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Characterization and identification of a ''mystery'' oil spill from Quebec (1999)

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Abstract

This paper describes a case study in which advanced chemical fingerprinting and data interpretation techniques were used to characterize the chemical compositions and determine the source of an unknown spilled oil from Quebec. On 28 February 1999, significant amounts of oil was reported on the river banks of St. Laurence River in front of a company named ''Thermex'' (in a town – Beauharnois, Quebec, about 50 km northwest of Montreal). The spilled oil was suspected to be released from a nearby factory. In response to this specific site investigation needs, a tiered analytical approach using GC–MS and GC–flame ionization detection was applied. A variety of diagnostic ratios of ''source-specific marker'' compounds, in particular isomers of biomarkers and alkylated series of polycyclic aromatic hydrocarbons within the same alkylation groups, were determined and analyzed. The hydrocarbon analysis results reveal the following: (1) the spilled oil is very ''specific'', and is significantly different from most crude oils in chemical composition; (2) the oil in samples come from the same source, however, the spill sample 2569 was identified to contain a small amount (~10%) of diesel; (3) the spilled oil was relatively ''fresh'', its chemical composition has not undergone significant alteration yet; (4) the spilled oil showed unusually high concentration of the US Environmental Protection Agency priority polycyclic aromatic hydrocarbons (PAHs). The ''Pyrogenic Index'' values were determined to be as high as 0.11–0.13, significantly higher than crude oils ($<$0.010) and heavy Bunker type fuels (0.015–0.060). This indicates significant contribution of PAH composition from pyrogenic components; (5) biomarkers were also detected, but their concentrations were unusually low in comparison to most crude oils.

Keywords: Oil spill identification; Biomarkers; Polynuclear aromatic hydrocarbons

1. Introduction

On 28 February 1999, a significant amount of spilled oil (estimated at about 10 tons) was reported on the river banks of St. Laurent River in front of a company named ''Thermex'' (in a small town – Beauharnois, Quebec, about 50 km northwest of Montreal). Oil from the storm sewer entering the river in front of Thermex was also noted. Samples of the spilled oil on the river bank and at the exit of the town storm sewer were collected with clean glass jars by the staff of Environment Canada, Quebec Region. Several other oil samples from inside of the factory building and from the factory oil Reservoir 2, which was suspected to be the source of the released oil, were also collected for purpose of this oil spill

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investigation. In order to determine the environmental impact of the unknown spilled oil, the responsibility for the spill clean-up, and the legal liability, the Emergencies Science Division oil laboratory of Environment Canada was requested to characterize the oil, determine if the source of the oil was from the factory and assess changes in the oil composition after the incident.

In response to the oil spill identification and specific site investigation needs, attention has recently focused on the development of flexible, tiered analytical approaches which facilitate the detailed compositional analysis by gas chromatography–mass spectrometry (GC–MS), GC–flame ionization detection (FID), and other analytical techniques to determine individual petroleum hydrocarbons and their relative distribution patterns in a complex mixture of compounds [1–11]. A variety of diagnostic ratios, especially ratios of source-specific oil constituents including polycyclic aromatic hydrocarbon (PAH) homologous groups at different alkylation levels (such as relative distribution of alkylated chrysene series and double ratios of alkylated dibenzothiophenes over alkylated phenanthrenes), isomeric PAHs within the same alkylation levels (such as relative ratios of three methyl-dibenzothiophenes), and biomarker compounds (such as ratios of C_{29} αβ-hopane to C_{30} αβ-hopane, terpane C_{23}/C_{24}, and steranes C_{27} αββ/C_{29} αββ) for interpreting chemical data from oil spills have been proposed and successfully used for oil source identification and monitoring of weathering and biological degradation processes [1–18]. Both high-molecular-mass PAHs and biological markers are degradation-resistant and can be highly source-specific. Their presence can make differentiation among similar contaminants possible. Many US Environmental Protection Agency (EPA) and American Society for Testing and Materials (ASTM) methods have been modified to improve specificity and sensitivity for measuring spilled oil and petroleum products in soils and waters. Compared to those older EPA methods, these modified methods are a clear advance because they can provide far more information directly useful for characterization and quantification of oil hydrocarbons and for oil spill identification and differentiation.

This paper will focus on forensic analytical methods used to characterize the oil spilled on the bank of the St. Laurent River, Quebec in 1999, and how to identify the source of the spilled oil by using advanced fingerprinting techniques and diagnostic ratios of a series of ''source-specific marker'' compounds.

2. Experimental

2.1. Materials

Distilled chromatographic solvents were used without further purification. Calibration standards used for determination of individual and total petroleum hydrocarbons include *n*-alkane standards from C_8 to C_{32} including pristane and phytane, PAH standards (SRM 1491) from the National Institute of Standards and Technology (NIST), and biomarker (hopanes and steranes) standards from Chiron Laboratory of Norway.

2.2. Sample preparation

The detailed description of three representative samples (one from the river bank, one from the inside of the company office building, and the last one from the suspected source, Reservoir 2, which were, respectively, numbered as 2569, 2570 and 2571 by sample collectors), oil density, and water content in oils (determined by the Karl Fischer titration method) are presented in Table 1. All these three samples had a bad and persistent odour, which was much stronger than the odours of most petroleum oils.

Approximate 0.4 g of the oil samples were accurately weighed, dissolved in hexane and made up to the final volume of 5.00 ml. A 200-μl volume of the oil solutions was spiked with appropriate surrogates (100 μl 200 ppm of *o*-terphenyl and 100 μl of mixture of deuterated acenaphthene, phenanthrene, benz[*a*]anthracene, and perylene, 10 ppm each), and then quantitatively transferred to a 3-g activated silica gel microcolumn, which was topped with about 1-cm anhydrous granular sodium sulfate and had been pre-conditioned using 20 ml of hexane, for sample clean-up and fractionation [13,19]. Hexane (12 ml) was used to elute aliphatic hydrocarbons,

Table 1
Hydrocarbon groups analysis results (after water content correction)

	Sample 2569	Sample 2570	Sample 2571
	Collected on the river bank black colour, strong persistent smell	Collected from the inside of the building, black colour, strong persistent smell	Collected from reservoir 2 (beside the building), black colour, strong persistent smell
Density (g/ml)	0.9363	0.9433	0.9583
Water content (%)[a] (3 determinations)	3.47±0.02	1.94±0.06	19.10±0.24
GC-TPH (mg/g oil)	847	813	830
Total GC-saturates (mg/g oil)	384	309	344
Saturates in TPH (%)	45	38	41
Aromatics in TPH (%)	55	62	59
Resolved saturates peaks/total saturates	0.17	0.13	0.13
Resolved (sat.+aro.) peaks/TPH	0.12	0.12	0.12
Total *n*-alkanes (mg/g oil)	32.9	16.1	14.9
CPI	1.13	1.19	1.18

