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Review

## Oil spill identification

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### Abstract

To unambiguously identify spilled oils and petroleum products and to link them to the known sources are extremely important in settling questions of environmental impact and legal liability. This article briefly reviews the most recent development and advances of chemical fingerprinting and data interpretation techniques which are most frequently used in oil spill identification studies, including recognition of relative distribution patterns of petroleum hydrocarbons, analysis of 'source-specific marker' compounds, determination of diagnostic ratios of specific oil constituents, isotopic analysis, and several other emerging techniques. The issue of how biogenic and pyrogenic hydrocarbons are distinguished from petrogenic hydrocarbons is also addressed. Finally, the example of the Exxon Valdez spill is reviewed to illustrate how complex hydrocarbon mixtures were identified and allocated to multiple sources by using these advanced chemical fingerprinting techniques. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Reviews; Environmental analysis; Oil spill identification; Petroleum; Carbon isotope ratio analysis; Polycyclic aromatic hydrocarbons

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## 1. Introduction

Petroleum is a complex mixture of thousands of different organic compounds formed from a variety of organic materials that are chemically converted under differing geological conditions over long periods of time. Crude oils contain primarily carbon and hydrogen (which form a wide range of hydrocarbons from light gases to heavy residues), but also contains smaller amounts of sulfur, oxygen and nitrogen as well as metals such as nickel, vanadium and iron. The infinitely variable nature of these factors results in distinct chemical differences between oils. Refined petroleum products are fractions usually derived by distillation of crude oil. Because of dissimilarities in characteristics of crude oil feed stocks and variations in refinery processes, refined oil products differ in their chemical compositions. Thus, all crude oils and petroleum products, to some extent, have chemical compositions that differ from each other. This variability in chemical compositions results in unique chemical ‘fingerprints’ for each oil and provides a basis for identifying the source(s) of the spilled oil.

As industrialization processes speed up and demands for energy grow worldwide, oil spills have become a global problem, in particular in industrialized countries. A historical review and analysis of reported oil spills over 37 800 liters (34 000 kg) in the International Oil Spill Database shows that since the early 1960s, nearly  $1.14 \cdot 10^6 \text{ m}^3$  ( $1.02 \cdot 10^9 \text{ kg}$ ) of oil have spilled into USA marine waters which occurred in 826 incidents involving tankers, barges, and other vessels [1], and about  $0.76 \cdot 10^6 \text{ m}^3$  ( $0.68 \cdot$

$10^9 \text{ kg}$ ) of oil onto USA soil from the land pipeline spills (on average, 99 land pipeline spills per year [2]). An estimated  $1.9 \cdot 10^6 \text{ m}^3$  ( $1.7 \cdot 10^9 \text{ kg}$ ) and over  $0.76 \cdot 10^6 \text{ m}^3$  ( $0.68 \cdot 10^9 \text{ kg}$ ) of oil have spilled from tankers in Europe [3] and Pacific Asia [4] since 1965, respectively. As an example, Table 1 summarizes oil spills over 37 800 l (34 000 kg) into USA marine waters from 1960 to 1997. The huge quantities of spilled oils and petroleum products enter our sea, territory and groundwater, causing extensive damage to marine life, terrestrial life, human health, and natural resources. To unambiguously characterize spilled oils in complex contaminated environmental samples and to link them to the known sources are extremely important for environmental damage assessment, prediction of the potential long-term impact of spilled oils on the environment, selecting appropriate spill response and taking effective clean-up measures. In addition, characterization of chemical compositions and identification of oil spill sources are, in many cases, critical for settling disputes related to liability.

The fate and behaviour of spilled oils in the environment depends on a number of physicochemical and biological factors including evaporation, dissolution, microbial degradation, photooxidation, and interaction between oil and sediments [5]. The combination of these processes, called ‘weathering’, reduces the concentrations of hydrocarbons in sediment and water and alters the chemical composition of spilled oils. The changes in the chemical composition of the spilled oil have profound effects on the oil’s toxicity and biological impact of the oil over the time, and hence add great difficulties to the

Table 1  
Oil spills over 378 00 liters (34 000 kg) into US marine waters (1962–1997)

Year	Total spills	Amount spilled ( $\times 10^3$ kg)
1962	1	10 000
1963	1	5 000
1964	5	6 861
1965	2	1 741
1966	3	21 350
1967	3	27 520
1968	6	84 245
1969	8	50 578
1970	7	33 139
1971	8	52 187
1972	11	17 844
1973	14	17 378
1974	14	24 071
1975	19	102 867
1976	15	53 912
1977	16	113 519
1978	46	43 724
1979	44	48 738
1980	64	18 833
1981	30	11 316
1982	22	2 486
1983	28	15 833
1984	36	38 007
1985	38	13 583
1986	38	14 582
1987	46	29 796
1988	43	23 925
1989	46	59 483
1990	52	37 622
1991	22	7 154
1992	26	4 335
1993	23	3 869
1994	31	11 182
1995	16	2 031
1996	26	6 260
1997	16	1 923
Total	826	$1.02 \cdot 10^9$ kg ( $1.13 \cdot 10^6$ m <sup>3</sup> )

identification of the residual spilled oil in the impacted environment. Obviously, how to efficiently and unambiguously identify sources of spilled oils of different nature, form and type is a challenge to geochemists and analytical chemists.

Hundreds of papers on the fate (the contamination extent and weathering behaviour), effects (impacts on biological communities), and sources of spilled oils and petroleum products have been published during the last two decades. Great advances have

been made on analyses of petroleum hydrocarbons in oils, petroleum products and complex oil-spill-related environmental samples. Rather than attempting to review all aspects of oil spills, this paper will focus on reviewing various advanced petroleum hydrocarbon fingerprinting and data interpretation techniques for oil spill identification. First, we will briefly review the most recent developments and advances of chemical fingerprinting techniques for oil spill. Second, we will address the issue of how biogenic and pyrogenic hydrocarbons are distinguished from petrogenic hydrocarbons. Third, we will review the techniques most frequently used for oil spill source identification, which include recognition of relative distribution patterns of petroleum hydrocarbons, analysis of 'source-specific marker' compounds, determination of diagnostic ratios of specific oil constituents, isotopic analysis, and several other techniques. Finally, the example of the Exxon Valdez spill will be reviewed to illustrate how complex hydrocarbon mixtures were identified and allocated to multiple sources by using these advanced chemical fingerprinting techniques.

## 2. Advances in chemical fingerprinting techniques for oil spill studies

A wide variety of instrumental and non-instrumental techniques are currently used in the analysis of oil hydrocarbons, which include gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC), size-exclusion HPLC, infrared spectroscopy (IR), supercritical fluid chromatography (SFC), thin-layer chromatography (TLC), ultraviolet (UV) and fluorescence spectroscopy, isotope ratio mass spectrometry, and gravimetric methods. Of all these techniques, GC techniques are the most widely used. Compared to the molecular measurements two decades ago, GC methods have now been enhanced by more sophisticated analytical techniques, such as capillary GC–MS, which is capable of analyzing the oil-specific biomarker compounds and polycyclic aromatic hydrocarbons. The accuracy and precision of analytical data has been improved and optimized by a series of quality assurance/quality control measures, and the laboratory data handling capability

has been greatly increased through advances in computer technology. Whittaker et al. [6] recently presented a review with 90 references on current analytical methodologies for the characterization of heavy oil-contamination extracted from waste-soil matrices. The applications and limitations of a variety of conventional and novel techniques for the rapid screening and extended analysis of refractory petroleum waste streams are discussed. In a report to the Marine Spill Response Corporation, Sauer and Boehm [7] provides a detailed guidance to chemical analytical methodologies related to oil spill response. Tiered analytical approach, benefits of certain methods and the method limitations are presented with over 110 references being cited. Krahn et al. [8] reviewed the application of rapid HPLC methods to screen for aromatic components in sediments, bile and tissue samples. These methods have been used to assess damage to natural resources after the Exxon Valdez oil spill. In addition, bile screening methods has also been used to evaluate contaminants in fish samples for a national monitoring program. Landance and Greibrokk [9] present a review with 109 references on employing various analytical techniques for fractionation and determination of main hydrocarbon classes and subgroups in fuels, heavy petroleum fractions and crude oils. In a recent review, Kaplan et al. [10] described the so-called Forensic Environmental Geochemistry (FEG) methodologies and their use for differentiating various hydrocarbon fuels (specifically for the light and middle distillate petroleum products in the  $C_3$ – $C_{25}$  hydrocarbon range) and solvents in environmentally altered samples. They also described how fuel additives can be used as tracers for estimating residence time in the environment and time of manufacture of gasoline. The methodologies have been used in numerous environmental cases throughout the USA to provide evidences in resolving legal disputes relating to the source identification of environmental contaminants.

Depending on chemical/physical information needs, the point of application and the level of analytical detail, the methods used for oil spill study can be, in general, divided into two categories: non-specific methods and specific methods for detailed component analysis [6,11].

### 2.1. Non-specific methods

The conventional non-specific methods include field screening gas chromatography with flame ionization detection (GC–FID) and photoionization detection (GC–PID) [12–16]; gravimetric and IR determinations [such as US Environmental Protection Agency (EPA) Method 418.1 and Method 9071, and American Society for Testing and Materials (ASTM) Method 3414 and 3921] [17–19]; ultraviolet fluorescence spectroscopy [20,21], TLC which has been extensively used in the component class characterization of various whole oils and oil fractions [22–25]; HPLC [8,26,27], size-exclusion chromatography [28,29], supercritical fluid chromatography (SFC) [30], and recently-developed infrared fibre optic sensor for identification of various petroleum samples [31]. Compared to the specific methods, these non-specific methods require shorter preparation and analytical time and are less expensive to use. These techniques have been used to screen sediments for petroleum saturate and aromatic compounds, to measure total petroleum hydrocarbons (TPHs), to assess site contamination, to determine the presence and type of petroleum products that may exist in soil or water, and to qualitatively examine and compare oil weathering/degradation.

In recognition of higher costs associated with extensive analysis of large numbers of environmental samples by more sophisticated GC–MS, Krahn et al. [28,29] determined the molecular mass (size) distribution of the residual oil in over three thousand Exxon Valdez spilled oil sediment samples by the rapid size-exclusion HPLC with fluorescence detection. The distinctive chromatographic patterns of different crude oils and crude oil fractions also demonstrated the utility of the technique in distinguishing between possible hydrocarbon sources (Fig. 1). As Fig. 1 shows, the chromatograms of diesel (Fig. 1a), marine lubricating oil (Fig. 1c), and Exxon Valdez crude oil (Fig. 1e), exhibit different chromatographic profiles. In contrast, numerous similarities exist between chromatograms of the crude oils from the Exxon Valdez (Fig. 1e) and Gulf spills (Fig. 1g). In addition, chromatographic profiles of diesel fuel (Fig. 1a) and No. 2 fuel oil from the North Cape (Fig. 1b) are similar, demonstrating that

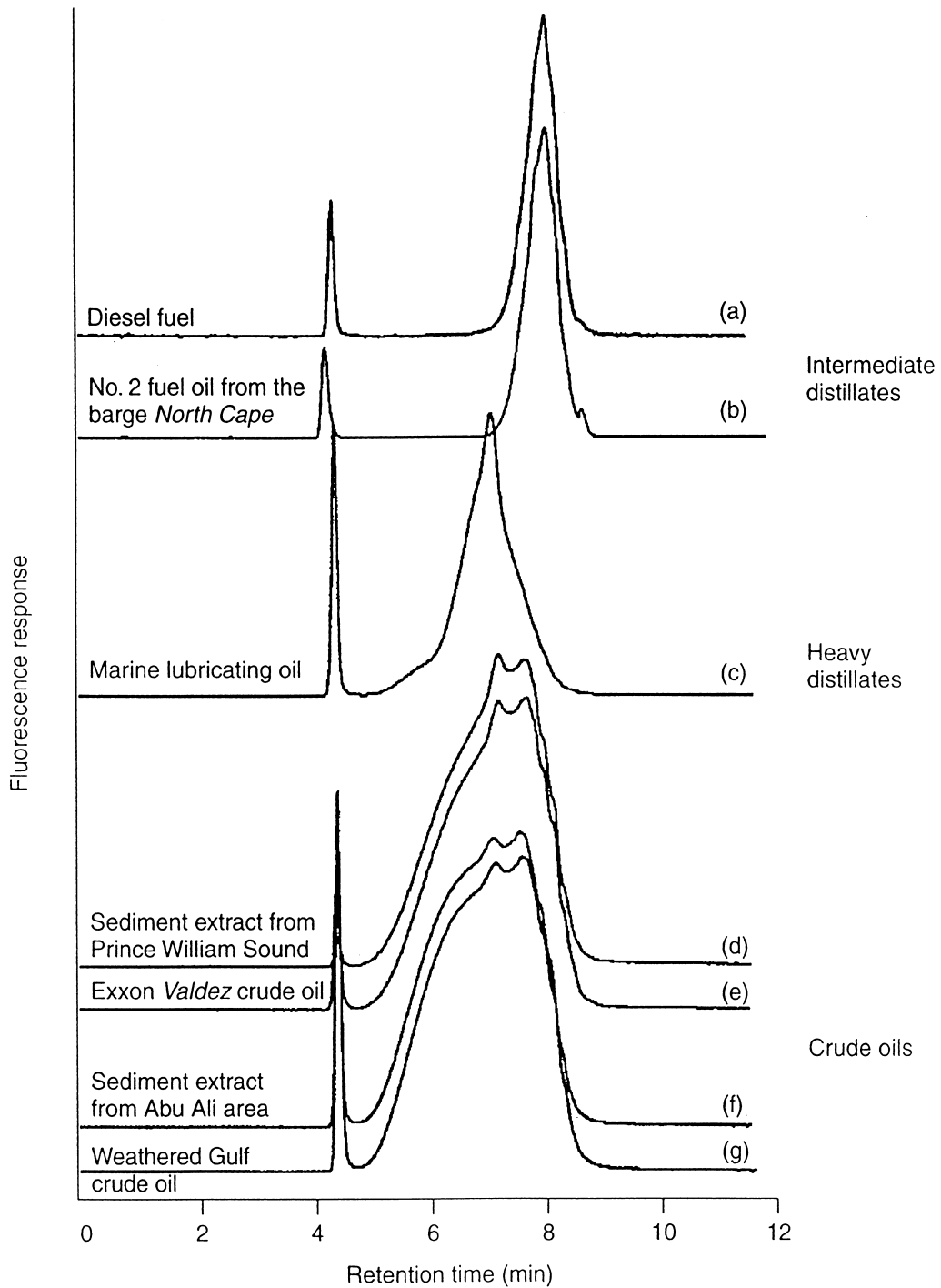


Fig. 1. Chromatograms from the size-exclusion HPLC/fluorescence analysis of petroleum fractions. (a) Diesel fuel; (b) No. 2. fuel oil spilled from the North Cape; (c) Marine lubricating oil (d) Extract of sediment from Knight Island in Prince William Sound, AD (e) Exxon Valdez crude oil; (f) Extract of sediment from the Abu Ali area of Saudi Arabia; (g) Weathered Persian Gulf crude. Fluorescence excitation was recorded at 260 nm and emission at 380 nm. The peak at about 4.5 min is the polystyrene internal standard (adapted from Ref. [29]).

these fractions distill in the same temperature range and contain compounds of similar molecular masses. Thus, the type of petroleum distillate and possible source can be suggested from the HPLC analysis, but detailed analyses are needed to provide a more definitive answer.

The major shortcoming associated with the non-specific methods is that the data generated from these methods generally lack detailed individual component and petroleum source-specific information [10,32], and therefore these methods are of limited value in many cases, for spilled oil characterization and source identification. For example, the EPA methods including 602, 610, 624 and some of the 8000 series methods [33] have been used as routine procedures for determination of volatile and semivolatile aromatic hydrocarbons presented in spilled oil and petroleum product samples. However, these methods were originally designed for waste water and industrial waste. Of the more than 160 priority-pollutant compounds determined by these methods, only 20 are petroleum-related. Further, only half of these 20 compounds are found in significant quantities in oils and petroleum products. Also, the polycyclic aromatic hydrocarbon (PAH) compounds in oils are dominated almost exclusively by the C<sub>1</sub>–C<sub>4</sub> alkylated homologues of the parent PAHs, in particular, naphthalene, phenanthrene, dibenzothiophene, fluorene and chrysene, none of which are measured by the standard EPA methods. Other important classes of petroleum hydrocarbons (e.g., aliphatics and biomarkers) are not measured by these methods at all. Another example is the use of the EPA 418.1 method to determine TPH content. The EPA 418.1 method [17], based on measuring the absorption of C–H bond in the 3200–2700 wavenumber range, was originally intended for use only with liquid waste but had been one of the most widely used methods for the determination of TPH in soils before its demise because of the use of a chlorofluorocarbon extractant. For some site assessments, Method 418.1 was the sole criterion for verification of site cleanup. However, there were some problems associated with this method such as inherent inaccuracy in the method (i.e., positive or negative biases caused by various factors) and the lack of effective reference standards when working with an unknown. The limitations of these standard

EPA methods have been discussed in detail by many authors [20,32,34–37].

## 2.2. Specific methods for detailed component analysis

In response to the oil spill identification need and specific site investigation needs, attention has recently focussed on the development of flexible, tiered analytical approaches which facilitate the detailed compositional analysis by GC–MS, GC–FID, and other analytical techniques that determine individual petroleum hydrocarbons [36,38–44]. Many EPA and ASTM methods have been modified to improve specificity and sensitivity for measuring spilled oil and petroleum products in soils and waters [18,19,27,45–48]. A variety of diagnostic ratios, especially ratios of PAHs and biomarker compounds, for interpreting chemical data from oil spills have been proposed for oil source identification and monitoring of weathering and biological degradation processes [34,36,38–40,49–59]. These modified methods are a clear advance over standard EPA methods because they can provide far more information directly useful for characterization and quantification of oil hydrocarbons and for oil spill identification.

### 2.2.1. Oil spill identification protocol

The oil spill identification system currently used is largely based on two analytical techniques: GC–FID and GC–MS. Data produced from these two methods are used to compare spill samples with samples taken from suspected sources. If significant differences in hydrocarbon fingerprints and diagnostic ratios are found at any stage in the identification process, the conclusion will be that the samples are not from the suspected source. When all data from the two methods have been compared and no such difference have been found, it can be concluded that identity of the spilled oil and the suspected source oil is the same. Fig. 2 outlines the oil spill identification protocol [10,36].

