environ. Sci. Technol.*; 2002b, **36**, 2822–2825.

Radke, M. Application of aromatic compounds as maturity indicators in source rocks and crude oils. In: *Advances in Organic Geochemistry — 1986*; Butterworth & Co. Ltd., London; 1988.

Radke, M., R.G. Schaefer, and D. Leythaeuser. Composition of soluble organic matter in coals: Relation to rank and liptinite fluorescence. *Geochim. Cosmochim. Acta*; 1980, **44**, 1787–1800.

Radke, M., H. Willsch, and D. Leythaeuser. Aromatic components of coal: Relation of distribution pattern to rank. *Geochim. Cosmochim. Acta*; 1982, **46**, 1831–1848.

Rasmussen, W.V. Characterization of oil spills by capillary column gas chromatography. *Anal. Chem.*; 1975, **48**, 1562–1566.

Reddy, C.M., T.I. Eglinton, A. Hounshell, H.K. White, L. Xu, R.B. Gaines, and G.S. Frysinger. The West Falmouth oil spill after thirty years: The persistence of petroleum hydrocarbons in marsh sediments. *Environ. Sci. Technol.*; 2002, **36**, 4754–4760.

Ronningsen, H.P., J. Sjoblom, and L. Mingyuan. Water-in-oil emulsions from Norwegian continental shelf 11. Aging of crude oils and its influence on the emulsion stability. *Colloids Surfaces A: Physicochem. and Eng. Aspects*; 1995, **97**, 119–128.

Rubinstein, I. and P. Albrecht. The occurrence of nuclear methylated steranes in a shale. *J. Chem. Soc., Chem. Commun.*; 1975, 957–958.

Sauer, T.C. and P.D. Boehm. Guidance document on hydrocarbon chemistry analytical methods for oil spill assessments. Marine Spill Response Corporation, Tech. Rpt. 95-032, Washington, D.C.; 1995.

Sauer, T.C. and A.D. Uhler. Pollutant source identification and allocation: Advances in hydrocarbon fingerprinting. *Remediation*; 1994/1995; Winter Issue, 25–50.

Seifert, W.K., J.M. Moldowan, and R.W. Jones. Application of biological marker chemistry to petroleum exploration. In: *Proc. 10th World Petroleum Congress, Bucharest, Hungary*; Special Paper SP 8; Heyden & Son Limited, London; 1979, 425–440.

Seifert, W.K. and J.M. Moldowan. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochim. Cosmochim. Acta*; 1978, **42**, 77–95.

Seifert, W.K., J.M. Moldowan, and G.J. DeMaison. Source correlation of biodegraded oils. *Org. Geochem.*; 1984, **6**, 633–643.

Short, J.W., K.A. Kvenvolden, P.R. Carlson, F.D. Hostettler, R.J. Rosenbauer, and B.A. Wright. Natural hydrocarbon background in benthic sediments of Prince William Sound, Alaska: Oil vs coal. *Environ. Sci. Technol.*; 1999, **33**, 34–42.

Short, J.W., M.R. Lindeberg, P.M. Harris, J.M. Maselko, J.J. Pella, and S.D. Rice. Estimate of oil persisting on the beaches of Prince William Sound 12 years after the *Exxon Valdez* oil spill. *Environ. Sci. Technol.*; 2004, **38**, 1–25.

Silliman, J.E., P.A. Meyers, B.J. Eadie, and J.V. Klump. A hypothesis for the origin of perylene based on its low abundance in sediments of Green Bay, Wisconsin. *Chem. Geo.*; 2001, **177**, 309–322.

Simoneit, B.R.T. Cyclic terpenoids of the geosphere. In: R.B. Johns (ed.), *Biological Markers in the Sedimentary Record*; Elsevier; Amsterdam, The Netherlands; 1986, 43–99.

Simoneit, B.R.T. and V.O. Elias. Organic tracers from biomass burning in atmospheric particulate matter over the ocean. *Mar. Chem.*; 2000, **69**, 301–312.

Song, C. *Introduction to Chemistry of Diesel Fuels*; Taylor and Francis, New York, NY; 2000.

Speight, J.G. *The Chemistry and Technology of Petroleum, 2nd ed.*, Marcel Dekker, Inc., New York, NY; 1991.

Staniloae, D., B. Petrescu, and C. Patroescu. Pattern recognition based software for oil spill identifi-

cation by gas chromatography and IR spectroscopy. *Environ. Forensics*; 2001, **2**, 363–366.

