

**Quantitative Characterization of PAHs in Burn Residue and Soot Samples
and Differentiation of Pyrogenic PAHs from Petrogenic PAHs
- The 1994 Mobile Burn Study**

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ABSTRACT

Several mesoscale burns were conducted in 1994 in Mobile Bay, Alabama, to study various aspects of diesel fuel burning *in situ*. Samples were taken from the oil, residue and the smoke plume during each burn and analysed by capillary gas chromatograph - mass spectrometry. The high temperatures reached during the *in situ* combustion resulted in nearly complete destruction of the diesel. The burn residue and soot produced from the burns were estimated to account for 0.1-0.3% and 8-14% of the diesel by weight, respectively. Increase in abundance of higher molecular weight PAHs relative to the low molecular weight species was noticeable in the residue, and was particularly significant in the soot samples. The high molecular weight PAHs with five or more rings were found to be largely generated by combustion. A simple model based on mass balance of individual petroleum PAHs pre- and post-burn is proposed to estimate the destruction efficiencies of the total petroleum PAHs. Considering that there were many variables which could affect soot and residue production and collection, three scenarios (Scenario A with soot production of 5% and residue production of 0.1%; Scenario B, 10% and 0.2%, and Scenario C, 15% and 0.3%, respectively) were chosen to calculate destruction efficiencies of target PAHs for the 1994 Mobile Burn Experiments. The total destruction efficiencies of target PAHs were determined to be greater than 99% for all three scenarios. Using this model, 27.3 kg of the diesel PAHs, mainly 2- and 3-ring PAHs and their alkylated homologues, were destroyed when 1000 kg of diesel were burned. At the same time only 0.032 kg of the 5- and 6-ring PAHs (at 10% and 0.2% level of soot and residue production yield) were generated during burning.

In addition to the conventional criteria (the predominance of higher molecular weight PAHs over the 2- and 3-ring PAHs, and the predominance of the unsubstituted parent PAHs over the alkylated homologues and decrease in relative abundances with increasing levels of alkylation), a new diagnostic ratio, $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$, is proposed as a quantitative indicator for identification of pyrogenic PAHs and for differentiating pyrogenic PAHs from petrogenic PAHs. This

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ratio is defined as the relative distribution of the total of 14 EPA priority 3-6 ring priority PAHs (see text) to the total of the 5 target petroleum-specific alkylated PAH homologous series. It is found that the ratio is significantly greater in the soot samples than in the starting oil. In addition, this ratio can be also used as a screening tool to distinguish heavy oils and heavy fuels from most crude oils and light petroleum products. The effectiveness of the criteria in distinguishing pyrogenic PAHs from petrogenic PAHs and in distinguishing heavy fuels including Bunker C type oils from crude oils, jet fuels and diesels is demonstrated by determination of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ in hundreds of various samples including crude, weathered oil, long-term spilled oil, and biodegraded oil samples and by comparison with that of the burn residue and soot samples.

1.0 INTRODUCTION

In situ burning of spilled oil as an oil spill cleanup countermeasure is gaining acceptance because of its distinct advantages over other countermeasures [Fingas *et al.*, 1996a; Walton *et al.*, 1995]. This technique can convert large quantities of oil into its primary combustion products, carbon dioxide and water. It requires less equipment and labour, and can be applied in areas where many other methods cannot due to lack of response infra-structure and/or lack of alternatives. Efficiency of oil removal from water was reported to be greater than 99% based on the results of the large-scale Newfoundland Offshore Burn Experiments (NOBE) [Fingas *et al.*, 1994]. In addition, because oil burn products, mainly smoke particulates and unburned residues, are only a small percentage of the spilled oil, the need to collect, store, and transport recovered fluid can be reduced to a minimum compared to those from the conventional methods.

In the last 14 years, numerous lab and tank tests and offshore burning experiments, from small to large scale, have been performed to study various aspects (such as type of oil, ignition technique, burning rate, oil thickness, and wind direction and speed) of burning *in situ* of crude oils and refined petroleum products [Fingas *et al.*, 1994; Benner *et al.*, 1990; Walavalkar and Kulkarni, 1996; Evans, 1994]. In 1991, the US Minerals Management Service (MMS) began sponsorship, in cooperation with several agencies, of a series of mesoscale burn tests of Louisiana crude oil. These tests were designed to measure a series of physical parameters as well as emissions. The facilities of the Fire and Safety Detachment at Little Sand Island situated in Mobile Bay, Alabama, were used. In 1992, a similar series of experiments were conducted. In 1994, diesel fuel was selected as the burn test fuel and a series of three mesoscale burns was conducted. A variety of parameters that might affect diesel burning, emissions, and smoke product were investigated. During each burn, samples were taken from the oil, residue and smoke plume itself. In addition to ground station samplers and airborne samplers, the National Institute of Standards and Technology (NIST), under the sponsorship of the US Coast Guard, developed a new smoke sampling package deployed from a helicopter to rapidly collect data on smoke and/or emissions from the burns. Environment Canada and the US Environmental Protection Agency (EPA) cooperated to set up a series of instruments and samplers to monitor all suspect emissions [Fingas *et al.*, 1996a] including CO₂, CO and SO₂, volatile organic compounds (VOC), carbonyls, polycyclic aromatic hydrocarbons (PAH),

dioxins and dibenzofurans, and particulates. The 1994 burn was conducted in a specially-constructed steel pan (15.2 x 15.2 m) with an outer berm filled with water. In a typical burn, diesel fuel was released and floated on 0.6 metres of salt water pumped from Mobile Bay. The fuel was ignited and the burn lasted about 25 minutes. Table 1 lists the general parameters from each of the three burns [Walton *et al.*, 1995]. The general analytical results of these trials have been reported [Fingas *et al.*, 1996b]. The data indicated that a relatively high temperature was reached during *in situ* combustion, resulting in nearly complete destruction of the diesel fuel. No analytes of concern were found in the water beneath the burns at the detection levels of the methods employed.

Table 1 Parameters of 1994 Mobile Burn Experiments

Burn No.	Burn Area (m ²)	Initial Fuel Depth (mm)	Fuel Volume (m ³)	Burn Time (s)	Burn Rate (kg/s.m ²)	Ave. Wind Speed (m/s)	Ave. Wind Direction (deg.)
1	199	86	17.1	1573	0.063	1.6	38
2	231	74	17.1	1600	0.067	5.1	358
3	231	74	17.1	1440	0.067	4.7	356

In situ combustion on water is a complex process, which is affected by many factors and surrounding dynamic conditions [Walavalkar and Kulkarni, 1996]. One recognized drawback to *in situ* burning is the smoke produced. This fact gives rise to public health concerns related to the chemical content of the smoke, in particular the levels of PAHs in the smoke. Since the late 1980s, a number of research projects have been carried out in the field of emissions from *in situ* oil combustion [Benner *et al.*, 1990; Walavalkar and Kulkarni, 1996; Evans, 1994]. However, there are no quantitative data on the distribution of the petroleum-specific alkylated PAHs of primary concern (that is, the naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene series) and other EPA-defined priority PAHs in the burn residue and in the smoke, on the relative amount of the total PAHs in the oil versus the amount in the smoke particulates, and on the total PAHs destructed. This information is extremely important for spill response staff and decision-makers to determine the most suitable countermeasures after an oil spill and for assessment of the impact of *in situ* burning products to the environment. This paper is directed at clarifying some aspects of the 1994 Mobile Burns, including examining and comparing the composition and levels of PAHs in the starting oil, burn residue and smoke, destruction and formation of PAHs, and development of quantitative differentiation criteria to distinguish pyrogenic PAHs from petrogenic PAHs. In addition, a simple model based on mass balance of individual petroleum PAHs pre- and post-burn is proposed to estimate the destruction efficiencies of the total PAHs of the oil.

2.0 EXPERIMENTAL

2.1 Burn Residue Samples

The background sample of the diesel fuel was collected from the barge which

delivered the fuel to the site prior to each burn. The diesel supplier was Midstream Fuel Service. The samples of the pre-burn diesel and residue were collected from the combustion tank prior to and following each burn. All samples were grab samples collected manually.

All pre-burn samples were collected from the northwest side of the tank. The fuel layer on the water was sufficiently thick that a water-free sample could be easily obtained. Titration analysis confirmed there was no water in the pre-burn samples. The post-burn residue samples were obtained by skimming the residue from the surface of the tank water. The average water content ($n=3$) in the residues was determined to be 8.0%, 1.8% and 0.3% for the residue samples MB-14, MB-16, and MB-18 respectively using the Karl-Fischer titration method.

The pre- and post-burn samples were directly dissolved in hexane at a concentration of ~100 mg/mL and spiked with surrogates prior to the column cleanup.

2.2 Soot Sampling

A series of different instruments and samplers were used to collect all suspect emissions [Fingas *et al.*, 1996b]. The Anderson (Smyrna, GA) PM-10 high-volume samplers and the Anderson TSP high-volume samplers were used to collect smoke particulates from the burns.

PM-10 samplers collect particulates less than 10 μm and TSP samplers feature accurate collection of total suspended particulates. Both samplers meet US EPA specification. A flow rate of 1.1 to 1.7 m^3/min was employed. The sampling media consisted of quartz fiber filters in 8 x 10" sheets. The inside of the samplers was rinsed with hexane prior to use. After sampling was completed, the filters were wrapped in aluminum foil, placed in an envelope and refrigerated. All filters were weighed on a precision balance before and after the burn to obtain the weight of the soot particulate.

2.3 Microwave Extraction Apparatus

The microwave apparatus used to extract PAHs and other hydrocarbons from the soot samples was the MES-1000 microwave solvent extraction system (CEM Corp, Mathews, NC). The system consists of a 950-W microwave instrument that has been specifically designed for use with organic solvents and is operated at a frequency of 2450 MHz. Extraction conditions are controlled by temperature using an in-board fiber optic system, which allows extraction temperatures to be selected from 20 to 200 $^{\circ}\text{C}$ in 1 $^{\circ}\text{C}$ increments. Temperature and pressure data can be copied to an external printer or downloaded to a computer.