### 2.2.2. Selection of source-specific target analytes

In the non-specific methods, only groups or fractions of chemical hydrocarbons (such as TPH, total saturates, EPA priority PAHs, and volatile content)

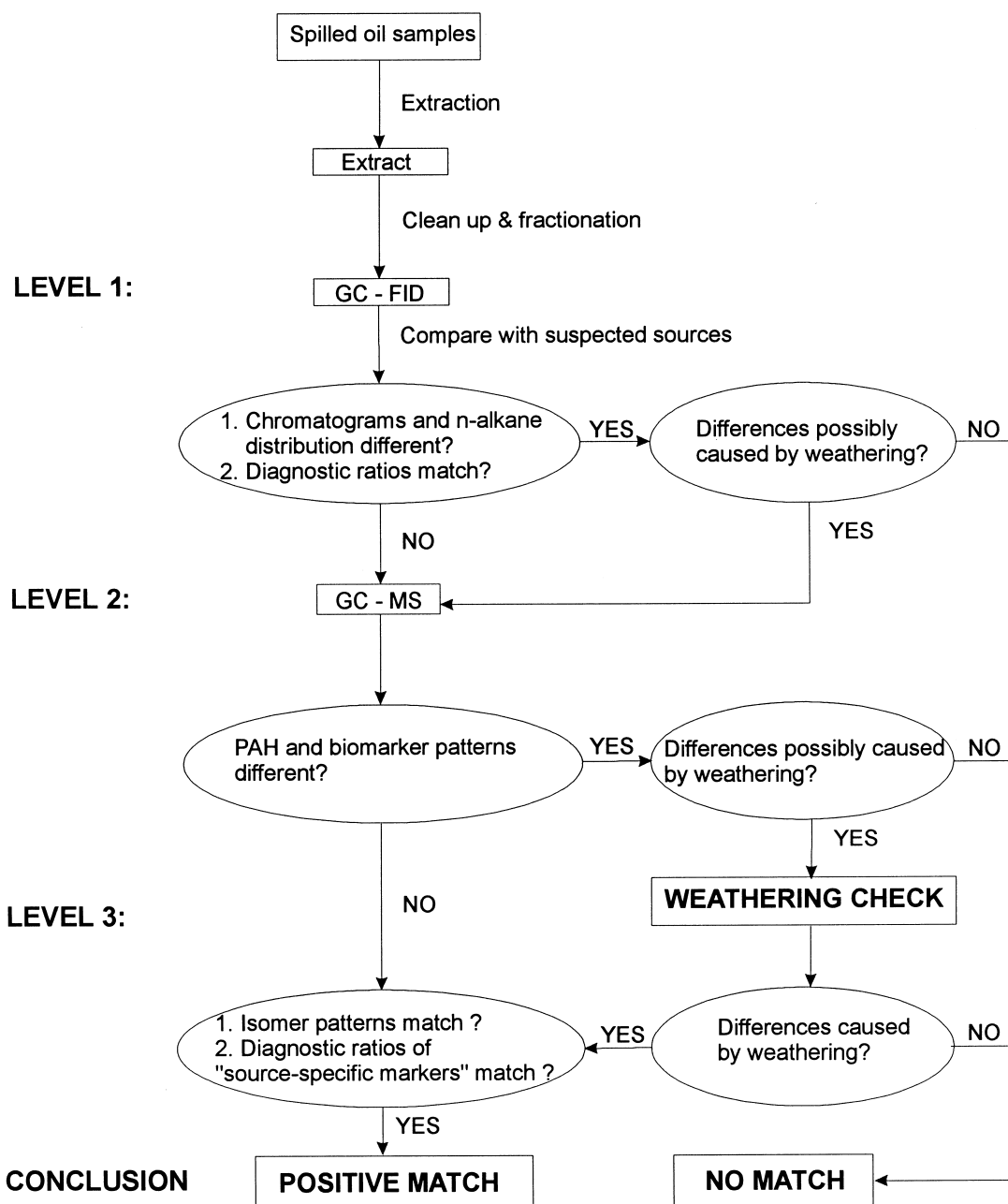


Fig. 2. Oil spill identification protocol chart (modified from Ref. [36]).

were identified. Oil spill identification requires further elaboration of oil target analytes to include identification of the individual specific target compounds and isomeric groups. The selection of appropriate target oil analytes is dependent mainly on the

type of oil spilled, the particular environmental compartments being assessed, and on expected needs for current and future data comparison [7,10]. In general, the major petroleum-specific target analytes [7,10,32,36,41,45,46,49–54] that may be needed to

be chemically characterized for oil source identification and environmental assessment include the following:

(1) Individual saturated hydrocarbons including *n*-alkanes (C<sub>8</sub>–C<sub>40</sub>) and selected isoprenoids pristane and phytane (in some cases, another three highly-abundant isoprenoid compounds farnesane, trimethyl-C<sub>13</sub>, and norpristane are also included);

(2) The volatile BTEX (benzene, toluene, ethylbenzene, and three xylene isomers) and alkylated benzenes (C<sub>3</sub>–C<sub>5</sub>-benzenes);

(3) The EPA priority parent PAHs and, in particular, the petroleum-specific alkylated (C<sub>1</sub>–C<sub>4</sub>) homologues of selected PAHs (that is, alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene series). These alkylated PAH homologues (Table 2) are the backbone of chemical characterization and identification of oil spill assessments;

(4) Biomarker terpane and sterane compounds (Table 3). Analysis of selected ion peaks produced by these characteristic, environmentally-persistent compounds generates information of great importance in determining source(s), weathered state and potential treatability;

Measurements of TPHs, the unresolved complex mixtures (UCMs), and stable carbon isotope ratio (δ<sup>13</sup>C) are also included in many cases.

Another potentially-valuable hydrocarbon group for oil spill identification is nitrogen and oxygen heterocyclic hydrocarbons. These heterocyclic hydrocarbons are generally only present in oils at quite relatively low concentrations compared to PAHs. However, they become enhanced with weathering because they are biorefractory and persistent in the environment [57]. Most organic nitrogen hydrocarbons in crude oils are present as alkylated aromatic heterocycles with a predominance of neutral pyrrolic structures over basic pyridine forms [64]. They are chiefly associated with high boiling fractions, much of the nitrogen in petroleum being in asphaltenes [58,60,61]. Individual and alkyl homologues of carbazole, quinoline, and pyridine have been identified in many crude oils [55,58–62]. These compounds may provide important clues for potential sources of hydrocarbons in the environment and for tracing petroleum molecules back to their biological precursors [55,56]. Compared to the PAHs and

Table 2

Source-specific target PAHs and alkylated homologous PAHs for oil spill studies

Compound	Code	Ring numbers	Target ions
Oil-characteristic alkylated PAHs			
Naphthalenes			
C <sub>0</sub> -naphthalene	C <sub>0</sub> N	2	128
C <sub>1</sub> -naphthalenes	C <sub>1</sub> N	2	142
C <sub>2</sub> -naphthalenes	C <sub>2</sub> N	2	156
C <sub>3</sub> -naphthalenes	C <sub>3</sub> N	2	170
C <sub>4</sub> -naphthalenes	C <sub>4</sub> N	2	184
Phenanthrenes			
C <sub>0</sub> -phenanthrene	C <sub>0</sub> P	3	178
C <sub>1</sub> -phenanthrenes	C <sub>1</sub> P	3	192
C <sub>2</sub> -phenanthrenes	C <sub>2</sub> P	3	206
C <sub>3</sub> -phenanthrenes	C <sub>3</sub> P	3	220
C <sub>4</sub> -phenanthrenes	C <sub>4</sub> P	3	234
Dibenzothiophenes			
C <sub>0</sub> -dibenzothiophene	C <sub>0</sub> D	3	184
C <sub>1</sub> -dibenzothiophenes	C <sub>1</sub> D	3	198
C <sub>2</sub> -dibenzothiophenes	C <sub>2</sub> D	3	212
C <sub>3</sub> -dibenzothiophenes	C <sub>3</sub> D	3	226
Fluorenes			
C <sub>0</sub> -fluorene	C <sub>0</sub> F	3	166
C <sub>1</sub> -fluorenes	C <sub>1</sub> F	3	180
C <sub>2</sub> -fluorenes	C <sub>2</sub> F	3	194
C <sub>3</sub> -fluorenes	C <sub>3</sub> F	3	208
Chrysenes			
C <sub>0</sub> -chrysene	C <sub>0</sub> C	4	228
C <sub>1</sub> -chrysenes	C <sub>1</sub> C	4	242
C <sub>2</sub> -chrysenes	C <sub>2</sub> C	4	256
C <sub>3</sub> -chrysenes	C <sub>3</sub> C	4	270
Other EPA priority PAH pollutants			
Biphenyl	Bph	2	154
Acenaphthylene	AcI	3	152
Acenaphthene	Ace	3	153
Anthracene	An	3	178
Fluoranthene	Fl	4	202
Pyrene	Py	4	202
Benz[ <i>a</i> ]anthracene	BaA	4	228
Benzo[ <i>b</i> ]fluoranthene	BbF	5	252
Benzo[ <i>k</i> ]fluoranthene	BkF	5	252
Benzo[ <i>e</i> ]pyrene	BeP	5	252
Benzo[ <i>a</i> ]pyrene	BaP	5	252
Perylene	Pe	5	252
Indeno[1,2,3- <i>cd</i> ]pyrene	IP	6	276
Dibenz[ <i>a,h</i> ]anthracene	DA	5	278
Benzo[ <i>ghi</i> ]perylene	BP	6	276
Surrogates and Internal Standard			
[ <sup>2</sup> H <sub>10</sub> ]Acenaphthene			164
[ <sup>2</sup> H <sub>10</sub> ]Phenanthrene			188
[ <sup>2</sup> H <sub>12</sub> ]Benz[ <i>a</i> ]anthracene			240
[ <sup>2</sup> H <sub>12</sub> ]Perylene			264
[ <sup>2</sup> H <sub>14</sub> ]Terphenyl			244



Table 3  
Source-specific target biomarker terpane and sterane compounds for oil spill studies

Peak	Compound	Empirical formula	Molecular mass
<b>Terpanes</b>			
1	C <sub>19</sub> tricyclic terpane	C <sub>19</sub> H <sub>34</sub>	262
2	C <sub>20</sub> tricyclic terpane	C <sub>20</sub> H <sub>36</sub>	276
3	C <sub>21</sub> tricyclic terpane	C <sub>21</sub> H <sub>38</sub>	290
4	C <sub>22</sub> tricyclic terpane	C <sub>22</sub> H <sub>40</sub>	304
5	C <sub>23</sub> tricyclic terpane	C <sub>23</sub> H <sub>42</sub>	318
6	C <sub>24</sub> tricyclic terpane	C <sub>24</sub> H <sub>44</sub>	332
7	C <sub>25</sub> tricyclic terpane	C <sub>25</sub> H <sub>46</sub>	346
8	C <sub>24</sub> tetracyclic terpane+C <sub>26</sub> tricyclic terpanes	C <sub>24</sub> H <sub>42</sub> +C <sub>26</sub> H <sub>48</sub>	
9	C <sub>28</sub> tricyclic terpane	C <sub>28</sub> H <sub>52</sub>	388
10	C <sub>28</sub> tricyclic terpane	C <sub>28</sub> H <sub>52</sub>	388
11	C <sub>29</sub> tricyclic terpane	C <sub>29</sub> H <sub>54</sub>	402
12	C <sub>29</sub> tricyclic terpane	C <sub>29</sub> H <sub>54</sub>	402
13	Ts: 18α(H),21β(H)-22,29,30-trisnorhopane	C <sub>27</sub> H <sub>46</sub>	370
14	17α(H),18α(H),21β(H)-25,28,30-trisnorhopane	C <sub>27</sub> H <sub>46</sub>	370
15	Tm: 17α(H),21β(H)-22,29,30-trisnorhopane	C <sub>27</sub> H <sub>46</sub>	370
16	17α(H),18α(H),21β(H)-28,30-bisnorhopane	C <sub>28</sub> H <sub>48</sub>	384
17	17α(H),21β(H)-30-norhopane	C <sub>29</sub> H <sub>50</sub>	398
18	18α(H),21β(H)-30-norneohopane	C <sub>29</sub> H <sub>50</sub>	398
19	17α(H),21β(H)-hopane	C <sub>30</sub> H <sub>52</sub>	412
20	17β(H),21α(H)-hopane	C <sub>30</sub> H <sub>52</sub>	412
21	22 <i>S</i> -17α(H),21β(H)-30-homohopane	C <sub>31</sub> H <sub>54</sub>	426
22	22 <i>R</i> -17α(H),21β(H)-30-homohopane	C <sub>31</sub> H <sub>54</sub>	426
23	17β(H),21β(H)-hopane	(Internal standard)	
24	22 <i>S</i> -17α(H),21β(H)-30,31-bishomohopane	C <sub>32</sub> H <sub>56</sub>	440
25	22 <i>R</i> -17α(H),21β(H)-30,31-bishomohopane	C <sub>32</sub> H <sub>56</sub>	440
26	22 <i>S</i> -17α(H),21β(H)-30,31,32-trishomohopane	C <sub>33</sub> H <sub>58</sub>	454
27	22 <i>R</i> -17α(H),21β(H)-30,31,32-trishomohopane	C <sub>33</sub> H <sub>58</sub>	454
28	22 <i>S</i> -17α(H),21β(H)-30,31,32,33-tetrakishomohopane	C <sub>34</sub> H <sub>60</sub>	468
29	22 <i>R</i> -17α(H),21β(H)-30,31,32,33-tetrakishomohopane	C <sub>34</sub> H <sub>60</sub>	468
30	22 <i>S</i> -17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	C <sub>35</sub> H <sub>62</sub>	482
31	22 <i>R</i> -17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	C <sub>35</sub> H <sub>62</sub>	482
<b>Steranes</b>			
32	C <sub>20</sub> 5α(H),14α(H),17α(H)-sterane	C <sub>20</sub> H <sub>34</sub>	274
33	C <sub>21</sub> 5α(H),14β(H),17β(H)-sterane	C <sub>21</sub> H <sub>36</sub>	288
34	C <sub>22</sub> 5α(H),14β(H),17β(H)-sterane	C <sub>22</sub> H <sub>38</sub>	302
35	C <sub>27</sub> 20 <i>S</i> -13β(H),17α(H)-diasterane	C <sub>27</sub> H <sub>48</sub>	372
36	C <sub>27</sub> 20 <i>R</i> -13β(H),17α(H)-diasterane	C <sub>27</sub> H <sub>48</sub>	372
37	C <sub>27</sub> 20 <i>S</i> -13α(H),17β(H)-diasterane	C <sub>27</sub> H <sub>48</sub>	372
38	C <sub>27</sub> 20 <i>R</i> -13α(H),17β(H)-diasterane	C <sub>27</sub> H <sub>48</sub>	372
39	C <sub>28</sub> 20 <i>S</i> -13β(H),17α(H)-diasterane	C <sub>28</sub> H <sub>50</sub>	386
40	C <sub>29</sub> 20 <i>S</i> -13β(H),17α(H)-diasterane	C <sub>29</sub> H <sub>52</sub>	400
41	C <sub>29</sub> 20 <i>R</i> -13α(H),17β(H)-diasterane	C <sub>29</sub> H <sub>52</sub>	400
42	C <sub>27</sub> 20 <i>S</i> -5α(H),14α(H),17α(H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372
43	C <sub>27</sub> 20 <i>R</i> -5α(H),14β(H),17β(H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372
44	C <sub>27</sub> 20 <i>S</i> -5α(H),14β(H),17β(H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372
45	C <sub>27</sub> 20 <i>R</i> -5α(H),14α(H),17α(H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372
46	C <sub>28</sub> 20 <i>S</i> -5α(H),14α(H),17α(H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386
47	C <sub>28</sub> 20 <i>R</i> -5α(H),14β(H),17β(H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386
48	C <sub>28</sub> 20 <i>S</i> -5α(H),14β(H),17β(H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386
49	C <sub>28</sub> 20 <i>R</i> -5α(H),14α(H),17α(H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386
50	C <sub>29</sub> 20 <i>S</i> -5α(H),14α(H),17α(H)-stigmastane	C <sub>29</sub> H <sub>52</sub>	400
51	C <sub>29</sub> 20 <i>R</i> -5α(H),14β(H),17β(H)-stigmastane	C <sub>29</sub> H <sub>52</sub>	400
52	C <sub>29</sub> 20 <i>S</i> -5α(H),14β(H),17β(H)-stigmastane	C <sub>29</sub> H <sub>52</sub>	400
53	C <sub>29</sub> 20 <i>R</i> -5α(H),14α(H),17α(H)-stigmastane	C <sub>29</sub> H <sub>52</sub>	400

biomarkers, the application of nitrogen and oxygen-containing heterocyclic hydrocarbons in source identification is still in its infancy, and more research is needed.

### 2.2.3. Using tiered analytical approach

Tiered analytical approaches have been increasingly applied for oil spill identification in recent years. Depending on the needs of spilled oil characterization, support for biological studies, monitoring weathering effects on chemical composition changes, or source differentiation, the tiered analytical approaches may vary. In the comprehensive study of the fates and effects of the Exxon Valdez oil spill in Prince William Sound (PWS) of Alaska, Boehm and Page et al. [39,40,50,51,63,64] have applied various tiered analytical approaches to obtain hydrocarbon fingerprints in thousands of sediment and biological samples and to allocate complex hydrocarbons to multiple sources. Wang et al. have reported application of a tiered analytical approach for identification of the source of an unknown oil on contaminated birds [65] and for identification and differentiation of unknown British Columbia and California tarball samples [66]. The tiered approach they used includes the following: tier 1, determination of hydrocarbon groups in oil residues; tier 2, product screening and determination of *n*-alkanes and TPHs; tier 3, distribution pattern recognition of target PAHs and biomarker components (sometimes the volatile hydrocarbons are monitored); tier 4, determination and comparison of diagnostic ratios of the 'source-specific marker' compounds with the potential source oil and with the corresponding data from database; tier 5, determination of weathered percentages of the residual oil.

### 2.2.4. Quality assurance

The reliability of analytical data for the advanced chemical fingerprinting is largely dependent on the quality assurance and quality control procedures used [34,41,43,46,51]. Quality control charts have been used to determine if analyses of a quality control samples are outside statistical limits [68,67]. Yancey et al. [69] described a quality control scheme to achieve reproducible capillary GC characterization of crude oils and petroleum condensates.

Besides the routine quality control measures re-

quired by standard EPA and ASTM methods such as instrument calibration, surrogate spiking, procedural blanks, matrix spike recoveries, replicate analyses, some refinements have been further implemented by many oil spill analysis laboratories in order to achieve improved analytical precision and accuracy [42,51,70–72]. The key refinements include the following:

- To establish 5-point calibration curves that demonstrate the linear range of the analysis;
- To analyze quality control standards prepared from the National Institute of Standards and Technology (NIST) certified standard reference materials (SRMs) with the sample batches for accuracy assessment;
- To apply more rigorous calibration check standards of  $\pm 15\%$ ;
- To determine relative response factors (RRFs) of target analytes of interest from authentic standards;
- To manually set the baselines for alkylated PAHs at various alkylation levels;
- To estimate the method detection limits (MDLs) for each target analytes using the procedure described in Appendix B, 40CFR (Code of Federal Regulations) Part 136;
- To increase sample size and to reduce the sample extract pre-injection volume for those sediment samples with very low concentrations of hydrocarbons;

These modifications substantially improved the precision and accuracy of the analytical data in the 0.1 to 10 ppb PAH concentration range in the hundreds of benthic sediment and tissue samples from Prince William Sound and the Gulf of Alaska following the Exxon Valdez oil spill [51,64,70,71].

## 3. Distinguishing biogenic hydrocarbons from petrogenic hydrocarbons

Characterization and differentiation of hydrocarbons from different sources is an essential part of any objective oil spill study. After oil spills, oil hydrocarbons often mix with other background hydrocarbon sources in the impacted area. One of the potential sources of hydrocarbons contributing to the background is biogenic hydrocarbons. Hydrocarbons

from both anthropogenic and natural sources including biogenic source are very common in the marine and inland environments [51,57,64,73–75].

Biogenic hydrocarbons are generated either by biological processes or in the early stages of diagenesis in recent marine sediments. Biological sources include land plants, phytoplankton, animals, bacteria, macroalgae and microalgae.

