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Characterization and identification of the Detroit River mystery oil spill (2002)

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Abstract

In this paper, a case study of the Detroit River mystery oil spill (2002) is presented that demonstrates the utility of detailed and integrated oil fingerprinting in investigating unknown or suspected oil spills. The detailed diagnostic oil fingerprinting techniques include determination of hydrocarbon groups and semi-quantitative product screening, analysis of oil-characteristic biomarkers and the extended suite of parent and alkylated polycyclic aromatic hydrocarbons (PAHs), and quantitative determination of a variety of diagnostic ratios of "source-specific marker" compounds. The detailed chemical fingerprinting data and results highlight the followings:

(1) The spill samples were largely composed of used lube oil mixed with smaller portion of diesel fuel.
(2) The diesel in the samples had been weathered and degraded.
(3) Sample 3 collected from N. Boblo Island on 14 April was more weathered (most probably caused by more evaporation and water-washing) than samples 1 and 2.
(4) All fingerprinting results clearly demonstrated oils in three samples were the same, and they came from the same source.
(5) Most PAH compounds were from the diesel portion in the spill samples, while the biomarker compounds were largely from the lube oil.
(6) Input of pyrogenic PAHs to the spill samples was clearly demonstrated. The pyrogenic PAHs were most probably produced from combustion and motor lubrication processes, and the lube oil in these spill samples was waste lube oil.

Keywords: Oils; Polynuclear aromatic hydrocarbons; Alkanes; Terpanes; Steranes

1. Introduction

An oil spill to the Rouge River and Detroit River was discovered and reported in the second week of April (8–13 April 2002). The oil of thousands of liters spilled into the Rouge River and travelled about 3 km to the Detroit River. It then floated in several small patches down the river into northern Lake Erie. Thousands of liters more spilled into the Rouge River during that weekend. The two spills were related, and heavy rains flushed the additional oil out of the sewer and into the river. Environment Canada (EC) Ontario Region conducted an aerial survey of the Detroit River. They also surveyed the majority of the areas by vessel. The spill impacted approximately 43 km of USA and Canadian shorelines. The presence of sheen over the majority of the impacted river area was observed. On the shore, it appeared as a black coat and typically 0.2–1.0 mm thick. EC Ontario Region collected a number of spill samples from various spots and sent 11 samples to the Oil Research Laboratory of the Emergencies Science and Technology Division (ESTD), Environment Canada, for analysis. The samples were received on 18 April 2002, and treated and analyzed as emergency samples.

Waterborne oil spills of unknown origin often occur in rivers, open water and in coastal waterways. These spills range from continuous leaks from land sources and illegal

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dumping at sea to large spill accidents. To precisely characterize spilled oil hydrocarbons in complex environmental samples and to defensibly identify the spill source(s) are extremely important for site contamination assessment, for prediction of the potential long-term impact of spilled oils on the environment, and for determining responsibility for the spill and settling disputes related to liability.

In recent years, numerous studies concerned with the origin, type, fate and behavior of spilled oils in various environments have been published. Great advances have been made on both interpretive and analytical methods for fingerprinting oil hydrocarbons. Flexible, tiered analytical approaches, which facilitate the detailed compositional analyses based primarily upon GC–MS and GC–flame ionization detection (FID), have been developed in response to the oil spill identification and specific site investigation needs [1–8]. Data produced from various analytical techniques are used to compare spill samples with samples taken from suspected sources. A variety of diagnostic ratios, especially ratios of source-specific oil constituents including polycyclic aromatic hydrocarbon (PAH) homologous groups at different alkylation levels, isomeric PAHs within the same alkylation levels (such as relative ratios of three methyldibenzothiophene and four methylphenanthrene isomers), 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 successfully used for oil source identification and monitoring of weathering and biological degradation processes.

For example, in order to meet further requirements of analytical methods for oil spill identification (being more *quantifiable*, *objective* and *defensible*), SINTEF Applied Chemistry of Norway [2], in cooperation with several other agencies, has recently improved and standardized the existing Nordtest methodology for oil spill fingerprinting, which includes four tiered "levels" of analyses and data treatment with focus on determination of quantitative diagnostic indices. Many US Environmental Protection Agency (EPA) and American Society for Testing and Materials (ASTM) methods have been modified accordingly to improve *specificity* and *sensitivity* for measuring spilled oil and petroleum products in soils, waters and contaminated sites [9–11]. For example, the modified EPA Method 8270 has been modified to expand the analyte list to include many oil-characteristic compounds such as the alkylated PAHs and biomarker compounds.

In this paper, a medium but practical case study is presented to demonstrate the utility of the detailed and integrated multi-criterion analytical approaches for fingerprinting, correlating and identifying unknown or suspected spills. We first determined the product type by recognizing distribution patterns of bulk hydrocarbon groups, then quantified biomarker and extended suite of parent and alkylated PAH compounds and compared their distribution profiles, finally we went the extra mile to verify our conclusions by determining a variety of diagnostic ratios of "source-specific marker" compounds. Furthermore, we defensibly identified and determined the input of pyrogenic PAHs to the spill samples.

2. Experimental

2.1. Reagents and materials

Distilled chromatographic solvents were used without further purification. Calibration standards used for the determination of individual and total petroleum hydrocarbons (TPHs) include *n*-alkane standards from C_8 to C_{34} including pristane and phytane, PAH standards (SRM 1491) from the US National Institute of Standards and Technology (NIST), and biomarker standards (hopanes and steranes) from Chiron Laboratory of Norway.

2.2. Sample preparation

As requested by the EC Ontario Region spill response officers, three representative samples from 11 spill samples, labeled as LS 44561, LS 44551 and N. Boblo Island, were characterized.

(i) *Sample 1 (TAG LS 44561)*: Collected from Amhersburg Channel, Detroit River (42°06′52″N, 083°07′03″W). Sampling time: 9:10 a.m., 10 April 2002. It is a black oil–water emulsion sample.
(ii) *Sample 2 (TAG LS 44551)*: Collected from Detroit River (42°16′25″N, 083°06′37″W). Sampling time: 10:05 a.m., 10 April 2002. It is an absorbent wipe sample with oil–water on it, black color, and the wipe was saturated by water.
(iii) *Sample 3 (N. Boblo Island)*: Collected from North Boblo Island. Sampling time: 18:08 p.m., 14 April 2002. It is an absorbent wipe sample with oil on it, lighter black color.

The samples were received on 18 April and analyzed on 20 and 21 April. Prior to analysis, the samples were tightly sealed and stored in a refrigerator at 4 °C. The detailed sample preparation procedures are as follows:

(1) *Sample 1*: An aliquot of the sample was accurately weighed (19.80 g), approximately 150 ml of anhydrous granular sodium sulfate was added and thoroughly mixed with the sample to dry the sample. The remaining sample was archived. The sample was serially extracted six times with 100 ml of dichloromethane (DCM) for 10 min each time using sonication. The extracts were combined, dried and filtered by passing through a sodium sulfate layer. The dried extracts were then concentrated to appropriate volume and solvent-exchanged with hexane by rotary evaporation. The final volume of the concentrated extract in hexane was 25.00 ml.
(2) *Sample 2*: The sample was weighed (122.00 g) and successively extracted six times with 50 ml of DCM for

10 min each time using sonication. Extracts were combined and transferred to a separatory funnel to separate the water layer. The remaining procedures were the same as for sample 1. The final volume of the concentrated extract in hexane was 100.00 ml.