[a] The water content was determined by Karl Fischer titration.

and 15 ml of 50% (v/v) benzene in hexane was used to elute aromatic hydrocarbons. Half of the hexane fraction (labeled F1) was used for analysis of aliphatics, *n*-alkanes, and biomarker terpane and sterane compounds; half of the 50% benzene fraction (labeled F2) was used for analysis of alkylated homologous PAHs and other EPA priority unsubstituted PAHs; the remaining halves of F1 and F2 were combined into a fraction (labeled F3) and used for the determination of the total GC-detectable petroleum hydrocarbons (TPH) and the unresolved complex mixture of hydrocarbons. These three fractions were concentrated under a stream of nitrogen to appropriate volumes, spiked with internal standards (5-α-androstane for GC-TPH and *n*-alkane determination, d_{14}-terphenyl for PAH analysis, and C_{30} ββ-hopane for biomarker analysis), and then adjusted to accurate pre-injection volumes for GC–MS and GC–FID analyses [13,19].

2.3. Capillary gas chromatography and gas chromatography–mass spectrometry

Analyses for *n*-alkane distribution and TPH were performed on a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a flame-ionization detector and an HP 7673 autosampler. Analyses of PAHs and biomarker compounds were performed on an HP Model 5890 GC system equipped with a Model HP 5972 mass-selective detector. System control and data acquisition were achieved with an HP G1034C MS ChemStation (DOS series). For detailed chromatographic conditions, analysis quality control, and quantification methodology, refer to Refs. [13,19,20].

3. Results and discussion

3.1. Product type screen and determination of hydrocarbon groups

Assessment of chemical composition features and degradation trends of the Quebec samples can be illustrated by qualitative and quantitative examination of their GC traces. Table 1 presents the hydrocarbon group analysis results of the spill samples. In addition to the GC-TPH values and percentages of saturates and aromatics in the TPH, the ratios of UCM/TPH and resolved peaks/TPH are listed in Table 1 as well. The GC-TPH are defined as the sum of all resolved and unresolved distillable hydrocarbon detected by GC. The unresolved complex mixture of hydrocarbons (UCM) appears as the ''envelop'' or hump area between the solvent baseline and the curve defining the base of resolvable

peaks. The GC-detectable TPH were only a portion of the oil; the remainder is composed of the asphaltenes and polars (which had been separated by and stayed on the clean-up column), as well a small amount of high-molecular-mass hydrocarbons retained on the GC column.

Fig. 1 shows the GC–FID chromatograms of F3 for TPH analysis. Fig. 2 shows the GC–MS chromatograms of the m/z 85 fragment of the saturated hydrocarbon. Because of the increased resolution and higher sensitivity of the MS detector, the distribution of *n*-alkanes and isoprenoid compounds can be more clearly distinguished. Table 2 summarizes the concentration values of *n*-alkanes including pristane and phytane in all samples. Fig. 3 depicts graphically the *n*-alkane distributions.

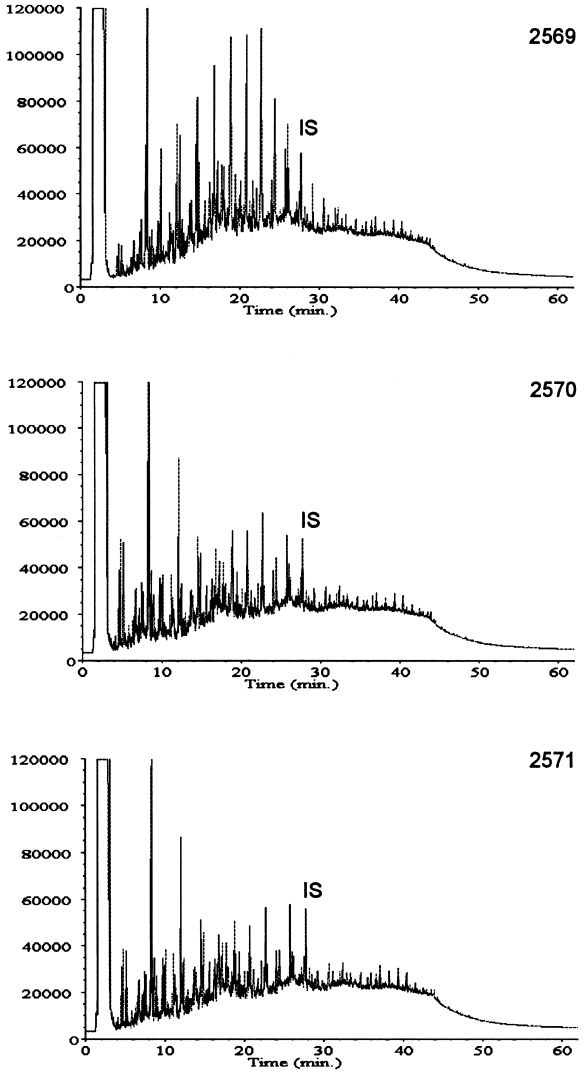

Fig. 1. GC–FID chromatograms of the total hydrocarbon fraction (F3) for TPH analysis of the spill samples. I.S. stands for internal standard 5-α-androstane. The GC traces, in particular the profile and shape of the UCM ''hump'', are significantly different from most crude oils, suggesting the spilled oil may be very special.

The major chemical composition features of TPH and saturate hydrocarbons in the samples are summarized as follows:

(1) The GC traces of F3 (Fig. 1) are significantly different from most crude oils, in particular the profile and shape of the UCM ''hump'', suggesting the spilled oil may be very special. The GC-TPH were determined to be 813–847 mg/g oil, significantly higher than most crude oils. Light refined products such as diesels and jet fuels have TPH values in this range, but the GC traces of the spill oil samples clearly indicated that they were not light refined petroleum products. The unusually high TPH values imply that this oil may only contains very small amount of, or even does not contain asphaltenes and polar compounds. The aromatic fractions in the TPH were determined to be greater than 55%, significantly higher than most oils (only heavy residues such as old type Bunker C fuels may have an aromatics-to-TPH ratio close to such high ratio values). Also, the Carbon Preference Index (CPI) values (1.13–1.20) were found to be significantly greater than 1.0 (most crude oils and refined products have CPI values around 1.0). All these findings further indicate that these oil sample were indeed ''special'' and different from most crude oils and refined products.

(2) GC traces (Fig. 1) clearly exhibit several ''humps''. The resolved GC peaks were mostly located in the lighter component portion and before 30 min retention time. The GC traces after 30 min were very much same for all three samples.