Stiver, W. and D. Mackay. Evaporation rates of spills and hydrocarbons and petroleum mixtures. *Environ. Sci. Technol.*; 1984, **18**, 834–840.

Stout, S.A. Applications of petroleum fingerprinting in known and suspected pipeline releases — Two case studies. *Appl. Geochem.*; 2003, **18**, 915–926.

Stout, S.A. and G.S. Douglas. Diamondoid hydrocarbons application in the chemical fingerprinting of natural gas condensate and gasoline. *Environ. Forensics*; 2004, **5**, 225–235.

Stout, S.A., A.D. Uhler, and K.J. McCarthy. A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environ. Forensics*; 2001, **2**, 87–98.

Stout, S.A., A.D. Uhler, and K.J. McCarthy. Middle distillate fuel fingerprinting using drimane-based bicyclic sesquiterpanes. *Environ. Forensics*; 2005, **6**, 241–251.

Stout, S.A., A.D. Uhler, and S.D. Emsbo-Mattingly. Characterization of PAH sources in sediments of the Thea Foss/Wheeler Osgood Waterways, Tacoma, Washington. *Soil & Sed. Contam.*; 2003, **12**, 815–834.

Stout, S.A., A.D. Uhler, and S.D. Emsbo-Mattingly. Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways. *Environ. Sci. Technol.*; 2004a, **38**, 2987–2994.

Stout, S.A., A.D. Uhler, and K.J. McCarthy. Chemical characterization and sources of distillate fuels in the subsurface, Mandan, North Dakota. *Environ. Forensics*; 2006, **7**(3), 267–282.

Stout, S.A., A.D. Uhler, K.J. McCarthy, and S. Emsbo-Mattingly. Chemical fingerprinting of hydrocarbons. In: B.L. Murphy and R.D. Morrison (eds.), *Introduction to Environmental Forensics*; Academic Press, Boston, MA; 2002a, 137–260.

Stout, S.A., G. Millner, D. Hamlin, and B. Liu. The role of chemical fingerprinting in assessing the impact of a crude oil spill following Hurricane Katrina. *Env. Claims J.*; 2006b, **18**, 169–184.

Stout, S.A., G.S. Douglas, and A.D. Uhler. Automotive gasoline. In: R.D. Morrison and B.L. Murphy (eds.), *Environmental Forensics, Contaminant Specific Guide*; Academic Press, Boston; 2006a, 465–531.

Stout, S.A., S. Emsbo-Mattingly, A.D. Uhler, and K.J. McCarthy. Particulate coal in soils and sediments — Recognition and potential influences on hydrocarbon fingerprinting and concentration. *Contam. Soil Sed. Water*; 2002b, Dec., 12–15.

Straughan, D. Distribution of tar and relationship to changes in intertidal organisms on sandy beaches in Southern California. In: *Proc. 1979 Oil Spill Conference*; Amer. Petrol. Inst., Washington, D.C.; 591–601.

Strom-Kristiansen T., P.S. Daling, and A. Lewis. Weathering properties and dispersability of crude oils transported in U.S. waters. *Technical Report No. 93-032, Marine Spill Response Corporation, Washington, D.C.*; 1993.

Strom-Kristiansen, T., A. Lewis, P.S. Daling, J.N. Hokstad, and I. Singsaas. Weathering and dispersion of naphthenic, asphaltenic, and waxy crude oils. *Proc. 1997 Int'l. Oil Spill Conf.*; Amer. Petrol. Inst., Washington, D.C.; 1997, 631–636.

Syndes, L.K., T.H. Hemmingsen, S. Skare, S.H. Hansen, I.-B. Falk-Petersen, S. Lonning, and K. Ostgaard. Seasonal variations in weathering and toxicity of crude oil on seawater under arctic conditions. *Environ. Sci. Technol.*; 2001, **19**, 1076–1081.

Teal, J.M., K. Burns, and J. Farrington. Analyses of aromatic hydrocarbons in intertidal sediments resulting from two spills of No. 2 fuel oil in Buzzards Bay, Massachusetts. *J. Fisheries Res. Board of Canada*; 1978, **35**, 510–520.

