

PAH DISTRIBUTION IN THE 1994 AND 1997 MOBILE BURN PRODUCTS AND DETERMINATION OF THE DIESEL PAH DESTRUCTION EFFICIENCIES

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ABSTRACT: In 1994 and 1997, several U.S. and Canadian government agencies jointly conducted a series of mesoscale burns in Mobile Bay, Alabama, to study various aspects of *in situ* diesel fuel burning. Samples were taken from the oil, residue and the smoke plume during each burn and analysed by capillary gas chromatograph/mass spectrometry (GC/MS). Analysis results reveal that the PAH distribution patterns in the diesel, residue, and soot samples are significantly different from each other. 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. The average destruction efficiency of the total diesel PAHs from three 1994 Mobile burns was estimated to be greater than 99%. The high molecular weight PAHs with five or more rings were found to be largely generated by combustion. These studies demonstrated that under certain circumstances, *in situ* burning is an effective measure to minimise the impact of an oil spill on the environment and to reduce the damage of an oil spill to the ecological system.

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.*, 1996; Walton *et al.*, 1995). In the last 14 years, numerous lab and tank tests and off-shore burning experiments, from small to large scale, have been performed to study various aspects of burning *in situ* of crude oils and refined petroleum products (Fingas *et al.*, 1994, 1996; Walton *et al.*, 1994, 1995). In 1994, diesel fuel was selected as the test fuel a series of three mesoscale burns was conducted in Mobile Bay, Alabama. A variety of parameters that might affect diesel burning, emissions, and smoke yield were investigated. In 1997, a total of twelve *in situ* burn experiments were performed. The primary goal of the 1997 *in situ* burns was the evaluation of five commercial fire booms under American Society for Testing and Materials protocols.

One recognised 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. However, there are no quantitative data on the distribution of the petroleum-specific alkylated PAHs of primary concern (that is, the alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene series) and other EPA priority PAHs (see detailed description of all target PAHs in Table 1) 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 destroyed. 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* burn products to the environment. This paper is directed at clarifying some basic aspects about alteration of PAH composition and levels in the starting oil, burn residue and smoke via detailed characterisation of all diesel PAHs, and destruction and formation of the diesel PAHs due to combustion. 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 diesel.

Experimental

Burn Residue and Soot Samples. All burn residue samples were collected manually by skimming the residue from the surface of the water in the test tank. The diesel and residue samples were directly dissolved in hexane at a concentration of ~100 mg/mL and spiked with surrogates prior to the column cleanup.

The Anderson (Smyrna, GA) PM-10 high-volume sampler and the Anderson TSP high-volume sampler were used to collect smoke particles of less than or equal to 10 µm in size and the total suspended particles from 0.3 to 50 µm from the burns,

Table 1. PAY quantitation results and diagnostic ratios of paired PAH isomers and alkylated PAH homologous series.

PAH	Concentrations (µg/g)							
	94-Mobile burn				97-Mobile burn			
	94-Diesel*	Residue-3	PM-10-B3	TSP-B3	97-Diesel* (8.5% weathered)	Residue-3	PM-10-B3	TSP-B3
Naphthalenes (C0 to C4)	15146	7461	30	26	16519	6902	18	4
Phenanthrenes (C0 to C4)	3000	5077	148	109	4113	5912	75	11
Dibenzothiophenes (C0 to C3)	5020	7229	85	56	6341	9486	35	7
Fluorenes (C0 to C3)	3902	4223	10	7	3473	3904	36	3
Chrysenes (C0 to C3)	25	272	29	35	50	147	33	11
Other PAH*	416	471	336	397	322	453	398	168
Total	27510	24734	639	630	30818	26805	557	202
Diagnostic Ratios								
Chrys/Naphs	0.001	0.04	0.99	1.38	0.003	0.02	18.33	2.75
Chrys/Phens	0.008	0.05	0.20	0.33	0.010	0.02	0.44	1.00
Chrys/Dibens	0.005	0.04	0.34	0.63	0.008	0.02	0.94	1.57
Chrys/Fluos	0.006	0.06	2.82	4.85	0.010	0.04	0.92	3.66
C2D/C2P : C3D/C3P	1.89 : 1.72	1.73 : 1.52	0.68 : 0.76	0.68 : 0.78	1.87 : 1.43	1.89 : 1.48	0.78 : 1.27	0.92 : 1.04
Phen/An	36.59	9.98	4.53	4.29	141.90	13.55	2.10	1.22
Chry/BaA	6.85	3.11	1.29	1.27	7.82	2.47	1.30	1.21
Σ Other (3-6 ring)PAHs/ Σ (5 PAH series)	0.004	0.01	0.86	1.28	0.003	0.01	0.61	1.35