The extraction vessels are double-walled Teflon vessels specifically designed for use with organic solvents. The vessel has a working range of 200 $^{\circ}\text{C}$, 200 psi, and a 100 mL volume. A maximum of 12 samples can be extracted simultaneously. All extraction vessels are connected to a sealed center collection vessel so that in the event of a vessel safety membrane rupture, solvent vapours will be contained.

2.4 Sample Extraction and Cleanup

Three to six pairs of 36 mm (ID) PM-10 or TSP filter discs, cut from the

whole PM-10 or TSP filter sheets (8 x10"), were placed into the Teflon vessels and spiked with 100 μ L of deuterated surrogate mixture containing 1 μ g each of 4 deuterated PAHs (d_{10} -acenaphthene, d_{10} -phenanthrene, d_{10} -benz(a)anthracene, and d_{12} -perylene). Sixty mL of a methanol/benzene/hexane solvent mixture (2:1:9) was added to the vessels, enough to cover the filter. The vessels were closed and placed on the sample carousel inside the microwave oven for extraction. The temperature was allowed to increase to 100 $^{\circ}$ C, at which temperature the extraction was performed for 10 min. The microwave-heating program was as follows: (1) increase to the set point temperature, (2) maintain at the set temperature for 10 min, and (3) upon removal of the vessels from the microwave oven, to allow them to cool to ambient room temperature. Satisfactory recoveries of PAHs from filters by using the microwave extraction have been demonstrated and reported [Shu *et al.*, 1995].

The extracts were dried by filtering through anhydrous sodium sulphate and then concentrated to approximately 1-2 mL by rotary evaporation and nitrogen blowdown techniques. The concentrated extracts were transferred (with 3 rinsings of 0.5 mL of hexane each to quantitatively complete the transfer) to a pre-conditioned 1.5 g silica gel microcolumn topped with 1 cm anhydrous sodium sulphate for sample cleanup. Ten mL of a benzene/hexane mixture (1:1) was used to elute the saturate and aromatic hydrocarbons. The eluent was collected in a pre-calibrated centrifuge tube and concentrated under a stream of nitrogen to appropriate volume (\sim 0.4 mL). Finally, the concentrated eluent was spiked with 50 μ L of 1 ppm internal standard d_{14} -terphenyl and made up to the accurate preinjection volume (0.5 mL) for GC analysis.

The pre-burn and post-burn residue samples were fractionated into saturate and aromatic fractions using a silica gel microcolumn fractionation technique, and spiked with internal standards for GC/MS and GC/FID analysis [Wang *et al.*, 1994a; Wang *et al.*, 1994b; Wang *et al.*, 1994c].

2.5 Gas Chromatography/Mass Spectrometry (GC/MS) Analysis

The analyses of target PAHs and other hydrocarbons were performed on an Hewlett Packard (HP) 5890 Series II GC equipped with a HP 7673 autosampler and interfaced directly to a HP 5972 mass selective detector (MSD). System control and data acquisition were achieved with an HP G1034C MS ChemStation software. For details of chromatographic conditions, temperature program, quality control, and quantitation methodology, refer to Ref. [Wang *et al.*, 1994a; Wang *et al.*, 1994b; Wang *et al.*, 1994c].

In order to achieve improved analytical precision and accuracy for the soot samples which only contain trace of PAHs, some refinements (such as more frequent and rigorous calibration check-up of instrument performance, manual integration of PAHs having low abundances, manually setting alkylated PAH baseline, and using one GC/MS through the entire program) were implemented in addition to the routine quality control measures.

3.0 RESULTS AND DISCUSSION

3.1 Fingerprints of Target PAHs in starting Oil, Burn Residue and Soot Samples

Table 2 summarizes the quantitation results of target PAHs in the diesel and

Table 2 Target PAH Quantitation Results (µg/g oil) for the Diesel and Burn Residues

Alkylated PAH	Starting Oil	Pre-burn				Post-burn	
	(MB-08)	(MB-013)	(MB-016)	(MB-017)	(MB-014)	(MB-016)	(MB-018)
Naphthalene							
C ₉ -N	232.1	239.1	219.2	233.4	24.1	47.7	54.6
C ₁ -N	1025.2	1065.4	1031.4	1020.6	90.9	82.1	160.6
C ₂ -N	4599.2	4785.5	5018.9	5172.2	1004.9	825.2	1499.5
C ₃ -N	6305.4	6746.1	6817.9	7015.8	2485.0	2261.7	3489.5
C ₄ -N	2984.1	3154.1	3282.4	3275.2	1744.0	1759.9	2257.1
Sum	16146	16990	16370	16717	6349	4977	7461
Phenanthrene							
C ₉ -P	253.6	270.4	291.9	297.7	260.5	374.5	384.6
C ₁ -P	909.6	993.6	957.9	985.4	1056.4	1137.8	1206.2
C ₂ -P	1066.8	1038.6	1148.3	1175.1	1654.0	1805.8	1763.7
C ₃ -P	570.5	613.6	609.8	624.6	1200.3	1221.2	1167.9
C ₄ -P	199.3	217.8	216.8	223.7	623.4	630.4	554.7
Sum	3000	3134	3226	3307	4796	6170	6077
Dibenzothiophene							
C ₉ -D	511.4	562.9	561.1	572.9	416.6	449.2	516.5
C ₁ -D	1507.1	1577.1	1637.3	1669.9	1557.4	1690.2	1827.5
C ₂ -D	2019.6	2105.3	2194.9	2222.0	2743.2	2955.8	3104.8
C ₃ -D	982.2	1034.3	1051.8	1083.6	1725.9	1843.3	1780.6
Sum	6020	6280	6446	6548	6443	6939	7229
Fluorene							
C ₉ -F	241.4	250.4	250.0	262.2	137.8	122.9	171.3
C ₁ -F	1002.3	1107.0	1086.2	1128.1	712.4	759.3	934.6
C ₂ -F	1421.7	1466.8	1495.1	1526.6	1259.6	1347.9	1515.5
C ₃ -F	1236.9	1223.4	1229.2	1262.5	1403.5	1490.0	1601.4
Sum	3902	4048	4060	4179	3613	3720	4223
Chrysene							
C ₉ -C	6.8	6.9	8.0	6.6	50.4	49.3	45.7
C ₁ -C	9.1	11.0	10.9	11.6	103.2	90.9	77.1
C ₂ -C	7.5	7.3	8.4	8.1	150.1	112.3	104.6
C ₃ -C	1.9	1.3	2.1	2.3	70.5	56.3	44.6
Sum	26	27	29	29	374	309	272
Total	27094	28478	29129	29780	20474	21114	24263
Other PAHs							
Biphenyl (Bp)	309.2	321.0	308.9	351.9	52.3	45.5	90.9
Acenaphthylene (Acl)	14.3	15.0	16.2	16.5	34.3	75.4	78.6
Acenaphthene (Ace)	74.1	72.9	65.2	70.0	22.6	31.4	36.0
Anthracene (An)	6.93	9.07	8.79	8.68	20.2	47.0	38.5
Fluoranthene (Fl)	2.57	2.38	2.48	2.94	28.0	58.4	46.3
Pyrene (Py)	7.30	7.47	7.43	8.11	42.4	91.8	72.7
Benz(a)anthracene (BaA)	1.00	1.02	1.12	1.18	9.78	19.9	14.7
Benzo(b)fluoranthene (BbF)	0.21	0.15	0.24	0.27	5.78	11.7	10.4
Benzo(k)fluoranthene (BkF)	0.13	0.10	0.13	0.05	6.22	18.1	12.0
Benzo(e)pyrene (BeP)	0.42	0.34	0.39	0.43	11.0	15.5	12.6
Benzo(a)pyrene (BaP)	0.05	0.04	0.05	0.05	9.84	23.3	18.1
Perylene (Pe)	0.16	0.15	0.15	0.14	4.21	5.69	4.12
Indeno(1,2,3 cd)pyrene (IP)	ND	ND	ND	ND	10.0	17.2	16.4
Dibenz(a,h)anthracene (DA)	ND	ND	ND	ND	1.30	1.34	1.31
Benzo(ghi)perylene (BP)	ND	ND	ND	ND	12.8	26.3	18.9
Total	416	430	411	460	271	488	471
Total of all PAHs	27510	28907	29540	30240	20745	21602	24734
Diagnostic Ratios							
Chrys/Naphs	0.002	0.002	0.002	0.002	0.070	0.062	0.036
Chrys/Phens	0.008	0.008	0.009	0.009	0.078	0.060	0.054
Chrys/Dibens	0.005	0.005	0.005	0.005	0.058	0.044	0.038
Chrys/Fluos	0.006	0.007	0.007	0.007	0.107	0.083	0.064
C2D/C2P : C3D/C3P	1.80 : 1.72	1.85 : 1.69	1.91 : 1.72	1.89 : 1.73	1.66 : 1.44	1.64 : 1.51	1.73 : 1.52
Phen/An	36.59	29.80	33.21	34.29	12.89	7.97	9.98
Chry/BaA	6.85	6.80	7.13	5.62	5.15	2.48	3.11
Σ Other (3-6 ring)PAHs/ Σ (5 PAH series)	0.004	0.004	0.004	0.004	0.009	0.019	0.014

* ND: under the detection limit.

burn residue samples. The suite of target PAHs was expanded, to include not only the 5 target petroleum-specific alkylated PAH homologous series, but other EPA-defined unsubstituted priority PAHs [Page *et al.*, 1995; Wang and Fingas, 1997a]. Figure 1 depicts representative fingerprints and distinguishing features of target PAHs for the starting oil and burn residue.

