DEVELOPMENT IN FINGERPRINTING ANALYSIS OF PETROLEUM HYDROCARBONS

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ABSTRACT: *Major advances have been made on analyses of petroleum hydrocarbons in oils, petroleum products and complex oil-spill-related environmental samples. This paper briefly describes how the advanced chemical fingerprinting and data interpretation techniques are used to identify the source(s) of tarballs from the coast of Vancouver Island and Northern California. Characterization of the unknown oil was achieved by not only a variety of "standard" analyses including distribution analyses of aliphatic, aromatic and biomarker hydrocarbons, but also analyses of diagnostic ratios of "source-specific marker" compounds, in particular the alkylated series of polycyclic aromatic hydrocarbons within the same alkylation isomeric groups. Results of the analysis revealed that (1) California/Oregon and British Columbia/Washington tarball samples were chemically similar, but were identified to be from two different types of bunker fuel; (2) the source of the tarball samples was neither Alaska North Slope oil nor California Monterrey Miocene oil; and (3) the spilled oil samples have been highly weathered since release, and the California samples were more heavily weathered than the British Columbia samples.*

Introduction

To unambiguously identify spilled oils and petroleum products and to link them to the known sources are extremely important in setting questions of environmental impact and legal liability. In this paper we report how the tiered analytical approach was used for characterization and differentiation by source for unknown spill oil samples.

During January and February 1996, a significant number of tarballs were found along the coasts of Vancouver Island of British Columbia (BC), Washington (WA), Oregon (OR), and California (CA). (Oil Spill Prevention and Response, 1996). Samples of the tarballs were collected from the affected beaches. The samples were characterized by analysing individual aliphatics, aromatics, highly degradation-resistant biomarkers, and also by diagnostic ratio analysis of "source-specific marker" compounds. When the samples had been precisely characterized, oil identification techniques were used to identify the type of product present, to differentiate an oil from another oil, and to evaluate the degree of weathering the product had undergone since release. These include systematic comparison of GC/MS and GC/FID data, hydrocarbon distribution pattern recognition, and matching diagnostic ratios of target source-specific markers in an unknown oil to that of the known oil. In this work, in addition to conventional diagnostic ratio analysis, a number of new source-specific marker compound ratios, particularly the relative abundance ratios of alkylated PAH derivatives within the same alkylation isomeric groups, were compared and used to identify the type(s) and differentiate the source(s) of the BC/WA and CA/OR tarballs. Selected samples were further analysed using a carbon isotopic technique.

Experimental

Sample preparation. Two tarball samples collected from Vancouver Island on January 12, designated BC-1 and BC-2, and one from the beach at MacKerricher State Park on the California north coast on January 29, 1996, designated CA-1, were chosen to represent the BC/WA and CA/OR sample groups. A possible source oil, Alaska North Slope crude (ANS) was also included in the analysis. The tarball samples were weighed, mixed with appropriate amount of anhydrous sodium sulphate and spiked with surrogates of deuterated PAH and o-terphenyl, and then serially extracted with dichloromethane.

Capillary gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Analyses for *n*-alkane distribution and total petroleum hydrocarbons (TPH) were performed on a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a flame-ionization detector (FID) and an HP 7673 autosampler. Analyses of target PAH and biomarker compounds were performed on an HP Model 5890 GC equipped with a Model HP 5972 mass selective detector (MSD) (Wang *et al.*, 1994a,b, 1997). The carbon isotopic composition of oil fractions was performed on a nuclide 3-60 dual collecting mass spectrometer and the results were reported in the usual delta-notation ($\delta^{13}C$) in parts per thousand ($^0/_{00}$) relative to the PeeDee belemnite (PDB) standard. The estimated standard deviation is $0.1^0/_{00}$.

Tiered analytical approach. A tiered analytical approach was used for the identification and differentiation of sources of tarball samples: tier 1, determination of hydrocarbon groups in oil residues; tier 2, product screen and determination of *n*-alkanes and

TPH; tier 3, distribution pattern recognition of target PAH and biomarker components; 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 residual oil.

Results and discussion

Product type screen and determination of aliphatic hydrocarbons. Figure 1 shows the GC/FID chromatograms for TPH and aliphatic hydrocarbon analysis. Aliphatic hydrocarbon analysis results and Figure 1 demonstrated that the BC/WA samples BC-1 and BC-2 were chemically similar, evidenced by nearly identical *n*-alkane distributions, very close values of C_{17}/pristane, C_{18}/phytane and pristane/phytane (Table 1), and almost identical GC chromatograms, especially the shape of the unresolved complex mixture of hydrocarbons (UCM). Sample CA-1 also has a UCM profile similar to the BC samples. However, there are two important differences between the CA and BC tarballs. First, unlike the BC samples, the second UCM hump of the chromatogram of CA-1 is higher than the first hump. Second, no *n*-alkane and isoprenoid compounds were detected for CA-1. Complete loss of *n*-alkanes plus pristane and phytane implies that the sample CA-1 was more weathered and its chemical composition had undergone greater alteration than the corresponding BC samples, assuming a similar source.

