

## The Fate of PAHs Resulting from In-situ Oil Burns

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### ABSTRACT

PAHs or Polyaromatic Hydrocarbons are ubiquitous in the environment and are found in crude oils. Many environmental PAHs are derived from combustion of many types including forest fires and barbeques. Some PAHs are toxic to biota and man. The concern addressed in this paper is the fate of PAHs found in crude oils when that oil is burned.

Crude oil burns result in PAHs downwind of the fire, mostly adsorbed to particulate matter, but the PAH concentration on the particulate matter, both in the plume and the particulate precipitation at ground level, is often an order-of-magnitude less than the concentration of PAHs in the starting oil. This includes the concentration of multi-ringed (5 or 6 rings) PAHs, which are often created in other combustion processes such as low-temperature incinerators and diesel engines. There is a slight increase in the concentration of multi-ringed PAHs in the burn residue. When considering the mass balance of the burn, however, most of the PAHs are destroyed by the fire. Destruction efficiencies are typically 99 % or greater.

Diesel fuel contains significant levels of PAHs of smaller molecular size, the 2 to 3-ring PAHs predominating. Burning diesel results in a greater concentration of pyrogenic PAHs of larger molecular sizes. Larger PAHs are either created or concentrated by the fire. Larger PAHs,

some of which are not even detectable in the diesel fuel, are found both in the soot and in the residue; however, the concentrations of these larger PAHs are low and often just above detection limits. Overall, more PAHs are destroyed by the fires than are created. As with crude oil burns, the destruction efficiencies for diesel burns are typically 99 % or greater, but often less than those for crude oils. This paper will help to answer the question, are more PAHs destroyed by the fires than are created?

## INTRODUCTION

PAHs are ubiquitous in the environment and are considered to be of concern for both man and the environment (Lima et al., 2005). There are many sources of PAHs, but primarily come from combustion sources. Natural sources such as forest fires, are a contributor. Crude oil contains PAHs, however oil spills themselves are not a significant contributor of PAHs to the environment. Burning of petroleum could constitute a significant input of PAHs into the environment. In particular, it has been pointed out that the two most significant contributors are diesel engines and home heating using a type of fuel similar to diesel fuel (Lima et al., 2005). Heating with wood also contributes some PAHs. Sootier flames appear to be associated with more PAHs. The amount of PAHs in the starting fuel also influences the amount of PAHs emitted by a burn. Generally low temperature sources such as diesel engines are larger emitters of PAHs than high temperature sources such as fires.

PAHs are compounds consisting of at least two benzene rings. Descriptions of common PAHs are found in the literature (Fingas, 2016). There exists a set of compounds designated by the U.S. EPA as priority PAHs (Wise et al., 2015). The concern with these compounds is that some of them are known to be relatively toxic and some to be carcinogenic. The amounts of

PAHs in a typical crude oil varies, but range from 0 to 5%. In crude oils, the alkylated compounds (branched hydrocarbons from the PAH rings) occur more frequently than the parent un-alkylated rings. This can be of use in identifying the source of contamination as many sources of PAH pollution have more abundant parent compounds than alkylated ones.

Diesel contains significant levels of PAHs of smaller molecular size, with 2- 3-ring PAHs predominating. Burning diesel results in more pyrogenic PAHs of larger molecular sizes. Larger PAHs are either created or concentrated by the fire. Larger PAHs, some of which are not even detectable in the Diesel fuel, are found both in the soot and in the residue. The concentrations of these larger PAHs are low and often just above detection limits. The question is, are more PAHs are destroyed by the fires than are created?

The PAHs in oil may have any or several of the following fates: 1) be burned to CO<sub>2</sub> and water, 2) be converted to other chemicals such as other PAHs or to oxygenated PAHs, 3) be transmitted through to the gaseous emissions of a fire, 4) be absorbed on the particulate emissions (soot) from the fire, or 5) accumulate on the residue or unburned portion. These processes are illustrated in Figure 1.