Telnaes, N. and B. Dahl. Oil–oil correlation using multivariate techniques. *Org. Geochem.*; 1986, **10**, 425–432.

ten Haven, H.L., M. Rohmer, J. Rullkotter, and P. Bisseret. Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. *Geochim. Cosmochim. Acta.*; 1989, **53**, 3073–3079.

Thominette, F. and J. Verdu. Photo-oxidative behaviour of crude oils relative to sea pollution. Part I. Comparative study of various crude oils and model systems. *Mar. Chem.*; 1984, **15**, 91–104.

Thominette, F. and J. Verdu. Photo-oxidative behaviour of crude oils relative to sea pollution. Part II. Photo-induced phase separation. *Mar. Chem.*; 1984, **15**, 105–115.

Tissot, B.P. and D.H. Welte. *Petroleum Formation and Occurrence*, 2nd ed. Springer-Verlag, New York, NY; 1984.

Uhler, R.M., E.M. Healey, K.J. McCarthy, A.D. Uhler, and S.A. Stout. Molecular fingerprinting of gasoline by a modified EPA 8260 gas chromatography/mass spectrometry method. *Int'l. J. Environ. Anal. Chem.*; 2002, **83**, 1–20.

Ukpabio, E.J., P.A. Comet, R. Sassen, and J.M. Brooks. Triterpenes in a Nigerian oil. *Org. Geochem.*; 1994, **22**, 323–329.

United States Environmental Protection Agency (U.S. EPA). Guidance for conducting remedial investigations and feasibility studies under CERCLA. Interim Final. EPA/540/G-89/004. Washington, D.C.: Office of Emergency and Remedial Response. 1988.

United States Environmental Protection Agency (U.S. EPA). Risk assessment guidance for Superfund, Vol. I, Human health evaluation manual (Part A). Interim Final. EPA/540/1-89/002. Washington, D.C.: Office of Emergency and Remedial Response. 1989.

United States Environmental Protection Agency (U.S. EPA). Options for addressing high background levels of hazardous substances at CERCLA sites. Draft Final Issue Paper. Washington, D.C.: Office of Emergency and Remedial Response. 1992.

United States Environmental Protection Agency (U.S. EPA). Determination of background concentrations of inorganics in soils and sediments at harzardous waste sites. Engineering Forum Issue Paper. EPA/540/S-96/500. Washington, D.C.: Office of Emergency and Remedial Response. 1995.

United States Environmental Protection Agency (U.S. EPA). Test methods for evaluating solid waste (SW-846). Update III; 1997.

Urdal, K., N.B. Vogt, S.P. Sporstol, R.G. Lichtenthaler, H. Mostad, K. Kolset, S. Nordenson, and K. Esbensen. Classification of weathered crude oils using multimethod chemical analysis, statistical methods and SIMCA pattern recognition. *Mar. Pollut. Bull.*; 1986, **17**, 366–373.

Volkman, J.K. Biological marker compounds as indicators of the depositional environments of petroleum source rocks. In: A.J. Fleets, K. Kelts, and M.R. Talbot (eds.), *Lacustrine Petroleum Source Rocks, Geol. Soc. Spec. Publ. No. 40*; Blackwell Scientific Publishers, Oxford; 1988, 103–122.

Volkman, J.K., A.T. Revill, and A.P. Murray. Applications of biomarkers for identifying sources of natural and pollutant hydrocarbons in aquatic environments. In: R.P. Eganhouse (ed.), *Molecular Markers in Environmental Geochemistry*; *Am. Chem. Soc.*, Washington, D.C.; 1997, 110–132.

Wade, T.L. and J.G. Quinn. Geochemical investigation of hydrocarbons in sediments from mid-Narragansett Bay, Rhode Island. *Org. Geochem.*; 1979, **1**, 157–167.

Wang, Z. and M. Fingas. Differentiation of the source of spilled oil and monitoring of the oil weathering process using gas chromatography-mass spectrometry. *J. Chromatogr. A*; 1995a, **712**, 321–343.

Wang, Z. and M. Fingas. Study of the effects of weathering on the chemical composition of a light crude oil using GC/MS and GC/FID. *J. Microcolumn Separations*; 1995b, **7**, 617–639.

Wang, Z. and M. Fingas. Use of methyldibenzothiophenes as markers for differentiation and source identification of crude and weathered oils. *Environ. Sci. Technol.*; 1995c, **29**, 2842–2849.

Wang, Z. and M. Fingas. Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil spill-related environmental samples by gas chromatography. *J. Chromatogr.*; 1997, **774**, 51–78.