It has been recognized [51,63,76–83] that the biogenic hydrocarbons have the following chemical composition characteristics: (1) *n*-alkanes show a distribution pattern of odd carbon-numbered alkanes being much abundant than even carbon-numbered alkanes in the range of *n*-C<sub>21</sub>–*n*-C<sub>33</sub>, resulting in unusually high carbon preference index (CPI) values, which is defined as the sum of the odd carbon-numbered alkanes to the sum of the even carbon-numbered alkanes (oils characteristically have CPI values around 1.0); (2) notable absence of the ‘unresolved complex mixture (UCM)’ hump in the chromatograms; (3) pristane is often more abundant than phytane, suggesting a phytoplankton input [84–86] and resulting in abnormally high pristane/phytane ratio values; (4) presence of ‘biogenic cluster’ (identified as olefinic hydrocarbons of biogenic origin) in the gas chromatograms of the aromatic fractions [77]; (5) wide distribution of the biogenic PAH perylene, an unsubstituted PAH produced in subtidal sediments by a process known as early diagenesis [76].

In a study of hydrocarbon biogeochemical setting of the Baffin Island oil spill (BIOS) experimental site, Cretney et al. [77] found that the BIOS subtidal samples showed very high pristane/phytane ratios (5 to 15) and CPI values (3 to 11). High concentrations of pristane relative to phytane in most of beach and subtidal sediments indicate biological hydrocarbon input from a marine biological source. In addition, the GC chromatograms of the aromatic fractions were typified by the olefinic hydrocarbon clusters. This cluster is a common feature of coastal marine subtidal sediments and is believed to be of marine biological (planktonic or bacterial) origin [78,79]. The possibility of in situ genesis of PAHs is indicated by the presence of perylene as a major PAH in almost all the beach and subtidal sediments, however, it should be noted that it cannot be used alone as a definitive source identification criterion because

perylene is also produced in combustion processes. In a recent study of chemical characterization of oil residues in the Baffin Island intertidal sediment samples, Wang et al. [80] noted that the BIOS sample S-3 demonstrated some distinct characteristics of biogenic hydrocarbons including much higher abundance of odd *n*-alkanes than even *n*-alkanes in the range of *n*-C<sub>21</sub>–*n*-C<sub>33</sub> and high CPI and pristane/phytane values. However, the presence of petrogenic hydrocarbons were also obvious, indicated by the distribution of *n*-alkanes in a wide range from C<sub>15</sub> to C<sub>40</sub> and the notable presence of the chromatographic UCMs. This conclusion was further confirmed by the presence of petrogenic PAH and biomarker compounds, which showed similar distribution pattern to other oil residue samples. Page et al. [51,63,87] found that the background alkane distribution in the PWS benthic sediments is dominated by biogenic components. Page et al. [88] also identified mangrove leaf waxes to be a major source of biogenic hydrocarbons in a tropical spill site. By evaluation of *n*-alkane and PAH distribution indexes in Rio de La Plata Estuary sediments of Argentina, Colombo et al. [89] concluded that high level of petrogenic contamination dominated in stations A1–A3 and A5, whereas biogenic compounds predominated at stations A4, B8, B9, and C12.

During the years 1970 to 1972 the Nipisi, Rainbow and Old Peace River pipeline spills occurred in the Lesser Slave Lake area of northern Alberta. The Nipisi spill was by far the largest of the three spills and is also one of the largest land spills in Canadian history. The most recent field survey was conducted in 1995 in order to determine which cleanup methods were most successful, and to provide up-to-date information about any changes in residual oil and vegetative recovery 25 years after the spills. The comprehensive chemical data [81] from analysis of the Nipisi samples indicate the following:

(1) The Nipisi samples can be categorized into three groups plus the background group, according to the contamination level and degradation degree of the samples.

(2) The background samples showed typical biogenic *n*-alkane distribution in the range of C<sub>21</sub>–C<sub>33</sub> with abundances of odd-carbon-number *n*-alkanes being much higher than that of even-carbon-number *n*-alkanes. The biogenic cluster was also

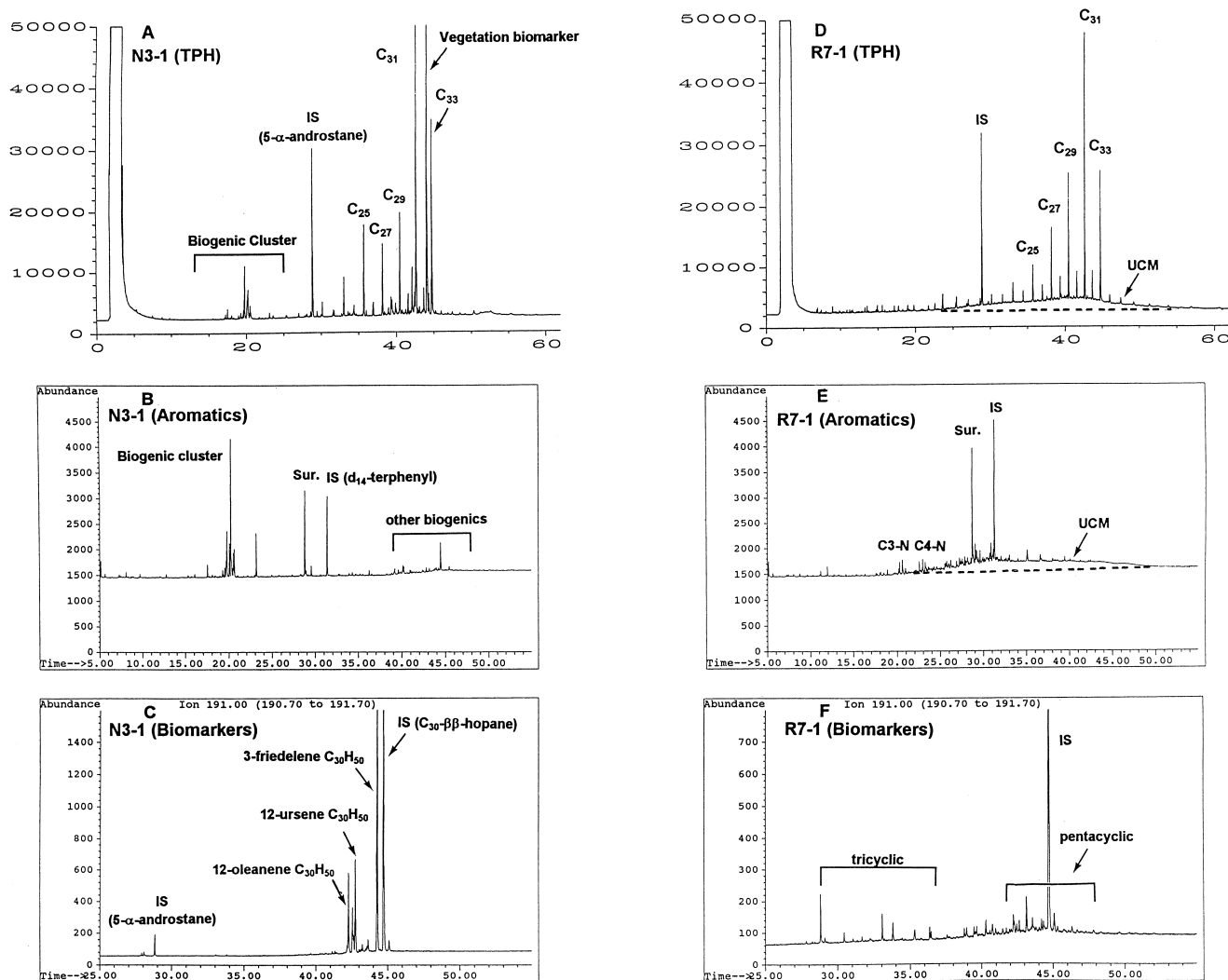


Fig. 3. Capillary gas chromatograms of two representative Nipisi samples: background sample N3-1 (left, biogenic hydrocarbons) and Group 3 sample R7-1 (right, mixture of vegetation hydrocarbons and lightly contaminated oil hydrocarbons), illustrating differences between petrogenic and biogenic hydrocarbon distributions. Top panel (A and D): GC-FID chromatograms for total petroleum hydrocarbon (saturates and aromatics) analysis. Sample R7-1 showed distribution of mixed petrogenic and biogenic *n*-alkanes, while Sample N3-1 showed only typical biogenic *n*-alkane distribution in the range C<sub>21</sub>–C<sub>33</sub>. The biogenic cluster was also obvious and no UCM was observed. Middle panel (B and E): total ion GC-MS chromatograms of aromatic fractions. Surrogate: *o*-terphenyl; internal standard (IS): [<sup>2</sup>H<sub>14</sub>]terphenyl. Bottom panel (C and F): GC-MS chromatograms (*m/z* 191) of saturated fractions. Petrogenic alkylated PAH homologues and biomarkers were detected in Sample R7-1. In contrast, no petrogenic PAHs and biomarkers were detected in Sample N3-1. However, three vegetation biomarkers with remarkable abundances were detected. Time scales in min.

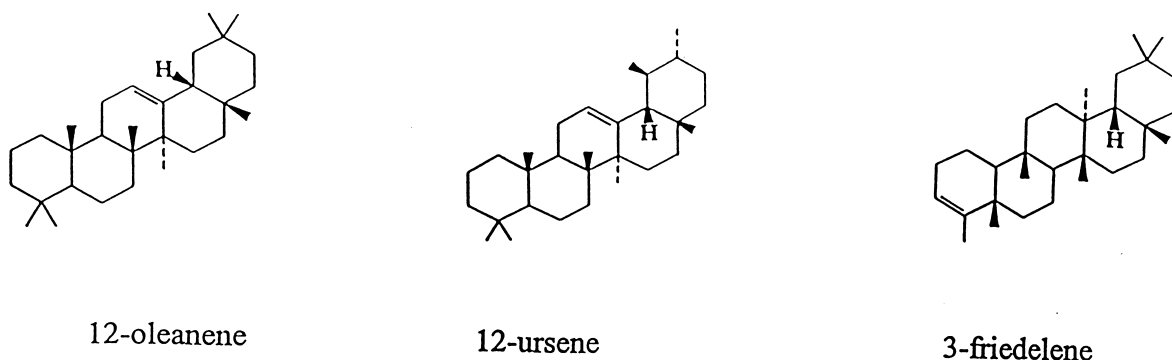


Fig. 4. Molecular structural formulas of three vegetation biomarkers identified from the Nipisi background samples.

obvious and no UCM was observed (see Fig. 3). No petrogenic hydrocarbons, in particular no alkylated PAH homologues and petroleum-characteristic biomarker compounds such as pentacyclic hopanes and  $C_{27}$ – $C_{29}$  steranes were detected. In addition, three vegetation biomarker (Fig. 4) compounds with remarkable abundances were detected and they were identified as 12-oleanene ( $C_{30}H_{50}$ ,  $M_r=410.7$ ,  $t_R=42.27$  min), 12-ursene ( $C_{30}H_{50}$ ,  $M_r=410.7$ ,  $t_R=42.74$  min), and 3-friedelene ( $C_{30}H_{50}$ ,  $M_r=410.7$ ,  $t_R=44.26$  min). Formation of a six-membered ring E from the baccharane precursor leads to the oleanane group. Oleananes and their derivatives form the largest group of triterpenoids and occur in the plant kingdom, specifically from higher plants [90]. The friedelene-type triterpenoids arise by increasing degrees of backbone rearrangement of the oleanane skeleton. Methyl migration in ring E of the oleanane precursor leads to the ursene skeleton [90].

(3) Hydrocarbons in the Group 3 samples taken from a depth of 40 to 100 cm were identified to be mixtures of vegetation hydrocarbons and lightly-contaminated oil hydrocarbons. As an example, Fig. 3 presents the GC chromatograms of two representative background and Group 3 samples, illustrating the differences between biogenic hydrocarbons from petrogenic hydrocarbons.

#### 4. Distinguishing pyrogenic hydrocarbons from petrogenic hydrocarbons

PAH distributions are the most useful tool in distinguishing pyrogenic hydrocarbons from petrogenic hydrocarbons. It has been recognized that in general, pyrogenic PAHs are characterized by the dominance of the unsubstituted compounds over their corresponding alkylated homologues and the dominance of the high-molecular-mass 4–6-ring PAHs over the low-molecular-mass 2–3-ring PAHs [73,87,91–97]. In contrast, petrogenic PAHs exhibit the characteristic bell-shaped distribution profiles, which are readily modified to the distribution profile of  $C_0 < C_1 < C_2 < C_3$  by weathering or degradation. As an example, Fig. 5 compares [98] PAH fingerprints for the 1994 Mobile Burn starting oil, burn residue, and soot sample, illustrating the distinguishing features of pyrogenic PAH distribution from the petrogenic PAH distribution. Fig. 6 compares extracted ion chromatograms at  $m/z$  178, 228, 252, and 276 for the 1994 Mobile diesel, residue sample MB-16 and soot sample TSP-B3. The changes in relative distribution patterns of selected PAHs clearly demonstrate the formation of pyrogenic PAH from 3-ring anthracene to 6-ring indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene due to combustion.

On 21 September 1978, a mechanical failure at the Strategic Petroleum Reserve Complex at West Hackberry, LA, USA, caused a well blowout at a salt-dome storage cavern. The blowout resulted in a major fire and subsequent release of approximately 72 000 barrels of Arabian light oil into Blake Lake and the surrounding marshland. Overton et al. [99] developed ratios of alkyl phenanthrenes to alkyl dibenzothiophenes as effective passive tags for distinguishing the source of petroleum hydrocarbons. The contamination from pyrogenic products of the fire was identified by elevated quantities of fluoran-

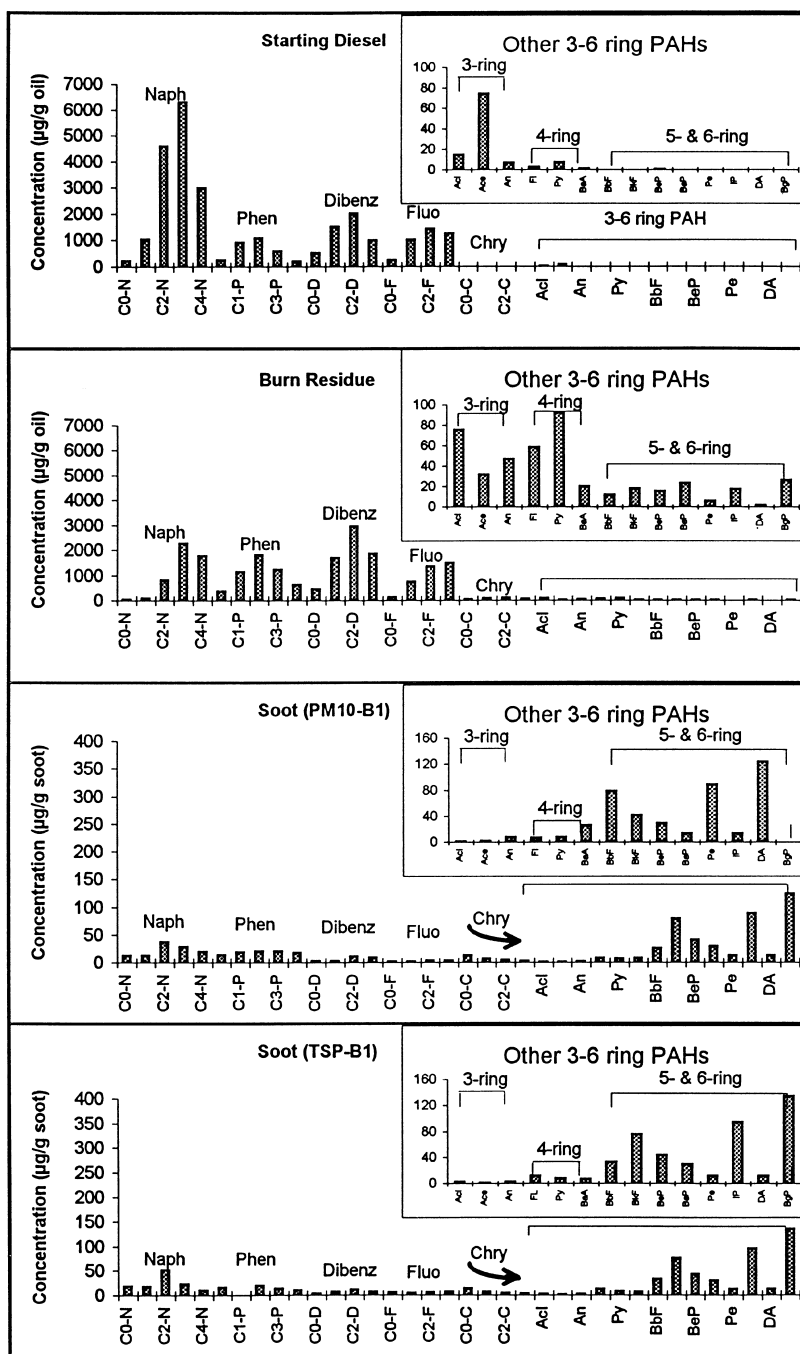


Fig. 5. PAH fingerprints and distinguishing features of distribution patterns between petrogenic and pyrogenic PAHs for the starting oil, burn residue, and soot samples from 1994 Mobile burn study. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0–4 represent carbon number of alkyl groups in the alkylated PAH homologous series. The abbreviations from Acl to BgP represent the other EPA priority unsubstituted PAHs (please refer to Table 2 for the full names of these PAHs). For comparison, the fingerprints of the other 3–6-ring PAHs have been enlarged and shown in the left insets. Note that for clarity, different Y-axis scales are used for soot samples.