(3) *Sample 3*: The sample was weighed (5.30 g) and successively extracted six times with 20 ml of DCM for 10 min each time using sonication. The extracts were combined, dried and filtered by passing through a sodium sulfate layer. The remaining procedures were the same as for sample 1. The final volume of the concentrated extract in hexane was 25.00 ml.

An aliquot of the concentrated extracts (1.00 ml) was quantitatively transferred to a pre-weighed vial and blown down to a residue with nitrogen to obtain a mass of the total solvent-extractable materials (TSEMs, expressed as mg/g of sample).

A chromatographic column with a PTFE stopcock (200 mm × 10.5 mm i.d.) was plugged with Pyrex glass wool at the bottom, serially rinsed with methanol, hexane, and dichrolomethane, and allow to dry. The column was dry-packed with 3 g of activated silica gel (100–200 mesh, pore size 150 Å, pore 1.2 cm^3/g, active surface 320 m^2/g, purchased from Fisher Scientific) and topped with about 1 cm anhydrous granular sodium sulfate. Then the columns were conditioned using 20 ml of hexane. Just prior to exposure of the sodium sulfate layer to air, appropriate volumes of the concentrated extracts (0.10, 0.10, and 0.50 ml for samples 1–3, respectively) containing approximately 30–40 mg of TSEMs were spiked with appropriate amounts of surrogates (100 μl of 200 ppm *o*-terphenyl and 100 μl mixture of deuterated acenaphthene, phenanthrene, benz[*a*]anthracene, and perylene, 10 ppm each), and then quantitatively transferred into chromatographic columns for sample cleanup and fractionation [12–14]. Hexane (12 ml) and 50% (v/v) benzene in hexane (15 ml) were used to elute the saturated and aromatic hydrocarbons, respectively. For each sample, half of the hexane fraction (labeled F1) was used for analysis of the total GC-detectable saturated compounds, *n*-alkanes and isoprenoids, 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 the hexane fraction and 50% benzene fraction were combined into a fraction (labeled F3) and used for the determination of the total GC-detectable petroleum hydrocarbons and the GC-unresolved complex mixture of hydrocarbons (UCMs). These three fractions were concentrated under a stream of nitrogen to appropriate volumes (∼0.4 ml), spiked with appropriate internal standards (50 μl of 200 ppm 5-α-androstane and 50 μl of 20 ppm C_{30}-ββ-hopane, 50 μl of 10 ppm [$^2H_{14}$]terphenyl, and 50 μl of 200 ppm 5-α-androstane for F1, F2, and F3, respectively), and then adjusted to an accurate pre-injection volume of 0.50 ml for GC–FID and GC–MS analyses.

2.3. Sample analysis

Analyses for *n*-alkane distribution (*n*-C_8 through *n*-C_{41}, pristane and phytane) and TPHs were performed on an Agilent 6890 gas chromatograph equipped with an FID system and an Agilent 7683 autosampler. Analyses of target PAH compounds (including five alkylated PAH homologous groups and other EPA priority PAHs) and biomarker terpanes and steranes were performed on an Agilent 6890 GC system equipped with an Agilent 5973 mass-selective detector (MSD). System control and data acquisition were achieved with the Agilent G1701 BA MSD ChemStation. The DB-5 (30 m × 0.32 mm i.d., 0.25 μm film thickness) and HP-5 (30 m × 0.25 mm i.d., 0.25 μm film thickness) fused silica columns were used for GC–FID and GC–MS analyses, respectively.

GC–FID analysis provides a baseline resolution of *n*-alkanes from *n*-C_8 to *n*-C_{41}. Quantitation of the analytes was based on the internal standard compound (5-α-androstane). GC–MS analysis was performed utilizing a selected ion monitoring (SIM) mode to improve detection limits. The ions monitored were 128, 142, 156, 170, and 184 for alkylated naphthalene homologous series; 178, 192, 206, 220, and 234 for alkylated phenanthrene homologous series; 184, 198, 212, and 226 for alkylated dibenzothiophene homologous series; 166, 180, 194 and 208 for alkylated fluorene homologous series; and 228, 242, 256, and 270 for alkylated chrysene homologous series. The concentrations of the individual PAH and biomarker compounds were determined based on the internal standards d_{14}-terphenyl and C_{30}-ββ-hopane, respectively. For detailed chromatographic conditions and temperature programs, analysis quality control, and quantification methodology, refer to [12–14].

3. Results and discussion

3.1. Product type screen and determination of hydrocarbon groups

In general, the product type and chemical composition features of oil samples can be illustrated by qualitative and quantitative examination of their GC traces [7,8]. Fig. 1 shows the GC–FID chromatograms of Fraction 3 for TPH and *n*-alkane analysis. The saturated fractions F1 demonstrated very similar GC–FID chromatogram profiles to their corresponding Fraction 3.

Table 1 summarizes the hydrocarbon group analysis results (gravimetrically determined TSEMs, GC-TPH values) of the spill samples. In addition, the important ratio parameters of resolved peaks/TPH, UCM/TPH, and *n*-alkane quantitation results are listed in Table 1 as well. Note that all hydrocarbon group data discussed below are expressed on the TSEM basis rather than on the sample weight basis. TSEMs supply an equal basis for the determination of the relative composition of saturates, aromatics, and asphaltenes