(3) Samples 2570 and 2571 show nearly identical GC chromatographic profiles, *n*-alkane distribution patterns, and relative ratios of pristane/phytane (0.87 and 0.86), implying these two samples were most likely from the same source.

(4) The total *n*-alkanes were determined to be 32.7, 16.0, and 14.7 mg/g oil for samples 2569, 2570, and 2571, respectively. One noticeable differ-

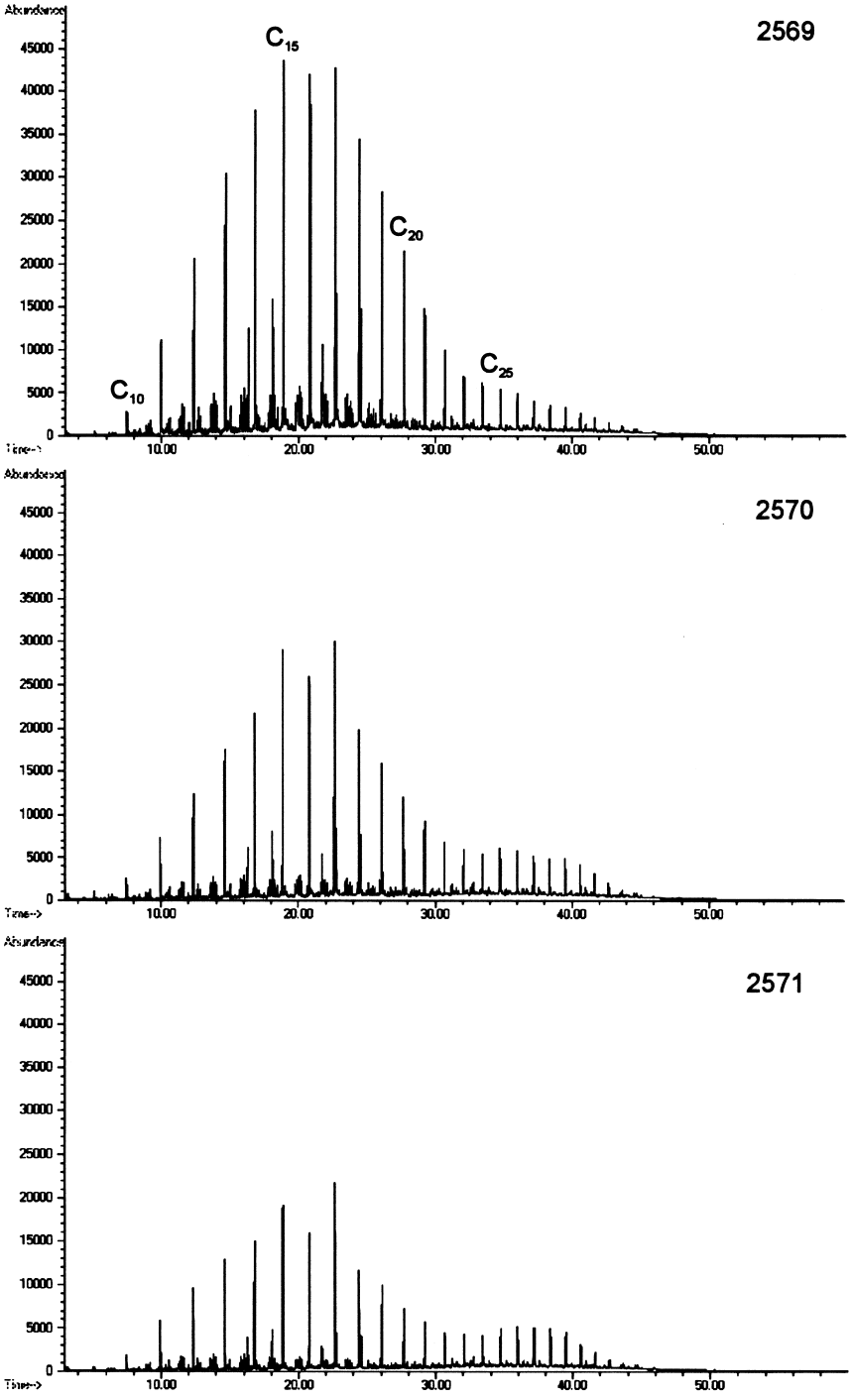

Fig. 2. GC–MS chromatograms of the m/z 85 fragment of the saturated hydrocarbons, clearly showing the distribution of *n*-alkane and isoprenoid compounds.

Table 2
n-Alkane analysis results (after water content correction)

	Sample 2569 (mg/g oil)	Sample 2570 (mg/g oil)	Sample 2571 (mg/g oil)
n-Alkanes			
n-C_8	0.03	0.08	0.07
n-C_9	0.13	0.15	0.13
n-C_{10}	0.66	0.48	0.56
n-C_{11}	1.95	0.91	1.07
n-C_{12}	2.30	1.01	1.10
n-C_{13}	2.78	1.19	1.21
n-C_{14}	3.30	1.27	1.18
n-C_{15}	3.62	1.66	1.47
n-C_{16}	3.31	1.28	1.09
n-C_{17}	3.98	1.84	1.52
Pristane	1.00	0.44	0.33
n-C_{18}	2.14	0.92	0.70
Phytane	1.21	0.51	0.38
n-C_{19}	1.53	0.69	0.48
n-C_{20}	1.03	0.47	0.36
n-C_{21}	0.73	0.36	0.29
n-C_{22}	0.47	0.26	0.22
n-C_{23}	0.31	0.19	0.19
n-C_{24}	0.22	0.18	0.19
n-C_{25}	0.22	0.18	0.19
n-C_{26}	0.18	0.18	0.19
n-C_{27}	0.37	0.39	0.43
n-C_{28}	0.21	0.21	0.28
n-C_{29}	0.36	0.39	0.41
n-C_{30}	0.34	0.39	0.40
n-C_{31}	0.14	0.15	0.14
n-C_{32}	0.10	0.11	0.09
n-C_{33}	0.09	0.07	0.06
n-C_{34}	0.04	0.06	0.05
n-C_{35}	0.04	0.03	0.03
n-C_{36}	0.04	0.03	0.03
n-C_{37}	0.03	0.03	0.02
Total	32.9	16.1	14.9
C_{17}/Pristane	3.97	4.18	4.66
C_{18}/Phytane	1.76	1.82	1.86
Pristane/phytane	0.83	0.87	0.86
CPI	1.13	1.19	1.18

ence between sample 2569 and the other two samples is that the sample 2569 shows much higher abundance of *n*-alkanes in the diesel carbon range from C_8 to C_{23} with the retention time in the range of 3–30 min (Table 2) and higher ratio value of resolved peaks to the total saturates (0.17 over 0.12, Table 1), implying that the spilled oil sample 2569 collected from the river bank may be contaminated by diesel. The portion of the diesel in the spilled oil sample was estimated to be around 10%. The 10% of diesel contributed about half of *n*-alkanes of the sample (the total *n*-alkanes of most diesels range from 120 to 180 mg/g oil).