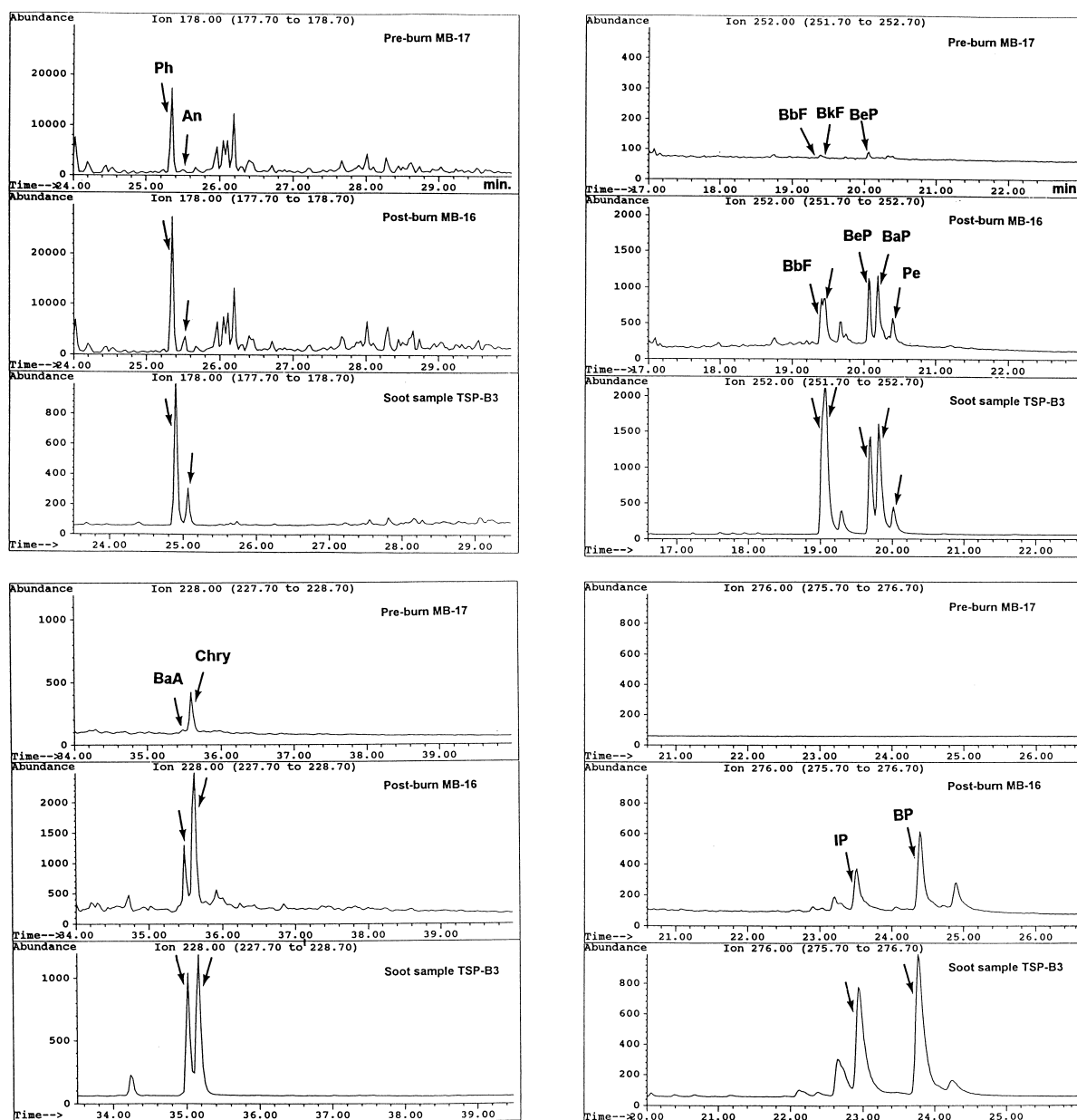


Fig. 6. Comparison of representative extracted ion chromatograms at  $m/z$  178, 228, 252, and 276 for the starting oil, burn residue MB-16, and soot sample TSP-B3, illustrating changes in the relative distribution of unsubstituted PAH isomers and demonstrating the formation of pyrogenic PAHs from 3-ring anthracene (An) to 6-ring indeno[1,2,3-*cd*]pyrene (IP) and benzo[*ghi*]perylene (BP) due to combustion. Refer to Table 2 for the full names of the remaining EPA priority unsubstituted PAHs shown in Fig. 2.

thene and pyrene in affected samples. In order to obtain an approximation of the hydrocarbon input by the river Elbe into the North sea, Theobald et al. [95] performed UV-Vis, GC and GC-MS measurements

for over 2.5 years at a fixed station at the freshwater edge of the Elbe to determine the composition and concentration of hydrocarbons in its water. The characterization results indicate three types of hydro-

carbons: some of them originate from natural sources (plant waxes with predominance of odd-chain *n*-alkanes); some originate from petroleum sources (unresolved complex mixture), and some originate from the incomplete combustion of fossil fuel (unsubstituted PAHs). Gonzalez-Vila et al. [100] investigated the influence of different burning conditions upon the PAH patterns generated from combustion of pine biomass and found that when burned at moderate temperature for a long period of time, the most abundant homologues generated were alkylated derivatives of naphthalene, whereas phenanthrene alkyl derivatives were predominant after a forest wildfire, where higher temperatures were reached in less time. More condensed PAHs were detected only in minor amounts. Benner et al. [101] studied the lab-scale combustion of crude oil on water and found that while burning the crude oil produced less total EPA priority PAHs than were in the original crude oil, the concentrations of PAHs with five or more rings were 10–20 times greater in the smoke than in oil. Sharma et al. [102] studied hydrocarbon distribution in sediments of Upper Laguna Madre (which is the Gulf Intracoastal Waterway) in the USA. It was determined that biogenic (marine phytoplankton and terrestrial vegetation) and anthropogenic sources are probably contributing to aliphatic hydrocarbon contamination, while PAH contamination include pyrogenic or combustion processes, spillage of petroleum products and disposal of dredged materials. Following the Gulf war, controversy and speculation have surrounded the extent to which the massive spillage of petroleum and the burning of oil wells have damaged marine ecosystems in the region. Readman et al. [103,104] performed a rapid assessment survey of hydrocarbon contamination in a area from Kuwait to Oman during mid-1991. They identified petrogenic and pyrogenic PAHs and found the concentrations of PAHs produced during burning of the oil wells were relatively low in sediments from even the most heavily contaminated sites. Bence et al. [51,63,105,106] identified combustion products throughout the marine environment in Prince William Sound and Gulf of Alaska. Two components of pyrogenic PAHs occur in the benthic sediments: a relatively uniform, low level, regional pre-spill background believed to be due to atmospheric input, and a local relatively high background, at some nearshore

locations, that is consequence of current or historical human activities. Probable local sources include the burning of coal, diesel fuel, and wood at communities, fish camps, and campsites, and creosote from marine installations. Identification of pyrogenic components in subtidal sediments is based entirely upon the PAH fraction. The dominance of the 4–6-ring unsubstituted PAHs was very distinct in the local source samples [51,63].

In field studies, it is often difficult to identify which PAHs have been introduced from petrogenic or pyrogenic sources. This is because there are many ways in which PAHs are introduced into the environment that the PAH signature from one source could be obscured by PAHs from another source(s). For example, except for the chrysene series, no obvious dominance of unsubstituted PAHs over the alkylated naphthalene, phenanthrene, dibenzothiophene, and fluorene homologous series was observed for the 1994 Mobile burn soot samples (see Fig. 5). Also, the absolute amount of PAHs generated during incomplete combustion is strongly dependent on temperature [91,107,108]. Under the comparable combustion conditions, the same amount of organic materials can yield largely different amount of PAHs at different temperatures [91]. Therefore, in addition to qualitative criteria, quantitative criteria should be defined to recognize sources of PAHs. Numerous quantitative diagnostic ratios have been defined to differentiate pyrogenic PAHs from other hydrocarbon sources [89,92,96,109–112], including phenanthrene/anthracene (Ph/An), phenanthrene/methylphenanthrene (Ph/m-Ph), fluoranthene/pyrene (Fl/Py), benz[*a*]anthracene/chrysene (BaA/Ch), Ph/(Ph+An), benzo[*e*]pyrene/(benzo[*e*]pyrene+benzo[*a*]pyrene), and indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene+benzo[*ghi*]perylene). Benlahcen et al. [96] reported a method using the ratio phenanthrene/anthracene < 10 and fluoranthene/pyrene > 1 to identify contamination sources of combustion processes. By determination of characteristic ratios of three pairs of unsubstituted PAHs, Bauza de Mirabo et al. [113] identified five pyrogenic hydrocarbon sources which might be potential sources of PAHs in aerosol samples collected from semi-rural stations in the island of Majorca (Spain). By analysing a series of diagnostic ratios of unsubstituted PAH isomers in a case study, Colombo et al. [89] con-



cluded that the industrial activities of La Plata Harbor (Argentina), which include catalytic cracking and coke combustion, were important sources of pyrogenic PAHs in several sampling stations. This contribution overwhelmed the background level of natural PAHs. Zeng [114] applied several compositional indices of PAHs to identify the sources of PAHs in the coastal environment off San Diego, CA, USA and concluded that PAHs detected in the microlayer and sediments collected in 1994 in San Diego Bay were mainly derived from combustion sources rather than oil spills, despite the heavy shipping activities in the area.

In the 1994 Mobile burn study [98], we found that the ratios of the total of the other EPA priority unsubstituted 3–6-ring PAHs to the total of five target alkylated PAH homologues,  $\Sigma(\text{other 3–6-ring PAHs})/\Sigma(\text{5-alkylated PAHs})$ , in the soot samples were significantly different from that for crude oils and petroleum products and can be positively used to differentiate the pyrogenic and petrogenic PAHs. For comparison, the PAH quantitation results and the relative ratios determined from over 60 oils and petroleum products including jet fuel, diesel, lube oil, Bunker C, and heavy fuel are also summarized in Table 4. Table 4 clearly indicates that the ratios of  $\Sigma(\text{other 3–6-ring PAHs})/\Sigma(\text{5-alkylated PAHs})$  determined for all listed oils and oil refined products are well under 0.05 without exception. However, this ratio dramatically increased to a range of 0.8 to 2.0 for the six 1994 Mobile burn soot samples. The difference in the magnitude of the data is very significant. Compared to other diagnostic ratios obtained from individual compounds, this ratio has its own distinct advantages: (1) petrogenic and pyrogenic PAHs are characterized by dominance of 5-alkylated PAH homologous series and by dominance of unsubstituted high-molecular-mass PAHs respectively, therefore, determination of the changes in this ratio more truly reflects the difference in the PAH distribution between these two sets of hydrocarbons; (2) this ratio can offer better accuracy with less uncertainty than those relative ratios determined from individual PAH compounds; and (3) this ratio shows great consistency from sample to sample and is subject to little interference from the concentration fluctuation of individual components within the PAH series. Also, long-term natural weathering/degrada-

tion and biodegradation only slightly alter the values of this ratio, but the ratio will be dramatically altered by combustion [98]. Fig. 7 depicts the relative ratios of  $\Sigma(\text{other 3–6 ring PAHs})/\Sigma(\text{5-alkylated PAHs})$  versus the relative ratios of phenanthrene to anthracene using the data obtained from this study. It can be clearly seen from Fig. 7 that the jet fuel, diesel, and most crudes show the ratios of  $\Sigma(\text{other 3–6 ring PAHs})/\Sigma(\text{5-alkylated PAHs})$  to be smaller than 0.01 versus very scattered ratios of phenanthrene/anthracene. Heavy oils (such as Cold Lake Bitumen and Orimulsion) and heavy fuels (such as IFO-180, A-02, IF-30, and Bunker C type oils) show significantly higher ratios falling in the range of 0.01 to 0.05 (clusters 1 and 2). In sharp contrast, the average ratio for the six soot samples of 1994 Mobile Burns is as high as 1.13 (in a range of 0.8 to 2.0). Obviously, this quantitative ratio, combined with other qualitative criteria, can be used to unambiguously differentiate sources of PAHs.

## 5. Oil spill identification

### 5.1. Oil and oil product type screening and differentiation by GC traces and *n*-alkane distribution

Oil and oil product type can be readily identified from their GC traces during the early stages of an oil spill, especially where the spilled oil is heavy and background hydrocarbon levels are low in an impacted environment. In addition to measuring TPHs in samples, GC–FID chromatograms provide a descriptive picture or fingerprint of the major oil components (e.g., individual resolved *n*-alkanes and major isoprenoids) and information on the weathering extent of the spilled oil. Comparing biodegradation indicators (such as *n*-C<sub>17</sub>/pristane and *n*-C<sub>18</sub>/phytane) for the spilled oil with the source oils can be also used to monitor the effect of microbial degradation on the loss of hydrocarbons at the spill site.

The publication ‘Analytical Methods for Petroleum Hydrocarbons’ by Washington State Department of Ecology [38] presents GC chromatograms of over 50 different petroleum products including vari-

Table 4

Relative distributions of the other 3–6-ring unsubstituted PAHs to five target alkylated PAH homologues for over 60 oils and petroleum products

	Total of 5- alkylated PAHs ( $\mu\text{g/g}$ )	Other 3–6- ring PAHs ( $\mu\text{g/g}$ )	Phen/Anth	$\Sigma$ (other 3–6-ring PAHs) $\Sigma$ (5 PAH series)
<i>Crude Oils</i>				
Arabian Light	22047	37	158.5	0.002
Arabian Medium	14697	42	80.3	0.003
Arrow oil	12233	111	17.5	0.009
ASMB	16770	109	27.4	0.007
Brent oil (UK,1993)	9006	65	353.4	0.007
California	5269	40	70.0	0.008
Cook Inlet 1 (Alaska,1996)	15511	127	52.8	0.008
Cook Inlet 2 (Alaska,1996)	12760	125	60.2	0.010
Cook Inlet 3 (Alaska,1996)	13608	81	61.0	0.006
Diesel #2 (Alaska,1996)	25696	117	33.3	0.005
Diesel of ESD 0%	8084	56	13.9	0.007
Diesel of ESD 8.20%	8367	61	16.7	0.007
Diesel of ESD 16.50%	8843	54	16.6	0.006
Eirini L (Sahara Crude)	6226	37	321.3	0.006
Federated	13354	66	167.9	0.005
Gulfaks oil (Norway,1993)	12294	98	175.0	0.008
Hibernia (1993)	11544	79	45.0	0.007
Hitra Hedrun Crude	45194	155	52.8	0.003
Iranian Heavy	19475	53	104.5	0.003
Jet Fuel B (Alaska,1996)	28103	53	27.1	0.002
Komi (Russia,1994)	10200	80	270.0	0.008
Lago Medio	7990	76	60.5	0.010
Lube oil	352	0	/	0.000
Maya	7218	25	40.7	0.003
MV Paean (Reduced crude)	4086	41	100.5	0.010
MV-Paean 6 (Fuel oil)	7744	59	31.6	0.008
New Valor (Arab Med Crude)	9524	38	77.9	0.004
Nipisi	11853	44	62.3	0.004
NOBE	11563	115	62.0	0.010
Norman Wells	7537	65	18.9	0.009
North Slope (BC, 1995)	9067	76	80.0	0.008
North Slope 1 (Alaska, 1996)	18130	82	194.0	0.004
North Slope 2 (Alaska, 1996)	17900	69	229.0	0.004
North Slope 3 (Alaska, 1996)	16368	80	189.0	0.005
Oseberg	7887	70	27.1	0.009
Prudhoe Bay	11871	115	26.9	0.010
Shell Diesel	15436	95	24.6	0.006
Statfjord Oil (Norway, 1993)	10787	55	287.9	0.005
Terra Nova (1989)	10723	70	76.9	0.007
<i>Heavy Oils and Spill Samples</i>				
A-02 (Heavy fuel oil, NF, 1997)	29544	650	7.9	0.022
Cold Lake Bitumen	5554	65	18.2	0.012
IF-30 (Heavy fuel oil, Norway, 1996)	7145	362	7.3	0.051
IFO-180	24469	693	17.2	0.028
Mouse MIX	33138	455	19.9	0.014
Orimulsion (before water content correction)	2128	31	16.8	0.015
Orimulsion (after water content correction)	3040	44	16.9	0.014
VC-01 (Reduced crude, Russia)	5008	70	31.4	0.014
W-02 (Heavy fuel oil, NF, 1997)	6720	92	13.1	0.014

Table 4 (continued)

	Total of 5-alkylated PAHs ( $\mu\text{g/g}$ )	Other 3–6-ring PAHs ( $\mu\text{g/g}$ )	Phen/Anth	$\Sigma(\text{other 3–6-ring PAHs})$ $\Sigma(5 \text{ PAH series})$
Bunker C (ESD)	16504	552	10.7	0.033
Bunker C (B.C.)	25456	862	12.3	0.034
Bunker C/Diesel Mix. (Alaska, 1996)	12484	590	25.2	0.047
Irving Whale (1990)	32096	706	13.1	0.022
Oil contaminated Bird 1 (1995)	14340	541	11.2	0.038
Oil contaminated Bird 2 (1995)	13239	543	19.0	0.041
Oil contaminated Bird 3 (1995)	12641	433	11.6	0.034
Oil contaminated Bird 4 (1995)	9739	303	10.7	0.031
Tarball-1 (BC, 1996)	5750	117	13.4	0.020
Tarball-2 (BC, 1996)	6268	125	12.8	0.020
Tarball-3 (CA, 1996)	3856	86	17.4	0.022
Tarball-1 (NF, 1997)	12538	379	8.6	0.030
Tarball-2 (NF, 1997)	13992	425	7.7	0.030
Tarball-3 (NF, 1997)	14657	382	9.2	0.026

ous gasolines, mineral spirits, jet fuel, kerosenes, diesel, engine oils, motor oils, transformer oils, and hydraulic fluids. Each petroleum product demonstrates its unique GC fingerprint. Even though the GC–FID approach is primarily qualitative, it can be

used to quickly screen the oil and oil product types, which are to be identified by GC profiles, carbon ranges, and major component distribution patterns. Karinen et al. [115] collected and analyzed samples of sediments and mussels mainly for alkane hydro-

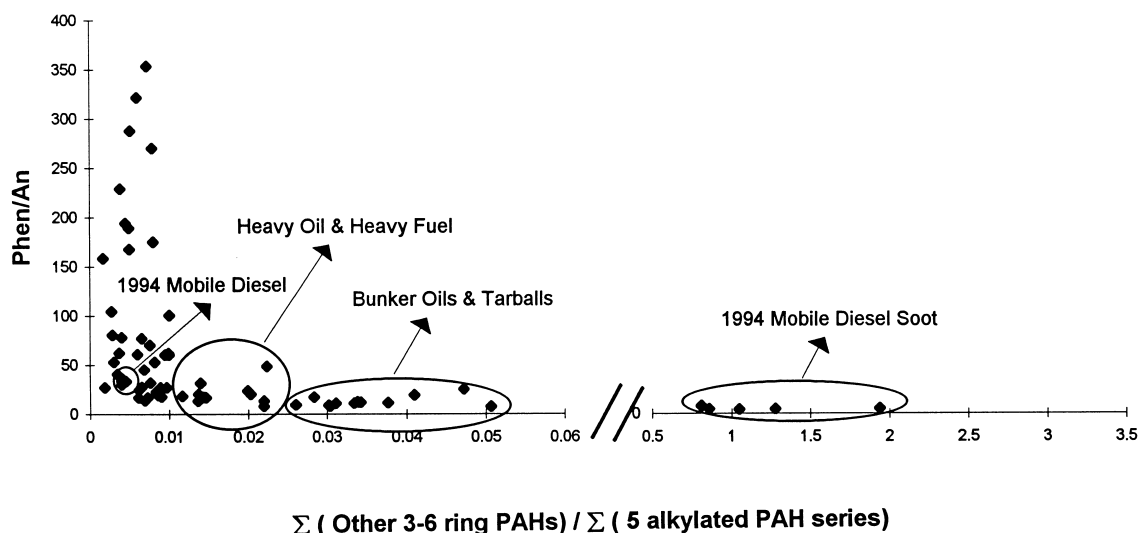


Fig. 7. Plot of the relative ratios of  $\Sigma(\text{other 3–6-ring PAHs})/\Sigma(5\text{-alkylated PAH series})$  over the relative ratios of phenanthrene/anthracene for over 60 oils and petroleum products. Lighter petroleum products and most crudes show the ratios of  $\Sigma(\text{other 3–6-ring PAHs})/\Sigma(5\text{-alkylated PAHs})$  fall into a range of 0 to 0.01, while heavy oils and heavy fuels show significantly higher ratios in the range of 0.01 to 0.05. The soot samples show the most striking increase in the ratio, indicated by the right circle.

carbons from eight sampling stations adjacent to the oil tanker vessel transportation corridor through PWS, Alaska, during the period from 1977 to 1980, to determine baselines prior to the start of oil tanker movement through the Sound. Extensive alkane analysis results indicate that except in areas affected by localized vessel traffic, intertidal sediments and mussels in PWS were remarkably free of petroleum-contaminant hydrocarbons during the period of the study. The hydrocarbons found in sediments and mussels unaffected by vessel traffic can be adequately explained by known, natural sources. Very recently, Wang [116] has identified an unknown spilled oil collected at exit of sewer outlet entering into Canal Lachine, Quebec, on 17 March 1998 for legal purposes to be diesel fuel by the fast GC screening-analysis approach. Following the identification of oil type, further detailed analyses were performed and the diesel fuel from a reservoir at pumping station of the City of Lachine, was identified to be the source of the unknown spill.

Fig. 8 shows GC–FID chromatograms for six different oils. Clearly, these six oils are very different, as not only are there large differences in the *n*-alkane distributions and UCMs, but also in relative ratios of isoprenoids to normal alkanes. Note that the Orimulsion sample, has nearly no *n*-alkanes in its GC–FID chromatogram.