Compared to most crude oils, the Mobile diesel is characterized by a narrower distribution of n-alkanes (n-C₈ to n-C₂₇) but with much higher concentrations of the total n-alkanes (~165 mg/g oil) than most crude oils. As well as containing relatively smaller quantities of BTEX (the collective name of benzene, toluene, ethylbenzene, and the xylene isomers, 4.40 mg/g oil) and C₃-benzenes (7.53 mg/g oil), the aromatic fraction of the diesel and pre-burn samples contains mainly alkylated naphthalene, dibenzothiophene, fluorene, and phenanthrene homologues (56, 19, 14, and 11% of the total of 5-target PAH homologues). The alkylated chrysene series were the least abundant (~0.1% of the total PAHs), resulting in the relative ratios of chrysene series to other four PAH series approaching zero. Among the other PAHs (Table 2), the dominance of 2- and 3-ring PAHs over the 4- and 5-ring PAHs is apparent. In addition, the diesel only contains extremely small amounts of 5- and 6-ring PAHs, and indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(ghi)perylene were not detected.

It was observed that "virtually all of the fuel was consumed by burning" [Walton *et al.*, 1995] and the residue was estimated no more than 0.1-0.3% of the starting diesel by weight. The burn residue was a mixture of burn products and some unburned oil. Therefore, the residue showed a mixed PAH fingerprint that retained some characteristics of the diesel oil but had some characteristics of additional pyrogenic PAHs. The most noticeable change in the aromatic hydrocarbon distribution was the complete loss of alkylbenzene compounds and dramatic decrease in abundances of naphthalene and its alkylated homologues relative to other PAH series. This feature is very similar to that of the highly weathered oils [Wang *et al.*, 1994c; Wang *et al.*, 1995a; Teal *et al.*, 1992; Farran *et al.*, 1987; Bence *et al.*, 1996]. However, there are several other compositional changes of PAHs which are significantly different from that caused by weathering or biodegradation. First, the concentration of chrysene and its alkylated homologues increased 10-14 times in the residue samples, resulting in significant increase in the relative ratios of chrysene series to the other 4 alkylated PAH series (Table 2). In contrast, the concentrations of the chrysene series in the long-term weathered *Arrow* [Wang *et al.*, 1994c] and *BIOS* [Wang *et al.*, 1995a] oil samples and highly lab-weathered ASMB oil (45% weathered) [Wang and Fingas, 1995b] were only altered in a range of 0.8 to 1.5 time of that in the corresponding source oils. This is because the chrysene series in these samples were only slightly degraded or virtually not degraded even many years after the spill. Second, for the other unsubstituted PAHs, additional PAHs, including indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(ghi)perylene, were detected. The increase in abundances of 4- to 6-ring PAHs plus 3-ring anthracene and their dominance over lower molecular weight 2- and 3-ring biphenyl, acenaphthylene and acenaphthene was pronounced. This implies that these high molecular weight PAHs may be largely formed from combustion, even though their absolute amount was very small (only in the µg level). Thirdly, the relative ratios of two pairs of

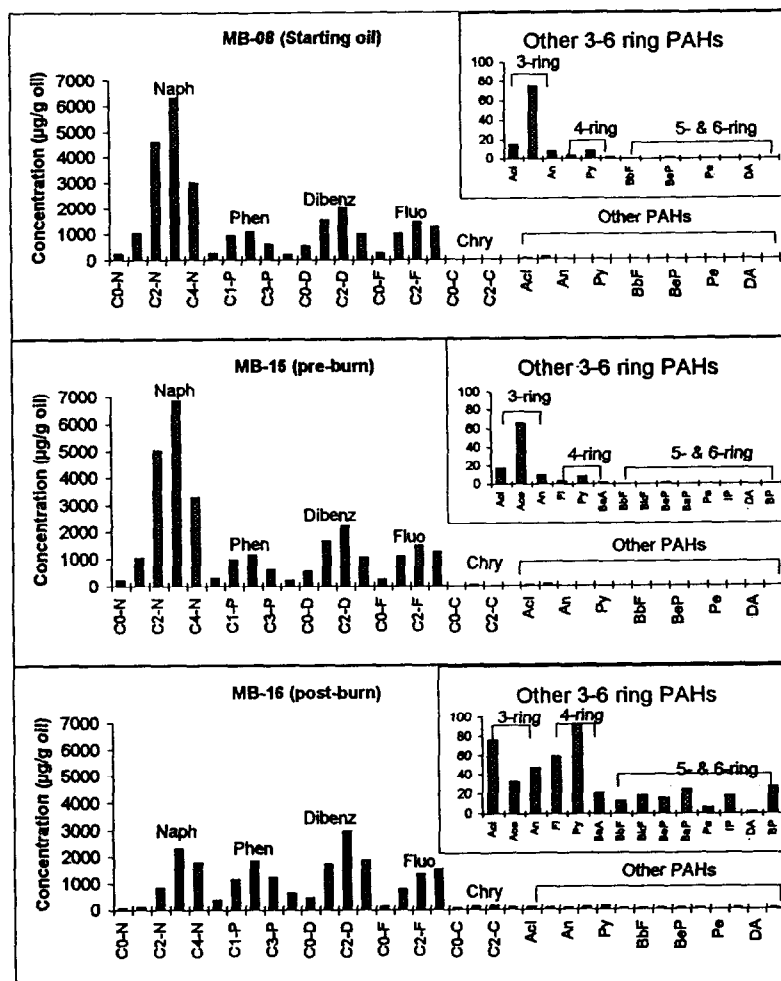


Fig. 1 PAH fingerprints and distinguishing features of different distribution of PAHs for the starting oil, pre-burn oil and burn residue. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0 - 4 represent carbon number of alkyl groups in the alkylated PAH homologous series. The abbreviations from Aci to Bp represent the other EPA-defined 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.

isomers, phenanthrene to anthracene (MW = 178) and chrysene to benz(a)anthracene (MW = 228), decreased to 8-10 and 2-5 from ~33 and ~7 for the diesel and pre-burn samples, respectively. As an example, Figure 2 compares extracted ion chromatograms at m/z 178 and 228 for the diesel, residue sample MB-16 and soot sample TSP-B3, illustrating the changes in the relative distribution patterns of target PAHs, and demonstrating the formation of pyrogenic PAHs, anthracene and benz(a)anthracene due to combustion.

If the changes of the PAH composition in the residue were considered to be significant and different from the weathered/degraded oils, then the next question will logically be "how about the chemical composition and its changes for the major and the most important burn product – smoke particulates". Table 3 summarizes the quantitation results of target PAHs in the soot samples. Figure 3 depicts the distribution of 5-target alkylated PAH homologues and other PAHs in the soot samples. From Table 3, it is apparent that six soot samples from three independent burns showed quite close quantitation results (expressed in $\mu\text{g/g}$ of particulate) and similar distributions of PAHs, even for Burn 1 in which there was an upward trajectory of the smoke plume (the average wind direction, 38 degrees). This may indicate that the chemical composition of the smoke depends more on the type of organic material burned than on the combustion conditions. In addition to PAHs, the petroleum n-alkane distribution was also apparent in the soot samples (Figure 4). The soot samples showed an n-alkane distribution similar to that of the diesel but with three important differences: complete loss of the light n-C8 to n-C14 fraction, shift of maximum from n-C17 for the diesel to around n-C30 for the soot sample, and enhancement of the ratio of phytane over pristane (2.1 for the soot sample TSP-B3 and 1.0 for the diesel, respectively).

Unlike other organic biomass materials, the diesel contains large quantities of PAHs before burning. Most of these PAHs would be destroyed during the *in situ* burn process but a very small portion of these PAHs may escape by volatilization and adsorption on the soot. On the other hand, however, trace amount of new pyrogenic PAHs may be generated, presumably through thermal aromatization of free-radicals pyrolyzed from precursor hydrocarbons [Bj  seth, 1985; Badger, 1962; Gonzalez-Vila, 1991; Brassell, 1980]. Therefore, the distribution profile and pattern of PAHs must be carefully examined and compared to distinguish the pyrogenic and petrogenic hydrocarbons. Compared to the diesel oil, two differences in the PAH distribution of the smoke particulates are distinguished. First, the dominance of parent chrysene over the alkyl-substituted homologues and the decrease in relative abundances with increasing level of alkylation in the chrysene series (that is, in the order of $C_0 > C_1 > C_2 > C_3$) are very pronounced. This is a typical characteristic of pyrogenic PAHs generated in combustion of organic materials including wood, coal, and refined petroleum products [Bence *et al.*, 1996; Bj  seth, 1985; Brassell, 1980; Boehm *et al.*, 1997; Volkman *et al.*, 1992]. In contrast, petroleum alkylated PAH homologous series show the characteristic bell-like distribution profiles, which are readily modified to the distribution profile of $C_0 < C_1 < C_2 < C_3$ by weathering or degradation. However, it is noted that such distribution profiles were not obvious for the other four 2- and 3-ring alkylated PAH series, which indicates, as described above, that these lower molecular weight PAHs in the smoke particulates may be