* The other 15 EPA priority PAH include: biphenyl (Bph), acenaphthylene (AcI), acenaphthene (Ace), anthracene (An), fluoranthene (Fl), pyrene (Py), benz(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (Pe), indeno(1,2,3-cd)pyrene (IP), dibenz(a,h)anthracene (DA), benzo(ghi)perylene (BP).

respectively. The soot sample were spiked with the deuterated PAH surrogates and extracted using microwave and Soxhlet extraction methods. The extracts were dried by filtering through anhydrous sodium sulphate and concentrated to approximately 1-2 mL. The concentrated extracts were then transferred to a pre-conditioned 1.5 g silica gel microcolumn topped with 1 cm anhydrous sodium sulphate for sample cleanup. The eluent was collected in a pre-calibrated centrifuge tube, concentrated, spiked with appropriate internal standards, and made up to the accurate pre-injection volume (0.5 to 1.0 mL) for GC analysis.

Gas chromatography/mass spectrometry (GC/MS) analysis. The analysis 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 (Wang *et al.*, 1994a, 1994b, 1997).

Results and discussion

Distributions of target PAHs in starting oil, burn residue and soot samples. Figure 1 compares representative fingerprints and distinguishing features of target PAHs in the starting diesel, burn residue, and soot samples.

The suite of target PAHs includes not only five target petroleum-specific alkylated PAH homologous series, but also other EPA priority unsubstituted PAHs. The 1997 diesel is very similar to the 1994 diesel in chemical compositions. Compared to most crude oils, the Mobile diesel is characterised by narrower

distribution of n-alkanes (n-C₈ to n-C₂₇) but with much higher concentrations of the total n-alkanes (~165 mg/g oil). As well as containing relatively smaller quantities of BTEX (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). In addition, the diesel only contains very 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 burned out and the residue was estimated to be 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. Compared to the starting diesel, the most noticeable changes in the aromatic and PAH distribution for the burn residues were (1) the complete loss of alkylbenzene compounds and dramatic decrease in abundances of naphthalene and its alkylated homologues relative to other PAH series; (2) the concentration of chrysene and its alkylated homologues increased 10-14 times; and (3) additional high-number-ring PAHs 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.

Compared to the diesel oil and burn residues, alteration in the PAH distribution of the smoke particulates was extremely striking. First, the dominance of parent compound over the alkyl-substituted homologues in the chrysene series is very pronounced,