(5) The depletion of the low-molecular-mass (M_r) C_8 and C_9 in the spill sample 2569 is apparent in comparison with high M_r *n*-alkanes of the sample itself and with samples 2570 and 2571 (Table 2 and Fig. 3). The alteration of the relative abundances of the low-M_r *n*-alkanes to the high-M_r *n*-alkanes indicated that the spill sample 2569 had been lightly weathered since the occurrence of the spill.

3.2. Distribution of target alkylated PAH homologues and other EPA priority PAHs

In general, PAH compounds, especially the high-molecular-mass PAHs and their alkylated homologues are relatively stable and, therefore, the distribution patterns and the diagnostic ratios of these oil-characteristic PAHs can be used as fate indicators of oil in the environment and oil source markers [5,11,17,21–26].

Table 3 summarizes quantitation results of five target petroleum-characteristic alkylated PAH homologues and other EPA priority PAHs. Some important ratio values of ‘‘source-specific marker’’ PAH compounds were also determined and presented in Table 3. Fig. 4 depicts the distribution of the target PAHs in the samples.

GC–MS measurements show that BTEX (the collective name of benzene, toluene, ethylbenzene, and the xylene isomers) and other lighter alkylbenzene compounds still existed in the spill sample, further confirming that the spill samples were relative fresh and were only lightly weathered.

The sum of the five target alkylated PAHs and other EPA priority PAHs were determined to be 21 570, 21 434, 19 530 μg/g of oil (Table 3) for samples 2569, 2570 and 2571, respectively, which are significantly higher than most crude oils. Three oil samples show very similar PAH distribution patterns and fingerprints. Slight differences in the PAH distribution (in particular, the differences in the distribution profile of the low-M_r alkylated naphthalene series) was noticed between the spill sample 2569 and the suspected source samples. This differ-

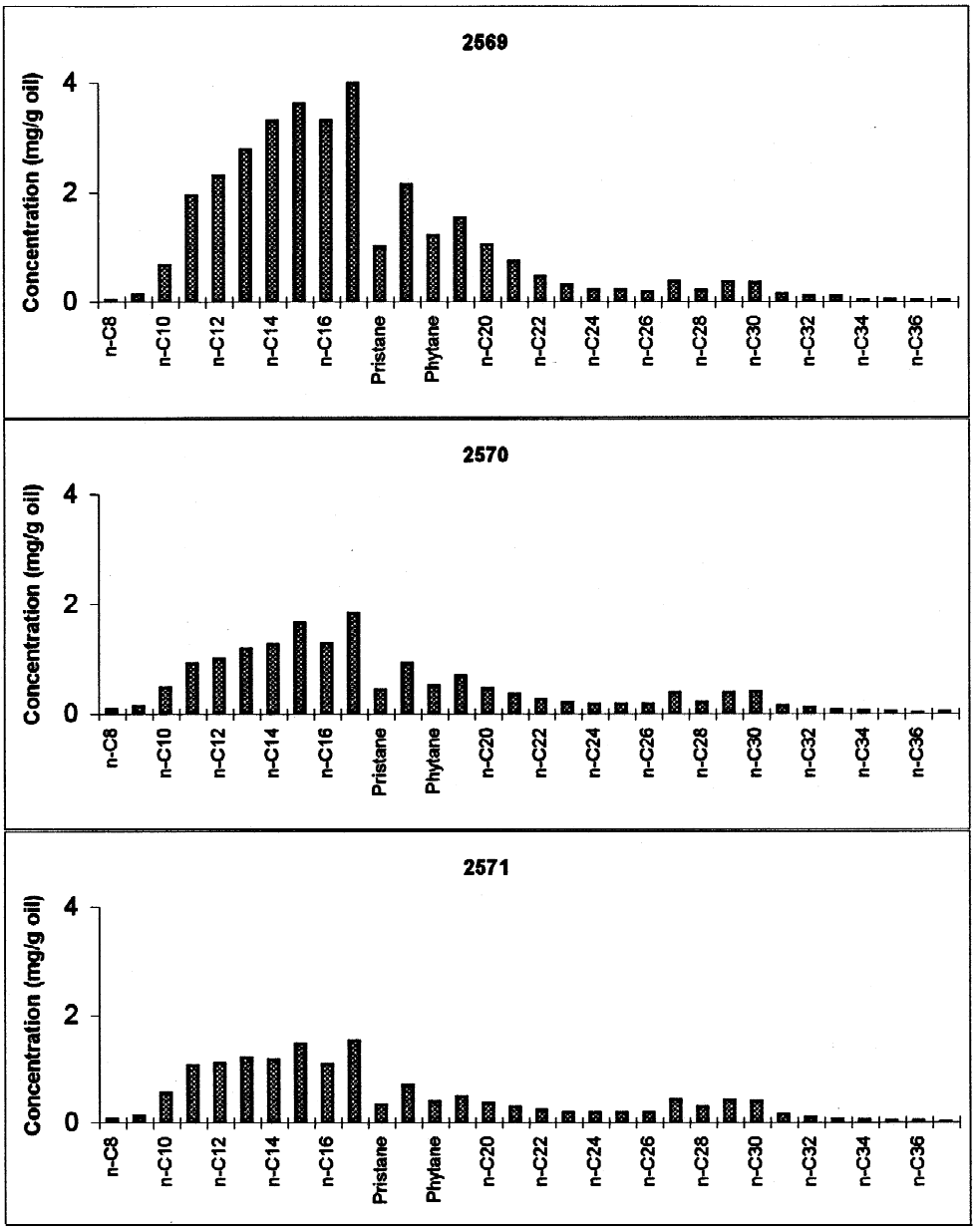

Fig. 3. *n*-Alkane quantitation results (mg/g oil) of the spill samples. The sample 2569 shows much higher concentrations of *n*-alkanes in the diesel carbon range from C_8 to C_{23}, implying that the spilled oil sample collected from the river bank may be contaminated by diesel.

ence may be attributed to the addition of highly abundant alkylated naphthalene series from the 10% of diesel in the spill sample. It has been well demonstrated that the alkylated naphthalene and chrysene series are the most (>55%) and least (<0.02%) abundant among the five target alkylated PAH series of diesel [27].