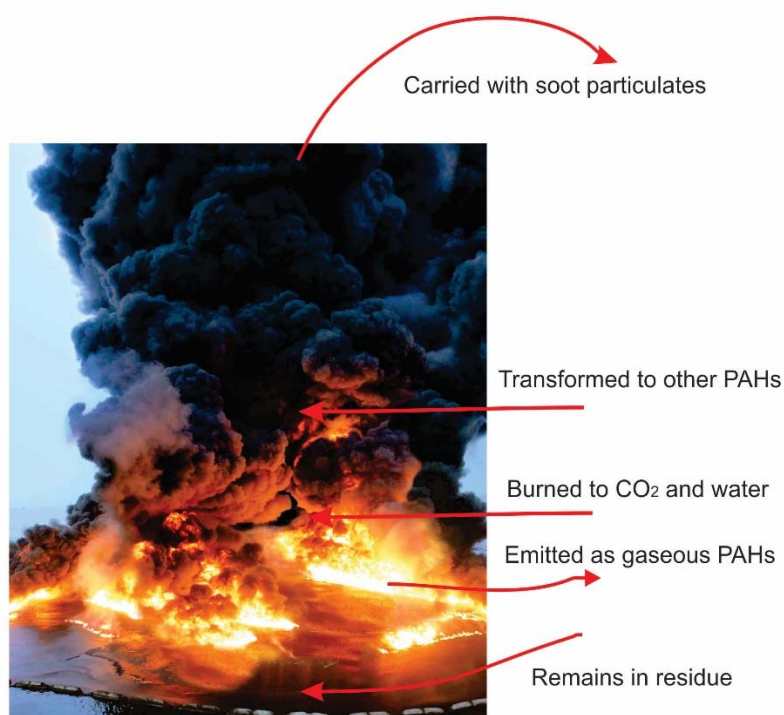


Figure 1 The possible fate pathways for PAHs in oil during a burn

## STUDIES OF THE FATE OF PAHs IN FIRES

Several early studies noted that the concentrations of PAHs were about the same in the residue as in the starting oil (Fingas et al., 1995; Li et al., 1992). The observations at the burn experiments reported at these trials included: 1) that generally the PAH concentrations in the residue and the starting oil were similar but never identical, 2) that for diesel burns there appeared to be more larger PAHs present in the residue and 3) tests of the volatile emissions showed low concentrations of PAHs during both crude and diesel burns. Several interpretations of these results ensued, however no firm conclusions could be made because the scientists were unsure of the mass balance of the burns between the soot and the residue compared to the starting oil. It is important to recognize that the concentration of PAHs in the starting oil and the

residue is only one facet. An important facet of the puzzle is the efficiency of the burn, or how much of the oil (and PAHs contained therein) were burned. To illustrate this, presume that 100 kg of oil were burned with a starting concentration of 1% PAHs - this would mean that there was 1 kg of PAHs. If the burn efficiency was 95% and the concentration of the PAHs was still 1% in the residue, then 95% of the PAHs were destroyed by the fire. In addition, one should consider the PAHs lofted in the soot and emitted as vapour.

A basic study on the fate of PAHs in diesel burns was carried out by Wang et al. (1999). This study used several mesoscale burns conducted in Mobile Bay, AL, to study various aspects of diesel fuel burning. The target PAHs in the diesel, residue, and soot samples collected during each burn were quantitatively characterized by GC/MS (Gas Chromatography/Mass Spectrometry). A simple model based on mass balance of individual petroleum PAHs pre- and post-burn was proposed to estimate the destruction efficiencies of the PAHs. This study demonstrated that distributions of PAHs in the original diesel and soot were actually different. The average destruction efficiencies for the total target diesel PAHs including five alkylated PAH series and other EPA priority unsubstituted PAHs were greater than 99%. Using the model, 27.3 kg of the diesel PAHs were destroyed for each 1000 kg of diesel burned. These were mostly two- and three-ring PAHs and their alkylated homologues. Combustion also generated trace amounts of high-molecular-weight five- and six-ring PAHs as well as the four-ring benz[a]anthracene. But the total mass of these pyrogenic PAHs was found to be extremely low: only 0.016, 0.032, and 0.048 kg of the five- and six-ring PAHs were generated by combustion in the three different scenarios for each 1000 kg of diesel burned. It was concluded that in-situ burning is an effective measure to minimize the impact of an oil spill on the environment, greatly

reducing exposure of ecosystems to the PAHs of spilled oils. This study showed several trends related to the destruction of PAHs in diesel burns:

1. It appears that the greater the number of rings, that the poorer the PAH destruction percent. For the priority PAHs, the trend is generally that as the ring numbers increases, the destruction percent decreases.
2. It appears that for the alkylated PAHs, the destruction percent decreases with increasing alkylation.

An examination of the vapour component shows that during three diesel burns, the concentrations of the only measureable PAH, naphthalene, was 0.2 out of 169  $\mu\text{g}/\text{m}^3$ ; 0.4 out of 153 and 0.7 out of 176 total  $\mu\text{g}/\text{m}^3$  of volatile organic compounds (for three different burns). The background was 0.7  $\mu\text{g}/\text{m}^3$ , therefore the PAHs in the vapour phase are negligible and often below background levels.

The next step was to examine the fate of PAHs in crude oil burns. The PAHs data set chosen for this study was that of the Newfoundland Offshore Burn Experiment (NOBE) which used a medium Alberta crude oil (Fingas et al., 1995). Table 1 shows the PAHs in the starting oil, soot and residue as measured from one burn at this study. Performing the mass balance calculation using the value of 1% for the soot and the measured oil burn efficiency of 99% (the maximum estimated at this burn), it was found that 99.99% of the PAHs were burned. This also shows that the PAH destruction was higher for crude oil than for diesel fuel. Data for some diesel burns are also shown in Table 1.

It is noted that the destruction of the PAHs in the soot is usually 99% indicating that this is not a strong route of PAH dissemination. This also indicates that PAHs on soot may be ignored in terms of the overall mass balance of PAHs in a burn.