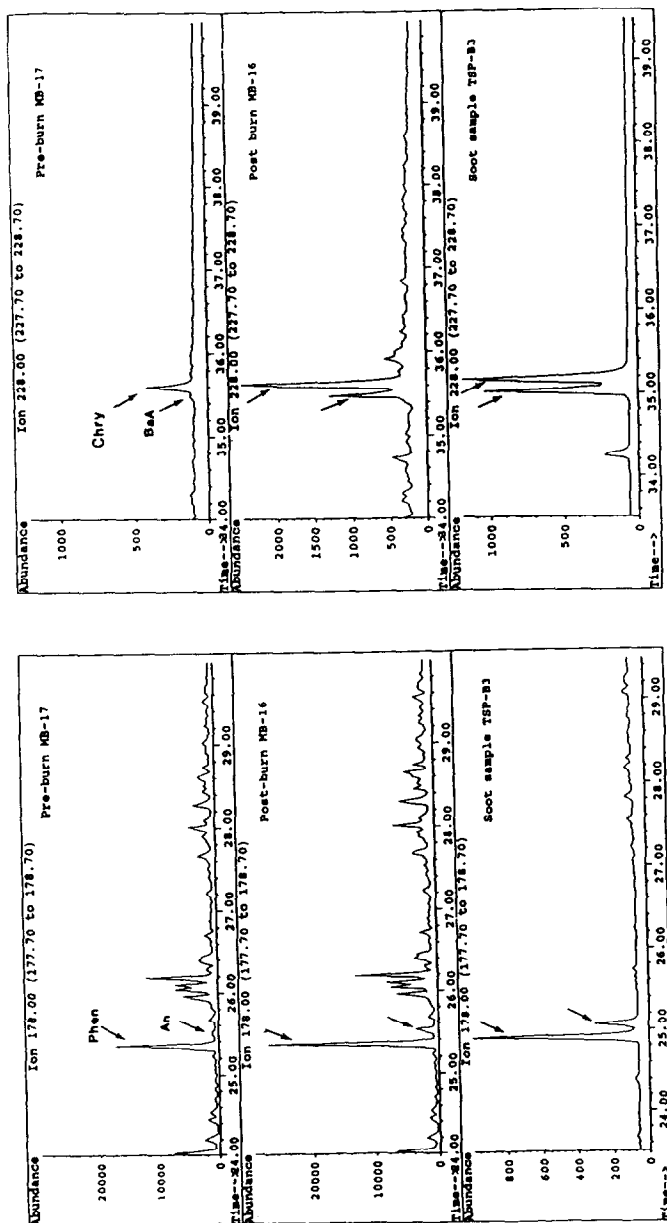


Fig. 2 Comparison of representative extracted ion chromatograms at m/z 178 and 228 for the starting oil, burn residue, and soot sample, illustrating changes in the relative distribution of two pairs of PAH isomer (phenanthrene and anthracene at m/z 178, and chrysene and benz(a)anthracene at m/z 228), and demonstrating the formation of pyrogenic PAHs anthracene and benz(a)anthracene due to combustion.

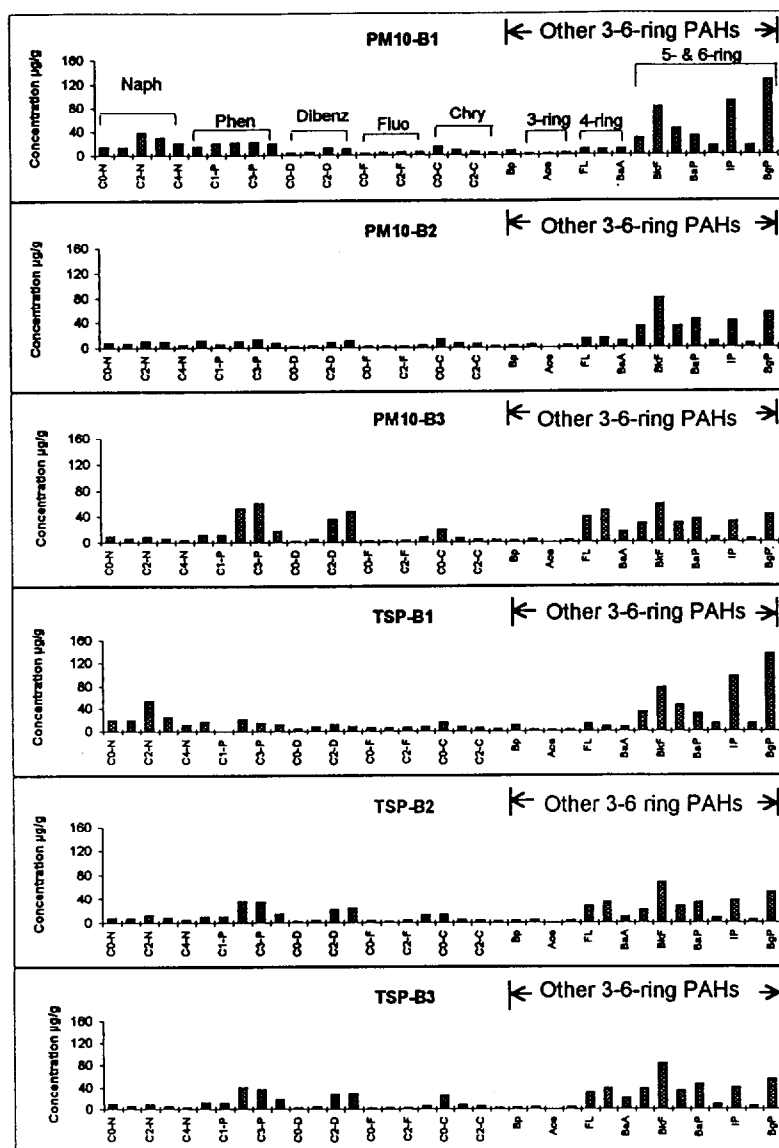


Fig. 3 Fingerprints of target alkylated PAH homologues and other EPA-defined substituted PAHs in soot samples from three independent burns of 1994 Mobile Burn Tests. Compared to the PAH distribution of the starting oil, the dominance of parent compound over the alkyl-substituted homologues in the chrysene series and the dominance of high molecular weight 5- and 6-ring PAHs over the other lower molecular weight PAHs are very pronounced.

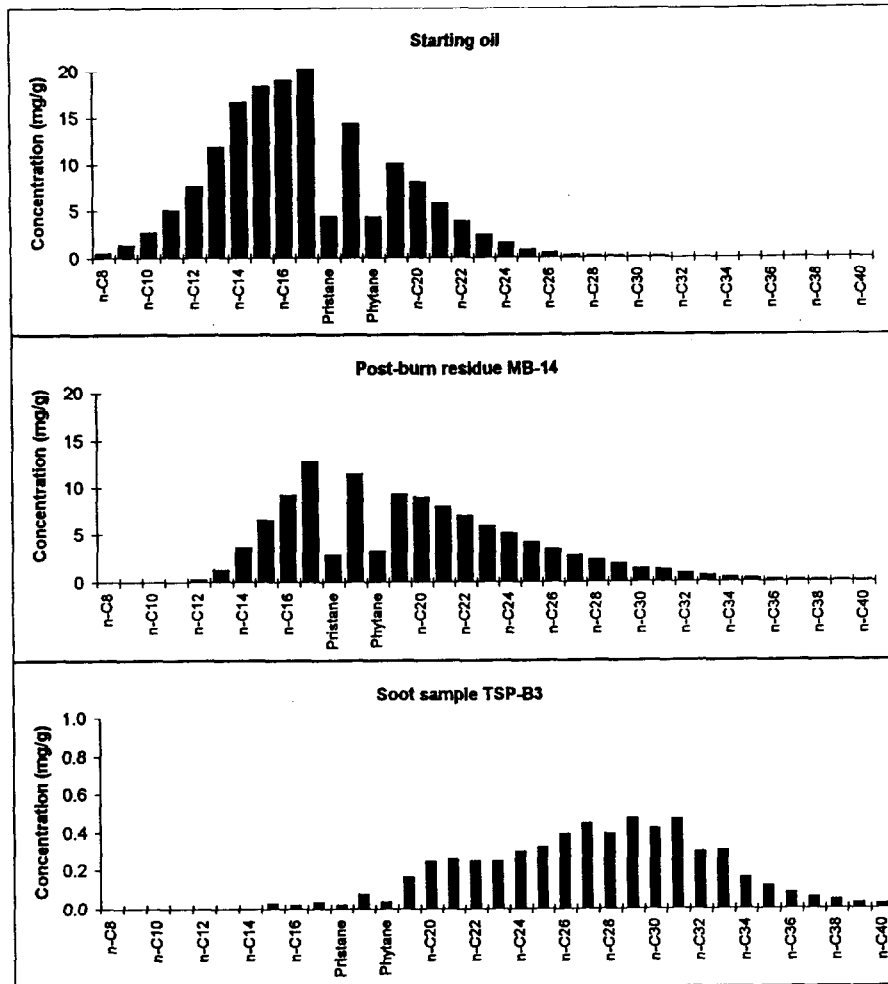


Fig. 4 Comparison of n-alkane distribution for the diesel, burn residue and soot sample. For clearness, a different concentration scale (0 - 1.0 mg/g particulate) is used for the soot sample TSP-B3

Table 3 Target PAH Quantitation Results ($\mu\text{g/g}$ particulate) for Soot Samples