Another pronounced compositional feature is that all three samples demonstrated extremely high concentrations of other EPA priority unsubstituted PAHs,

Table 3
PAH analysis results (after water content correction)

Sample	Aromatic ring number	2569 (μg/g oil)	2570 (μg/g oil)	2571 (μg/g oil)
Alkylated PAHs				
Sum of naphthalenes	2	13 191	13 115	11 341
Sum of phenanthrenes	3	4282	4225	4156
Sum of dibenzothiophenes	3	662	553	527
Sum of fluorenes	3	2647	2807	2738
Sum of chrysenes	4	779	803	823
Total		21 560	21 503	19 585
Other EPA priority PAHs				
Biphenyl (Bph)	2	621	623	573
Acenaphthylene (Acl)	3	570	628	635
Acenaphthene (Ace)	3	278	289	286
Anthracene (An)	3	288	317	321
Fluoranthene (Fl)	4	299	282	306
Pyrene (Py)	4	376	365	390
Benz[*a*]anthracene (BaA)	4	156	157	166
Benzo[*b*]fluoranthene (BbF)	5	78	78	89
Benzo[*k*]fluoranthene (BkF)	5	98	98	93
Benzo[*e*]pyrene (BeP)	5	69	68	72
Benzo[*a*]pyrene (BaP)	5	108	107	110
Perylene (Pe)	5	16	15	16
Indeno[1,2,3-*cd*]pyrene (IP)	6	55	57	58
Dibenz[*a,h*]anthracene (DA)	5	15	16	16
Benzo[*ghi*]perylene (BP)	6	66	70	69
Total		3094	3170	3200
Diagnostic ratios				
$C_0C:C_1C:C_2C:C_3C$		0.20:0.28:0.33:0.19	0.19:0.27:0.34:0.20	0.19:0.28:0.34:0.19
$C_2D/C_2P:C_3D/C_3P$		0.21:0.26	0.18 :0.22	0.19:0.22
4-:2-/3-:1-*m*-DBT[a]		1:0.74:0.48	1:0.82:0.50	1:0.84:0.52
(3-+2-Methyl-phenanthrene)/(4-/9-+1-methyl-phenanthrene) (*m/z* 192		0.89	0.89	0.88
2-Methyl-naphthalene/1-methyl-naphthalene (*m/z* 142)		1.27	1.25	1.27
Anthracene/phenanthrene (*m/z* 178)		0.32	0.35	0.36
BaA/Chry (*m/z* 228)		0.99	0.97	0.99
BeP/BaP (*m/z* 252)		0.64	0.64	0.65
IP/BP (*m/z* 276)		0.83	0.82	0.84
Pyrogenic index[b]		0.11	0.12	0.13

[a] DBT represents dibenzothiophene.
[b] Pyrogenic index is defined as the relative ratio of the sum of the other EPA priority three- to six-ring PAHs to the sum of the five target alkylated PAH homologues.

especially the high-M_r PAHs from four-ring fluoranthene to six-ring benzo[*ghi*]perylene. The total of other EPA priority PAHs were determined to be in the range of 3100–3200 μg/g oil, significantly higher than in crude oil and refined products. In most oils, the abundances of anthracene relative to phenanthrene (*m/z* 178) and benz[*a*]anthracene relative to chrysene (*m/z* 228) is quite low. As for diesel, the concentrations of four- to six-ring other EPA priority PAHs plus three-ring anthracene are extremely low, and indeno[123-*cd*]pyrene, dibenzo[*ah*]anthracene and benzo[*ghi*]perylene are even under the GC–MS detection limits in many diesels. However, the spill and suspected source samples showed unusually high