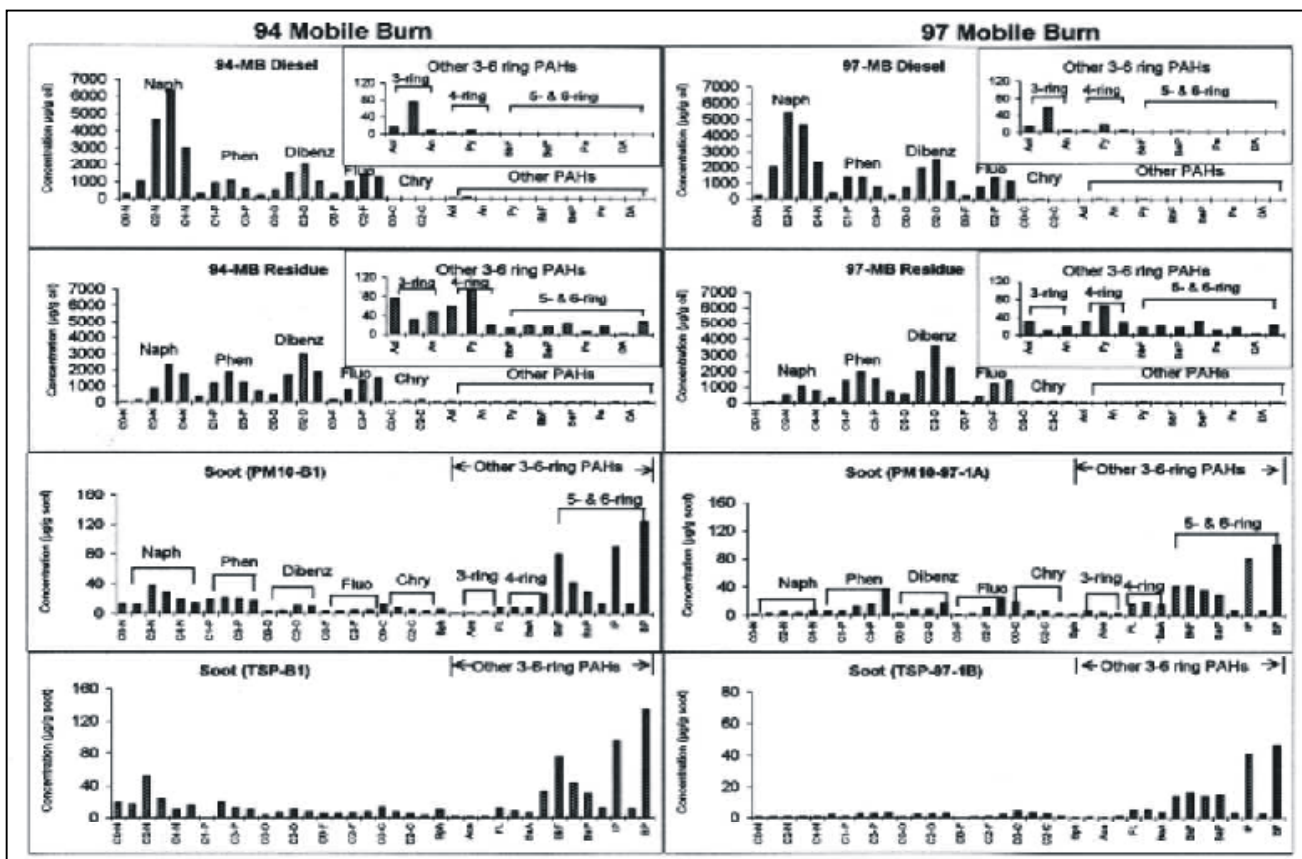


Figure 1. PAH fingerprints and distinguishing feature of different distribution of PAHs for the 1994 (left) and 1997 (right) Mobile burn diesel, burn residue, and soot samples. N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively; 0 - 4 represent carbon number of alkyl groups in the alkylated PAH homologous series. The abbreviations from Acl to Bp represent the other 14 EPA priority unsubstituted 3-6 ring PAH from acenaphthylene to benzo(ghi)perylene (refer to Table 1 for the full names of these PAHs). For comparison, the fingerprints of the other 3-6 ring PAH have been enlarged and shown in the left insets. Note that for clarity, different Y-axis scales are applied to chromatograms of the diesel, residue, and soot.