Alkylated PAH	(PM10-B1)	(PM10-B2)	(PM10-B3)	(TSP-B1)	(TSP-B2)	(TSP-B3)
Naphthalene						
C ₀ -N	13.1	6.4	9.0	18.5	6.9	8.7
C ₁ -N	12.3	5.6	5.2	17.5	6.2	5.1
C ₂ -N	36.9	9.3	8.2	51.5	10.9	7.1
C ₃ -N	28.4	8.4	4.8	22.9	7.1	3.5
C ₄ -N	19.4	3.0	2.2	9.7	3.3	1.2
Sum	110	33	30	120	34	26
Phenanthrene						
C ₀ -P	13.3	10.3	10.8	15.5	8.9	10.1
C ₁ -P	18.5	4.3	10.3	20.4	8.9	9.7
C ₂ -P	20.4	8.7	51.3	19.7	34.2	38.3
C ₃ -P	20.0	11.9	59.6	12.6	33.2	34.4
C ₄ -P	17.8	6.1	16.4	10.0	13.3	16.2
Sum	90	41	148	78	99	109
Dibenzothiophene						
C ₀ -D	2.7	1.1	0.9	2.9	0.5	0.6
C ₁ -D	3.2	1.3	4.2	6.7	2.2	2.7
C ₂ -D	10.4	6.4	34.7	10.6	20.4	25.9
C ₃ -D	8.8	8.9	45.6	6.9	22.3	26.8
Sum	26	18	86	27	46	66
Fluorene						
C ₀ -F	2.1	1.2	1.0	5.0	1.4	0.8
C ₁ -F	2.3	1.0	0.7	4.9	0.8	0.6
C ₂ -F	3.9	0.6	1.8	5.8	2.8	1.2
C ₃ -F	3.9	2.3	6.9	6.8	11.7	4.8
Sum	12	6	10	22	17	7
Chrysene						
C ₀ -C	12.3	11.7	18.4	13.6	11.8	23.8
C ₁ -C	6.9	5.8	5.5	6.8	3.7	6.4
C ₂ -C	4.6	5.0	3.3	4.9	2.7	4.1
C ₃ -C	2.8	1.6	2.1	2.9	1.9	1.1
Sum	27	24	29	28	20	35
Total	264	121	303	276	215	233
Other PAHs						
Biphenyl (Bp)	6.0	2.1	2.0	9.7	2.3	1.6
Acenaphthylene (Acl)	0.9	3.5	3.4	2.2	3.7	3.1
Acenaphthene (Ace)	0.9	0.4	0.4	1.1	0.3	0.1
Anthracene (An)	1.7	2.1	2.4	2.2	2.3	2.4
Fluoranthene (Fl)	7.7	12.3	37.4	11.9	26.6	30.5
Pyrene (Py)	6.9	13.7	47.2	7.5	32.8	37.8
Benz(a)anthracene (BaA)	7.7	9.6	14.3	6.5	9.0	18.7
Benzo(b)fluoranthene (BbF)	25.8	31.9	27.4	32.3	19.8	36.9
Benzo(k)fluoranthene (BkF)	79.1	78.4	58.1	75.5	66.9	82.3
Benzo(e)pyrene (BeP)	41.3	31.7	28.2	43.1	26.3	33.4
Benzo(a)pyrene (BaP)	29.2	42.6	34.4	29.1	32.5	45.5
Perylene (Pe)	12.9	8.7	6.3	11.9	6.7	7.6
Indeno(1,2,3 cd)pyrene (IP)	88.6	39.9	30.1	94.9	35.3	38.9
Dibenz(a,h)anthracene (DA)	13.0	4.8	4.1	11.6	3.2	4.4
Benzo(ghi)perylene (BP)	123.9	53.3	40.8	134.5	50.1	53.3
Total	446	335	336	474	318	397
Total of all PAHs	710	456	639	750	533	630
Diagnostic Ratios						
Chrys/Naphs	0.24	0.73	0.99	0.23	0.58	1.38
Chrys/Phens	0.30	0.58	0.20	0.36	0.20	0.33
Chrys/Dibens	1.06	1.36	0.34	1.04	0.44	0.63
Chrys/Fluos	2.20	4.71	2.82	1.25	1.20	4.85
C ₂ D/C ₂ P : C ₃ D/C ₃ P	0.51 : 0.44	0.74 : 0.75	0.68 : 0.76	0.54 : 0.55	0.60 : 0.67	0.68 : 0.78
Phen/An	7.73	4.90	4.53	7.19	3.92	4.29
Chry/BaA	1.59	1.22	1.29	2.10	1.31	1.27
Σ Other (3-6 ring)PAHs/ Σ (5 PAH series)	0.81	1.94	0.86	0.81	1.05	1.28

largely from volatilized and un-combusted diesel PAHs under the present combustion conditions, rather than newly-generated. Second, the high molecular weight 5- and 6-ring PAHs, which were mostly generated from incomplete combustion of the diesel, are remarkably abundant relative to the other lower molecular weight PAHs. Quantitatively, the relative ratios of the total of other 3- to 6-ring PAHs to the total of 5 alkylated PAH series, expressed in $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$, were in a range of 0.8 to 2.0 for the six soot samples. These ratios are far greater than that of crude oils and petroleum products, which will be discussed in detail later. The relative ratios of phenanthrene to anthracene and chrysene to benzo(a)anthracene were found to fall in a range of 4-8 and 1-2 respectively, which were significantly smaller than that obtained from the residue samples.

For comparison purposes, the values of the double ratio of C2D/C2P:C3D/C3P are presented in Tables 2 and 3. This ratio, as an important fingerprinting criterion, has been successfully used to correlate the 1989 *EXXON VALDEZ* spilled oil sediment samples to the source oil [Page *et al.*, 1995; Boehm *et al.*, 1997; Volkman *et al.*, 1992; Page *et al.*, 1996]. However, unlike the *EXXON VALDEZ* spilled oil, the double ratio determined in the Mobile Burn Experiments demonstrated the order of pre-burn samples > post-burn residue >> soot samples (Figure 5). This fact clearly indicate that the burn situation is greatly different from the slow natural weathering process. In the slow natural weathering process, weathering may occur at comparable rates for each level of alkylation of dibenzothiophene and phenanthrene series. But under the long-term heavy weathering/degradation conditions [Wang *et al.*, 1994c; Wang *et al.*, 1995a] or the burn situation, the loss rate of sulphur-containing dibenzothiophenes was obviously greater than the loss rate of the phenanthrene series. The plot of double ratios in Fig. 5 can be best described by a linear equation " $Y = 0.8292 X + 0.1345$ ($r^2 = 0.99$)". This plot may be useful for tracing the relative distribution of PAHs of the diesel burn products in the future experiments.

3.2 Estimation of Destruction Efficiencies of The Diesel PAHs

The best estimation of destruction efficiencies of PAHs in the *in situ* burn diesel largely depends on "true values" of soot produced, in addition to depending on analytical precision and accuracy. Since the late 1980s, several groups have published data in the literature on soot production from *in situ* oil fires [Fingas *et al.*, 1995; Benner *et al.*, 1990; Walavalkar and Kulkarni, 1996; Evans, 1994]. However, these data do not agree and often vary from each other by as much as an order of magnitude. A very common approach used to estimate the soot production is the carbon balance method. The major assumption of this method is that all carbons resulting from the fire are in the smoke plume. The carbon balance method may be somewhat applicable for very small burns where sampling is performed directly in the chimney and where the gases do not have a chance to escape from the smoke. However, *in situ* observations and extensive data obtained from a three dimensional array of dozens of carbon dioxide metres, sampling stations, and helicopter sampling packages from the NOBE experiments [Fingas *et al.*, 1994; Fingas *et al.*, 1995] and from the mesoscale 1994 Mobile Burn Experiments [Fingas *et al.*, 1996a; Fingas *et al.*, 1996b] demonstrated that there was a significant gas separation between the

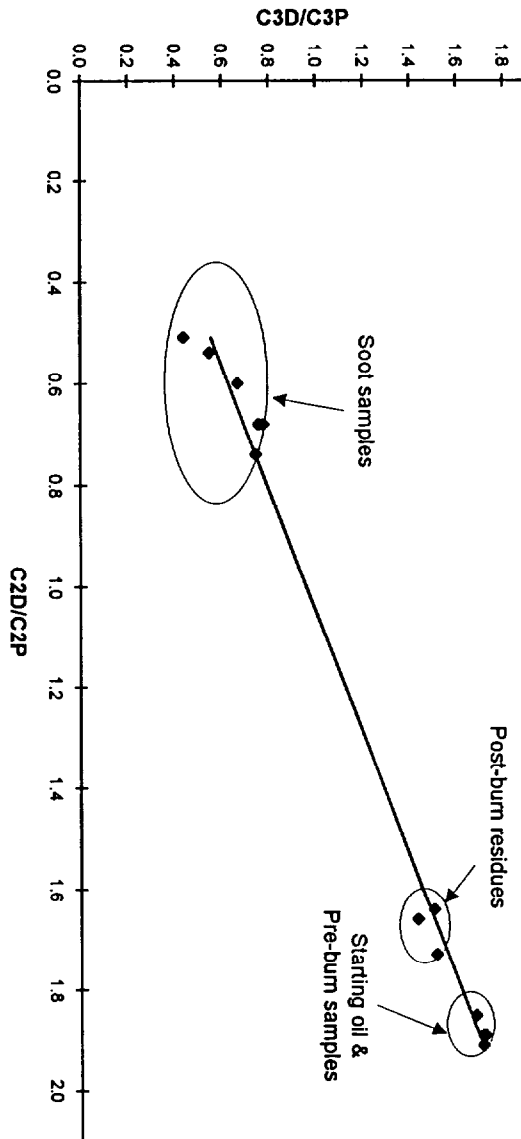


Fig. 5 Double ratio plot of C2D/C2P to C3D/C3P in diesel, burn residue, and soot samples. The plot shows the double ratio in the order of the starting oil and pre-burn samples > post-burn residue >> soot samples, demonstrating the loss rate of allylated dibenzothiophene series was significantly greater than the loss rate of allylated phenanthrene series under burn situation. The plot of double ratios can be best described by a linear equation of $Y = 0.8292 X + 0.1345$.

plume and the surface and the ground concentrations of carbon dioxide were always greater than those found in the air and in the plume, often by as much as a factor of 30. Therefore, a single carbon balance measurement in the plume over-estimates soot production of *in situ* burns. Very recently, two new methods of estimating soot production, integration of the soot concentration by volume under the plume and integration of soot deposition weight over the area under the plume, have been proposed. The NOBE and Mobile experimental data were fed into the model of integration by volume under plume to estimate the soot production. For the Mobile diesel, the average value of soot production obtained was 8.6% [Fingas *et al.*, 1996b]. Walton and co-workers [Walton *et al.*, 1994] reported the smoke particulate yields of 9.3 to 13.7% of the mass of fuel burned determined by the carbon balance method. The soot samples were collected by using a newly designed helicopter transported sampling package. It should be understood that current measurement and estimation techniques are fraught with numerous difficulties, therefore, "true experimental values" may not be forthcoming for a period of time.