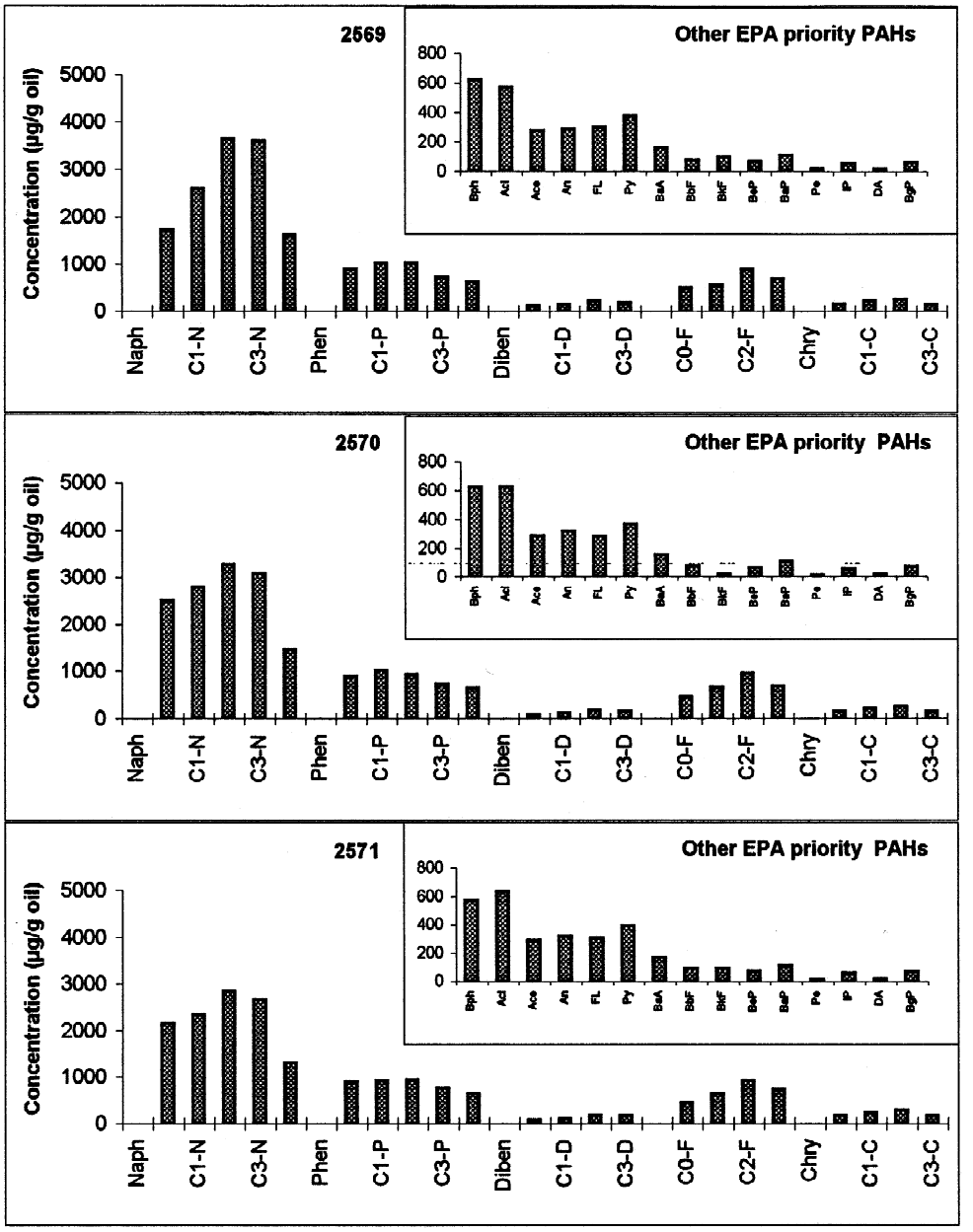

Fig. 4. Alkylated PAH fingerprints of the spill samples, illustrating the PAH compositional features. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0, 1, 2, 3, and 4 represent carbon numbers of alkyl groups in alkylated PAH homologues. The left insets are enlarged fingerprints of the other EPA priority PAHs. The abbreviations from Bph to BgP represent biphenyl, acenaphthylene, acenaphthene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, dibenz[*a*,*h*]anthracene, and benzo[*ghi*]perylene, respectively.

values in relative ratios of target paired PAH isomers (Table 3). As an example, Fig. 5 presents extracted ion chromatograms of anthracene and phenanthrene at m/z 178 and benz[*a*]anthracene and chrysene at m/z 228 for the three spill samples. The relative ratios of anthracene to phenanthrene and ben-

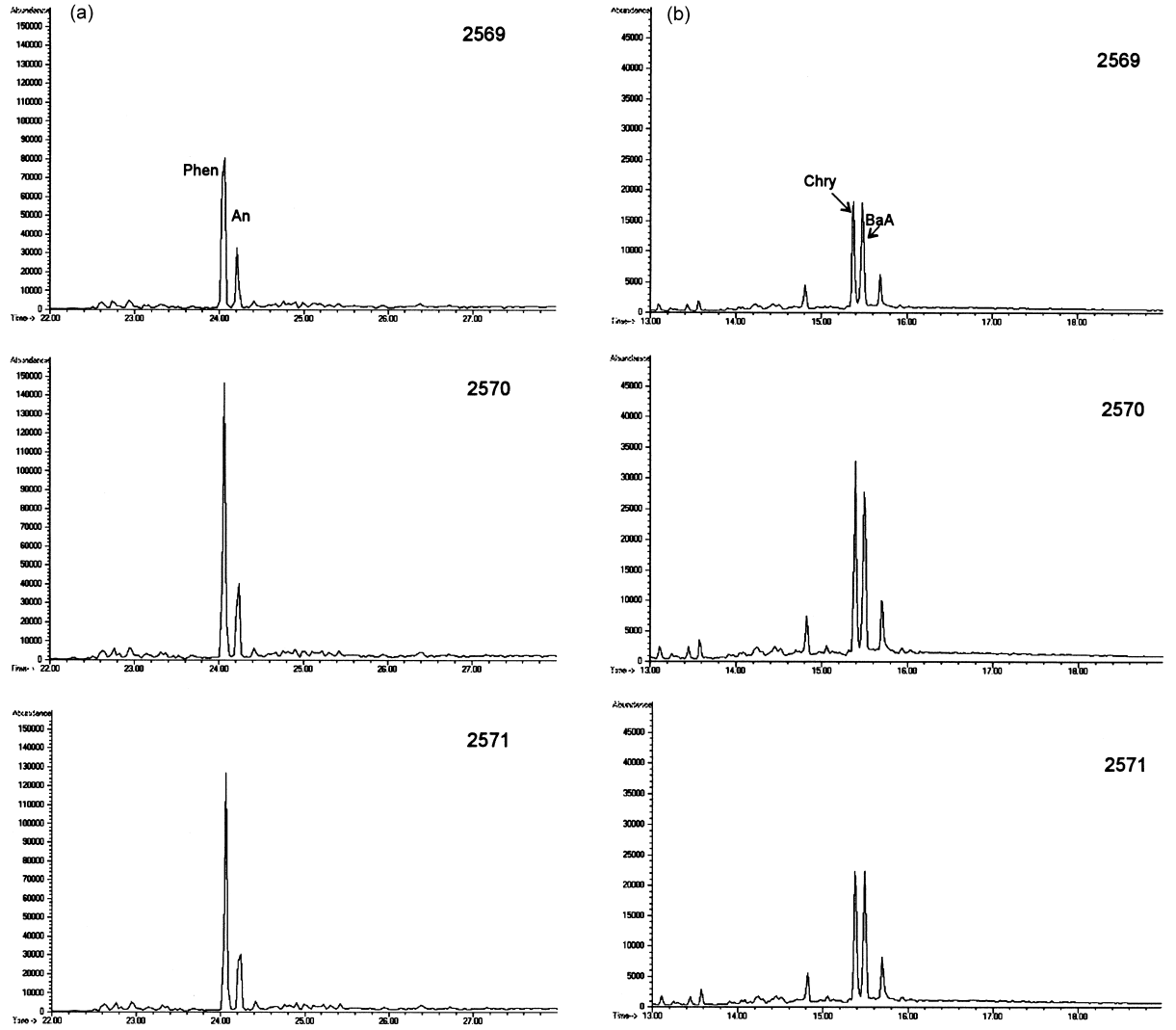

Fig. 5. Comparison of extracted ion chromatograms for PAH compounds phenanthrene and anthracene (at m/z 178, A) and benz[a]anthracene and chrysene (at m/z 228, B), The relative abundance distribution of these two pair PAH isomers were determined to be about 0.35 and 1.0, respectively, far higher than the corresponding ratio values of crude oils. This compositional feature is very distinct, and only pyrogenic hydrocarbons has demonstrated that kind of PAH compositional features.

z[a]anthracene to chrysene were determined to be about 0.35 and near 1.0, respectively, far higher than the corresponding ratios in crude oils. This PAH compositional feature is very distinct and only pyrogenic hydrocarbons has demonstrated that kind of PAH compositional features [12,27].