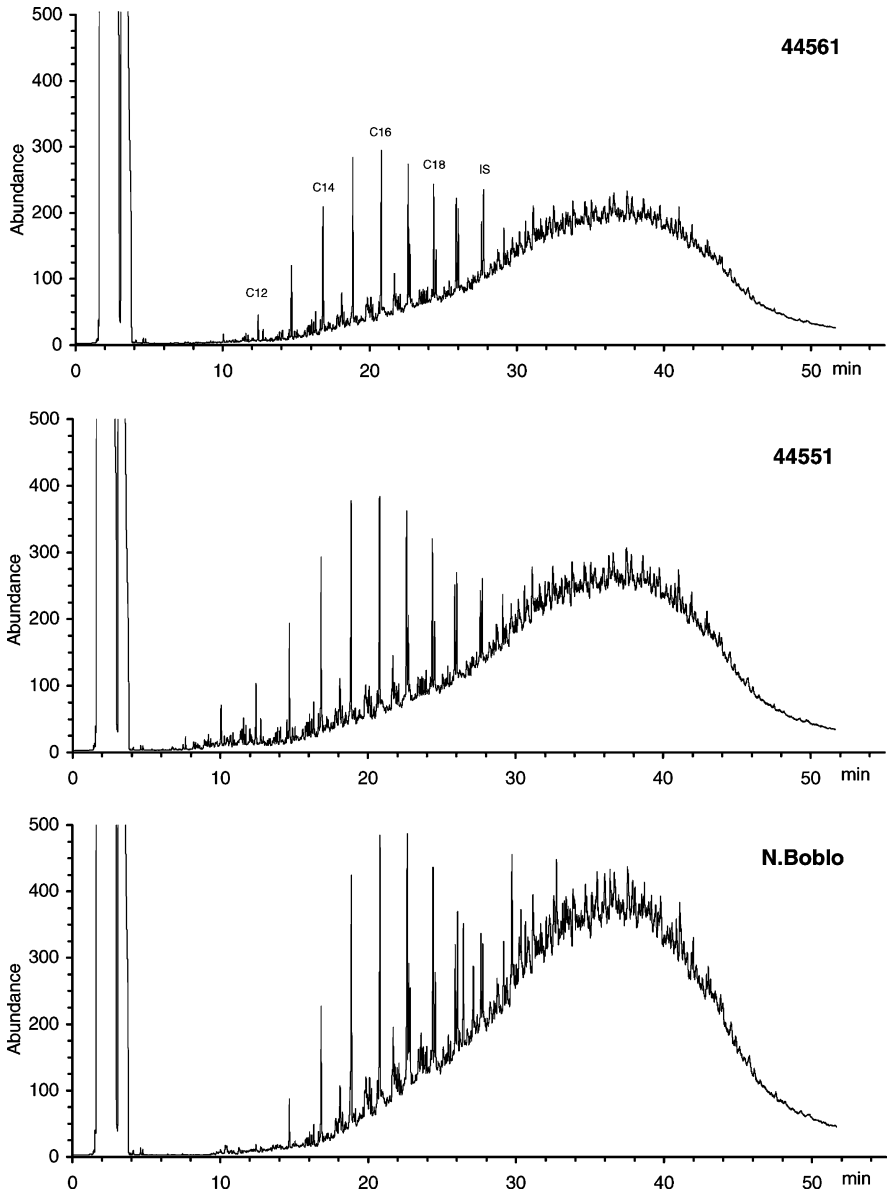

Fig. 1. GC–FID chromatograms of Fraction 3 of the Detroit River spill samples 44561, 44551, and N. Boblo for *n*-alkane and TPH analysis. The GC traces are featured by dominance of unresolved complex mixture (UCM) of hydrocarbons with very small amount of resolved peaks being detected in the lube oil carbon range (retention time: 24–50 min).

plus polars in samples. It is only by this way that the quantitation results are comparable. The total GC-TPH value, defined as the sum of all resolved and unresolved hydrocarbons detected by GC, is calculated using the following equation:

$$\text{TPHs } (\mu\text{g/g}) = \frac{A_{\text{TPH}} W_{\text{IS}} D}{A_{\text{IS}} (\text{RRF}_{\text{TPH}}) W_{\text{S}}}$$

where A_{TPH} is the total area of the sample chromatogram corrected with the solvent dichloromethane blank; RRF_{TPH} the average relative response factor of all target *n*-alkanes plus pristane and phytane, which are obtained from the *n*-alkane (from C_8 to C_{36}) calibration standards; A_{IS} the response for the internal standard 5-α-androstane in the sample; W_{IS} the amount (μg) of internal standard added to the sample; D the dilution factor (if no dilution was made, $D = 1$) (dimensionless); and W_{S} the mass (g) of the sample extracted.

Fig. 2 graphically depicts the quantitative *n*-alkane distributions. The major chemical composition features of TPHs and saturate hydrocarbons in the samples are summarized as follows:

(1) The GC-TPH values were determined to be 449, 494, and 513 mg/g TSEM for samples 1–3. Clearly, the GC-TPH values are exclusively smaller than the corresponding TSEM values. The solvent-extractable impurities from samples, asphaltenes plus polar compounds (which were retained on the silica gel cleanup column), as well as a small amount of high-molecular-mass

Table 1
Hydrocarbon group analysis results of the Detroit River spill samples

	Samples		
	44561	44551	N. Boblo
Sample mass (g)	19.8	122	5.30
Final volume of extract (ml)	25.0	100	5.0
Total TSEM (g)	7.59	40.9	0.46
TSEM concentration (mg/g sample)	384	335	87.5
GC-TPH (mg/g TSEM)	449	494	513
GC-saturates (mg/g TSEM)	398	442	452
GC-saturates/GC-TPH (%)	89	90	88
GC-aromatics/GC-TPH (%)	11	10	12
Resolved peaks/total GC area (F3)	0.06	0.06	0.06
UCM/GC-TPH (F3)	0.94	0.94	0.94
Total *n*-alkanes (mg/g TSEM)	9.30	10.4	8.58
n-C_{17}/pristane	1.93	2.00	2.09
n-C_{18}/phytane	1.78	1.79	1.83
Pristane/phytane	1.19	1.14	1.09

hydrocarbons (which are called GC-undefined hydrocarbons and were retained on the GC column) account for the differences between the TSEM and GC-TPH.

(2) The GC traces of both F1 and F3 of the spill samples are clearly dominated by large UCM (located in the *n*-C_{18} to *n*-C_{36} range) with almost no *n*-alkane being detected after *n*-C_{20} (at retention time ~28 min). The ratios of the all GC-resolved peaks to the total GC area were determined to be only 0.06 for three samples (Table 1). The GC chromatographic profile and shape of the UCM "humps" are significantly different from crude oils and most refined products [7,8]. In addition, the ratios of the total saturates to the GC-TPH were determined to be around 90%, much higher than most crude oils.

Crude oil compositions vary widely. Depending on the sources of carbon from which the oils are generated and the geologic environment in which they migrated and from which reservoir, they can have dramatically varied compositions in C_6 to C_{41} carbon range such as relative amounts of paraffinic, aromatic and asphaltenic compounds, large differences in the *n*-alkane distributions and UCM, and significantly different relative ratios of isoprenoids to normal alkanes. Refined petroleum products are obtained from crude oil through a variety of distillation, blending, and catalytic processes. Light distillates are typically products in the C_3 to C_{12} carbon range. They include aviation gas, naphtha, and automotive gasoline. The GC trace of fresh light distillates are featured with dominance of light-end, resolved hydrocarbons and a minimal UCM. Mid-range distillates are typically products in a relative broad carbon range (C_6 to C_{26}) and include kerosene, jet fuel, and diesel products. The GC chromatograms of Jet fuels, for example, are dominated by abundant resolved peaks in the C_8 to C_{20} range and show the characteristic and nearly symmetrical UCM. Heavy fuels are typified with a broad resolved alkanes in the C_{14} to C_{36} range and a large UCM that can make up more than 60% of the total GC area. Lube oils are specialty products. The GC chromatograms of most lube oils are generally featured with very significant UCM "hump" in a relatively narrow carbon range (*n*-C_{18} to *n*-C_{36}) and with very limited resolved peaks. All the GC trace features (Fig. 1) suggest that the major portion of the spilled oil might be a lube oil.

(3) The resolved *n*-alkanes mainly distributed in the diesel carbon range (C_8 to C_{27}). No *n*-alkane with the carbon number smaller than C_{10} and greater than C_{24} was detected. The total *n*-alkanes including pristane and phytane were determined to be only 9.3, 10.4, and 8.6 mg/g of TSEMs for samples 1–3, respectively.

For fresh diesels, the *n*-alkanes mainly distribute in a carbon range of *n*-C_8 to *n*-C_{27} (much narrower than the carbon range of *n*-C_8 to *n*-C_{41} for crude oils) with maximum being around *n*-C_{11} to *n*-C_{14} [4,7,8]. In general, the concentrations of *n*-alkanes in diesels are very high (often greater than 120 mg/g diesel). The UCM of diesels are nearly symmetrical with the maximum being in the center of the chromatograms. Using the estimation value of 120 mg *n*-alkanes per gram diesel and in consideration of weathering effect, therefore, the percentage of diesel in the spill samples may be estimated not exceeding 20% of the total hydrocarbons detected (that is, ~10 mg *n*-alkanes/g TSEM for samples 1–3 is divided by 120 mg *n*-alkane/g diesel, and the resulting percentage of diesel in the spill samples would be no greater than 20%).