The destruction efficiency of the individual PAHs, E_{PAH} , is defined as the mass of target PAHs destroyed in burns, $m_{B, PAH}$, over the mass of the same PAHs in the starting fuel, $m_{f, PAH}$. The amount of PAHs burned, which is equal to the difference between the total PAHs in the starting oil, $m_{f, PAH}$, and the sum in the smoke particulate, $m_{p, PAH}$, and in the residue, $m_{r, PAH}$:

$$\begin{aligned} E_{PAH} &= m_{B, PAH} / m_{f, PAH} \\ &= (m_{f, PAH} - m_{p, PAH} - m_{r, PAH}) / m_{f, PAH} \\ &= 1 - m_{p, PAH} / m_{f, PAH} - m_{r, PAH} / m_{f, PAH} \end{aligned} \quad (1)$$

Two assumptions are made in the calculation. The first is that the target PAHs in the smoke particulate and in the residue are predominant ones during burns. The second assumption is that the samples were collected over a suitable time period to average out natural fluctuations in the fire and plume, therefore, the PAHs in the samples represent the averaged "true" PAH distribution. The mass of target PAHs in smoke particulate is equal to the concentrations of target PAHs in smoke particulate samples, $C_{p, PAH}$, multiplying the mass of the smoke particulate, which can be readily obtained by the fuel mass (m_f) multiplied by the smoke yield (Y_s). The mass of the PAHs in the starting fuel can be simply obtained by the concentrations of PAHs in the fuel, $C_{f, PAH}$ multiplying the fuel mass m_f .

$$\begin{aligned} m_{p, PAH} &= m_p \times C_{p, PAH} \\ &= m_f \times Y_s \times C_{p, PAH} \end{aligned} \quad (2)$$

$$m_{f, PAH} = m_f \times C_{f, PAH} \quad (3)$$

The mass of the PAHs in the residue can be readily obtained by the same method.

$$m_{r, PAH} = m_r \times C_{r, PAH} \quad (4)$$

Combining equations (2), (3) and (4) yields:

$$\begin{aligned}
 E_{\text{PAH}} &= 1 - (m_f \times Y_s \times C_{\text{P, PAH}}) / (m_f \times C_{\text{f, PAH}}) - (m_r \times C_{\text{r, PAH}}) / (m_f \times C_{\text{f, PAH}}) \\
 &= 1 - (C_{\text{P, PAH}} / C_{\text{f, PAH}}) \times Y_s - (m_r \times C_{\text{r, PAH}}) / (m_f \times C_{\text{f, PAH}}) \\
 &= 1 - (C_{\text{P, PAH}} / C_{\text{f, PAH}}) \times Y_s - C_{\text{r, PAH}} / C_{\text{f, PAH}} \times m_r / m_f \quad (5)
 \end{aligned}$$

Because there were many variables which could affect soot and residue production and collection, three scenarios with a range of yield from 5% to 15% of soot production were chosen to estimate destruction efficiencies of target PAHs for 1994 Mobile Burn Experiments. The calculated results using Equation 5 are presented in Table 4. The three scenarios used were: Scenario A with soot production of 5% and residue production of 0.1%, Scenario B with soot production of 10% and residue production of 0.2%, and Scenario C with soot production of 15% and residue production of 0.3% to the starting oil by weight. Compared with the published estimated data for soot production yields of 8.6 to 13.7% [Fingas *et al.*, 1996b; Walton *et al.*, 1994], these three scenarios can be considered to represent a reasonable range for the diesel soot and residue production under the present burn conditions.

From Table 4, the following observations are apparent: (1) Distribution of PAHs in the soot and residue is very different from the starting diesel, and the destruction efficiencies of PAH congeners greatly differ; (2) The total destruction efficiencies of target diesel PAHs including 5 alkylated PAH series and other EPA-defined unsubstituted 3-6 ring PAHs (27,510 µg per gram of oil) were greater than 99% for all three scenarios, primarily due to the high destruction efficiencies of the 2- and 3- ring PAH series; (3) Among the 5 alkylated PAH series, the 4-ring chrysene series (only 25 µg/g of oil) had the lowest destruction efficiency. The net destruction efficiency of the whole chrysene series was determined to be in a range of 93% to 80% for the three scenarios, while the destruction efficiencies were all greater than 99% for all four of the other alkylated PAH series; (4) The destruction efficiencies of the other 3- to 6-ring PAHs were determined to be 82, 64, and 46% for Scenarios A, B, and C, respectively; (5) The destruction efficiencies of the other EPA-defined PAHs dramatically decreased with increasing ring number. For example, the destruction efficiency of three 3-ring PAHs was around 98% for Scenario B, and decreased to 15% and 65% for 4-ring fluoranthene and pyrene; (6) Eight target 5- and 6-ring PAHs from benzo(a)anthracene to benzo(ghi)perylene plus 4-ring benz(a)anthracene were largely generated from combustion of diesel. The mass of these PAHs in the soot and residue (the great majority of these compounds were found in the soot rather than in the burn residue) were estimated to be 3 to 36 times, 6 to 70 times, and 9 to 108 times of that in the starting oil for Scenarios A, B, and C, respectively. It is important to note, however, that even though these high ring PAHs were in much higher abundance in the burn products than in the starting oil, the total mass of these PAHs generated by combustion was very small. By estimation using our model, 27.3 kg of the diesel PAHs, mainly 2- and 3-ring PAHs and their alkylated homologues, were destroyed when 1000 kg of diesel was burned. At the same time only 0.016, 0.032, and 0.048 kg of the 5- and 6-ring PAHs were generated during burning for the three different scenarios. Therefore, these results should not be misinterpreted as "burning makes PAHs".

Table 4 Estimation of Destruction Efficiencies of Target PAHs for 1994 Mobile Burn Experiments

Alkylated PAHs	Aromatic Ring Numbers	Starting Oil (Cr,PAH) (μg/g)	Residues (Cr,PAH) (μg/g, n=3)	Soot (Cr,PAH) (μg/g, n=6)	% Destruction* (Scenario A)	% Destruction* (Scenario B)	% Destruction* (Scenario C)
Naphthalene							
C ₀ -N	2	232.1	42.1	10.4	99.8	99.1	98.8
C ₁ -N	2	1025.2	111.2	8.7	99.9	99.9	99.8
C ₂ -N	2	4599.2	1109.8	20.7	99.9	99.9	99.8
C ₃ -N	2	8305.4	2745.4	12.5	99.9	99.9	99.8
C ₄ -N	2	2984.1	1920.4	8.5	99.9	99.9	99.8
Sum		15146	5929	59	99.9	99.9	99.8
Phenanthrene							
C ₀ -P	3	253.6	339.9	11.5	99.8	99.3	98.9
C ₁ -P	3	909.6	1133.5	12.0	99.8	99.5	99.3
C ₂ -P	3	1069.6	1741.2	28.6	99.7	99.4	99.1
C ₃ -P	3	570.5	1198.5	28.6	99.5	99.1	98.6
C ₄ -P	3	199.3	602.8	13.3	99.4	98.7	98.0
Sum		3000	6014	94	99.7	99.3	99.0
Dibenzothiophene							
C ₀ -D	3	511.4	460.8	1.4	99.9	99.8	99.7
C ₁ -D	3	1507.1	1891.7	3.4	99.9	99.7	99.5
C ₂ -D	3	2019.6	2934.6	16.1	99.8	99.6	99.4
C ₃ -D	3	982.2	1783.2	19.9	99.7	99.4	99.1
Sum		5020	6870	43	99.8	99.6	99.4
Fluorene							
C ₀ -F	3	241.4	144.0	1.9	99.9	99.8	99.7
C ₁ -F	3	1002.3	802.1	1.7	99.9	99.8	99.7
C ₂ -F	3	1421.7	1374.3	2.7	99.9	99.8	99.7
C ₃ -F	3	1236.9	1496.3	6.0	99.8	99.7	99.6
Sum		3902	3819	12	99.9	99.8	99.7
Chrysene							
C ₀ -C	4	8.8	48.4	15.3	98.0	76.0	64.0
C ₁ -C	4	9.1	90.4	5.8	96.0	90.0	85.0
C ₂ -C	4	7.5	122.4	4.1	96.0	91.0	87.0
C ₃ -C	4	1.9	57.1	2.1	91.0	83.0	74.0
Sum		25	318	27	93.0	96.0	90.0
Total		27094	21950	235	99.8	99.7	99.6
Other PAHs							
Biphenyl (Bp)	2	309.2	62.9	4.0	99.9	99.8	99.7
Acenaphthylene (Acl)	3	14.34	62.7	2.8	99.0	97.9	96.8
Acenaphthene (Ace)	3	74.05	30.0	0.5	99.9	99.8	99.7
Anthracene (An)	3	6.93	35.2	2.2	97.9	95.8	93.7
Fluoranthene (Fl)	4	2.57	44.2	21.1	57.0	15.0	(1.2 times)
Pyrene (Py)	4	7.30	69.0	24.3	82.0	65.0	47.0
Benz(a)anthracene (BaA)	4	1.00	14.8	11.0	43.0	(1.1 times)	(1.7 times)
Benzo(b)fluoranthene (BbF)	5	0.21	9.3	29.0	(7 times)***	(14 times)	(21 times)
Benzo(k)fluoranthene (BkF)	5	0.13	12.1	73.4	(28 times)	(56 times)	(85 times)
Benzo(e)pyrene (BeP)	5	0.42	13.1	34.0	(4 times)	(8 times)	(12 times)
Benzo(a)pyrene (BaP)	5	0.05	17.1	35.8	(36 times)	(72 times)	(108 times)
Perylene (Pe)	5	0.16	4.7	9.0	(3 times)	(8 times)	(9 times)
Indeno(1,2,3-cd)pyrene (IP)	6	ND**	14.5	54.8	newly generated	newly generated	newly generated
Dibenz(a,h)anthracene (DA)	5	ND	1.3	6.9	newly generated	newly generated	newly generated
Benzo(ghi)perylene (BP)	6	ND	19.4	76.0	newly generated	newly generated	newly generated
Total of 3-6 ring PAHs		107	347	380	82	64	46
Total of 5-6 ring PAHs		0.97	92	319	(16 times by weight)	(32 times by weight)	(48 times by weight)
Total of all PAHs		27610	22300	620	99.8	99.6	99.4

* Three scenarios were chosen to estimate the destruction efficiencies of PAHs using Equation 5:

Scenario A, soot = 6%, residue = 0.1%

Scenario B, soot = 10% residue = 0.2% ; Scenario C, soot = 15%, residue = 0.3% of the starting oil by weight.