The diagnostic ratios of ''source-specific'' PAH compounds were also determined and summarized in Table 3. In recent years, in addition to determination of ratios of the conventional diagnostic PAH and biomarker compounds, research has been further expanded to use individual source-specific isomers within the same alkylation levels and isomeric groups and to determine the relative isomer-to-isomer distribution for source identification of spilled oil [11,23,28]. The differences between the isomer distribution reflect the differences of the deposional 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 distributions of isomers at the same ratios of m/z are subject to little interference from weathering in the short term or lightly weathered oils. Hence they can be more positively used for oil spill identification. Analysis of the diagnostic ratios of ''source-specific'' hydrocarbons (Table 3) clearly reveals the following:

(1) The relative distribution of the highly degradation-resistant alkyl (C_0- to C_3-) chrysene series (C_0C:C_1C:C_2C:C_3C) were determined to be nearly identical for all three samples.

(2) Isomeric distributions of 2-methyl-naphthalene to 1-methyl-naphthalene at m/z 142, (3-+2-methyl-phenanthrene) to (4-/9-+1-methyl-phenanthrene) at m/z 192, benz[*a*]anthracene to chrysene at m/z 228, benzo[*e*]pyrene to benzo[*a*]pyrene at 252, and indeno[123-*cd*]pyrene to benzo[*ghi*]perylene at m/z 276 were found to be closely matching.

(3) It is well known that diesel PAHs are largely composed of two- and three-ring PAHs and their alkylated homologues, and diesels only contain (or even do not contain in some diesels) extremely low amounts of high-M_r PAH and biomarker compounds. This is because refining processes have removed most high-M_r hydrocarbons from the corresponding crude oil stocks. Therefore, the slight differences in isomeric distribution of 4-, 2-/3-, and 1-methyl-dibenzothiophene and the double ratios of C2D/C2P:C3D/C3P between the spill and suspected source samples may be attributed to the contribution of ~10% of diesel in the spill oil. Obviously, for the reasons discussed above, the ~10% of diesel had little effects on determination of diagnostic ratios of other high-molecular-mass PAH isomers or alkylated PAH homologous series such as the chrysene series.

(4) A new parameter ''pyrogenic index'', Σ(other 3–6 ring PAHs)/Σ(5 alkylated PAHs), has been recently defined and proposed as a quantitative indicator for identification of pyrogenic PAHs and for differentiating pyrogenic and petrogenic PAHs [27]. Also, this index has demonstrated to be a useful tool for distinguishing heavy fuels from crude oils and light refined products. It is interesting to note that all three samples had extremely high ''Pyrogenic Index'' values (0.11–0.13), far higher than the corresponding values for oils and refined products (<0.010), Bunker C fuel and other types of heavy residual fuels (<0.06) and biodegraded oils (<0.014), but lower than the ''pyrogenic index'' values of soot samples from the burning of oil or diesel (>0.5) [27]. This fact further implies that the spilled and the suspected source oil is a very ''unique'' oil, and it was very possibly related to some pyrogenic process of organic materials.

3.3. Analysis of biomarker compounds

Fig. 6 shows GC–MS distribution profiles of the highly degradation-resistant biomarker terpane and sterane compounds at m/z 191. A wide range of terpanes are present in the samples from C_{20} to C_{35} with the C_{30} and C_{29} αβ-hopanes being the most abundant. As for steranes at m/z 217 and 218, in addition to C_{21} and C_{22} 5α(H), 14β(H), 17β(H)-sterane, the dominance of C_{27}, C_{28}, and C_{29} 20S/20R steranes, particularly the epimers of αββ-steranes, is observed. Table 4 summarizes quantitation results for the target terpanes and two groups of αββ-steranes (C_{27} and C_{29}). These biomarker compounds have been increasingly used in recent years for the purposes of source identification and differentiation of oils, and monitoring the weathering and degradation process of oil hydrocarbons under a wide variety of conditions [7,11,13,14,17,29–34].

From Fig. 6 and Table 4, it can be seen that the distribution pattern and profile of biomarker terpanes and steranes are nearly identical for all three samples. The concentrations of terpanes and steranes are quite low, in comparison to most crude oils. The total target biomarkers were determined to be 275 μg per gram of oil for the spill sample and 275 and 278 μg per gram of oil for the suspected source oils.

In addition, the presence of C_{30} βα-hopane with relatively-high abundance in the samples is identified. This feature is quite unique and has rarely been seen in crude oils and petroleum products, further indicating that the spilled oil and the suspected source oil were the same. It has been recognized that the ''specific'' biomarker compounds including several geologically rare cyclic alkanes were found to exist only in certain oils and therefore can be used as unique markers to provide an