(4) Three samples showed nearly identical GC chromatographic profiles, *n*-alkane distribution patterns, as well as the nearly identical diagnostic ratios of *n*-C_{17}/pristane (Table 1: 1.93, 2.00, and 2.09), *n*-C_{18}/phytane (1.78, 1.79, and 1.83), and pristane/phytane (1.19, 1.14, and 1.09). This implies that they were most likely the same oil and from the same source, and some small differences were likely caused by weathering.

(5) Quantitative examination of all chromatographic features of spilled samples implies the following:
   (i) the spill samples were largely composed of lube oil mixed with smaller portion of diesel fuel;
   (ii) the diesel in the samples had been weathered and degraded, evidenced by the significant reduction of the lower end *n*-alkanes (*n*-C_8 to *n*-C_{12}) and shifting of the maximum of *n*-alkanes from *n*-C_{11}–*n*-C_{14} to *n*-C_{15}–*n*-C_{17};
   (iii) the *n*-alkanes with the lowest carbon number detected in samples 1 and 2 are *n*-C_{11} (0.07 mg/g TSEM) and *n*-C_{10} (0.10 mg/g TSEM), respectively. Sample 3 collected from N. Boblo Island showed complete loss of *n*-C_8 to *n*-C_{12}, indicating that the diesel portion in the sample had been more weathered (most probably by more evaporation and water-washing in its longer journey from spill source to the destination) than samples 1 and 2.

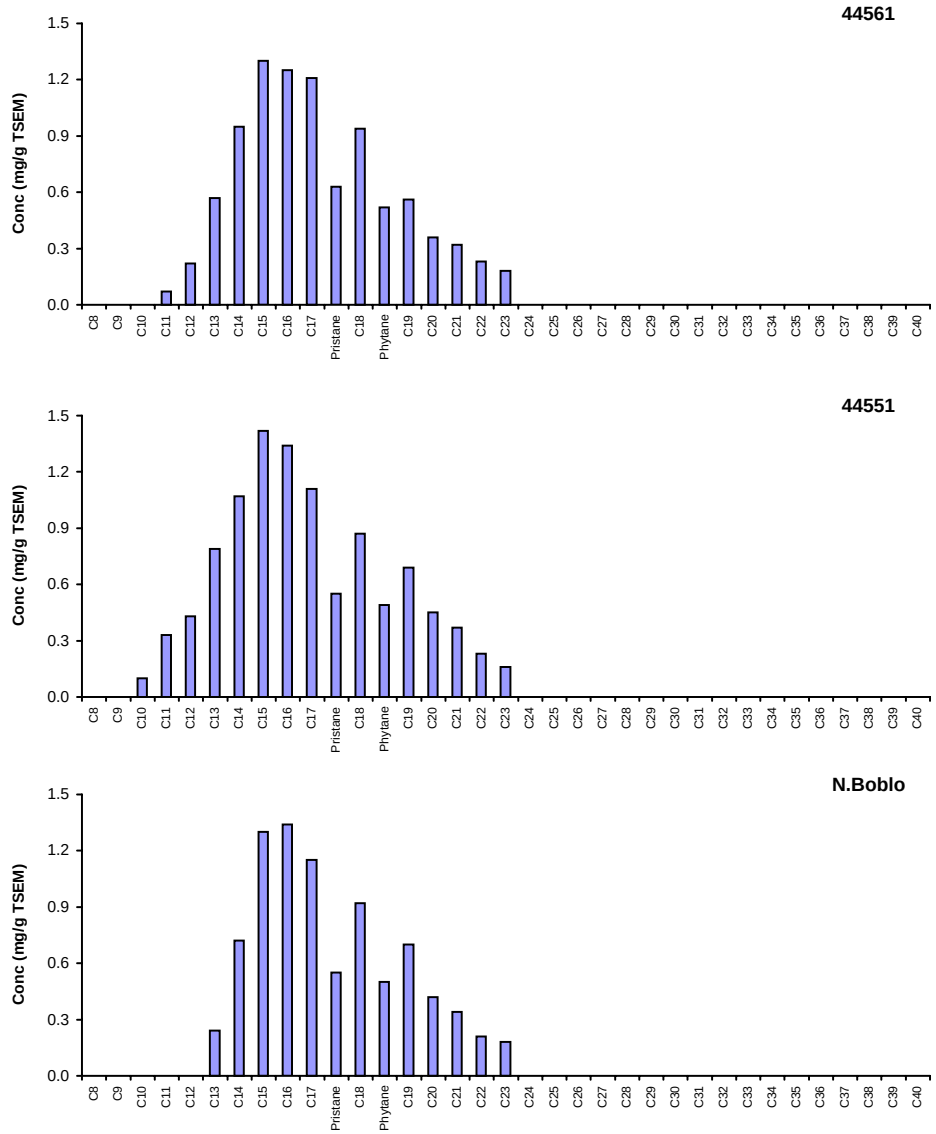

Fig. 2. *n*-Alkane distribution of the spill samples. The *n*-alkanes mainly distributed in the diesel carbon range (*n*-C_8 to *n*-C_{25}). No *n*-alkane with the carbon number smaller than C_{10} and greater than C_{25} was detected.

When crude oils and petroleum products are accidentally released to the environment, they are immediately subject to a wide variety of weathering processes, including evaporation, dissolution, dispersion, emulsification, adsorption on suspended materials, microbial degradation, photooxidation, and others [15,16]. These processes can be generally categorized into abiotic (physical) and biotic weathering. Weathering cause considerable changes in the physical properties and chemical compositions of spilled oils. The biotic weathering is a long-term weathering process, it is usually more isomer specific, and affects the *n*-alkanes more than the other hydrocarbon classes [17]. While abiotic weathering is more predictable, especially for the *n*-alkanes [16] and PAHs [18]. Too often the term "weathering" is misunderstood by some to mean processes that are entirely biological, or entirely physical by others. In the samples considered here, the extent of weathering of any kind was light, and was probably mostly abiotic (evaporation and water washing) if in consideration of the brief duration of environmental residence of the spilled oil which allows little time for microbial action.

3.2. Determination of oil-characteristic alkylated PAH homologues and their diagnostic ratios

PAH compounds in oil, especially the high-molecular-mass PAHs and their alkylated homologues, are relatively stable and source-specific. Compared to the saturated hydrocarbons, in particular the *n*-alkanes, they are less affected by weathering. Therefore, quantitative determination of the distribution and the diagnostic ratios of these target PAH compounds can be used as fate indicators of oil in the environment and oil source markers [19–22].