Fig. 9A compares the GC–MS (*m/z* 85) chromatograms of four petroleum products: lightly weathered Jet B Fuel, Diesel Fuel No.2, Bunker C/Diesel mixture, and Lube oil. In contrast to the corresponding GC–FID chromatograms, the GC–MS (selected ion monitoring, SIM) chromatograms of the four petroleum products have much simpler traces for the saturated hydrocarbons. The unresolved complex mixture ‘envelope’ seen in the GC–FID chromatograms is significantly reduced. Differentiation between samples is considerably simplified by comparing the chromatogram profiles and *n*-alkane elution range. The lube oil, eluted late in 23 to 53 min range, is dominated by a broad hump of unresolved saturated hydrocarbons and can be readily distinguished from the Jet B Fuel and Diesel Fuel No.2. The Jet B Fuel and Diesel No.2 can be readily distinguished from the *n*-alkane distribution ranges ( $C_8$ – $C_{17}$  for Jet B Fuel and  $C_8$ – $C_{23}$  for Diesel No.2, respectively) and relative amounts of pristane and

phytane. Bunker C/Diesel is clearly demonstrated to be a mixture of heavy residue oil and lighter diesel fuel. The *n*-alkane distribution is featured by two ‘humps’, with the maxima around *n*- $C_{13}$  and *n*- $C_{24}$  on the early-eluted and the late-eluted ‘hump’, respectively. For comparison, Fig. 9B depicts graphically the quantitative distribution of *n*-alkanes for these four products.

## 5.2. Weathering effects on oil chemical composition changes

Weathering causes considerable changes in the chemical and physical properties of spilled oils [10,51,53,54,63,64,70,80,81,87,117–126]. The extent and rate of weathering is different for each spill and is controlled by a number of spill conditions and natural processes such as type of the spilled oil, environmental conditions and microbiological activities. In the first few days following a spill, the weathering is largely caused by evaporation and the loss can be up to 70 and 40% of the volume of light and medium crudes, respectively. For heavy or residual oils the losses are only about 5–10% of volume [127]. Major compositional changes due to weathering include the following:

- For lightly weathered oils, significant losses occur in the low-molecular-mass *n*-alkanes, however the ratios of *n*- $C_{17}$ /pristane and *n*- $C_{18}$ /phytane have been found to be virtually unaltered from those measured for the source oil [80,128]. Therefore, for fresh or mildly weathered oil products, alkane and isoprenoid analysis may be used for oil source identification. In heavily weathered oils, the *n*-alkanes, and even the isoprenoids in some cases, may be completely lost [66,80,81]. Under such circumstances, GC–FID analysis is of little value for suspect source identification.
- Rapid loss of volatile aromatic compounds including BTEX (benzene, toluene, ethylbenzene, and xylenes) and  $C_3$ -benzenes. When oils are weathered to a certain degree (approximately in the range of 20–25% weathering), the BTEX and  $C_3$ -benzenes are completely lost [72].
- Pronounced decrease in the naphthalenes relative to other alkylated PAH series.
- Development of a profile in each alkylated PAH

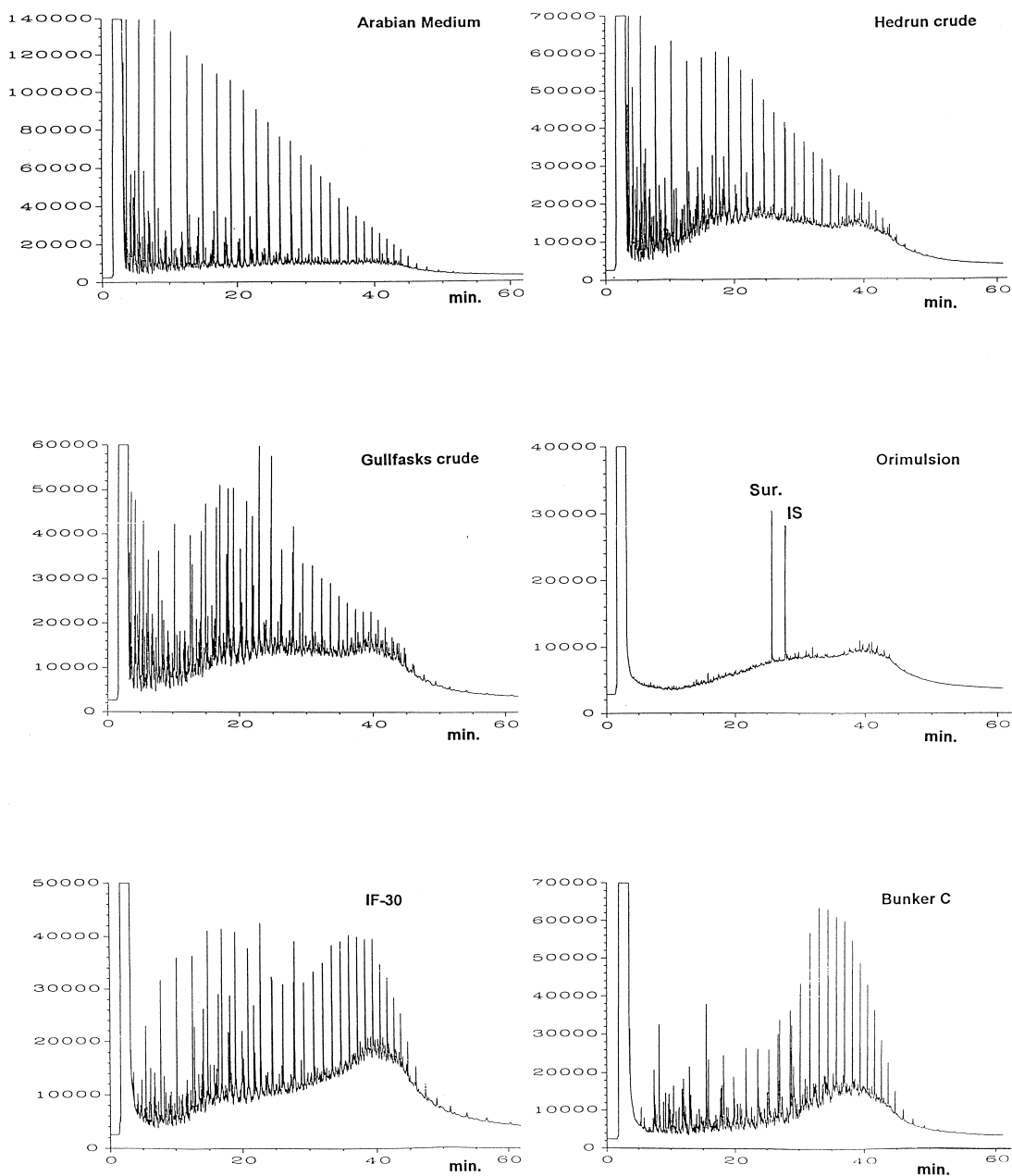


Fig. 8. GC–FID chromatograms for six oils. These six oils are different, as not only are there large differences in the *n*-alkane distributions and UCMs, but also in relative ratios of isoprenoids to normal alkanes. Note that the Orimulsion sample, has nearly no *n*-alkanes on its GC–FID chromatogram.

family showing the distribution of  $C_0 < C_1 < C_2 < C_3$ .

- Enhancement of the chrysenes relative to other PAH series and significant decrease in the relative ratios of the sum of naphthalenes, phenanthrenes, dibenzothiophenes, and fluorenes to chrysenes.
- The relative consistency of the double ratios ( $C_2$ -D/ $C_2$ -P: $C_3$ -D/ $C_3$ -P, see Table 2 for definitions of

these codes) as each degrades in many cases. The double ratio method have been considerably used for Exxon Valdez spill identification and correlation. As an example, Fig. 10 plots  $C_2$ -D over  $C_2$ -P and  $C_3$ -D over  $C_3$ -P for several oil sources

associated with PWS. The straight lines in Fig. 10 demonstrated an important weathering feature of crude oils. It should be noted, however, that no such obvious correlation was observed for long-term heavily weathered oil samples such as the

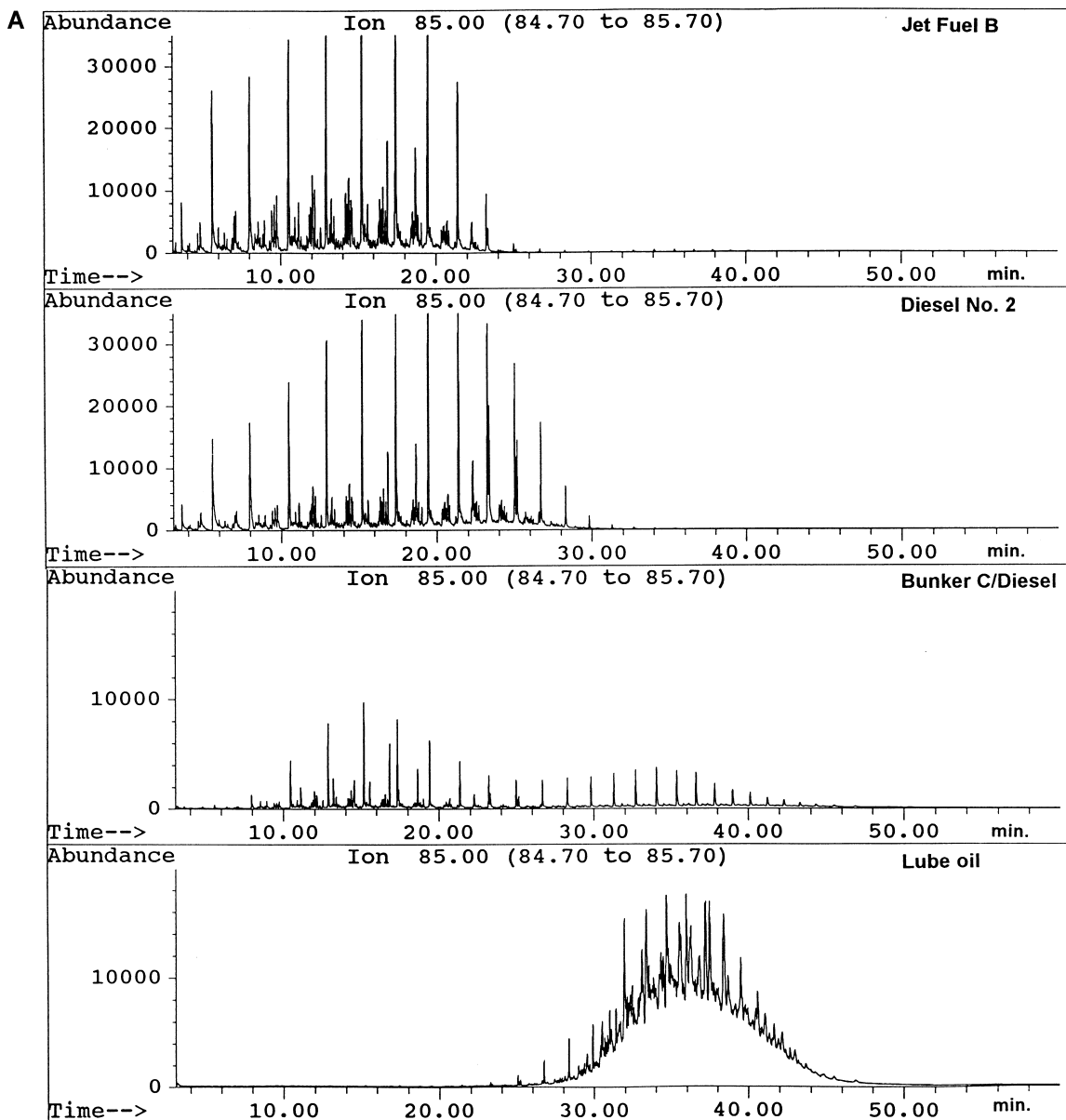


Fig. 9. GC-MS ( $m/z$  85) chromatograms (A) and the corresponding  $n$ -alkane distribution (B) of four petroleum products, illustrating distinguishing features of  $n$ -alkane distribution patterns between these oil products.

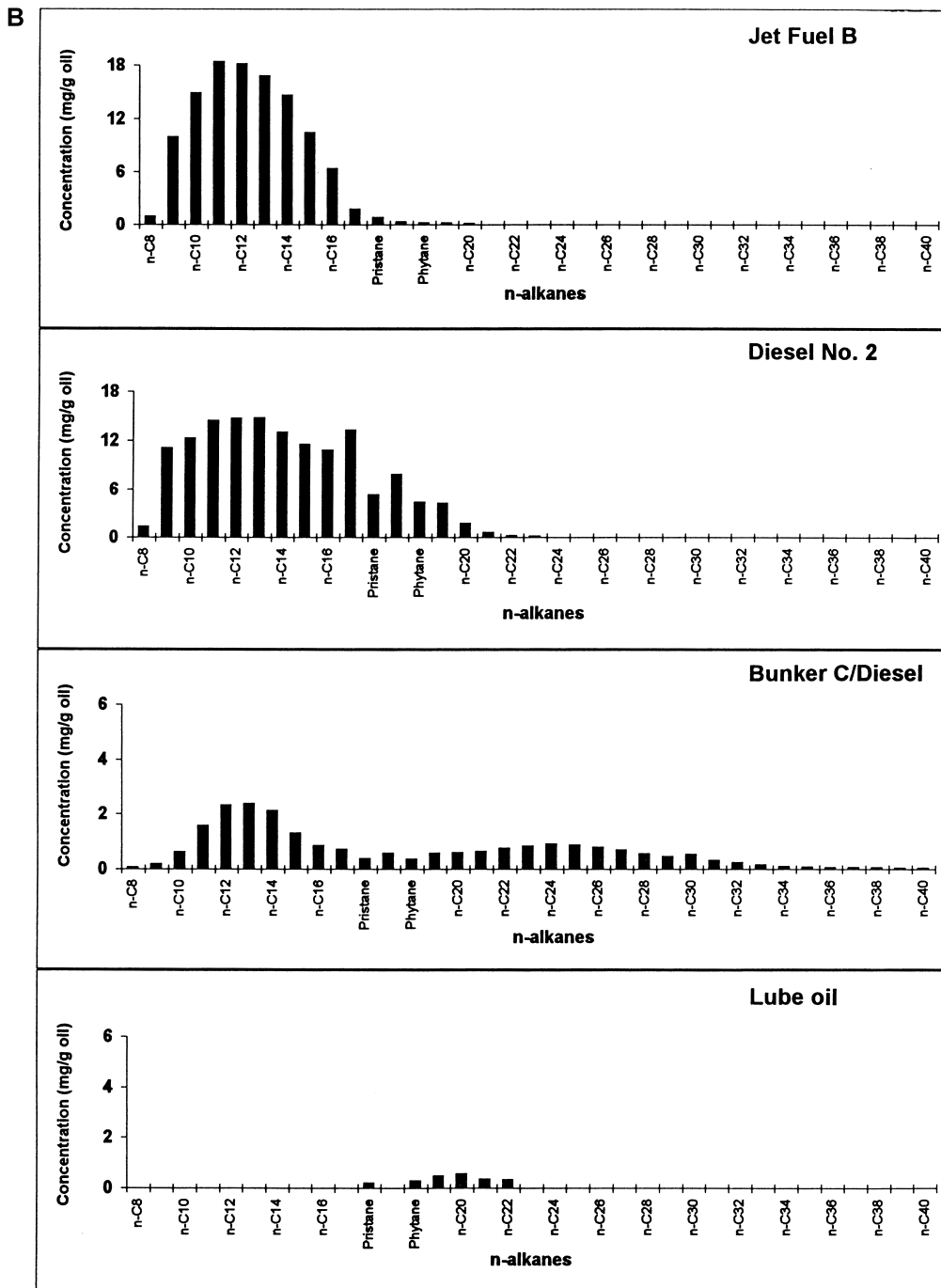


Fig. 9. (continued)

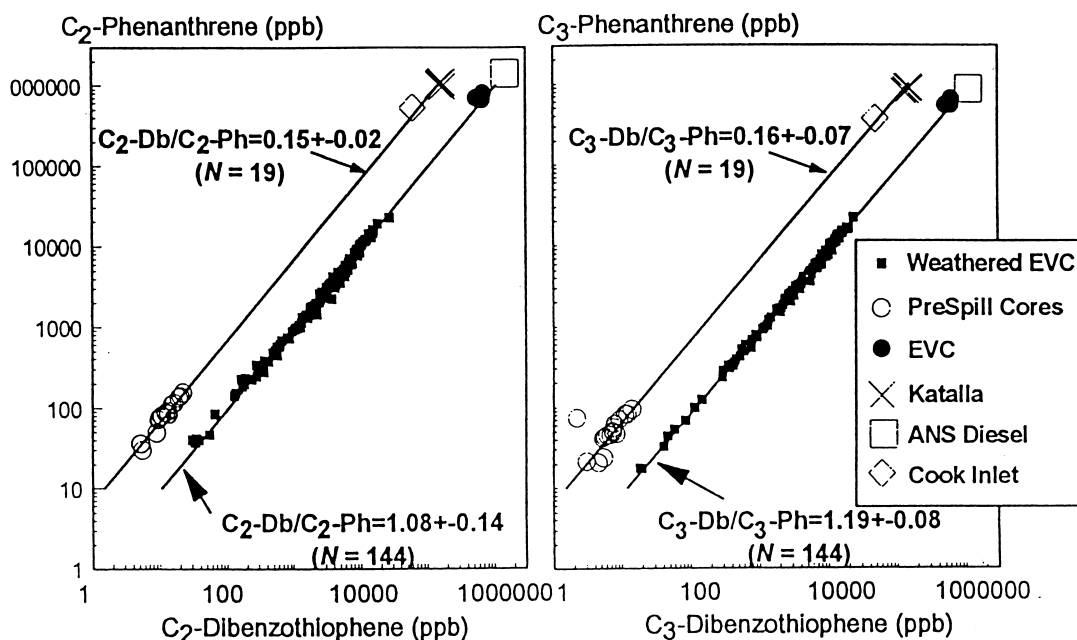


Fig. 10.  $C_2$ -D/ $C_2$ -P and  $C_3$ -D/ $C_3$ -P relationships of weathered Exxon Valdez crude (EVC), diesel refined from Alaska North Slope feedstock at a Kenai Refinery, PWS regional background hydrocarbons from deep subtidal cores, and Katalla and Cook Inlet crude oils. The weathered EVC data are analyses of 1990 oiled intertidal sediments (surface and subsurface samples) reported by Prince et al. (Refs. [200] and [201]). Wide ranges of weathering states and concentrations are represented (adapted from Ref. [51]).

22-year-old spilled Arrow oil [54] samples in which the aromatic compounds have been degraded and altered extensively.

- Gradual buildups in the relative abundances of biomarker compounds (terpanes and steranes) because of their refractory nature and high resistance to biodegradation [53,129–133]. Also, the relative ratios of paired terpane compounds including Ts/Tm,  $C_{23}/C_{24}$ ,  $C_{29}/C_{30}$ ,  $C_{31}$  22S/(22S+22R),  $C_{32}$  22S/(22S+22R),  $C_{33}$  22S/(22S+22R) (see Table 3 for definitions of these biomarker compounds) are almost not altered by weathering [53,65,80,129,145].