** ND: under the detection limit.

*** Eight 5- and 6-ring PAHs were largely generated from combustion of the diesel. The total mass of these PAHs were 16, 32, and 48 times of that in the starting oil for scenarios A, B, and C, respectively (see text for details).

3.3 Differentiation of Pyrogenic and Petrogenic PAHs

It has been recognized that pyrogenic PAHs are featured by the dominance of the unsubstituted compounds over their corresponding alkylated homologues and the dominance of the high molecular weight 4-6 ring PAHs over the low molecular weight 2-3 ring PAHs [Bj  seth, 1985; Brassell *et al.*, 1980; Boehm *et al.*, 1997; Volkman *et al.*, 1992; Page *et al.*, 1996; Theobald *et al.*, 1995; Benlahcen *et al.*, 1997]. In field studies, however, 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 Table 3). Also, the absolute amount of PAHs generated during incomplete combustion is strongly dependent on temperature. Under the comparable combustion conditions, the same amount of organic materials can yield hugely different amount of PAHs at different temperatures [Bj  seth, 1985]. Therefore, in addition to qualitative criteria, quantitative criteria should be defined to recognize sources of PAHs. Benlahcen and co-workers [Benlahcen *et al.*, 1997] have reported a method using the ratio phenanthrene/anthracene < 10 and fluoranthene/pyrene > 1 to identify contamination sources of combustion processes. In this study, we found that the ratios of the total of the other EPA-defined unsubstituted 3-6 ring PAHs to the total of 5 target alkylated PAH homologues, $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$, 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.

The ratios for the diesel, burn residues, and soot samples are presented in Tables 2 and 3. Table 5 summarizes 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. Tables 2, 3, and 5 clearly indicate that the ratios of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ 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) as discussed above, petrogenic and pyrogenic PAHs are characterized by dominance of 5 alkylated PAH homologous series and by dominance of unsubstituted high-molecular-weight 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) determination of these two sets of PAHs has become conventional measurement for many environmental labs, and 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/degradation and biodegradation only slightly alter the values of this ratio, but the ratio will be dramatically altered by combustion, as

Table 5 Relative distributions of 5 target alkylated PAH homologue to other 3- to 6-ring unsubstituted from over 60 oils and petroleum products

Oils	Total of 5-alkylated PAHs (µg/g)	Other 3-6 ring PAHs (µg/g)	Phen/Anth	Σ other (3-6) ring PAHs Σ 5 PAH series
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 from Norway)	6226	37	321.3	0.006
Federated	13354	66	167.9	0.005
Gulfasko 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
KOM (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 Paen (Reduced crude)	4086	41	100.5	0.010
MV-Paeen # 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
Osenberg	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

Table 5 Relative distributions of 5 target alkylated PAH homologue to other 3- to 6-ring unsubstituted from over 60 oils and petroleum products

Heavy Oils	Total of 5-alkylated PAHs (µg/g)	Other 3-6 ring PAHs (µg/g)	Phen/Anth	$\frac{\sum \text{other (3-6) ring PAHs}}{\sum \text{5 PAH series}}$
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
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

discussed in this paper. Tables 6 and 7 summarize the ratio data of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ determined from two artificially weathered oil series, the heavily weathered/degraded 25-year old Nipisi spill oil samples and NOBE burn samples, and from biodegradation samples of nine Alaskan oils, respectively. For comparison purposes, the ratios of phenanthrene/anthracene for biodegraded samples are also listed in Table 7. Figure 6 depicts the relative ratios of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ versus the relative ratios of phenanthrene to anthracene using the data from Tables 2, 3, and 5-7.

It can be clearly seen from Figure 6 that the jet fuel, diesel, and most crudes show the ratios of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ 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). An interesting feature observed from Fig. 6 is that the ratios for the unknown tarball samples collected from the coasts of British Columbia (BC) and California (CA) in 1996 and Newfoundland in 1997 also fell in this ratio range, implying that these tarballs might be from a source of heavy oils or heavy fuels. A comprehensive study has revealed that the tarball samples from BC and CA were chemically similar and both from bunker type fuels [Wang *et al.*, 1997b]. Fig. 6 indicates that the ratio of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ can be also used as a screening tool to distinguish heavy oils and heavy fuels from most crude oils and light petroleum products.

The ratios for the burn residue samples vary, from several times up to over 20 times of that for the starting oils, depending on the portion of burn products in the residues. The soot samples show the most striking increase in the ratio (over two hundred times). For example, 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), while the same ratio for the diesel is only 0.004.

It is noted that some heavy fuels (such as IF-30 and A-02) and unknown tarball samples from Newfoundland in 1997 show the ratios of phenanthrene to anthracene smaller than 10. In particular, the nine sets of the biodegraded Alaskan oils show the ratios of phenanthrene to anthracene also smaller than 10, due to the obviously preferential degradation of phenanthrene over anthracene by the defined inoculum [Foght *et al.*, 1998]. An incorrect conclusion could be derived if this ratio was used alone to identify the contamination source of PAHs by combustion. In contrast, however, the ratios of $\Sigma(\text{other 3 - 6 ring PAHs}) / \Sigma(5\text{-alkylated PAHs})$ only show slight changes regardless of the type of oils and whether oils were weathered or biodegraded. Hence, this quantitative ratio, combined with other qualitative criteria, can be unambiguously used to differentiate sources of PAHs.

4.0 CONCLUSIONS

For the 1994 Mobile diesel burns, quantitative results for the PAH composition and relative distribution of five alkylated PAH homologues and an additional 14 EPA-defined unsubstituted priority PAHs in the smoke particulate have been obtained. These data, together with the initial oil volume and the residue volume, the amount of smoke produced, and the PAH contents of the diesel and

Table 6 Relative ratio data of Σ other (3-6) ring PAHs/ Σ 5 PAH series for artificially weathered oil series, heavily-weathered 25-year-old Nipisi samples, and NOBE burn samples.

Oils	Total of 6-alkylated PAHs ($\mu\text{g/g}$)	Other 3-6 ring PAHs ($\mu\text{g/g}$)	Σ other (3-6) ring PAHs / Σ 5 PAH series
Artificially Weathered Oils			
ASMB oils series			
0%	13459	70.2	0.005
9.80%	14171	65.8	0.005
19.50%	15819	76.0	0.005
29.80%	18195	73.2	0.004
34.50%	18737	80.9	0.004
45%	16010	81.4	0.005
California oils series			
0%	5269	40.0	0.008
4.60%	5988	45.3	0.008
9.55%	6087	48.8	0.008
14.60%	4943	49.5	0.010
25-year-old Nipisi Spill Samples			
Ref. Oil (fresh)	11853	43.5	0.004
Ref. Oil (weathered)	11837	43.9	0.004
N1-2*	1979	11.9	0.007
N2-1A	1996	24.4	0.012
N2-2	805	7.7	0.010
N2-3A	1602	8.3	0.005
N4-2	2112	19.7	0.009
N5-1A	1543	16.6	0.011
N6-1	2317	12.7	0.005
N6-2	1157	9.3	0.008
R1-1	1706	11.8	0.007
R2-1A	2375	15.3	0.006
R5-1	2139	16.4	0.008
R6-1	2535	21.7	0.009
P2-1	2939	21.5	0.007
NOBE Burn Samples			
2A (fresh)	11563	115.2	0.010
2B (fresh)	11752	97.0	0.008
3 (fresh)	11933	105.4	0.009
4 (pre-burn)	11383	111.1	0.010
5A (pre-burn)	11603	117.1	0.010
5B (pre-burn)	11525	98.7	0.009
7 (weathered)	8467	69.7	0.008
11 (residue)	4304	290.3	0.067
12 (residue)	2985	216.1	0.072
14 (residue)	2917	651.1	0.223
15 (residue)	3468	417.4	0.120
16 (residue)	2991	497.2	0.166

* The Nipisi spill oil samples from N1-2 to P2-1 were high contaminated and highly weathered/degraded sediment samples.