Table 2
Quantitation results of target PAHs for the spill samples

PAHs		Samples		
		44561 (μg/g TSEM)	44551 (μg/g TSEM)	N. Boblo (μg/g TSEM)
Alkylated PAHs				
Naphthalene	C_0–N	17.8	53.5	1.10
	C_1–N	73.0	106	11.9
	C_2–N	133	179	55.8
	C_3–N	203	184	134
	C_4–N	116	115	95.5
Sum		543	636	298
Phenanthrene	C_0–P	134	132	104
	C_1–P	131	126	114
	C_2–P	124	119	111
	C_3–P	73.0	70.7	67.8
	C_4–P	51.7	51.5	45.0
Sum		513	498	441
Dibenzothiophene	C_0–D	11.6	11.1	8.42
	C_1–D	15.7	14.8	13.9
	C_2–D	27.6	26.5	25.4
	C_3–D	22.4	21.2	20.1
Sum		77.3	73.6	67.8
Fluorene	C_0–F	49.7	51.5	28.2
	C_1–F	43.8	44.5	33.4
	C_2–F	67.8	66.9	70.4
	C_3–F	68.3	65.9	56.0
Sum		230	229	188
Chrysene	C_0–C	15.2	15.4	10.8
	C_1–C	11.0	11.1	8.80
	C_2–C	9.72	9.91	7.91
	C_3–C	6.02	6.12	4.94
Sum		41.9	42.4	32.4
Total alkylated PAHs		1404	1479	1028
Other EPA priority PAHs				
Biphenyl (Bph)		14.2	17.2	3.88
Acenaphthylene (Acl)		3.07	3.78	1.14
Acenaphthene (Ace)		34.2	35.3	13.0
Anthracene (An)		15.0	16.2	5.15
Fluoranthene (Fl)		66.1	65.9	55.5
Pyrene (Py)		49.6	49.4	34.9
Benz[*a*]anthracene (BaA)		15.8	15.4	11.1
Benzo[*b*]fluoranthene (BbF)		9.70	10.0	8.84
Benzo[*k*]fluoranthene (BkF)		8.53	8.59	7.89
Benzo[*e*]pyrene (BeP)		6.67	6.93	5.65
Benzo[*a*]pyrene (BaP)		9.80	10.3	4.63
Perylene (Pe)		2.20	2.59	1.53
Indeno[1,2,3-*cd*]pyrene (IP)		6.27	6.46	6.06
Dibenz[*a*,*h*]anthracene (DA)		1.50	1.54	1.16
Dibenzo[*ghi*]perylene (BgP)		7.20	7.41	6.19
Total EPA priority PAHs		250	257	167
Diagnostic ratios				
Ratios of 3-*m*-DBT isomers		1.00:0.65:0.27	1.00:0.65:0.28	1.00:0.66:0.27
Chrysene/BaA		0.99	1.00	0.97
(3- + 2-*m*-phen)/(4-/9- + 1-*m*-phen)		1.57	1.59	1.66
(C_2–D/C_2–P):(C_3–D/C_3–P)		0.22:0.31	0.22:0.30	0.23:0.30
Pyrogenic index		0.168	0.162	0.159

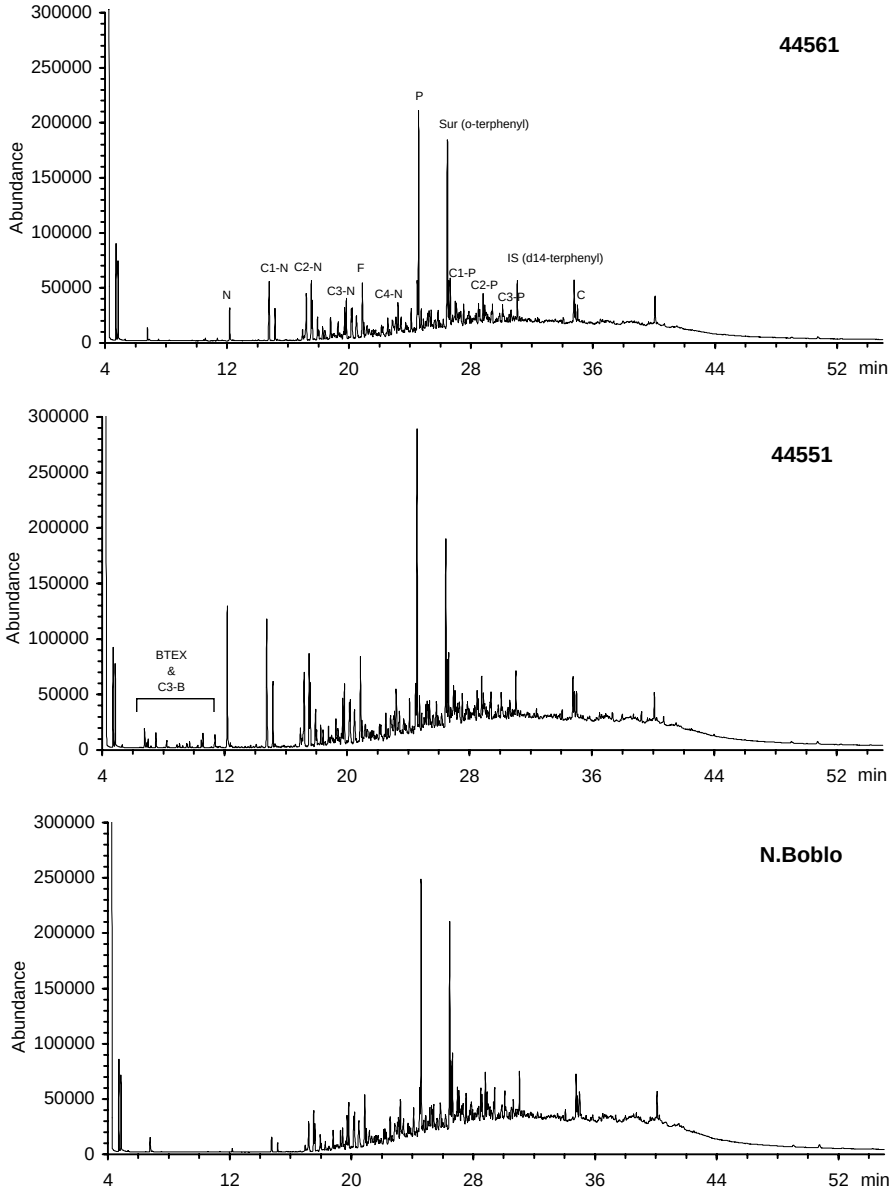

Fig. 3. The GC–MS total ion chromatograms (in SIM mode) for analyses of BTEX and C_3-B (C_3-benzenes) and PAH compounds. N, F, P, and C represent naphthalene, fluorene, phenanthrene, and chrysene, respectively. C_1, C_2, and C_3 represent carbon numbers of alkyl groups in alkylated PAH homologues. Sur and IS represent surrogate *o*-terphenyl, and internal standard [$^2H_{14}$]terphenyl.

Fig. 3 shows GC–MS total ion chromatograms for benzene, toluene, ethylbenzene and xylenes (BTEX) and PAH analysis. Table 2 summarizes quantitation results of five target petroleum-characteristic alkylated PAH homologous series and other EPA priority PAHs. Some important ratio parameters of "source-specific marker" PAH compounds were also determined and presented in Table 2. Fig. 4 depicts the distribution of petroleum-characteristic alkylated PAH homologues and other EPA priority PAHs. PAH analysis results demonstrate the following:

(1) The relative distribution patterns and profiles of alkylated PAHs are very much the same for the spilled samples, in particular for samples 1 and 2, further implying that they were from the same source.
(2) The five target alkylated PAH homologous series and other EPA priority PAHs were determined to be 1404, 1479, and 1028 μg/g TSEM, and 250, 257, and 167 μg/g TSEM for samples 1–3, respectively. Compared to crude oils and most refined products such as Jet fuel and diesel (>10,000 μg/g for most oils), the PAH concentrations in these spill samples are quite low.