The early effect of microbial degradation is monitored by the ratios of biodegradable to less degradable compounds such as the  $n$ - $C_{17}$ /pristane and  $n$ - $C_{18}$ /phytane ratios. It has been demonstrated, however, that changes in these ratios may substantially underestimate the extent of biodegradation because isoprenoids also biodegrade to a significant degree [53,80,129]. Later, highly degradation-resistant components such as  $C_{30}$  17 $\alpha$ (H), 21 $\beta$ (H)-hopane are

selected to serve as conserved 'internal standards' for determining rate and extent of weathering for the spilled residual oil [129,130]. For distilled oil products, such as diesel and jet fuel samples, which may not contain significant quantities of biomarker compounds and chrysenes, less 'conservative' PAHs with a high degree of alkylation such as  $C_4$  or  $C_3$ -phenanthrenes can be selected and used as alternative internal standards [34].

Short and Heintz [70] have developed a first-rate kinetic model of PAH weathering to evaluate 7767 environmental samples collected for the Exxon Valdez oil spill for the presence of spilled oil. The modelled PAHs included the 14 most persistent compounds of 31 analyzed by GC-MS. Parameters include loss-rate constants related to energy required for PAHs to escape from petroleum and a quantitative index of weathering. The model accounts for 91% of the temporal variability of modelled PAH concentrations. This model can be related to currently accepted protocols for oil spill source identification based on PAH analysis.



Figs. 11A and 11B shows the GC chromatograms for TPHs and *n*-alkane analysis and GC–SIM–MS chromatograms for alkylated benzene and alkylated PAH distribution analysis for 25-year-old Nipisi spilled oil samples [81], illustrating the effect of field weathering conditions and sample depths on chemical composition changes of the spilled oil during the 25 year period. Fig. 11 clearly demonstrates that 25 years after the spill, the remaining underground oil is still relatively 'fresh' in comparison with the reference oil and the surface residual oil. Subsurface oil degradation has been demonstrated to be slow and will proceed at a very slow rate because the peat in this wetland habitat system is acidic, and water saturated, i.e., largely anaerobic. Also, the annual temperature is only 1.7°C, based on 22 years of weather records [81].

### 5.3. Oil spill identification by PAH fingerprint analysis

#### 5.3.1. PAH distribution pattern recognition

Crude oils and refined products from different sources can have very different PAH distributions. Also, many PAH compounds are more resistant to weathering than their saturated hydrocarbon counterparts (*n*-alkanes and isoprenoids) and volatile alkylbenzene compounds, thus making PAHs one of the most valuable fingerprinting classes of hydrocarbons for oil identification [41,49,64,75,80,81,87,118,134–136]. Even differences between the same types of products are discernible through examination of the PAH distribution [39,51,63]. Examples of PAH distribution of some oil and petroleum product types are illustrated in Fig. 12. The oil products differ significantly in the PAH distribution from the crude oils and from each other. Jet B fuel has extremely high content of the naphthalene series (99%) with the other four alkylated PAH series being only 1% in total. In addition, no 4–6-ring PAHs were detected in the other 15 EPA priority PAHs. Diesel No. 2 has a high naphthalene content (86%), a low phenanthrene content (5%), and no chrysenes. In the Bunker C/Diesel mixture, the unusually high contents of the alkyl phenanthrenes and chrysenes were pronounced, accounting for approximately 35% and 18%, respectively [137].

Numerous studies have been reported using dis-

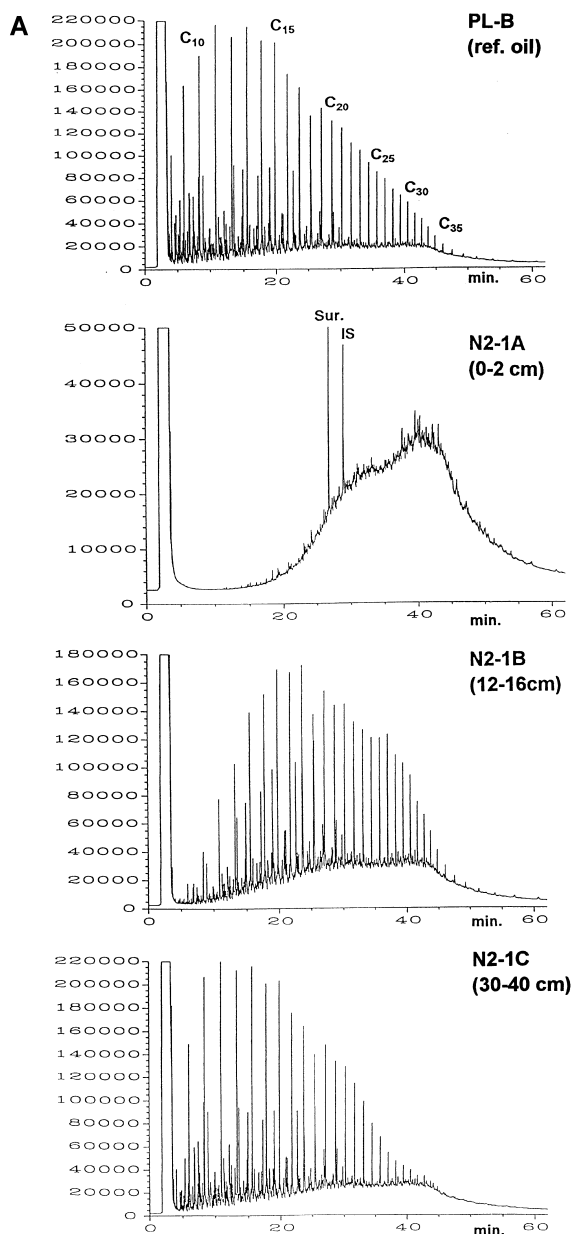


Fig. 11. GC–FID (A) and GC–SIM–MS (B) chromatograms of saturated and aromatic fractions for the Nipisi reference source oil PL-B, and samples N2-1A (0–2 cm), N2-1B (12–16 cm), and N2-1C (30–40 cm), illustrating the effects of field weathering conditions and sample depths on chemical composition changes of aliphatic (in particular *n*-alkanes) and alkylbenzenes and alkylated PAHs, respectively. Sur. and I.S. represent surrogate and internal standard. B and N represent benzene and naphthalene respectively, n, 0, 1, 2, and 3 represent carbon numbers of alkyl groups in alkylbenzenes and alkylated naphthalene homologues.

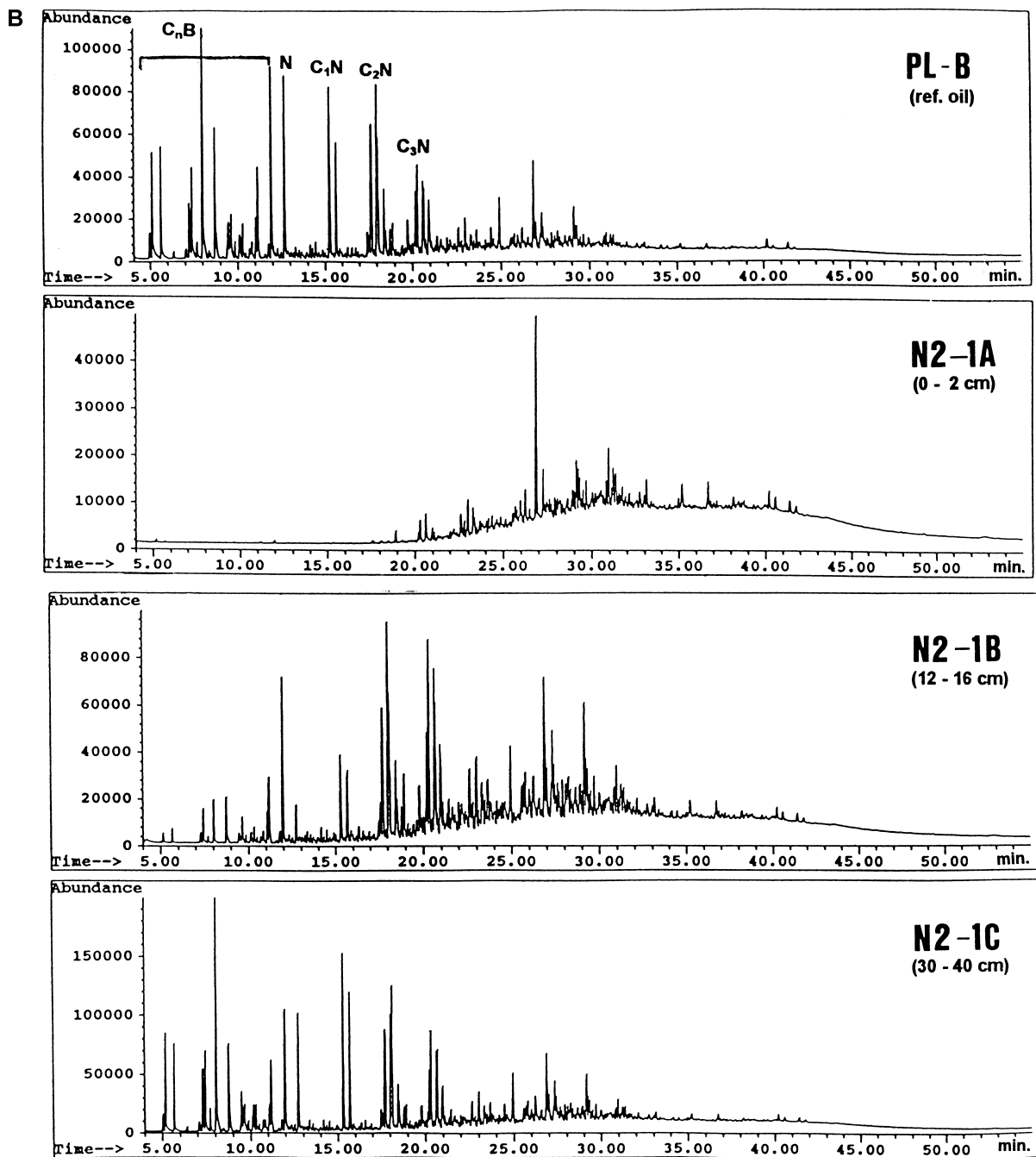


Fig. 11. (continued)

tributions of the alkylated PAH homologues as environmental fate indicators and source-specific markers of oil in sediments [54,118], marine biota

[64,138] and water samples [34]. For example, one year after the Gulf war oil spill, Sauer et al. [125] compared PAH alkyl homologue and triterpane dis-

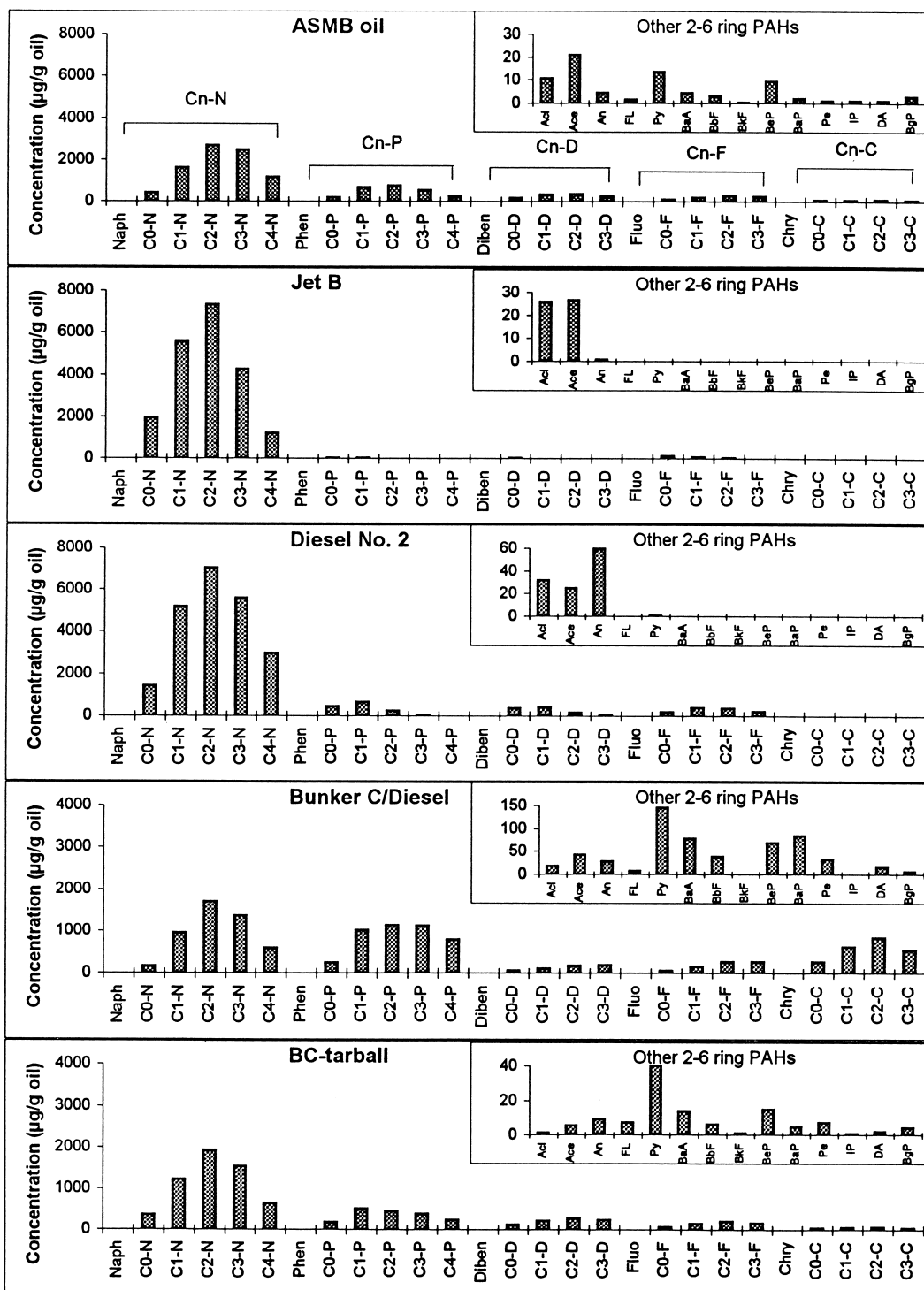


Fig. 12. Alkylated homologous PAH and other EPA priority PAH distributions for the ASMB crude, three oil products, and a tarball sample from British Columbia, illustrating differences in PAH distribution features between different oil and oil products. Note that for clarity, different y-axis scales are used.

tribution in approximately 200 intertidal and subtidal samples with reference crude oils including Kuwait crude oil, light Arabian crude oil, and Iranian crude oil and determined that the Kuwait reference crude oil was very similar to the Gulf War spilled oil collected during a shoreline survey of oil-impacted beaches of Saudi Arabian in June 1991. As part of the scientific studies following the 1989 Exxon Valdez spill, a number of deep subtidal sediment chemistry studies were completed within PWS and outside the spill zone in the Gulf of Alaska [51,87,139]. Analysis of PAH distribution from PWS identified two major type of petrogenic sources: Alaska North Slope oil with high relative alkyl

dibenzothiophene content, and natural oil seep petroleum with a low relative alkyl dibenzothiophene content [42,140].

### 5.3.2. Diagnostic ratios

A number of diagnostic ratios of target alkylated PAH species have been successfully used as indicators for oil spill identification. These are briefly summarized in Table 5.

Weathering and biodegradation alter the chemical composition of spilled oil, making the unambiguous identification of the source of an oil something of a challenge. A method using the double ratio plots of alkylated PAH homologues, in particular the

Table 5  
Diagnostic ratios of 'source-specific' PAH compounds used for oil spill studies

Diagnostic Ratios	Application	Ref.
Double ratio plots (C <sub>2</sub> D/C <sub>2</sub> P vs. C <sub>3</sub> D/C <sub>3</sub> P)	-distinguishing between sources with similar chemical composition -useful in establishing statistical models for source allocation -examples: Exxon Valdez oil spill study Gulf War oil spill study	[7,51,54,63,64,93,99,125,141,143,144]
Double ratio plots (C <sub>3</sub> D/C <sub>3</sub> P vs. C <sub>3</sub> D/C <sub>3</sub> C)	-distinguishing among weathered crude oils -distinguishing spilled oil from other sources -examples: to describe oil depletion and to identify in subtidal data from the M/C Haven spill in Italy, Exxon Valdez spill, and a North Sea spill	[145,146]
(4–6-ring <sup>a</sup> non-alkylated PAH)/Σ PAH <sup>b</sup> Σ Naphs/Σ PAH Σ phens/Σ dibens Σ phen/Σ phens	-used for multi-source hydrocarbons identification in the study hydrocarbon contamination on the Antarctic Peninsula	[7,93,147,148]
Ratios of 3 m-DBT <sup>c</sup> isomers	-used for source identification of unknown spilled oils -distinguishing between oils with similar chemical compositions -differentiation between oils due to physical weathering and biodegradation -marker of biodegradation	[54,65,66,81,116,126,137,149]
C <sub>0</sub> C: C <sub>1</sub> C: C <sub>2</sub> C: C <sub>3</sub> C Σ chrys/Σ phens Σ chrys/Σ dibens	-used for source identification in the Arrow and BIOS spill studies -weathering indicator	[7,54,80,126]
Relative distribution of PAH in each homologous family	-differentiation between composition changes due to physical weathering and biodegradation	

<sup>a</sup> 4–6-ring non-alkylated PAH include fluoranthene, pyrene, benzofluoranthenes, benzopyrenes, indenopyrene, dibenzoanthracene and benzoperylene.

<sup>b</sup> Σ PAH: the sum of total PAH including five target alkylated PAH homologues and the other EPA priority PAH.

<sup>c</sup> m-DBT: methyl-dibenzothiophene.

alkylated dibenzothiophenes and phenanthrenes ( $C_2D/C_2P$  versus  $C_3D/C_3P$ ), for identification and differentiation of petroleum product sources has been developed and extensively used in the studies of the Gulf War oil spill [125,141] and of the 1989 Exxon Valdez oil spill to distinguish Alaska North Slope (ANS) crude, its weathering products, and diesel refined from ANS feed stock from other petrogenic hydrocarbons [51,54,63,64,93,142–144]. The double ratios also distinguished two petroleum sources or ‘suspects’ in the Amoco Cadiz spill [124] and hydrocarbon inputs from the Ixtoc blowout and Burmah Agate oil spills in heavily weathered oil residues [142]. These ratios were previously reported by Overton et al. [99] and used to identify the source of petroleum residues after a fire and oil spill. Table 6 lists the double ratio values for some representative crude oils and petroleum products from the ref. [145]. Furthermore, Douglas et al. [145] have defined the  $C_3D/C_3P$  and  $C_3D/C_3C$  as source ratios (the ratios that be almost constant because the compounds degraded at the same rate) and ‘weathering ratios (the ratios that change substantially with weathering and biodegradation)’, respectively. They were applied to described oil depletion and to

identify sources in subtidal sediment data from the Exxon Valdez spill and a North sea oil spill. Recently, the double ratios were used in assessment of the M/C Heaven oil spill to distinguish high-sulfur heavy Iranian cargo crude from a low-sulfur pre-spill background [146].

In studies of hydrocarbon contamination on Antarctic Peninsula, Kennicutt et al. [147,148] applied PAH diagnostic ratios for multi source hydrocarbon identification including diesel fuel and combustion-derived PAHs in subtidal sediments and limpet samples. In the studies of characterization of spilled oil residues from the Arctic environments and northern inland, Wang et al. [54,80,81] utilized a number of diagnostic ratios of selected source-specific alkylated PAHs in combination with determination of ratios of selected paired biomarkers for source identification and differentiation, determination of weathering extent and degree of surface and subsurface samples, and distinguishing between composition changes due to physical weathering and biodegradation.