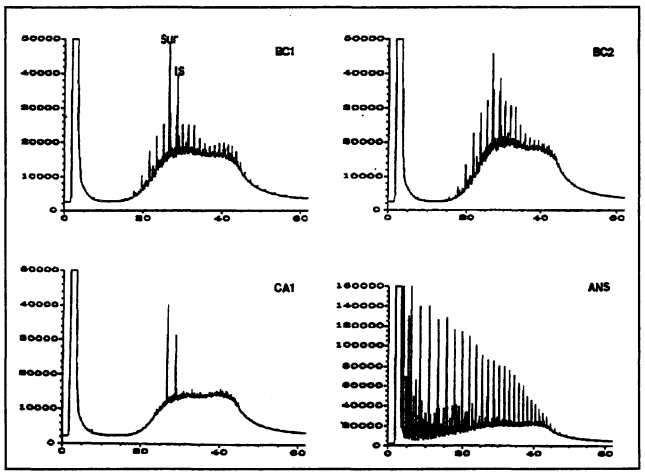

Figure 1. GC/FID chromatograms for total petroleum hydrocarbon analysis of the tarball samples BC-1, BC-2, CA-1, and the suspected source Alaska North Slope (ANS) oil, illustrating the similarities and differences in the distribution patterns and profiles of n-alkanes and unresolved complex mixture (UCM) between samples. IS and Sur represent internal standard 5-α-androstane and surrogate *o*-terphenyl, respectively.

Table 1. Diagnostic ratios of source-specific marker: compounds for source identification of British Columbia (BC) and California (CA) tarball samples.

	BC-1	BC-2	CA-1	ANS
Target aliphatics compounds				
C17/pristane	3.70	3.82	/*	2.39
C18/phytane	1.87	1.93	/*	1.82
pristane/phytane	0.51	0.54	/*	0.98
CPI	1.03	1.01	/*	0.99
Diagnostic ratios of PAH compound groups				
C2D/C2P : C3D/C3P	0.31 : 0.52	0.29 : 0.50	0.58 : 0.84	0.50 : 0.62
C0P:C1P:C2P:C3P:C4P (C2P=1.00)	0.12 : 0.68 : 1.0 : 0.71 : 0.44	0.13 : 0.69 : 1.0 : 0.70 : 0.43	0.08 : 0.57 : 1.0 : 0.83 : 0.65	0.31 : 0.91 : 1.0 : 0.69 : 0.42
C0C:C1C:C2C:C3C (C2C=1.00)	0.42 : 0.78 : 1.0 : 0.82	0.41 : 0.79 : 1.0 : 0.83	0.39 : 0.72 : 1.0 : 0.86	0.64 : 0.89 : 1.0 : 0.81
Naphthalenes / Chrysenes	2.6	3.2	0.8	26.4
Phenanthrenes / Chrysenes	7.0	8.0	4.4	8.6
Dibenzothiophenes / Chrysenes	1.9	2.1	2.1	3.9
Fluorenes / Chrysenes	1.4	1.6	0.8	2.6
Biomarkers				
Terpane C23/C24	2.15	2.19	2.07	1.69
Hopane C29/C30	0.84	0.84	0.84	0.61
Ts/Tm	0.31	0.33	0.29	0.50
C32(S)/C32(R)	1.46	1.49	1.52	1.46
C33(S)/C33(R)	1.56	1.56	1.52	1.44
C23/C30	1.22	1.22	1.07	0.51
C24/C30	0.57	0.56	0.52	0.30
Sterane C27aßß/C29aßß	1.11	1.09	1.14	0.84
PAH isomers				
Alkylated naphthalenes				
C3N: isomer1/isomer2/isomer3	4.37 : 3.42 : 1.0	4.46 : 3.50 : 1.0	3.17 : 2.35 : 1.0	4.58 : 3.16 : 1.0
C4N: isomer1/isomer2/isomer3	1.0 : 0.68 : 0.37	1.0 : 0.72 : 0.37	1.0 : 0.50 : 0.44	1.0 : 1.05 : 0.58
Alkylated phenanthrenes				
C1P: (3 + 2-methyl-P)/(4/9 + 1-methyl-P)	1.37	1.42	0.89	0.74
C2P: isomer2/isomer1	3.11	3.00	4.85	4.10
isomer3/isomer1	1.74	1.70	2.50	2.09
C4P: isomer1/isomer2	1.43	1.48	0.95	0.61
Alkylated fluorenes				
C1F: isomer1/isomer2/isomer3	1.0 : 1.02 : 0.43	1.0 : 1.00 : 0.42	1.0 : 1.42 : 0.53	1.0 : 1.94 : 0.42
Alkylated dibenzothiophenes				
C1D: 4- : 2-/3- : 1-methyl-dibenzothiophene	1.0 : 0.92 : 0.55	1.0 : 0.93 : 0.53	1.0 : 0.92 : 0.60	1.0 : 0.64 : 0.32