and the decrease in relative abundances with increasing level of alkylation in the chrysene series (that is, in the order of $C_0 > C_1 > C_2 > C_3$) is also significant. This is a typical characteristic of pyrogenic PAHs generated in combustion of organic materials including wood, coal, and refined petroleum products. 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. Table 1 briefly summarises the PAH quantitation results and a series of diagnostic ratios of paired PAH isomers and alkylated PAH homologous series. Figure 2 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 for over 60 oils and petroleum products. PAH analysis results clearly shows that in addition to other diagnostic ratios, the relative ratio of the total of other 3- to 6-ring EPA priority PAHs to the total of five alkylated PAH series, expressed in $\Sigma(\text{other 3-6 ring PAHs}) / \Sigma(5 \text{ alkylated PAHs})$, was in a range of 0.8 to 4.9 for the 1994 and 1997 soot samples. In sharp contrast, the ratio of $\Sigma(\text{other 3-6 ring PAHs}) / \Sigma(5 \text{ alkylated PAHs})$ for the diesels is only 0.003 to 0.004. 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. As Figure 2 shows, this ratio exclusively falls in the range of 0.01 to 0.05 for crude oils and oil products analysed, while it dramatically in-

creases to a range of 0.8 to 2.0 for the six 1994 Mobile burn soot samples. It has been also demonstrated that weathering and biodegradation only slightly change this ratio (Wang *et al.*, 1998). Therefore, this quantitative ratio can be used to unambiguously differentiate pyrogenic PAHs from petrogenic PAHs.

Determination of destruction efficiencies of the diesel PAHs. The destruction efficiency of the individual PAHs, E_{PAH} , defined as the mass of target PAHs destroyed in burns, $m_{B, PAH}$, over the mass of the same PAHs in the starting fuel, $m_{f, PAH}$, can be estimated using the following equation where m_f and m_r are the fuel mass and the residue mass respectively, $C_{P, PAH}$, $C_{f, PAH}$ and $C_{r, PAH}$ represent the concentrations of target PAHs in smoke particulate samples, in the fuel and in the residue respectively, Y_s is the smoke production yield:

$$E_{PAH} = 1 - (m_f \times Y_s \times C_{P, PAH}) / (m_f \times C_{f, PAH}) - (m_r \times C_{r, PAH}) / (m_f \times C_{f, PAH})$$

$$= 1 - C_{P, PAH} / C_{f, PAH} \times Y_s - (m_r \times C_{r, PAH}) / (m_f \times C_{f, PAH})$$

$$= 1 - C_{P, PAH} / C_{f, PAH} \times Y_s - C_{r, PAH} / C_{f, PAH} \times m_r / m_f \quad (1)$$

Fingas *et al.* (1996) reported the average value 8.6% of soot production. Walton and co-workers (1994) reported the smoke particulate yields of 9.3 to 13.7% of the mass of fuel burned determined by the carbon balance method. Because there were