### 5.3.3. PAH isomer analysis

The use of the sum of the alkylated PAHs as multicomponent analytes in deriving diagnostic ratios for oil characterization and spill assessment have been made considerable advances as described above. Recently, research has been further expanded to use individual source-specific isomers within the same alkylation level and to determine the relative isomer-to-isomer distribution for source identification of spilled oil. For example, chromatographically well-separated  $C_1$ -dibenzothiophene isomers [149,150] present in all oils at relatively high concentrations and their relative abundance distributions vary significantly from different sources. As the alkylation levels increase, more isomers will be detected (for example, the  $C_3$ -dibenzothiophenes as a group, contain more than 20 individual isomers with different relative abundances). The differences between the isomer distributions reflect the differences of the depositional environment during oil formation. Compared to PAH homologous groups at different alkylation levels, higher analytical accuracy and precision may be achieved due to the close match of physical/chemical properties of the isomers. Also, the relative distribution of isomers are subject to

Table 6  
 $C_2D/C_2P$  and  $C_3D/C_3P$  ratios of representative crude oils and petroleum products (adapted from Ref. [145])

Oil type	$C_2D/C_2P$	$C_3D/C_3P$
JP 4 fuel	0.14	0.26
Jet A fuel	1.09	0.00
No. 1 Arctic diesel	0.98	1.02
No. 2 fuel oil	0.54	0.74
No. 2 EPA fuel oil	0.32	0.58
Union 76 diesel	0.85	1.39
Alaska diesel	0.61	0.62
Diesel fuel marine	0.41	0.64
No. 4 fuel oil 1% fuel sulfur	0.22	0.28
EPA Bunker C residual fuel	1.05	1.03
No. 6 fuel oil	0.29	0.20
Lube oil	0.36	0.41
Coal tar	0.09	0.15
Texas intermediate crude	0.61	0.54
Argo Merchant cargo oil	0.74	1.08
API Ref Arabian light crude oil	3.68	3.99
Merban crude oil	3.77	4.59
Karachaganak condensate	6.72	11.47
Alaska North Slope oil	0.87	1.08
Cook Inlet crude oil	0.11	0.12

little interference from weathering in short-term or lightly weathered oils. Hence this approach can be positively used for oil spill identification. On the other hand, it has been demonstrated that the position of the alkylation on the PAHs can influence the biodegradation rate of the isomers within an isomer group [126,151]. This information can be used to sort out environmental factors such as the impact of biodegradation on the PAH distribution and to differentiate oil compositional changes due to physical weathering from those due to biodegradation.

Wang et al. [149] has developed a GC–MS method for the differentiation and source identification of crude, weathered and biodegraded oils using the relative abundances of three isomeric methyl-dibenzothiophene (4-:2-/3-:1-m-DBT) compounds. A database of the ratios of the C<sub>1</sub>-DBT isomers for several hundred crude, weathered and biodegraded oils, and petroleum products has been established. Table 7 presents data of isomeric distribution within C<sub>1</sub>-DBT determined from 49 oils and oil products. Fig. 13 plots 2-/3-methyl-dibenzothiophene versus 1-methyl-dibenzothiophene (both isomers are normalized relative to 4-methyl-dibenzothiophene) using data from Table 7. Fig. 13 shows how scattered the data points representing the various oils are. Another pronounced feature observed from Fig. 13 is that related oils produce tight clusters on the plot. The use of these ratios complements existing methods of oil characterization, but has its own distinct advantages. The ratios of the C<sub>1</sub>-DBT compounds have been used to successfully discriminate different oil samples [81,126], to identify the source of oil on contaminated birds [165], unknown spilled fuel [116], and on tarball samples [66]. This selectivity has been found to be a very powerful fingerprinting technique for the differentiation of oils and petroleum products.

During January and February 1996, a significant number of tarball/patty incidents occurred along the coast of Vancouver Island (British Columbia, Canada) and Washington, Oregon, and California, USA [66]. In addition of determination of conventional diagnostic PAH and biomarker ratios, a number of 'source-specific' isomeric PAHs within the same alkylation levels were quantified, and their relative abundance ratios were computed in order to definitively identify and differentiate the sources of

the tarballs. The selected isomers include three isomers each within C<sub>3</sub>-naphthalenes and C<sub>4</sub>-naphthalenes, four isomers each within C<sub>1</sub>-phenanthrenes and C<sub>2</sub>-phenanthrenes, two isomers within C<sub>4</sub>-phenanthrenes, and three isomers each within C<sub>1</sub>-fluorenes and C<sub>1</sub>-dibenzothiophenes [66]. Comprehensive analysis results revealed that California/Oregon tarball samples were chemically similar to the British Columbia/Washington tarball samples, but they originated from two different Bunker type fuels, which were indicated by striking different isomeric ratios between California/Oregon and British Columbia/Washington samples. This approach has been also used in biodegradation studies of crude oils [65,137,151].

#### 5.4. Oil spill identification by biomarker fingerprint analysis

Biomarker fingerprinting has historically been used by petroleum geochemists in characterization of marine oils in terms of source rock, genetic family, migration and maturation properties, and in identification of petroleum deposits. Chemical analysis of source-characteristic and environmentally-persistent biomarkers generates information of great importance in determining the source of spilled oil, differentiating oils, monitoring the degradation process and weathering state of oils under a wide variety of conditions. In the past decade, use of biomarker fingerprinting techniques to study spilled oils has greatly increased, and biomarker parameters have been playing a prominent role in almost all oil spill work. The effects of biodegradation on biomarkers have been investigated by many authors. Several *in vitro* and *in situ* studies [53,54,131,152–155] have shown that hopane and sterane compounds are very resistant to biodegradation. In laboratory studies of biodegradation of nine Alaska oils and oil products [151] and eight Canadian oils [65] by a defined bacterial consortium incubated under freshwater and cold/marine conditions, Wang et al. found that the fingerprint patterns of triterpanes and steranes showed no changes after incubation, despite extensive saturate and aromatic losses, and the ratios of selected paired biomarkers also remained constant. Therefore, biomarkers can, in many cases, be and have been used as conserved internal references

Table 7  
Isomeric distribution within the C<sub>1</sub>-dibenzothiophene group from 49 crude oils and petroleum products

Crude oils	Relative ratios <sup>a</sup>
ASMB	1.0:0.76:0.28
Arabian Light	1.0:0.77:0.51
Arabian Medium	1.0:0.79:0.50
Arrow oil	1.0:0.68:0.36
Bent Horn	1.0:0.60:0.07
Brent (British)	1.0:0.56:0.39
Bunker C	1.0:1.15:0.29
Bunker C/Diesel mixture (Alaska)	1.0:0.76:0.27
California	1.0:0.70:0.43
Cold Lake Bitumen	1.0:0.74:0.58
Cook Inlet (Granite Point)	1.0:0.27:0.13
Cook Inlet (Trading Bay)	1.0:0.33:0.17
Cook Inlet (Swanson River)	1.0:0.22:0.16
Diesel (Montreal, 1998)	1.0:0.28:0.24
Diesel No.2 (Alaska)	1.0:0.61:0.27
Erini (Sahara crude, from Norway)	1.0:0.30:0.09
Federated	1.0:0.69:0.24
Gulfaks (Norway)	1.0:0.55:0.32
Hibernia	1.0:0.47:0.44
Hidra (Hedrun crude)	1.0:0.50:0.26
IF-30 (Norway)	1.0:0.36:0.28
IFO-180	1.0:0.96:0.29
Iranian Heavy	1.0:0.70:0.41
Irving Whale	1.0:0.89:0.20
Jet B (Alaska)	1.0:0.56:0.25
Lago Medio	1.0:0.65:0.39
Lloyd Minister	1.0:0.68:0.49
Maya oil	1.0:0.74:0.55
Mobile Diesel	1.0:0.67:0.12
Mousse Mix	1.0:0.92:0.35
Nipisi	1.0:0.57:0.19
NOBE (Western oil, Canada)	1.0:0.51:0.25
Norman Wells	1.0:0.51:0.21
North Slope 1 (ESD stock)	1.0:0.64:0.31
North Slope 2 (ESD stock)	1.0:0.62:0.32
North Slope 3 (ESD stock)	1.0:0.64:0.32
Orimulsion 100	1.0:0.73:0.87
Orimulsion 400	1.0:0.81:0.92
Oseberg	1.0:0.51:0.34
Prudhoe Bay	1.0:0.62:0.30
KOMI (Russia,1994)	1.0:0.46:0.32
Shell Diesel	1.0:0.38:0.18
Staffjord (Norway)	1.0:0.53:0.31
Terra Nova	1.0:0.57:0.56
British Columbia tarball (1996)	1.0:0.92:0.60
California tarball (1996)	1.0:0.92:0.54
Oil-contaminated birds from Newfoundland (1997)	1.0:1.02:0.40
Newfoundland tarball (1997)	1.0:1.00:0.41
Oil-contaminated birds from Quebec (1995)	1.0:1.00:0.29

<sup>a</sup> 4-methyl-DBT:2-/3-methyl-DBT:1-methyl-DBT.

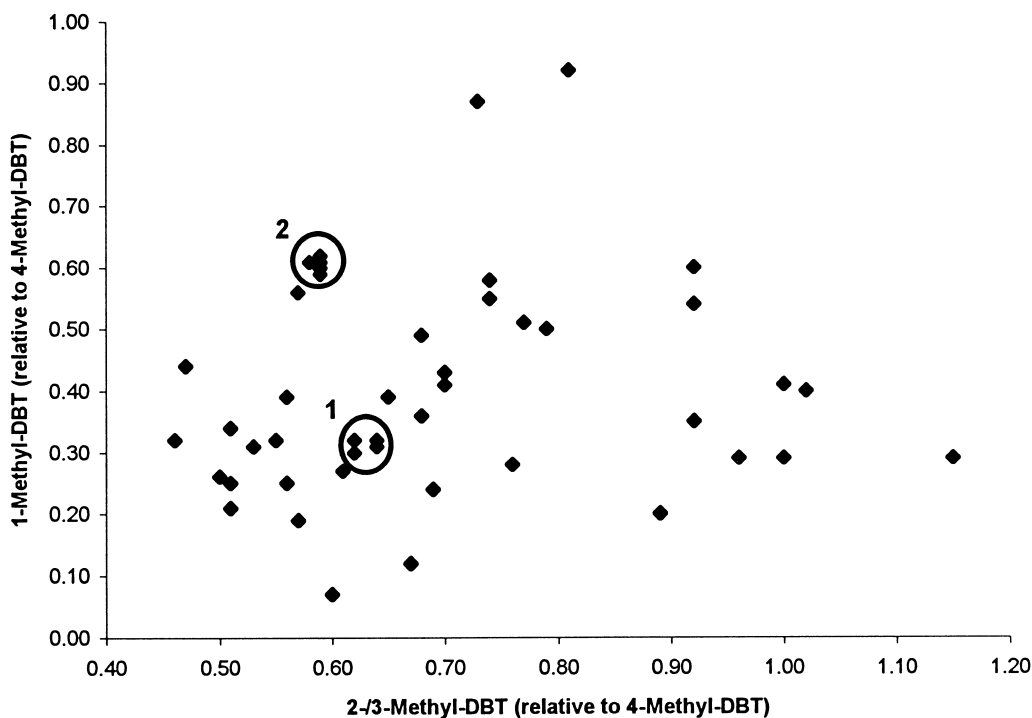


Fig. 13. Plot of the relative ratios of 2-/3-methyldibenzothiophene to 4-methyldibenzothiophene versus the relative ratios of 1-methyldibenzothiophene to 4-methyldibenzothiophene for 49 different oils and oil products. The circles 1 and 2 indicate related samples from origins of North Slope and Terra Nova, respectively.

[129,130] for oil weathering and biodegradation studies, in particular for those highly degraded or long-term weathered residual oils and complex petroleum-contaminated environmental samples.

However, it should be noted that in severely weathered or long-term weathered oil, degradation of some biomarkers was observed [81,152,155]. In a recent study, Munoz et al. [156] found that isoprenoids were severely degraded and biomarkers were more or less altered eight years after an oil spill in a peaty mangrove in a tropical ecosystem. They also found that norhopanes were the most biodegradation-resistant among the studied terpane and sterane groups and the  $C_{30}$   $\alpha\beta$ -hopane appeared more sensitive to weathering than its higher homologues. Because of the differential resistance of biomarkers to biodegradation, comparisons of their relative ratios can be used to rank oils as to the extent of biodegradation [153,154]. Peter and Moldovan [131] have created a 'quasi-stepwise' sequence for assessing the extent to which an oil has

been biodegraded, based on the relative abundances of the various biomarker hydrocarbon classes.

#### 5.4.1. Biomarker distributions

A wide variety of biomarkers have been identified as being of use in characterization of crude oils and oil fractions [43,52,131], including tricyclic, tetracyclic and pentacyclic terpanes ( $m/z$  191), methylhopanes ( $m/z$  205), steranes ( $m/z$  217/218), methylsteranes ( $m/z$  217/231), and diasteranes ( $m/z$  217/259). The distribution patterns are, in general, different from oil to oil. As an example, Fig. 14 shows GC-MS chromatograms at  $m/z$  191 for North Slope, Cook Inlet, Diesel No. 2, and Jet B fuel from Alaska. The Cook Inlet oil showed significantly different biomarker distribution from the North Slope oil with much lower total concentration of terpanes and with only  $C_{30}$   $\alpha\beta$  hopane being prominent. No biomarker compounds were detected in Jet B fuel and only trace  $C_{20}$ - $C_{24}$  terpanes were present in the diesel. Obviously, refining processes have removed



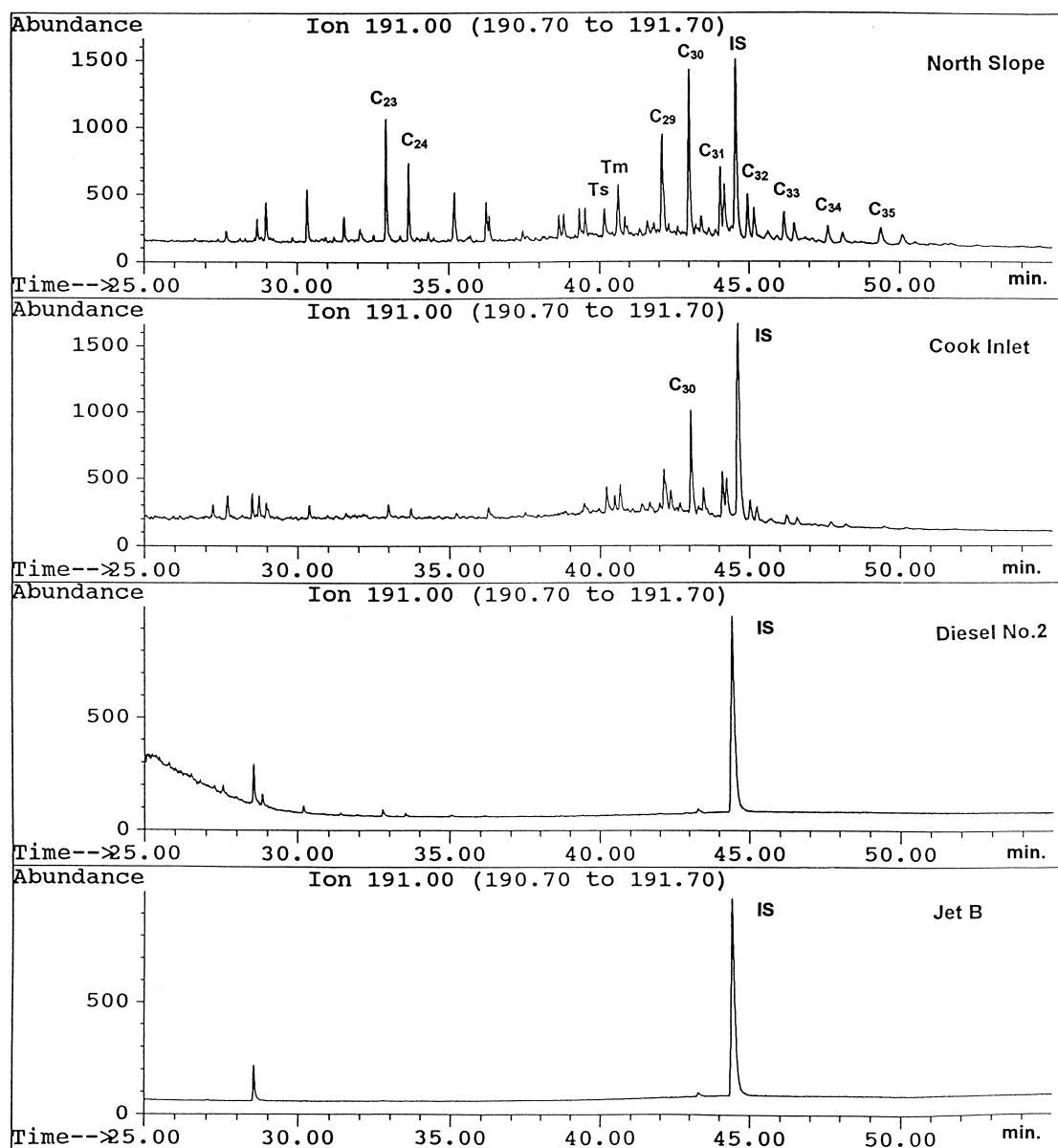


Fig. 14. GC-MS chromatograms of biomarker terpanes at  $m/z$ 191 for North Slope, Cook Inlet, Diesel No. 2, and Jet B fuel from Alaska. The Cook Inlet oil showed significantly different biomarker distribution from the North Slope oil with much lower total concentration of terpanes and with only C30  $\alpha\beta$  hopane being prominent. No biomarker compounds were detected in Jet B fuel and only trace C<sub>20</sub>-C<sub>24</sub> terpanes present in the diesel. Obviously, refinery processes have removed most high molecular weight biomarkers from the corresponding crude oil feed stocks.

most high-molecular-mass biomarkers from the corresponding crude oil feed stocks.

Based on analysis of triterpane distribution patterns and determination of two pentacyclic C<sub>27</sub>

triterpanes, Shen [157] distinguished four Arabian crudes, which in their weathered forms were extremely similar to one another. Volkman et al. [75] determined the distribution of various biomarker

compounds in a range of aquatic and sediment samples to confirm the presence of oil contamination and identify possible oil sources. Among a number of pollution sources, lubricating oils were identified as a major source of hydrocarbon pollution in many estuaries and coastal areas in Australia. A study by Bieger et al. [158] demonstrated the use of tricyclic and pentacyclic terpanes as indicators of the origin of diffuse lubricating oil contamination in plankton and sediments around St. John's, Newfoundland, Canada. In this study, variable inputs of automotive and outboard motor oils in different areas were clearly recognized and identified.

Biomarker fingerprinting and indices have also been successfully used in determining the extent of biodegradation undergone by spilled oils [54,80,81,124,130,159] and predicting the natural attenuation or bioremediation potential of heavy oil waste matrices [160].

#### 5.4.2. Unique biomarker compounds

Biomarker terpanes and steranes are common constituents of crude oils. The terpanes include a wide range of compounds, ranging from  $C_{19}$  to  $C_{35}$  with various pentacyclic hopanes (e.g.,  $C_{29}$   $\alpha\beta$ - and  $C_{30}$   $\alpha\beta$ -hopane) predominating. In the sterane distributions, the  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  steranes have the highest abundances in most oils. Some oils also exhibit significant contributions of diasterane compounds. However, a few 'specific' biomarker compounds including several geologically rare acyclic alkanes are found to exist only in certain oils and, therefore, can be used as unique markers to provide an interpretational advantage in fingerprinting sources of spilled oils.