Table 1	Comparison of Crude Oil and Diesel Fuel PAH Fate in Burns									
	Crude Oil (Alberta Sweet Mixed Blend)					Diesel Fuel				
	Concentrations (µg/g)			Burn destruction %		Concentrations (µg/g)			Burn destruction %	
	Starting Oil	Residue	Soot	as residue	as soot	Starting Oil	Residue	Soot	as residue	as soot
<b>Naphthalenes</b>										
C0-N	206	61	9	99.998	100.000	232.1	42.1	10.4	100.000	100.000
C1-N	1049	220	8	99.999	100.000	1025.2	111.2	8.7	100.000	100.000
C2-N	2246	578	11	99.998	100.000	4599.2	1109.8	20.7	100.000	100.000
C3-N	1749	589	3	99.998	100.000	6305.4	2745.4	12.5	100.000	100.000
C4-N	859	333	2	99.997	100.000	2984.1	1920.4	6.5	100.000	100.000
SUM	6109	1780	104	99.998	100.000	5929	59	99.9	100.000	100.000
<b>Phenanthrenes</b>										
C0-P	109	106	5	99.993	100.000	253.6	339.9	11.5	99.999	100.000
C1-P	407	301	5	99.995	100.000	909.6	1133.5	12	99.999	100.000
C2-P	450	361	12	99.995	100.000	1066.8	1741.2	28.8	99.999	100.000
C3-P	342	299	17	99.994	100.000	570.5	1196.5	28.6	99.999	99.999
C4-P	173	145	12	99.994	100.000	199.3	602.8	13.3	99.998	99.999
SUM	1481	1211	30	99.994	100.000	5014	94	99.7	100.000	100.000
<b>Dibenzothiophenes</b>										
C0-D	14	8	0	99.997	100.000	511.4	460.8	1.4	100.000	100.000
C1-D	28	21	0	99.995	100.000	1507.1	1691.7	3.4	99.999	100.000
C2-D	46	37	0	99.995	100.000	2019.6	2934.6	18.1	99.999	100.000
C3-D	26	26	1	99.993	100.000	982.2	1783.2	19.9	99.999	100.000
Sum	114	91	2	99.994	100.000	6870	43	99.8	100.000	100.000
<b>Fluorenes</b>										
C0-F	82	50	1	99.996	100.000	241.4	144	1.9	100.000	100.000
C1-F	176	92	0	99.996	100.000	1002.3	802.1	1.7	100.000	100.000
C2-F	176	93	0	99.996	100.000	1421.7	1374.3	2.7	100.000	100.000
C3-F	144	95	1	99.995	100.000	1236.9	1498.3	6	99.999	100.000
Sum	578	329	15	99.996	100.000	3819	12	99.9	100.000	100.000
<b>Chrysenes</b>										
C0-C	35	45	79	99.991	100.000	6.8	48.4	15.3	99.995	99.976
C1-C	45	58	29	99.991	100.000	9.1	90.4	5.8	99.996	99.993
C2-C	55	75	30	99.991	100.000	7.5	122.4	4.1	99.991	99.994
C3-C	50	58	55	99.992	100.000	1.9	57.1	2.1	99.983	99.988
Sum	185	235	54	99.991	100.000	318	27	93	100.000	99.997
total alkylated	8467	3645	76	99.997	100.000	27094	21950	235	100.000	100.000
<b>Priority PAHs</b>										
Biphenyl	70.8	14	1	99.999	100.000	309.2	62.9	4	99.998	99.998
Acenaphthylene	7.61	33	1	99.971	100.000	14.3	62.7	2.8	100.000	100.000
Acenaphthene	15.95	6	0	99.997	100.000	74.1	30	0.5	99.995	99.997
Anthracene	2.09	11	1	99.967	100.000	6.9	35.2	2.2	99.988	99.915
Fluoranthene	2.45	42	20	99.881	99.999	2.6	44.2	21.1	99.996	99.965
Pyrene	18.28	173	61	99.934	100.000	7.3	69	24.3	100.000	99.825
Benz(a)anthracene	2.94	44	32	99.901	99.999	1	14.8	11		
Benzo(b)fluoranthene	2.94	137	426	99.687	99.990	0.2	9.3	29		
Benzo(k)fluoranthene	0.49	59	360	99.159	99.950	0.1	12.1	73.4	100.000	99.455
Benzo(e)pyrene	8.71	285	740	99.774	99.994	0.4	13.1	34		
Benzo(a)pyrene	0.86	147	306	98.985	99.979	0.1	17.1	35.6		
Perylene	1.72	40	77	99.844	99.997	0.2	4.7	9		
Indeno(1,2,3cd)pyrene	0.74	14.5	54.6	99.868	99.995		14.5	54.6		
Dibenz(a,h)anthracene	1.35	1.3	6.9	100.000	100.000		1.3	6.9		
Benzo(ghi)perylene	2.94	19.4	76	99.959	99.998		19.4	76	100.000	99.990
<b>Overall</b>	<b>8607</b>	<b>4671.2</b>	<b>2239</b>	<b>100.000</b>	<b>100.000</b>	<b>27510.4</b>	<b>22360</b>	<b>619</b>	<b>99.993</b>	<b>99.993</b>

Table 1 also includes data from a diesel fuel burn. The alkylated PAHs burn with approximately the same efficiency with a greater degree of alkylation.

A look at the vapour component shows that during the two NOBE burns, the concentrations of the only measureable PAH, naphthalene was 0 to 7.3  $\mu\text{g}/\text{m}^3$  out of 6000 to 24,000 total  $\mu\text{g}/\text{m}^3$  of volatile organic compounds (for each of the two burns). The background was 0 to 6  $\mu\text{g}/\text{m}^3$ , therefore the PAHs in the vapour phase are negligible and sometimes below background levels.