    The dominance of alkylated naphthalene and phenanthrenes among five target alkylated PAH homologous series is pronounced for all three samples.
(3) Sample 2 still contained a small amount of BTEX and C_3-benzene compounds (Fig. 3). In comparison, almost

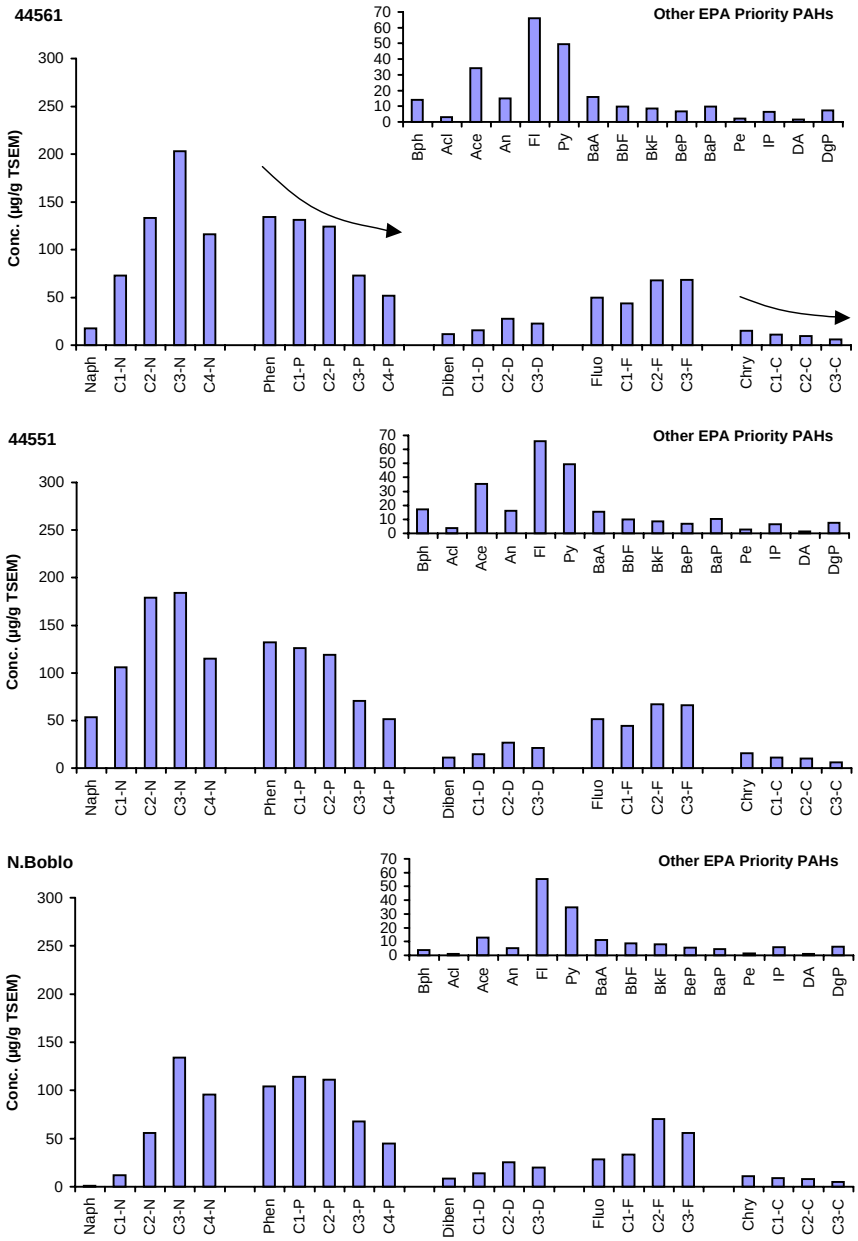

Fig. 4. Alkylated PAH fingerprints of the spill samples, illustrating the PAH compositional features. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0–4 represent carbon numbers of alkyl groups in alkylated PAH homologues. The fingerprints of the other EPA priority PAHs are shown in the left insets. Refer to Table 2 for the abbreviations of these PAHs. The input of pyrogenic PAHs are clearly demonstrated.

no BTEX and other alkyl benzene compounds were detected in samples 1 and 3. This fact further demonstrates that sample 2 was least weathered.

The loss of lower-molecular-mass naphthalene and C_1- and C_2-naphthalenes was obvious for all three samples, resulting in development of the relative distribution of C_0–N < C_1–N < C_2–N < C_3–N. This relative distribution pattern is particularly obvious for the more weathered sample 3. For other EPA priority PAHs, the more weathered sample 3 also demonstrated lower concentrations of lighter two- and three-ring PAHs (biphenyl, acenaphthylene, and acenaphthene).

It has been well demonstrated that in general, lube oils only contain small quantities of PAH compounds while PAH concentrations are high in diesel [7,8]. Obviously, detected PAHs in these spill samples were largely contributed by the small portion of diesel in spill samples.

In the PAH fingerprinting, we simply do not quantify PAH alone, but determine a number of diagnostic ratios of "source-specific marker" PAH compounds as well (see Table 2). In recent years, determination of ratios of the conventional diagnostic PAH and biomarker compounds, in particular determination of relative distribution of source-specific isomers within the same alkylation levels

and isomeric groups, has been used for oil source identification. The differences between the isomer distribution 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 for determination of ratios of source-specific isomers within the same alkylation levels, 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. Hence they can be more positively used for oil spill identification and differentiation. Analysis of the diagnostic ratios of "source-specific" PAHs clearly reveals the following: (1) the relative distribution of PAH isomers 4-, 2-/3-, and 1-methyl dibenzothiophene at *m*/*z* 198, and (3-+2-methyl-phenanthrene) to (4-/9-+1-methyl-phenanthrene) at *m*/*z* 192 were found to be very closely matching (Table 2); (2) the double ratios ((C_2–D)/(C_2–P):(C_3–D)/(C_3–P)) were also nearly identical (0.22:0.31, 0.22:0.30, and 0.23:0.30 for samples 1–3, respectively).

3.3. Input of pyrogenic PAHs to the spill samples

Another pronounced PAH compositional feature (Fig. 4) is that among the alkylated phenanthrene, fluorene, and chrysene series, the parent PAH phenanthrene, fluorene, and chrysene are most abundant, their concentrations are even higher than their corresponding alkylated homologous con-