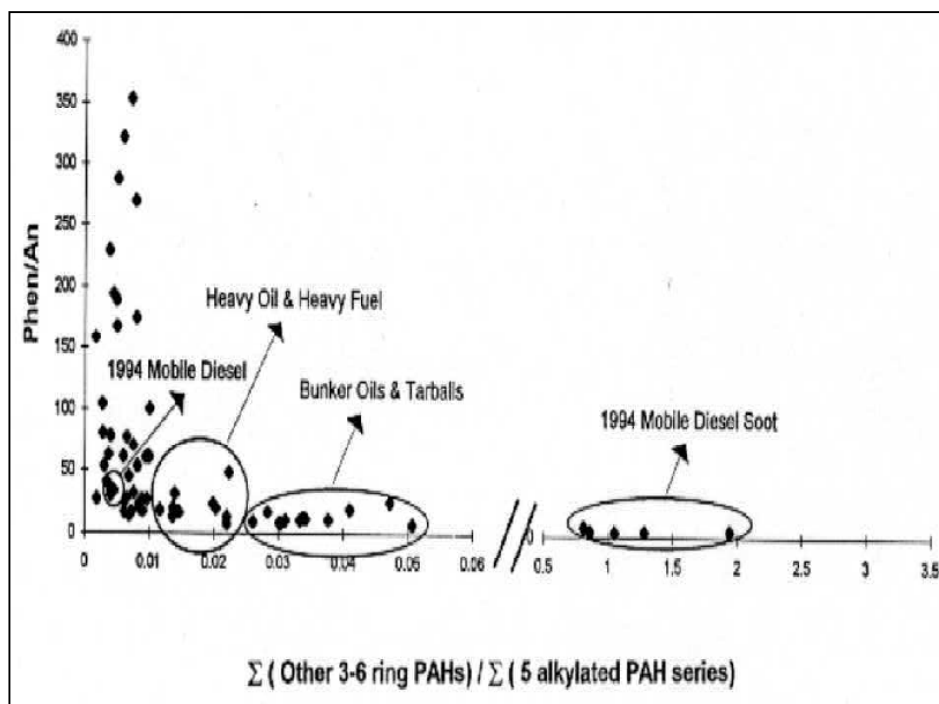


Figure 2. Plots of the relative ratios of $\Sigma(\text{other 3-6 ring PAHs}) / \Sigma(5 \text{ alkylated PAH series})$ over the relative ratios of phenanthrene/anthracene for over 60 oils and petroleum products.

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 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.*, 1996; Walton *et al.*, 1994), these three scenarios can be considered to represent a reasonable range for the soot and residue production under the present burn conditions. The calculated results using Equation 1 are presented in Table 2.

From Tables 1 and 2, it can be seen that:

- Distributions of PAHs in original diesel and soot are very different.
- The average destruction efficiencies for the total target diesel PAHs including 5 alkylated PAH series and other EPA priority unsubstituted PAHs (27510 μg per gram of oil) were greater than 99%.
- Using the Equation 1, 27.3 kg of the diesel PAHs were destroyed for each 1000 kg of diesel burned. These were mostly 2- and 3-ring PAHs and their alkylated homologues.
- Combustion also generated trace amounts of high molecular weight 5- and 6-ring PAHs as well as the 4-ring benz(a)anthracene. But it is important to note that the total mass of these pyrogenic PAHs was extremely low: only 0.016, 0.032, and 0.048 kg of the 5- and 6-ring PAHs were generated by combustion in the three different scenarios for each 1000 kg of diesel burned.

From these points, we conclude that *in situ* burning is an effective measure to minimise the impact of an oil spill on the environment, greatly reducing exposure of ecosystems to the PAHs of spilled oils.

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 characterisation of oil components, environmental assessments of oil and petroleum product spills, spill treating agent studies and analyses of dispersants.

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Table 2. Estimation of destruction efficiencies of target PAHs for the 1994 Mobile burn experiments.

Alkylated PAHs	Aromatic ring numbers	Starting Oil (Cr,PAH) (μg/g)	Residues (Cr,PAH) (μg/g, n=3)	Soot (Cp,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	6305.4	2745.4	12.5	99.9	99.9	99.8
C ₄ -N	2	2984.1	1920.4	6.5	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	99.6	99.3	98.9
C ₁ -P	3	909.6	1133.5	12.0	99.8	99.5	99.3
C ₂ -P	3	1066.8	1741.2	28.8	99.7	99.4	99.1
C ₃ -P	3	570.5	1196.5	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	5014	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	1691.7	3.4	99.9	99.7	99.5
C ₂ -D	3	2019.6	2934.6	18.1	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	1498.3	6.0	99.8	99.7	99.6
Sum		3902	3819	12	99.9	99.8	99.7
Chrysene							
C ₀ -C	4	6.8	48.4	15.3	88.0	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	86.0	80.0
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	5	0.21	9.3	29.0	(7 times)***	(14 times)	(21 times)
Benzo(k)fluoranthene	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	35.6	(36 times)	(72 times)	(108 times)
Perylene (Pe)	5	0.16	4.7	9.0	(3 times)	(6 times)	(9 times)
Indeno(1,2,3-cd)pyrene	6	ND**	14.5	54.6	newly generated	newly generated	newly generated
Dibenz(a,h)anthracene	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		27510	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 = 5%, 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).

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