From Table 1 it can be seen that the PAHs in the crude oil soot are 2239  $\mu\text{g}/\text{g}$  or 2% of that in the residue if considering the alkylated compounds, more if considering the target PAHs. With approximately the same percentages (<0.1%) of residue or soot, it can be concluded that the PAHs on the soot are not as significant fate for PAHs as in the residue. In the case of the crude oil, this is more pronounced than for diesel fuel.

Test burns of diesel fuel were again conducted in 1997 at Mobil, AL (Fingas et al., 1999; Wang et al., 1999). Similar results were obtained as before, namely that the destruction was nearly complete for all burns and all compounds. Similar burn tests were conducted in 1998 at Mobile, AB. (Fingas et al., 2000). Similar results were obtained, namely that the destruction was nearly complete for all burns and all compounds. Again, there does not appear to be differences in destruction percentages among the various alkylated PAHs nor among the priority PAHs. However, there are some higher concentrations of priority PAHs in the residue.

Garrett et al. (2000) carried out burn tests at small scale on Statfjord crude oil and found that the PAHs were reduced through burning. In addition to the 85% burned, an additional 40% of the PAHs were removed.



Burn tests on heavy and residual oils were conducted (Fingas et al., 2005). These burns were special in that they were carried out on heavy oils and bitumen, some mixtures and waste oils. The chosen heavy oils were poorly characterized before the burn. The Bunker C was somewhat characterized, while the test oil was several years old and was used to test skimmers. Its origin was unknown, however it was very viscous and low in PAHs. The Orimulsion and Bitumen were of similar origin and were mixed samples from the supplier of the product in Venezuela. The PAH destruction was variable and low for the two Orimulsion burns and the test oil burns. Burn efficiency was low for the test oils, as low as 2%. The Bitumen burns also had a lower burn efficiency. The PAH destruction percentages were higher compared to what one would expect, but that is because the boiling points of the PAHs are lower than the rest of the components in the oil and would be burned early in the combustion process.

Lin et al. (2005) performed a series of test burns in 30 cm pots containing marsh plants. Both diesel fuel and Louisiana crude oil were used. PAH removals of 99.4 and 98.9 for the diesel and crude were observed. It was also noted that there were increases in the priority PAHs as had been observed by Wang et al. (1999), especially for the diesel fuel. However, overall the PAH destruction was quantitative.

During the Deepwater Horizon spill in the USA, 411 successful burns of weathered and sometimes emulsified oil were carried out. Shigenaka et al. (2014, 2015) carried out a series of test burns as well as collected samples of oil burn residue at the site of the Deepwater Horizon burns. The PAHs in the collected samples and the starting oil was determined. The results show that the destruction percent of the burns are typically well over 99% with some of the priority PAHs being less – typically around 98%. This is consistent with previous data. It should be noted that some of the samples were scraped from the fire-resistant boom and thus they may have a

slightly different composition from the residue. Shigenaka et al. (2014) indicated that these samples may not be burned as much as the residue, however from this analysis it appears that they are.

Fritt-Rasmussen et al. (2013) conducted several small scale burns on Troll B crude oil and noted that there was an increase in some of the 16 priority PAH compounds. A mass balance was not calculated. Fritt-Rasmussen et al. (2015) carried out a review of burn residue noting that there was an increase in some of the 16 priority PAH compounds

Shigenaka et al. (2014) also carried out a series of small test burns to assess the chemical changes that burns undergo. These include a very small burn of Macondo oil, pan burns of South Louisiana crude and burns of emulsified Macondo oil. The burn efficiencies were not measured, however can be estimated from comments about the burnability. The Macondo oil burned with a high destruction percent. The Louisiana crude oil similarly. With the estimation of 80% burn efficiency for the Macondo emulsion, PAHs were still largely destroyed.