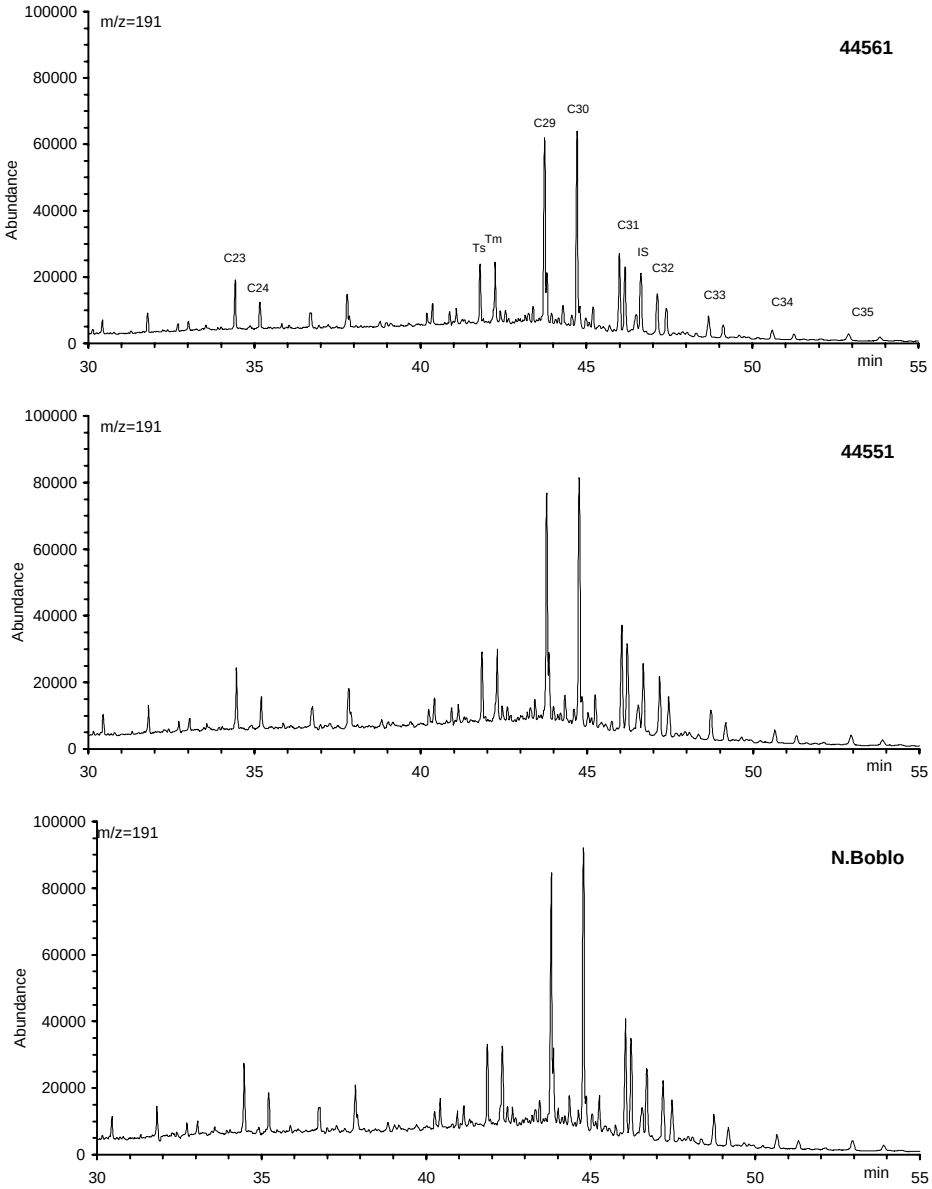

Fig. 5. Comparison of distribution of biomarker terpane compounds (*m*/*z* 191). C_{23}, C_{24}, C_{29}, C_{30}, C_{31} to C_{35}, Ts, Tm represent C_{23} and C_{24} tricyclic terpanes, C_{29}- and C_{30}-αβ-hopanes, 22*S*/22*R* epimer pairs of C_{31} to C_{35} homohopanes, and 18α(H),21β(H)-22, 29,30-trisnorhopane (Ts) and 17α(H),21β(H)-22,29,30-trisnorhopane (Tm), respectively.

stituents. In particular, the highest abundance of parent chrysene over its alkyl-substituted homologues and the decrease in relative abundances with increasing level of alkylation (that is, in the order of C_0–C > C_1–C > C_2–C > C_3–C) was very pronounced. This kind of PAH distribution profile has been generically termed as "*skewed or sloped*". In addition, the relative ratios of chrysene to benz[*a*]anthracene were determined to be very close to 1.0, far higher than the same ratios for crude oils and refined products. All these features indicate the input of pyrogenic PAHs [23,24].

Wang et al. [24] have recently proposed a new "pyrogenic index (PI)", defined as ∑(other 3–6 ring EPA priority PAHs)/∑(the five target alkylated PAHs), as a quantitative indicator for identification of pyrogenic PAHs and for differentiating pyrogenic and petrogenic PAHs. This ratio demonstrates great consistency from sample to sample and is subject to little interference from concentration fluctuation of individual components within the PAH series [24]. The PI parameter has been successfully used for differentiation of pyrogenic PAHs from petrogenic PAHs in a number of studies including the study of "Distribution and sources of PAHs in sediments of Guanabara Bay, Brazil" [25] and the case study for source identification of a mystery oil spill from Quebec [26]. This index is also a useful tool for distinguishing heavy petroleum products from crude oils and light refined products. The "pyrogenic index" were determined to be as high as 0.16 for three samples, far higher than the corresponding values for crude oils and refined products