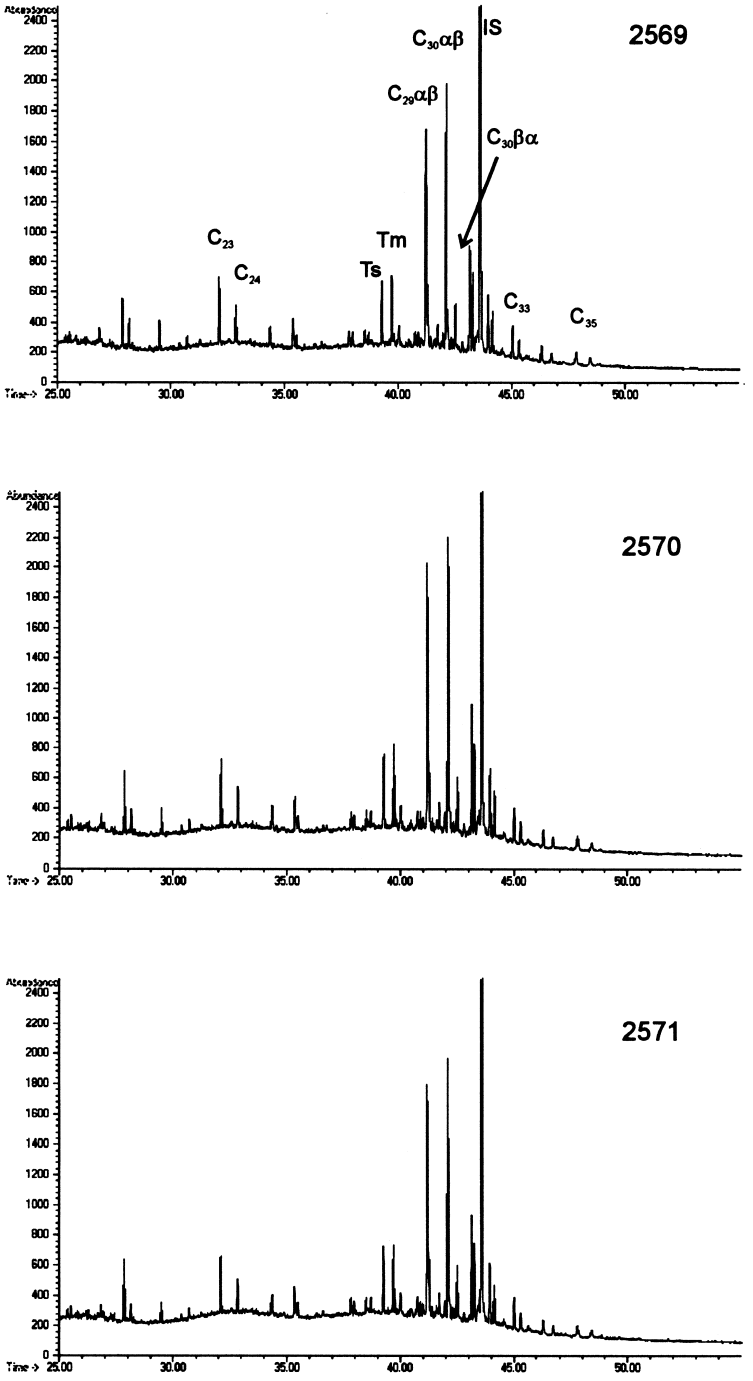

Fig. 6. Comparison of distribution of biomarker terpanes (m/z 191) in the QR samples. The presence of C_{30} βα-hopane (moretane) with relatively-high abundance in the samples is identified. I.S. represents the internal standard C_{30} ββ-hopane; C_{23}, C_{24}, C_{29}, C_{30}, C_{32} to C_{35}, and Ts and Tm represent C_{23} and C_{24} terpane, C_{29} and C_{30} αβ-hopane, 22*S*/22*R* isomer pairs of C_{32} to C_{35} hopanes, and 18α(H), 21β(H)-22, 29,30-trisnorhopane (Ts) and 17α(H), 21β(H)-22,29,30-trisnorhopane (Tm), respectively.

Table 4
Analysis results of biomarker compounds and diagnostic ratios of ''source-specific marker'' biomarker compounds (after water correction)

	Quantitation results (μg/g oil)		
	Sample 2569	Sample 2570	Sample 2571
Parameters			
C_{23}-terpane	13.7	11.8	12.1
C_{24}-terpane	8.6	7.8	7.9
Ts	13.7	14.2	13.7
Tm	14.4	14.7	14.3
C_{29} αβ-hopane	50.9	49.8	51.0
C_{30} αβ-hopane	60.7	60.2	60.5
C_{30} βα-hopane	10.8	11.2	12.0
C_{31} (*S*)-hopane	23.1	23.8	23.7
C_{31} (*R*)-hopane	17.7	18.3	18.8
C_{32} (*S*)-hopane	15.4	16.1	15.8
C_{32} (*R*)-hopane	9.2	9.6	9.3
C_{33} (*S*)-hopane	9.1	10.0	10.2
C_{33} (*R*)-hopane	5.8	6.6	6.9
C_{27} αββ-steranes	13.3	12.6	14.0
C_{29} αββ-steranes	19.5	19.1	20.1
Total of target terpanes (μg/g oil)	286	286	290
Diagnostic ratios			
Terpane C_{23}/C_{24}	1.59	1.53	1.52
Hopane C_{29} αβ/C_{30} αβ	0.84	0.83	0.84
Ts/Tm	0.95	0.97	0.96
Hopane C_{30} βα/C_{30} αβ	0.18	0.19	0.20
$C_{31}(S)/C_{31}(S+R)$	0.57	0.56	0.56
$C_{32}(S)/C_{32}(S+R)$	0.63	0.63	0.63
$C_{33}(S)/C_{33}(S+R)$	0.61	0.60	0.60
C_{23}/C_{30}	0.23	0.20	0.20
C_{24}/C_{30}	0.14	0.13	0.13
Steranes C_{27} αββ/C_{29} αββ	0.68	0.66	0.69

interpretational advantage in fingerprinting sources of spilled oils [11,13,14,28,29,32,35].

The relative ratios of target biomarker terpanes C_{23}/C_{24}, C_{23}/C_{30}, Ts/Tm [Ts: 18α(H), 21β(H)-22,29,30-trisnorhopane; Tm: 17α(H), 21β(H)-22,29,30-trisnorhopane], C_{29} αβ-hopane/C_{30} αβ-hopane, C_{30} βα/C_{30} αβ-hopane, $C_{31}(22S)/C_{31}(22S+22R)$, $C_{32}(22S)/C_{32}(22S+22R)$ and $C_{33}(22S)/C_{33}(22S+22R)$ hopanes are very much same for all three samples. The only noticeable differences between them are that the spilled oil had slightly higher concentration of C_{23} terpane (13.7 μg/g oil over 11.8 and 12.1 μg/g oil) and higher relative ratios of C_{23} terpane/C_{30} αβ-hopane (0.23 over 0.20) than the other two suspected source oil samples. This may be also explained by the presence of the 10% of diesel in the spilled oil. Analysis of various diesels has demonstrated that most diesels still contain very small amount of relatively low-M_r C_{23} and C_{24} terpanes after refining.

4. Conclusions

This paper describes a detailed analytical approach using ''source-specific marker'' compounds and their diagnostic ratios for characterization of chemical compositions of the spill and suspected source samples and for source identification of the spill. The analytical evidences and data interpretation results indicates that: (1) the spilled oil is very ''specific'' and different from crude oils and petroleum products not only in physical properties, but also in chemical composition; (2) the spilled oil samples showed

unusually high TPH and CPI values and unusually high concentration of other EPA priority PAHs. The ''Pyrogenic Index'' values were determined to be as high as 0.11–0.13, significantly higher than crude oils (<0.010) and heavy Bunker type fuels (0.015–0.060). Significant contribution of PAHs from pyrogenic components was obvious. This indicates that the spilled oil may be related to pyrogenic processing of some organic materials; (3) the oil in three samples were the same and had the same origin, however, the spill sample 2569 contained a small percentage of diesel (~10%), which contributes about half of the total *n*-alkanes; (4) the spilled oil was relatively ''fresh'', its chemical composition had not undergone significant alteration in comparison with the suspected source oil; (5) biomarkers were also detected, but their concentrations were quite low in comparison with most crude oils; (6) the spilled oil may be more toxic than most crude oils due to its high concentrations of PAHs, in particular the high concentration of high-molecular-mass unsubstituted 4–6 ring PAHs.

Note: We were recently informed that this case has been closed, some clean-up work has been done, and the company ''Thermex'' has agreed to pay for the expenses of clean-up. We have been also told that the company was producing and recycling oil from waste tires. Therefore, the spilled oil was indeed ''special'' and indeed related to some pyrogenic processing of organic materials – tires. The successful characterization and identification of the spilled oil clearly demonstrates the usefulness of advanced fingerprinting and data interpretation techniques for oil spill studies.

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