Gullett et al. (2016) studied the particulate matter emanating from the Deepwater Horizon burns. They sampled PAHs on particulate matter captured by volumetric samplers as well as on the sail of an aerostat flown in the smoke plumes. The mean sum of PAHs detected in the sail PAH extract and PM 2.5 Filters were 80.1  $\mu\text{g/g}$  and 68.2  $\mu\text{g/g}$  of the particulate matter, respectively, accounting for less than 1% of the total particulate matter mass. At the PM collection rate from the fires of 0.088 g particulate matter/g C12, this resulted in an emission factor of 4.5 mg PAH/kg of oil burned. These results are much lower than would be expected by PAH content of the oil, indicating an overall destruction of PAHs.

Stout and Payne (2016) gathered 4 residue samples from the DeepWater Horizon burns both on the surface and sub-surface. They analysed the PAHs and other composition factors and concluded that the burns resulted in 89% destruction of PAHs.

## SUMMARY AND CONCLUSIONS

The data summarized in Table 2 show that for the most part PAHs are destroyed in fires. Further this analysis shows that there are slight differences between crude oil and diesel burns, in that crude oil burns appear to be slightly more efficient in terms of destroying PAHs. The analysis of the PAHs going to various compartments clearly shows that most PAHs are destroyed in the fire, with some remaining with the residue. Burn efficiency does not appear to change the PAH distribution to any extent.

The main points concerning PAHs in oil burns can be summarized as:

1. Some diesel burns ended up with minor production of higher molecular weight PAHs. This was not found to be significant in any of the crude oil burns. The concentration of the 16 EPA priority compounds is higher in the burn residue than the starting concentrations and the concentrations of the alkylated PAHs are lower in the residue than that of the starting oil.
2. Diesel burning is somewhat less efficient than crude oil burning in the destruction of PAHs and does result in more soot with its incumbent PAH load.
3. The amount of PAHs emitted as vapour is negligible.
4. The amount of PAHs on the soot is variable, however in most cases is negligible. The amount of priority PAHs on the soot maybe somewhat elevated.
5. Burn conditions vary and result in variable PAH destruction results.
6. PAH destruction is dependent on the total burn efficiency.