* The n-alkanes and isoprenoids were completely lost for CA-1.

The GC traces clearly indicate that both BC and CA samples were composed of a blend of two oils. The resolved GC peaks in the lighter oil consists of saturated hydrocarbons, mostly *n*-alkanes with maximum around *n*-C_{18}, while the heavier oil has a maximum at around *n*-C_{31}. This kind of GC trace is often the characteristic of a "Bunker C" type oil. It appears likely that both BC/WA and CA/OR tarballs had Bunker C as the source oil.

Analysis of distributions of petroleum-specific alkylated PAH and biomarkers. The distribution of alkylated PAHs for samples BC-1, BC-2, and CA-1, and the suspected source oil ANS is depicted in Figure 2. PAH analysis results indicate that:

1. The relative distribution patterns of alkylated PAH of samples BC-1 and BC-2 are identical.
2. The PAH distribution pattern of CA-1 looks different from BC samples.
3. The high abundances of the alkyl phenanthrene and chrysene series relative to other alkylated PAH homologous series are pronounced for the tarball samples, which is a characteristic feature of Bunker C oil. Both the BC and CA samples have characteristics of a Bunker C type fuel, but may not be from a single source.
4. The BC and CA samples were highly weathered compared to the ANS oil and "fresh" Bunker C fuel.

As for biomarkers, the distribution pattern and profile of biomarker terpanes and steranes are identical for BC-1 and BC-2. Also, the concentrations of the most abundant biomarker compounds are very close to each other for these two samples. CA-1 has a very similar distribution pattern of biomarkers to the BC samples but the concentrations of all target biomarkers are slightly higher than those of the BC samples. There is a marked dissimilarity between biomarker distribution profiles of all the tarball samples and the ANS crude.

Comparison of diagnostic ratios of the source-specific marker compounds. Table 1 compares diagnostic ratio values of the source-specific marker compounds. In addition to the conventional diagnostic PAH and biomarker ratios, several other source-specific marker compounds, especially the alkylated PAH hydrocarbons within homologous alkylation isomeric groups, were also selected and their relative ratios were compared, in order to definitively identify and differentiate the source(s) of the tarballs. Table 1 clearly indicates the following:

1. Almost all of source-specific marker compound ratios for ANS oil differ significantly from those of the tarball samples.
2. The relative ratios of biomarker terpanes C_{23}/C_{24}, Ts/Tm (Ts: 18α(H), 21β(H)-22, 29,30-trisnorhopane; Tm: 17α(H), 21β(H)-22,29,30-trisnorhopane), C_{29}/C_{30},C_{32}(22S)/C_{32}(22R) and C_{33}(22S)/C_{33}(22R) for the BC and CA samples are similar, but the CA-1 sample has noticeably lower ratios of C_{23}/C_{30} and C_{24}/C_{30} than the corresponding BC samples.
3. Diagnostic ratios of PAH groups (such as double ratios of C_2D/C_2P to C_3D/C_3P) are different between BC and CA samples.
4. More convincingly, all diagnostic ratios of the selected paired PAH isomers within the same alkylation groups are nearly identical for BC-1 and BC-2, and strikingly different from those for the CA-1 sample.

Analysis of carbon-isotopic compositions. The carbon-isotopic compositions ($\delta^{13}C$) of ten CA/OR tarball samples average -26.8±0.1 for both saturate and aromatic fractions. These $\delta^{13}C$ values show very little variation and are distinct from those of ANS oil ($\delta^{13}C$ = -29.0) and another potential source, California Monterrey Miocene oil (CMM, $\delta^{13}C$ = -23.7). These data, along with the GC/MS and GC/FID analysis results indicate that samples collected from all California beaches, and Beverly State Beach in Oregon, were chemically similar and consistent with the same source, and further, that the source of CA/OR and BC tarballs was neither Alaska North Slope nor California Monterrey Miocene oil, but rather some other unidentified source.