Table 7 Relative ratio data of Σ other (3-6) ring PAHs/ Σ 5 PAH series for biodegradation samples of nine Alaskan oils

Oils*	Total of 5-alkylated PAHs ($\mu\text{g/g}$)	Other 3-6 ring PAHs ($\mu\text{g/g}$)	Phen/An**	Σ other (3-6) ring PAHs Σ 5 PAH series
ASMB series				
ASMB (+)NP1	8643	54.4	2.4	0.006
ASMB (+)NP2	8796	46.5	9.3	0.005
ASMB (+)NP3	7956	48.1	3.7	0.006
ASMB (-)NP1	6555	52.9	1.1	0.008
ASMB (-)NP2	8048	45.0	4.1	0.006
ASMB (-)NP3	7106	62.2	1.4	0.009
ASMB-SC1	13763	90.6	35.6	0.007
ASMB-SC2	13764	93.5	46.4	0.007
ASMB-W	16770	109.4	27.4	0.007
North Slope series				
N S # 1(+)NP1	9007	45.0	(An. under ND)	0.005
N S # 1(+)NP2	7258	44.0	(An. under ND)	0.006
N S # 1(+)NP3	6850	44.0	(An. under ND)	0.006
N S # 1(-)NP1	6189	45.0	(An. under ND)	0.007
N S # 1(-)NP2	5750	42.0	(An. under ND)	0.007
N S # 1(-)NP3	6013	43.0	(An. under ND)	0.007
N S # 1-SC1	13997	72.5	106.0	0.005
N S # 1-SC2	15273	71.8	218.0	0.005
N S # 1-W	18130	81.5	194.0	0.004
N S # 2(+)NP1	7131	31.0	(An. under ND)	0.004
N S # 2(+)NP2	7352	30.0	(An. under ND)	0.004
N S # 2(+)NP3	6550	29.0	(An. under ND)	0.004
N S # 2(-)NP1	6557	29.0	(An. under ND)	0.004
N S # 2(-)NP2	6272	29.0	(An. under ND)	0.005
N S # 2(-)NP3	6145	30.0	(An. under ND)	0.005
N S # 2-SC1	15112	54.8	215.0	0.004
N S # 2-SC2	15532	61.0	214.0	0.004
N S # 2-W	17900	68.8	229.0	0.004
N S # 3(+)NP1	6591	41.0	(An. under ND)	0.006
N S # 3(+)NP2	6682	40.6	(An. under ND)	0.006
N S # 3(+)NP3	6904	40.8	(An. under ND)	0.006
N S # 3(-)NP1	6461	41.8	(An. under ND)	0.006
N S # 3(-)NP2	6888	42.3	(An. under ND)	0.006
N S # 3(-)NP3	5824	40.5	(An. under ND)	0.007
N S # 3-SC1	14171	66.0	226.0	0.005
N S # 3-SC2	13552	67.3	129.0	0.005
N S # 3-W	16368	80.4	189.0	0.005

* (+)NP: flasks contained oil, nutrients and microbial inoculum; (-)NP: flasks contained oil, the microbial inoculum, but no nutrients; SC: sterile controls, flasks contained oil, nutrients, but no microbial inoculum; W: weathered oil

** Phen: phenanthrene; An: Anthracene; ND: under the detection limit.

Table 7 Relative ratio data of Σ other (3-6) ring PAHs/ Σ 5 PAH series for biodegradation samples of nine Alaskan oils

Oils	Total of 5-alkylated PAHs ($\mu\text{g/g}$)	Other 3-6 ring PAHs ($\mu\text{g/g}$)	Phen/An	Σ other (3-6) ring PAHs / Σ 5 PAH series
Cook Inlet Series				
C I # 1(+)-NP1	6316	69.6	1.1	0.011
C I # 1(+)-NP2	6021	69.9	0.7	0.012
C I # 1(+)-NP3	5489	61.7	0.5	0.011
C I # 1(-)-NP1	4639	67.1	0.4	0.014
C I # 1(-)-NP2	5365	67.8	0.7	0.013
C I # 1(-)-NP3	5092	66.8	0.6	0.013
C I # 1-SC1	11772	86.7	54.3	0.007
C I # 1-SC2	12973	125.0	59.3	0.010
C I # 1-W	15511	127.2	53.0	0.008
C I # 2(+)-NP1	5917	59.0	1.9	0.010
C I # 2(+)-NP2	5310	54.0	0.7	0.010
C I # 2(+)-NP3	5849	50.0	3.1	0.009
C I # 2(-)-NP1	3917	56.0	1.5	0.014
C I # 2(-)-NP2	3786	57.0	1.2	0.015
C I # 2(-)-NP3	3864	57.0	1.1	0.015
C I # 2-SC1	11117	133.5	57.6	0.012
C I # 2-SC2	10924	127.3	62.9	0.012
C I # 2-W	12760	151.2	60.2	0.012
C I # 3(+)-NP1	6029	37.7	3.7	0.006
C I # 3(+)-NP2	5521	40.9	1.4	0.007
C I # 3(+)-NP3	5371	45.2	1.2	0.008
C I # 3(-)-NP1	3869	47.4	0.3	0.012
C I # 3(-)-NP2	4755	46.0	0.4	0.010
C I # 3(-)-NP3	4386	41.6	0.4	0.009
C I # 3-SC1	11509	79.2	56.4	0.007
C I # 3-SC2	10705	68.4	54.3	0.006
C I # 3-W	13608	81.2	61.0	0.006
Jet Fuel B Series				
JF(+)-NP1	4224	36.1	4.0	0.009
JF(+)-NP2	4680	37.2	4.0	0.008
JF(+)-NP3	4736	26.3	2.0	0.006
JF(-)-NP1	7154	45.7	8.0	0.006
JF(-)-NP2	7662	34.3	4.0	0.004
JF(-)-NP3	7418	21.8	5.0	0.003
JF-SC1	22314	52.3	46.8	0.002
JF-SC2	27178	51.9	50.3	0.002
JF-W	28103	53	27.1	0.002

Table 7 Relative ratio data of Σ other (3-6) ring PAHs/ Σ 5 PAH series for biodegradation samples of nine Alaskan oils

Oils	Total of 5-alkylated PAHs ($\mu\text{g/g}$)	Other 3-6 ring PAHs ($\mu\text{g/g}$)	Phen/An	Σ other (3-6) ring PAHs / Σ 5 PAH series
Diesel # 2 series				
DF # 2(+)NP1	7099	16.9	4.4	0.002
DF # 2(+)NP2	6983	15.8	3.0	0.002
DF # 2(+)NP3	8376	23.4	3.3	0.003
DF # 2(-)NP1	11752	25.1	5.0	0.002
DF # 2(-)NP2	11287	33.5	4.8	0.003
DF # 2(-)NP3	10343	35.5	4.2	0.003
DF # 2-SC1	24545	78.7	31.0	0.003
DF # 2-SC2	23628	89.1	33.5	0.004
DF # 2-W	25696	116.6	33.3	0.005
Bunker C/Diesel Mixture series				
BC/Diesel(+)NP1	7331	372.3	14.9	0.051
BC/Diesel(+)NP2	7485	368.5	11.6	0.049
BC/Diesel(+)NP3	7087	353.9	7.5	0.050
BC/Diesel(-)NP1	7392	433.4	2.7	0.059
BC/Diesel(-)NP2	7215	402.0	4.0	0.056
BC/Diesel(-)NP3	7285	433.9	4.5	0.060
BC/Diesel-SC1	10627	510.3	24.6	0.048
BC/Diesel-SC2	9481	481.8	24.8	0.051
BC/Diesel-W	12484	589.7	25.2	0.047

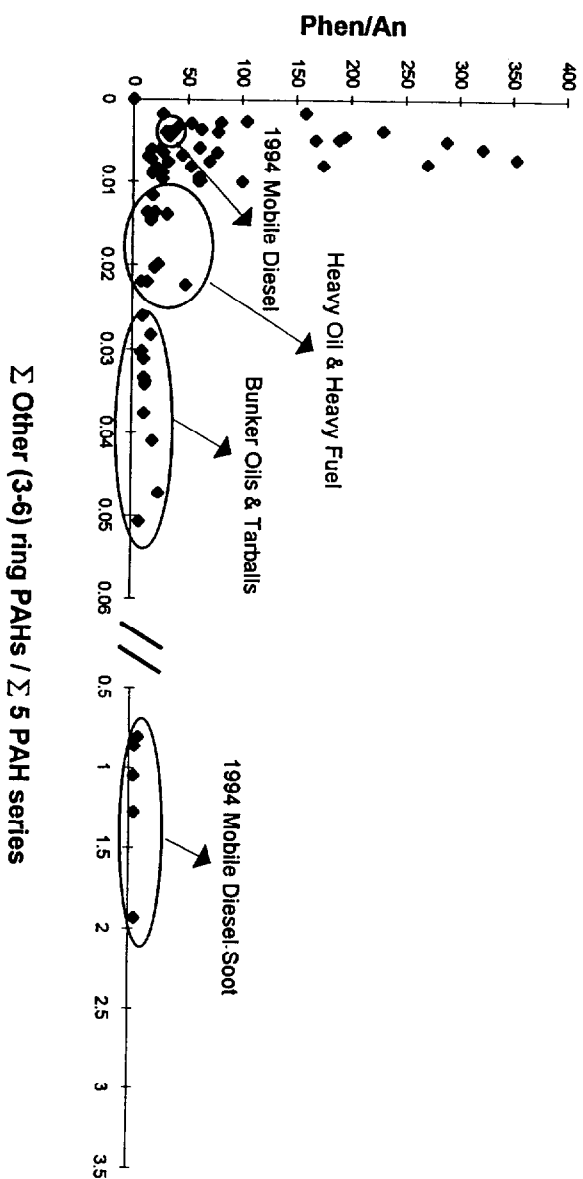


Fig. 6 Plot of the relative ratios of Σ (other 3 - 6 ring PAHs) / Σ (5-alkylated PAHs) over the relative ratios of Phenanthrene/Anthracene for over 60 oils and petroleum products. Lighter petroleum products and most crudes show the ratios of Σ (other 3 - 6 ring PAHs) / Σ (5-alkylated PAHs) fall into 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.

residue, are the basic parameters necessary for estimation of the destruction efficiencies of the diesel PAHs and assessment of the environmental impact of an *in situ* burn. Overall, *in situ* burning can help to mitigate the environmental impact of an oil spill by consuming much of the spilled oil and consequently, dramatically reducing the total amount of PAHs in the oil.

The relative ratios of the total of the other 3- to 6-ring PAHs to the total of the 5 target alkylated PAH homologous series are demonstrated to be useful means to distinguish heavy oils and fuels from most crude oils and light petroleum products and to differentiate pyrogenic and petrogenic PAHs. This method, combined with other criteria, is expected to be applicable to such situations as oil spill investigations, site assessment, and apportioning of legal responsibility for pollution cleanup.

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