<b>Oil Type</b>	<b>Burn Type</b>	<b>Location</b>	<b>Year</b>	<b>Reference</b>	<b>% Burn Efficiency</b>	<b>Measured or estimated</b>	<b>Measurements</b>	<b>Overall PAH Destruction</b>
Alberta Medium	Field burn	Offshore	1993	Fingas et al. 1994a	99.9	meas.	soot, gas, residue	99.95
Alberta Medium	Field burn 1	Offshore	1993	Fingas et al. 1994a	99.9	meas.	residue	99.94
Alberta Medium	Field burn 1	Offshore	1993	Fingas et al. 1994a	99.9	meas.	residue	99.95
Alberta Medium	Field burn 2	Offshore	1993	Fingas et al. 1994a	99.9	meas.	residue	99.95
Alberta Medium	Field burn 2	Offshore	1993	Fingas et al. 1994a	99.9	meas.	residue	99.95
Alberta Medium	Field burn 2	Offshore	1993	Fingas et al. 1994a	99.9	meas.	residue	99.95
Diesel Fuel	Test burn 1	Meso tank	1992	Fingas et al. 1993	98	meas.	residue	99.85
Diesel Fuel	Test burn 2	Meso tank	1992	Fingas et al. 1993	98	meas.	residue	99.81
Diesel Fuel	Test burn 3	Meso tank	1992	Fingas et al. 1993	98	meas.	residue	99.78
Diesel Fuel	Test burn 4	Meso tank	1992	Fingas et al. 1993	98	meas.	residue	99.82
Diesel Fuel	Test burn 5	Meso tank	1992	Fingas et al. 1993	98	meas.	residue	99.87
Diesel fuel	Tank burn	Meso tank	1994	Wang et al., 1999a	99	meas.	soot, gas, residue	99.19
Diesel Fuel	Test burn 1	Meso tank	1994	Fingas et al., 1996	98	meas.	residue	99.21
Diesel Fuel	Test burn 2	Meso tank	1994	Fingas et al., 1996	98	meas.	residue	99.01
Diesel Fuel	Test burn 3	Meso tank	1994	Fingas et al., 1996	98	meas.	residue	98.86
Diesel fuel	Test burn 1	Meso tank	1997	Fingas et al., 1998	99	meas.	soot, gas, residue	99.25
Diesel Fuel	Test burn 2	Meso tank	1997	Fingas et al., 1998	99	meas.	soot, gas, residue	99.22
Diesel Fuel	Test burn 3	Meso tank	1997	Fingas et al., 1998	99	meas.	soot, gas, residue	99.02
Diesel Fuel	Test burn 4	Meso tank	1997	Fingas et al., 1998	99	meas.	soot, gas, residue	98.9
Diesel fuel	Tank burn	Meso tank	1998	Fingas et al., 2000	99	meas.	soot, gas, residue	99
Statfjord crude	Tank burn	Small Tank	1999	Garrett et al., 2000	85	meas.	residue	85 + 40%
Bunker C	Tank Burn 2	Small Tank	2003	Fingas et al., 2005	63.8	meas.	soot, residue	99.96
Test Oil -residual	Tank Burn 3	Small Tank	2003	Fingas et al., 2005	2	meas.	soot, residue	64.81
Test Oil -residual	Tank Burn 4	Small Tank	2003	Fingas et al., 2005	2	meas.	soot, residue	51.1
Orimulsion	Tank Burn 5	Small Tank	2003	Fingas et al., 2005	65.6	meas.	soot, residue	69.95
Orimulsion	Tank Burn 6	Small Tank	2003	Fingas et al., 2005	61.3	meas.	soot, residue	64.94
Bunker C	Tank Burn 7	Small Tank	2003	Fingas et al., 2005	65.9	meas.	soot, residue	98.8
Bunker C	Tank Burn 8	Small Tank	2003	Fingas et al., 2005	70	meas.	soot, residue	99.96
Bitumen	Tank Burn 9	Small Tank	2003	Fingas et al., 2005	12.3	meas.	soot, residue	87.60
Bitumen	Tank Burn 10	Small Tank	2003	Fingas et al., 2005	12.5	meas.	soot, residue	91.27
Diesel fuel	Test burn	Small Tank	2004	Lin et al., 2005			residue	99.40
Louisiana Crude	Test burn	Small Tank	2004	Lin et al., 2005			residue	98.90
Macondo	Field burn 1	offshore	2010	Shigenaka et al., 2014	98	est.	residue	99.26
Macondo	Field burn 2	offshore	2010	Shigenaka et al., 2014	98	est.	residue	97.77
Macondo	Field burn 3	offshore	2010	Shigenaka et al., 2014	98	est.	residue	99.73
Macondo	Field burn 4	offshore	2010	Shigenaka et al., 2014	98	est.	residue	99.2
Macondo	Field burn 5	offshore	2010	Shigenaka et al., 2014	98	est.	residue	99.25
Macondo	Field burn 6	offshore	2010	Shigenaka et al., 2014	98	est.	residue	99.61
Macondo	small 5 g	lab	2012	Shigenaka et al., 2014	98	est.	residue	99.8
South Louisiana	test 500 mL	lab	2012	Shigenaka et al., 2014	98	est.	residue	99.11
Weathered Lou	test 500 mL	lab	2012	Shigenaka et al., 2014	98	est.	residue	99.31
Emulsified Mac	test 500 mL	lab	2012	Shigenaka et al., 2014	80	est.	residue	93.07
Emulsified Mac	test 500 mL	lab	2012	Shigenaka et al., 2014	80	est.	residue	80.13
Macondo	Actual burn	offshore	2010	Garrett et al. 2016	large	est.	particulate matter	large
Macondo	Actual burn	offshore	2010	Stout and Payne, 2016	89	est.	residue	89

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