Wang, Z. and M. Fingas. Development of oil hydrocarbon fingerprinting and identification techniques. *Mar. Pollut. Bull.*; 2003, **47**, 423–452.

Wang, Z., C. Yang, M. Fingas, B. Hollebone, X. Peng, A.B. Hansen, and J. Christensen. Characterization, weathering, and application of source identification of spilled lighter petroleum products. *Environ. Sci. Technol.*; 2005, **39**, 8700–8707.

Wang, Z., M. Fingas, and D.S. Page. Oil spill identification. *J. Chromat. A*; 1999a, **842**, 369–411.

Wang, Z., M. Fingas, and G. Sergy. Study of 22-year-old *Arrow* oil samples using biomarker compounds by GC/MS. *Environ. Sci. Technol.*; 1994b, **28**, 1733–1746.

Wang, Z., M. Fingas, and K. Li. Fractionation of a light crude oil and identification and quantitation of aliphatic, aromatic, and biomarker compounds by GC-FID and GC-MS, part I. *J. Chromat. Sci.*; 1994a, **32**, 361–382.

Wang, Z., M. Fingas, and L. Sigouin. Characterization and identification of a "mystery" oil spill from Quebec (1999). *J. Chromat. A*; 2001b, **909**, 155–169.

Wang, Z., M. Fingas, and L. Sigouin. Characterization and source identification of an unknown spilled oil using fingerprinting techniques by GC–MS and GC–FID. *LC GC N. Am.*; October 2000, **18**, 1058–1067.

Wang, Z., M. Fingas, M. Landriault, L. Sigouin, B. Castle, D. Hostetter, D. Zhang, and B. Spencer. Identification and linkage of tarballs from

the coasts of Vancouver Island and Northern California using GC/MS and isotopic techniques. *J. High Resol. Chromat.*; 1993, **21**, 383–395.

Wang, Z., M. Fingas, S. Blenkinsopp, G. Sergy, M. Landriault, L. Sigouin, and P. Lambert. Study of the 25-year-old Nipisi oil spill: Persistence of oil residues and comparisons between surface and subsurface sediments. *Environ. Sci. Technol.*; 1998, **32**, 2222–2232.

Wang, Z., S.A. Stout, and M. Fingas. Biomarker fingerprinting for spill oil characterization and source identification (Review). *Environ. Forensics*; 2006, **7**(2), 105–146.

Wang, Z.D., B.P. Hollebone, M. Fingas, B. Fieldhouse, and J. Weaver. *Characteristics of spilled oils, fuels, and petroleum products: 1. Composition and properties of selected oils*; U.S. EPA/600/R-03/072, National Exposure Research Laboratory (NERL), EPA, 2003. Also available at the EPA website: www.epa.gov/epahome/recentadditions.htm.

Waterborne Commerce of the United States (WCUS), Part 5 — National Summaries. *U.S. Army Corps of Engineers*; 2003. Also available at the EPA website; also available at the USACE website: http://www.iwr.usace.army.mil/ndc/wcsc/pdf/wcusnatl03.pdf.

Westerholm, R.N., T.E. Alsberg, A.B. Frommelin, M.E. Strandell, U. Rannug, L. Winquist, A. Grigoriadis, and K.-E. Egebäck. Effect of fuel polycyclic aromatic hydrocarbon content on the emissions of polycyclic aromatic hydrocarbons and other mutagenic substances from a gasoline-fueled automobile. *Environ. Sci. Technol.*; 1988, **22**, 925–930.

White, C.M. and M.L. Lee. Identification and geochemical significance of some aromatic components of coal. *Geochim. Cosmochim. Acta*; 1980, **44**, 1825–1832.

Wolfe, D.A., M.J. Hameedi, J.A. Galt, G. Watabayashi, J. Short, C. O'Claire, S. Rice, J. Michel, J.R. Payne, J. Braddock, S. Hanna, and D. Sale. The fate of the oil spilled from the *Exxon Valdez*. *Environ. Sci. Technol.*; 1994, **28**, 561A–568A.

Wu, Q., M.R. Gray, M.A. Pickard, P.M. Fedorak, J.M. Foght. Biocatalytic ring opening of dibenzothiophene and phenanthrene as model substrates dissolved in crude oil. *Petrol. Chem. Div. Preprints No. 615061*; *Am. Chem. Soc.*; 2002, 47.