McKirdy et al. [161] identified geologically rare acyclic alkane botrycocane ( $C_{34}H_{70}$ ) in a new class of Australian non-marine crude oils. The presence of this biomarker, which was derived from the freshwater green alga, in the Australian coastal bitumens suggested that the parent oils of the bitumens were generated from lacustrine source beds. Based on the fact that methyl hopanes are major polycyclic alkanes in oils from carbonate source rocks (such as those from the Middle East) but are uncommon in Australian oils, Volkman et al. [75] identified that lubricating oils, which contaminated many estuaries and coastal areas around Australia, were originated

from Middle East crudes. In a study to re-evaluate the petroleum prospective potential in southeast Australia, the same authors [94] examined ten bitumen samples collected between 1880 and 1915. The high proportions of  $C_{27}$  steranes and presence of  $C_{30}$  steranes suggested that the bitumens were derived from a marine source rock containing mainly marine organic matter. The unusual absence of  $2\alpha$ -methylhopanes and low abundance of tricyclic terpanes ruled out carbonates or the tasmanite oil shales respectively as sources.

The biomarkers  $18\alpha(H)$ -oleanane and  $17\alpha(H),18\alpha(H),21\beta(H)$ -28,30-bisnorhopane have been of special interest [162,163]. The presence of  $18\alpha(H)$ -oleanane in benthic sediments in PWS, coupled with its absence in Alaska North Slope crude and specifically in Exxon Valdez oil and its residues, confirmed another petrogenic source [63,87].

The search for unique geochemical biomarker compounds continues to be a fertile area of research for fingerprinting similar sources of petroleum.

#### 5.4.3. Diagnostic ratios of biomarkers

A number of ratios of selected terpanes and steranes has been defined and increasingly used for tracking spilled oils and identifying spill sources. The diagnostic ratios of biomarkers mostly used include the following [53,54,65,66,126,162–166]:

- Tm/Ts:  $17\alpha(H),21\beta(H)$ -22,29,30-trisnorhopane/ $18\alpha(H),21\beta(H)$ -22,29,30-trisnorhopane.
- Triplet ratio: [ $C_{26}$ -tricyclic terpane (S?) +  $C_{26}$ -tricyclic terpane (R?)]/ $C_{24}$ -tetracyclic terpane.
- $C_{23}/C_{24}$ :  $C_{23}$ -tricyclic terpane/ $C_{24}$ -tricyclic terpane.
- $C_{29}/C_{30}$ :  $17\alpha(H),21\beta(H)$ -norhopane/ $17\alpha(H),21\beta(H)$ -hopane.
- $C_{23}/C_{30}$  and  $C_{24}/C_{30}$ . These ratios are used as source parameters in biodegradation assessments.
- $C_{31}$  S/(S+R),  $C_{32}$  S/(S+R),  $C_{33}$  S/(S+R): These alkylhopane epimer ratios is typical terpane-maturity parameter used extensively in petroleum geochemistry.
- BTO:  $17\alpha(H),18\alpha(H),21\beta(H)$ -28,30-bisnorhopane (B),  $17\alpha(H),18\alpha(H),21\beta(H)$ -25,28,30-trisnorhopane (T) and oleanane (O).
- steranes  $C_{27}$   $\alpha\beta\beta/C_{29}$   $\alpha\beta\beta$ ,  $C_{28}$   $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ , and  $C_{29}$   $\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha)$ .

The triplet ratio, in general, varies in oils from different sources and is dependent upon sources, depositional environment and maturity. The triplet ratio was first used in a chemistry study of North Slope crude by Kvenvolden et al. [167], in which the ratio is  $\sim 2$ . Exxon Valdez oil (an Alaska North Slope crude) and its residues also have triplet ratios of  $\sim 2$ ; in contrast, many tarballs collected from the shorelines of the Sound have triple ratios of  $\sim 5$ . By using carbon-isotopic and a biomarker parameters, these tarballs were identified originally from California, and likely sourced from Monterey Formation [163]. Several biomarker parameters, in combination with other diagnostic ratios, were applied by the same authors [168] for source identification of complicated hydrocarbons in sediments from San Francisco Bay after the Shell oil spill in 1988. Barakat et al. [169] characterized organic geochemical parameters (such as high relative abundance of gammacerane, indices of  $C_{35}$  over  $C_{34}$ ,  $17\alpha(H)$ -homohopanes, and oleanane indices) of five crude oils from some producing wells from the Gulf of Suez, Egypt. The analysis results reveal significant difference within oils that suggest two oil types and one mixed type. Wang et al. [54] identified 32 terpane and 15 sterane biomarkers in 22-year-old No. 6 fuel oil spilled from the tanker Arrow.  $C_{29}$  and  $C_{30}$  hopane were found to be both the most abundant and degradation-resistant; the  $C_{29}/C_{30}$  ratio was therefore considered to be the most reliable source indicator in this case. For steranes, degradation resistance increased with increasing carbon number from  $C_{27}$  to  $C_{29}$ . Similar approaches, combined with determination of a number of other 'source-specific marker' ratios, were applied to characterize the Arctic Baffin Island [80] and the wetland Nipisi [81] spills and to identify unknown spilled oil on contaminated birds [65] and the origin(s) of tarballs from Vancouver Island and California shorelines [66].

### 5.5. Oil spill identification by carbon isotope ratio analysis

The stable carbon composition of oils and their refined products is essentially a manifestation of the myriad physical and biological processes that influence oil formation and refinery [6]. The complex isotopic fractionation patterns induced by these

processes result in characteristic  $^{13}C/^{12}C$  ratios that can be used to classify crude oils, petroleum products and tars and can be interpreted to elucidate oil depositional environment, maturity, migration and biodegradation [6,170,171]. This technique involves combustion of samples to  $CO_2$  and  $H_2O$  at high temperature followed by analysis of isotopic composition of purified  $CO_2$  using isotope ratio mass spectrometry (IRMS). The ratio of  $^{13}C/^{12}C$  is reported in the usual delta-notation ( $\delta^{13}C$ ) in parts per thousand (‰) relative to the PeeDee belemnite (PDB) standard. In a recent review [6], Whittaker et al. placed particular emphasis on a critical evaluation of the potential use of bulk and compound specific carbon isotope ratio mass spectrometry in the elucidation of waste source terms and extent of weathering. In another recent review, Fan et al. [35] briefly summarized the application of the isotope technique for determining petroleum hydrocarbons in soils.

The primary advantage of using the carbon-isotopic technique lies in the analysis of samples that have undergone extensive weathering, since the isotopic compositions of the whole oil remains largely unaffected and can therefore be used as a correlation parameter. This was demonstrated by Kvenvolden et al. [163,165,172], who used similarity and dissimilarity in isotopic composition as further evidence of correlation between weathered shoreline Exxon Valdez oils ( $\delta^{13}C = -29.4 \pm 0.1\text{‰}$ ) and North Slope oil ( $\delta^{13}C = -29.2$  to  $-29.5\text{‰}$ ), and differentiation between Exxon Valdez oils, the pre-spill petroleum hydrocarbon background Katalla seep oil ( $\delta^{13}C = -25.7\text{‰}$ ), and non-EVC Monterey-type (California-source) shoreline tars ( $\delta^{13}C = -23.7 \pm 0.2\text{‰}$ ), respectively. In certain cases particularly with lighter refined products, GC-IRMS can provide valuable correlation data in the absence of biomarker data [173]. Following the division of the  $\delta^{13}C$  values of 621 crude oil samples into three discrete ranges, Chung et al. [171] distinguished four groups of oils based on the age and nature of oil source rock and the environmental conditions at, and prior to, oil generation. A method using combined  $^{14}C$  and  $\delta^{13}C$  as a complimentary means to GC and GC-MS, to monitor in situ biodegradation of petroleum hydrocarbons has been also reported recently [174].

Isotopic fingerprinting may be particularly useful

for characterization of heavy oil contaminated land since it does not rely upon GC resolution of waste components and therefore avoids the primary analytical constraint associated with refractory wastes. Whittaker et al. [175] have reported utility of the IRMS technique as a screening tool for identifying a predominance of polar and asphaltenic material in heavy oils and for providing an additional source correlation parameter for undegraded oily contaminants.

As a result of the development of GC–IRMS, the isotopic composition of individual compounds can now be also determined [176,177], and several studies have already appeared that describe the use of this technique to elucidate the origin of various hydrocarbon products found in the aquatic environment [178,179]. In conjunction with the existing tools, Mansuy et al. [173] utilized GC–IRMS as a correlation tool for hydrocarbons spilled in aquatic environments with their suspected source(s) based on comparison of the isotopic composition of the bulk saturates and aromatics and individual *n*-alkanes. In this work, a method for the correlation of severely biodegraded oils based on the isotopic characterization of asphaltene pyrolysates was also discussed. O'Malley et al. [177] performed compound-specific carbon isotope analysis on individual PAH compounds isolated from environmental samples and concluded that the dominant signatures identified in the surface sediments of St. John's Harbour and Conception Bay were attributed to crankcase oil.

### 5.6. Oil spill identification by statistical analysis

Pattern recognition and various statistical methods including principal components analysis, discriminant analysis and cluster analysis, have been reported for source identification of oil spills [50,51,87,180–184] and for interpreting the effectiveness of bioremediation for the Exxon Valdez spill [185,186].

Jackson et al. [187] reported a method using the cumulative frequency function to deconvolute the data of PAH contaminants in oysters from the Gulf of Mexico into two probability density functions and calculate summary statistics for each population. The two populations with lower and higher PAH concentrations were determined to be probably due to background contamination and associated with local

point sources of PAH input, respectively. Xu et al. [180] developed a mathematical model which is based on cluster analysis of the Euclid approach for oil identification. This approach was reported to be used for classifying types of fourteen common crude oils and refined products of China and for source identification of spilled oils in Dalian Bay.

Principal components analysis (PCA) is the most widely used multivariate analysis technique in science and engineering. It is used to transform original sample composition data into new, smaller and uncorrelated variables called principle components. Each principal component is a linear combination of the original measurement data sets. Samples with similar chemical composition are clustered together and separated from those samples that are compositionally different. For data sets with large number of interrelated variables, PCA is a powerful tool for analyzing the structure of the data and reducing the dimensionality of the pattern vectors. Ruyken and Pijpers [181] reported identification of oil spills in Europort harbours (between Rotterdam and the North Sea) by means of pattern recognition as early as in 1987. Lavine et al. [182] have applied the pattern recognition methods (PCA and Statistical Discriminant Analysis) to classify high-speed GC chromatograms of weathered and unweathered jet fuels. A total of 228 neat jet fuel samples representing common aviation fuels sold in United States were characterized by 85-peak gas chromatograms. Discriminants were developed by parametric and nonparametric pattern recognition procedures that correctly classified the GC chromatograms of neat jet fuels according to fuel type (JP-4, Jet-A, JP-&, JPTS, or JP-5), and these discriminant functions were then used to successfully classify GC chromatograms of jet fuels which had undergone weathering in a subsurface environment. Another good example utilizing comprehensive chemical inventories and detailed PCA approach for source identification was reported for a study of Casco Bay, ME, sediments by Kennicutt et al. [84]. The large number of analytical data of a wide variety of analytes were analyzed using PCA. The most widespread contaminants in Casco Bay was identified to be petroleum and petroleum byproducts. The highest concentrations of contaminants were associated with population centres, effluent outfalls, and spills. The majority of

PAHs in sediments were identified to be the product of high-temperature combustion processes.

Aboul-Kassim and Simoneit [183,184] have used a variety of statistical techniques for source oil identification. In their analysis of the aliphatic and aromatic compositions in particulate fallout samples (PFS) in Alexandria [183], multivariate statistical analyses, including extended Q-mode factor analysis and linear programming, were performed in order to reduce the hydrocarbon data set into a meaningful number of end members (sources). Their analysis indicated that there are two significant end members explaining 90% of the total variation among the samples and confirming petrochemical (79.6%) and thermogenic/pyrolytic (10.4%) sources in the PFS model. In a study of sediment samples in the Eastern Harbour (EH) of Alexandria [184], a similar multivariate statistical approach, including both factor analysis and linear programming techniques, was used to determine the end member compositions and evaluate sediment partitioning and transport in the EH area. In this study, Aboul-Kassim and Simoneit determined that the untreated sewage was the main source of petroleum hydrocarbons in the EH area rather than direct inputs from boating activities or urban run-off.

The application of sophisticated statistical analysis techniques to oil analysis is a relatively new and dynamic area of research which enhances the interpretive power of petroleum hydrocarbon fingerprinting and promises to greatly improve the identification of oil spill sources.

#### *5.7. Oil spill identification by petroporphyrins analysis*

Porphyrins are naturally occurring pigments that are composed of four pyrrole rings. These near-planar structures are usually found in nature in the form of metal complexes. For example, the chlorophylls, which are the green pigments used by plants in photosynthesis, are magnesium porphyrin complexes. The metalloporphyrins, also known as petroporphyrins, found in crude oil are the product of the metabolism of chlorophyll by microorganisms and are usually complexed with metals they have scavenged from the environment, predominately nickel and vanadium. The chemical identity of

petroporphyrins varies between sources, depending upon the biological conditions inherent to each site. Using HPLC [188], these various compounds can be differentiated based on the different alkyl substituents attached to each porphyrin ring. Each oil sample produces a distinct petroporphyrin ‘fingerprint’ which links the sample to its geographic origins. By comparing these fingerprints, oils from different origins can then be distinguished. Similar to biomarker compounds, petroporphyrins break down very slowly in the environment. This means that oil spills can be matched to their sources even years after the spill occurred by the use of petroporphyrin analysis.

Papers by Lesage et al. [189,190] have been published on source identification using petroporphyrins as chemical indicators of soil contamination by crude oils. Characterization of petroporphyrins in crude oils by high-temperature GC–MS [191] and high-temperature GC with atomic emission detection [192] and potential of the methods for oil spill identification have been also reported.

#### *5.8. Oil spill identification by characterization of unresolved complex mixtures*

Unresolved complex mixtures (UCMs), or ‘hump’ of hydrocarbons, are a common feature of the gas chromatograms of crude oils and certain refined products such as lubricating oils, and it is especially pronounced for weathered and biodegraded oils and oil-polluted sediment extracts. It is perhaps surprising that virtually little is known about UCM compositions and molecular structures, even though the concentrations of these components in oils are significant. Work by several authors [193–195] have shown that oxidative degradation of UCMs yields some gas chromatographically resolved products. It has been suggested that these products, which were identified to be acids, lactones and ketones, may be useful for ‘fingerprinting’ UCMs. Actually, the oxidation products of UCMs isolated from sediments known to be contaminated with fresh Nigeria crude [196] and a tank oil [197] were successfully used to identify the source oils.

Revill et al. [198] analysed the UCM oxidation products of ten different oils and oil-contaminated sediment extracts using GC–MS. The GC–MS pro-

files of the oxidation products were shown to be useful for differentiating and correlating oils. In order to further enhance the reliability of oil identification, the GC–MS data were used to calculate inter-sample Euclidean distances. These values were then input into a multi-dimensional scaling program which allows similar samples to be clustered.

There is much to be learned about UCMs and the subject should provide a fruitful area for further research.

### 5.9. Oil spill identification by enantiomer analysis

Since 1995, a research group at the University of Missouri at Rolla, under the support of the US Department of Energy, has conducted a study [199] on enantiomers in crude oils in bid to improve identification of source of oil spilled into the sea. Enantiomers, the left- and right-hand mirror image molecules, exist in almost all oils, and the ratio of enantiomers do not tend to change with weathering. Enantiomers may hold geological information about how old the oil is and what conditions were like when it was buried in the earth for millions of years. With further development this new technique may be useful for identification of spill origin and assessment of liability.

## 6. Allocation of complex hydrocarbons to multiple sources

Chemical fingerprinting techniques to identify the sources of environmental pollutants have been in use for the last two decades and major advances have been made in recent years to address difficult oil spill issues on source identification and, in particular, quantitative allocation of complex hydrocarbons to multiple sources. The major approach used in source identification and allocation in complex mixtures include pattern recognition, source-specific diagnostic ratios of target analytes, and principal component analysis. This section will use the Exxon Valdez oil spill as a recent example to briefly review how the multi-sources can be differentiated from each other and how each contribution is allocated to its respective source.

After the 1989 Exxon Valdez oil spill, contract research organizations and university scientists collected and analyzed thousands of sediment samples from the spill area. These samples were found to contain hydrocarbons from spill oil, diesel fuel, combustion products, creosote, products of natural biological processes, and oil from natural oil seeps. Page et al. [39,51,87] used these advanced fingerprinting techniques, in particular distributions of PAHs and double ratios of C2D/C2P to C3D/C3P, to identify and allocate four major PAH sources in the sediment samples: biological PAHs; combustion product PAHs; natural petrogenic background PAHs derived from oil seeps outside of the Sound; and petroleum PAHs from ANS sources (i.e., either spill oil or diesel oil refined from ANS oil). Carbon isotopes and terpane distribution distinguished Exxon Valdez residues found on shorelines from tars from other sources. Diesel and diesel soot were identified by the absence of alkylated chrysenes and a narrow distribution of *n*-alkanes, whereas pyrogenic products were distinguished by the dominance of 4–6-ring PAHs over 2–3-ring PAHs and by the dominance of non-alkylated over alkylated homologues of each PAH series. The presence of 18 $\alpha$ (H)-oleanane in benthic sediments, coupled with its absence in Exxon Valdez oil and its residues, confirm another petrogenic source.

Shoreline residues from sources other than the spill were also identified and are widespread throughout the Sound [63,163,165]. These residues include (1) geochemically distinct tars and oils imported from California oil fields to Alaska for fuel and construction purposes prior to the discovery of the Cook Inlet and North Slope oil fields; (2) diesel and diesel soot; and (3) more highly refined products.

Page et al. [51,87] found that the ANS oil was generally a small part of the total PAHs in subtidal sediments. A source-ratio allocation model [51,87] have been developed to determine the approximate amount of ANS-derived PAHs in sediments.

Very recently, a more detailed method has been developed by Burns et al. [136] to more precisely allocate PAHs in sediment samples to the PAH sources from which they came. This new approach uses principal component analysis to identify possible sources and a least-squares model to find the

source mix that gives the best fit of 36 PAH analytes (including chrysenes) in each sample. The method identified 18 possible PAH sources in a large set of field data collected in PWS of Alaska, including diesel oil, diesel soot, spilled crude oil in various weathering states, natural background, creosote, and combustion products from human activities and forest fires. The PCA and least-squares modelling procedures can be generalized to allocate PAHs or other complex hydrocarbons to multiple sources in other situations, including other spills.

## 7. Conclusions

The advances in petroleum hydrocarbon fingerprinting and data interpretation methods and approaches in the last two decades have now allowed for detailed qualitative and quantitative characterization of spilled oils. This review focuses on recent applications of various advanced chemical fingerprinting and data interpretation techniques for the source identification of spilled oils. The techniques discussed include oil-characteristic hydrocarbon distribution pattern recognition, analysis of 'source-specific marker' compounds and determination of various diagnostic ratios, carbon isotope measurements, improved data treatments such as principal component analysis and multivariate statistical analyses, and several other emerging techniques. The issues on distinguishing biogenic and pyrogenic hydrocarbons from petrogenic hydrocarbons are also discussed.

In many cases, however, particularly for complex hydrocarbon mixtures or extensively weathered and degraded oil residues, there is no single technique which can unambiguously identify the source(s) of unknown spills and quantitatively allocate hydrocarbons to their respective sources. Combined fingerprinting approaches are necessary under such situations.

Advances in fingerprinting techniques will continue as analytical and statistical methods evolve. It can be anticipated that these advances will allow for even more detailed approaches to the fingerprinting of oil components and other complex hydrocarbon mixtures in the environment.

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