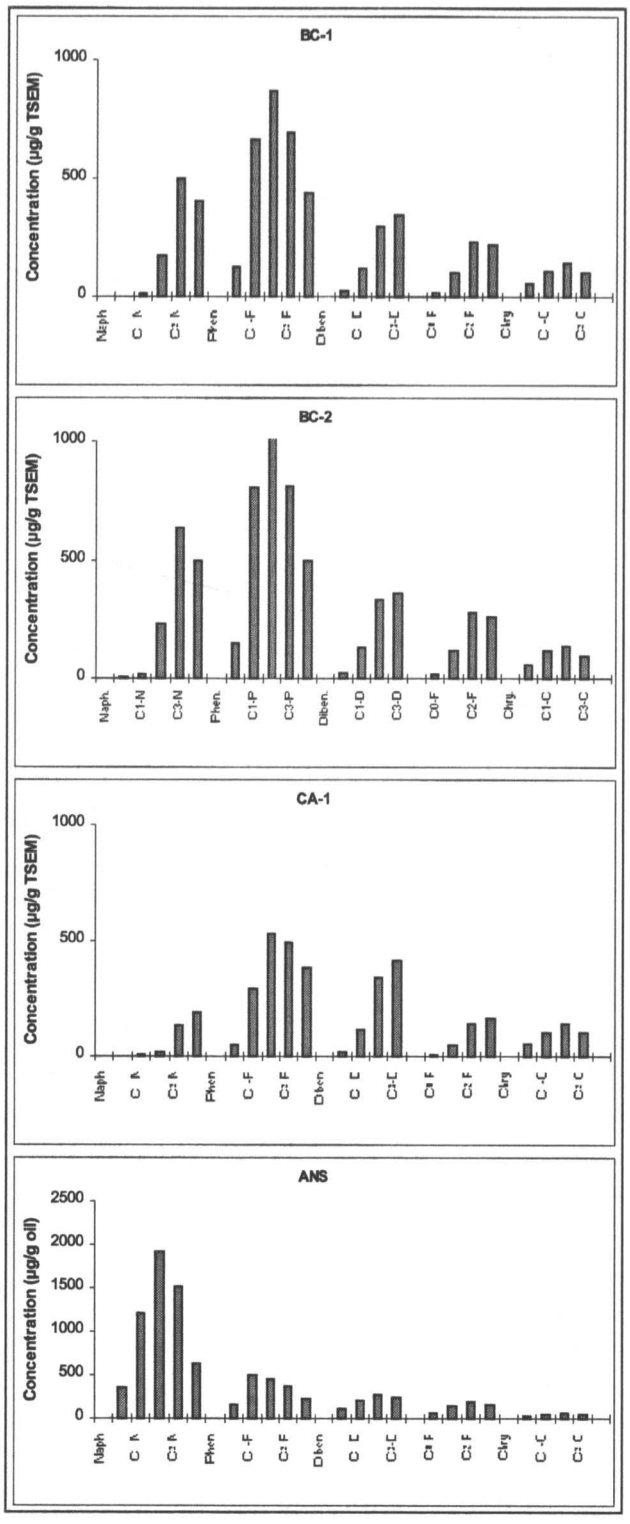

Figure 2. Alkylated PAH distributions for samples BC-1, BC-2, CA-1, and ANS oil, illustrating similarity and difference of petrogenic PAH compositions between oils

Conclusion

The California/Oregon samples collected from affected beaches including Pt. Reyes National Seashore, CA; Steamboat Rock, Cape Mendocino, CA; South Beach, Crescent City, CA; and Beverly State Beach, OR were chemically similar and consistent with a single Bunker C type source oil. The tarball samples collected from British Columbia and Ocean Shores, Washington were chemically similar and also consistent with a single "Bunker C" type source fuel. The British Columbia/Washington samples were similar, but not identical to the California/Oregon samples and had a different source. Alaska North Slope and California Monterrey Miocene oils were definitely not the source oils for either incident. The tarballs have been highly weathered since their release, and the CA/OR samples are more heavily weathered than the BC/WA samples.

Biography

Zhendi Wang is a senior research scientist working in environmental research and development. His specialities and research interests include: oil properties and analyses, fate and behaviour of oil and other hazardous organics in the environment, identification and characterization of oil components, environmental assessments of oil and petroleum product spills, spill treating agent studies and analyses of dispersants.

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