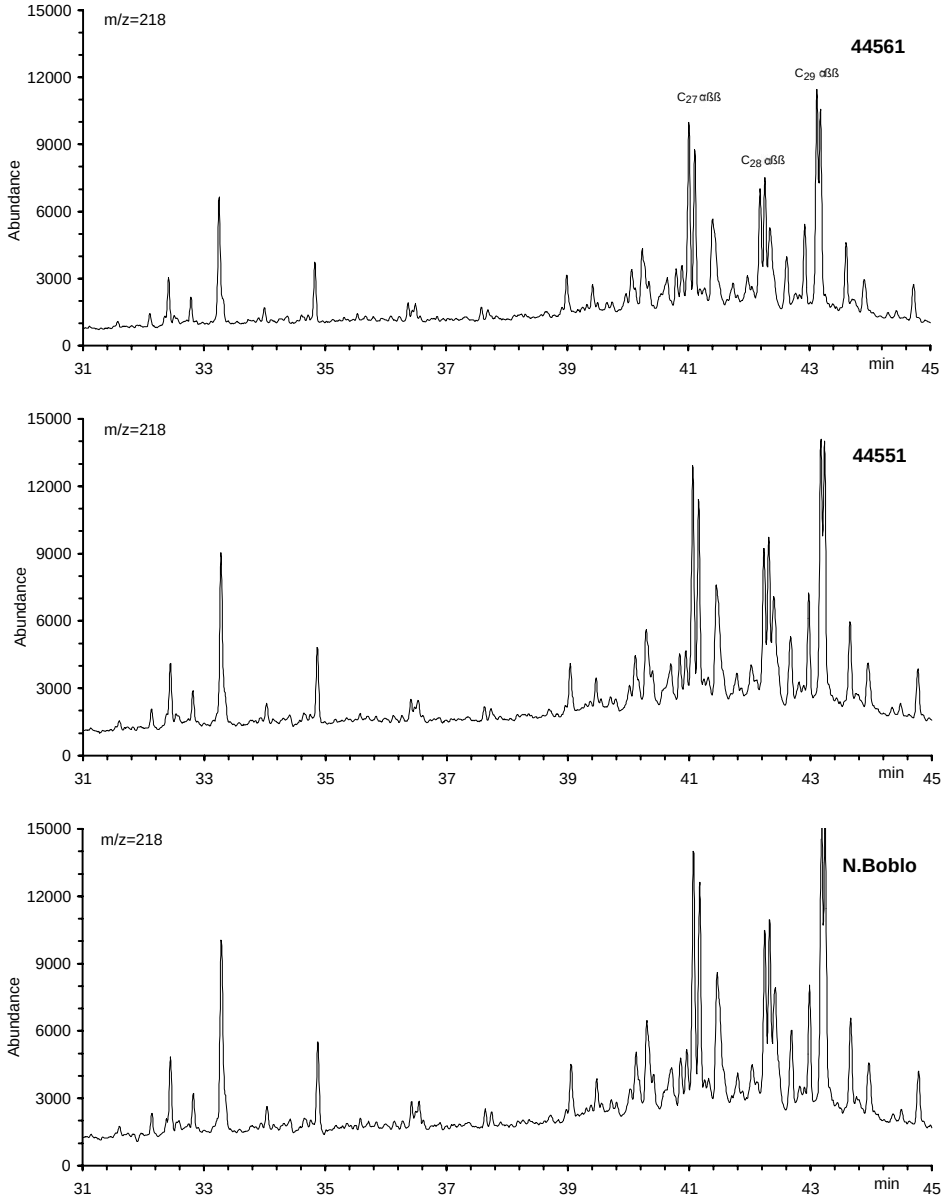

Fig. 6. Comparison of distribution of biomarker sterane compounds (*m*/*z* 218). C_{27}, C_{28}, and C_{29} represent four ααα and αββ (20*S*/20*R*) epimers of C_{27}-cholestanes, C_{28}-ergostanes, and C_{29}-stigmastanes.

(<0.06), defensively indicating the formation and presence of pyrogenic PAHs in the spill samples.

The most likely source of pyrogenic PAHs in used motor oils is combustion "blow-by" past the piston rings of exhaust gasses directly into the crankshaft cavity. Excessive heat in the motor lubrication process can also increase the concentration of PAHs, in particular the high-molecular-mass PAHs, in used lube oil [7]. Therefore, it can be reasonably concluded that the pyrogenic PAHs found in the spilled oil were most probably produced from combustion and motor lubrication process, and the lube oil in these spill samples was waste lube oil.

3.4. Characterization of biomarker compounds

Figs. 5 and 6 show GC–MS distribution profiles of biomarker terpane and sterane compounds in samples at *m*/*z* 191 and 218, respectively. Table 3 summarizes the quantitation results of target biomarker compounds. A wide range of terpanes are present in the samples from C_{19} to C_{35} with the C_{30}- and C_{29}-αβ-hopanes, Ts and Tm, and 22*S*/22*R* C_{31} homohopanes being the most abundant. As for steranes at *m*/*z* 218, in addition to the presence of diasteranes (at *m*/*z* 217, not presented here), the dominance of C_{27}, C_{28}, and C_{29} 20*S*/20*R* steranes, particularly the epimers of αββ-steranes, is obvious. 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 recent years, 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 [8,13,14,17,27–35]. Diagnostic ratios of target "source-specific" biomarker compounds were also determined and presented in Table 3.

It can be seen from Figs. 5 and 6 and Table 3 that:

(1) The samples show nearly identical distribution patterns of biomarker compounds and these petroleum-characteristic biomarker compounds were mostly from the lube oil portion of the spill samples. Diesels do not contain

Table 3
Quantitation results for major biomarker compounds of the spill samples

	Samples		
	44561 (μg/g TSEM)	44551 (μg/g TSEM)	N. Boblo (μg/g TSEM)
Biomarkers			
C_{23}	45.5	40.6	42.3
C_{24}	25.1	22.7	24.0
C_{29}	184	165	161
C_{30}	208	190	192
C_{31} (*S*)	89.2	87.3	84.7
C_{31} (*R*)	79.0	77.2	75.6
C_{32} (*S*)	56.8	53.4	51.8
C_{32} (*R*)	39.6	37.0	36.2
C_{33} (*S*)	32.6	31.5	30.2
C_{33} (*R*)	20.9	20.1	18.8
C_{34} (*S*)	16.4	15.5	14.7
C_{34} (*R*)	11.2	9.75	9.52
C_{35} (*S*)	14.5	14.5	13.2
C_{35} (*R*)	8.10	8.22	7.24
Ts	54.4	45.5	45.4
Tm	51.8	43.0	43.7
C_{27}-αββ-steranes	41.6	36.8	37.9
C_{29}-αββ-steranes	58.1	50.6	53.2
Total	1035	949	941
Diagnostic ratios			
C_{23}/C_{24}	1.82	1.79	1.76
C_{23}/C_{30}	0.22	0.21	0.22
C_{24}/C_{30}	0.12	0.12	0.13
C_{29}/C_{30}	0.89	0.87	0.84
Ts/Tm	1.05	1.06	1.04
C_{31} (*S*)/C_{31} ($S + R$)	0.53	0.53	0.53
C_{32} (*S*)/C_{32} ($S + R$)	0.59	0.59	0.59
C_{33} (*S*)/C_{33} ($S + R$)	0.61	0.61	0.62
C_{34} (*S*)/C_{34} ($S + R$)	0.61	0.61	0.61
C_{35} (*S*)/C_{35} ($S + R$)	0.64	0.64	0.65
$C_{30}/(C_{31} + C_{32} + C_{33} + C_{34} + C_{35})$	0.56	0.54	0.56
C27-αββ-steranes/C29-αββ-steranes	0.72	0.73	0.71

high-molecular-mass biomarkers and only contain trace of low-molecular-mass biomarker compounds (C_{20} to C_{24}). This is because high-molecular-mass biomarkers and most small biomarkers have been removed from their stocks during the refining processes.

(2) The total of the target biomarker compounds were determined to be 1103, 941, and 941 μg/g TSEM for samples 1–3. Obviously, the absolute concentrations of biomarker compounds in these three samples were matching closely each other.

(3) The diagnostic ratios of target biomarker compounds C_{23}/C_{24}, C_{29}-αβ-hopane/C_{30}-αβ-hopane, Ts/Tm, $C_{31}(22S)/C_{31}(22S + 22R)$, $C_{32}(22S)/C_{32}(22S + 22R)$, $C_{33}(22S)/C_{33}(22S + 22R)$, $C_{34}(22S)/C_{34}(22S + 22R)$, $C_{35}(22S)/C_{35}(22S + 22R)$, and C_{31}/(C_{31} to C_{35}), are also found to be very much the same. All these evidences, in combination with the TPH and PAH analysis results, unambiguously point toward to the conclusion that the three spill samples came from the same source.

It is important to note that the fingerprinting results described above highlight the necessity to analyze for more than one suite of analytes in source identification. Characterization of PAH and biomarker compounds must include determination of both concentrations and relative distributions, and should not be just measuring peak ratios alone. This is important because it is possible to have situation where a source might have similar biomarker ratio but very different actual amounts of biomarkers.

4. Conclusion

This paper describes a case study of using advanced chemical fingerprinting and data interpretation techniques to characterize the chemical composition and to determine the type, nature and source(s) of the Detroit River mystery oil spill. The chemical fingerprinting evidences and data interpretation results reveal the following:

(1) The spill samples were largely composed of used lube oil mixed with smaller portion of diesel fuel.
(2) The diesel in the samples had been weathered and degraded.
(3) The diesel portion in sample 3 collected from N. Boblo Island on 14 April was more weathered (most probably by more evaporation and water-washing) than samples 1 and 2.
(4) All fingerprinting results clearly demonstrated oils in three samples were the same, and they came from the same source.
(5) Most PAH compounds were from the diesel in the spill samples, while the biomarker compounds were largely from the lube oil.
(6) Input of pyrogenic PAHs to the spill samples was clearly demonstrated. The pyrogenic PAHs were most probably produced from combustion and motor lubrication processes.

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