Electronic Supplementary Material (ESI) for Environmental Science: Advances.

Photochemical Formation of Water-Soluble OxyPAHs, Naphthenic Acids, and Other Hydrocarbon Oxidation Products from Cook Inlet, Alaska Crude Oil and Diesel in Seawater

Supporting Information for Publication

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LC-Orbitrap Instrument Parameters

SPE- DOC extracts were analyzed using a Vanquish Flex Binary ultra-high performance liquid chromatograph coupled to an Exploris 120 high resolution orbitrap mass spectrometer (Thermo Scientific). Samples were injected (20 µL) onto a Kinetix C18 column (150 x 2.1mm; 1.7µ) with a UHPLC C18 2.1 mm Security Guard Column (Phenomenex) and eluted at 0.4 mL min^{-1} using with a gradient of water (A) and acetonitrile (B) each containing 0.1% formic acid (v/v). The column was maintained at 60 °C while the mobile phase composition was ramped from 5 to 99% B over 15 min and held for 10 min before resetting to initial conditions; total run time was 32 min. Eluted compounds were ionized via negative mode electrospray ionization (3200V). The nitrogen sheath gas, auxiliary gas, and sweep gas flows were 50, 5, and 5 (arbitrary units), respectively. The vaporizer and ion transfer tube temperatures were 350 and 300 °C. Ionization parameters were optimized by infusing the calibration solution (FlexMix, Thermo Scientific) into 0.4 mL/min 50% A post column at 5 µL/min. Full scans were collected over the range 150-1500 *m/z* with a resolution of 120,000 and RF lens set to 70%. Automatic gain control was used to accumulate 1e6 ions in the trap allowing a maximum injection time of 200 ms. Orbitrap mass accuracy was externally calibrated prior to analysis via infusion of the calibration solution while a mass lock was established during each scan using the fluoranthene (M^-, 202.0788 *m/z*) internal calibrant discharge source (Easy-IC, Thermo Scientific). A standard solution containing 10 µg/mL each of metsulfuron methyl, chlorsulfuron, capsaicin, rotenone, usnic acid, and ibuprofen was analyzed after every ten samples for quality assurance.

Targeted oxyPAH and PAH Instrument Paramters

Oxy-PAHs and PAHs were analyzed separately using a 1260 Infinity series liquid chromatograph coupled to a 6410A triple quadrupole mass spectrometer controlled by Mass

Hunter v. B.06.00 (Agilent). 10 µL injections were made onto a Zorbax Eclipse PAH (2.1x100 mm; 3.5µm) column with matching guard cartridge (2.1x12.5 mm; 5µ) (Agilent) and eluted at 0.2 mL min^{-1} with a gradient of water (A) and methanol (B) each containing 0.1% formic acid, the column compartment was maintained at 40 °C. Gradient parameters for Oxy-PAHs and PAHs are available in the supporting information (**Table S8 and S9**). Oxy-PAHs were ionized via negative mode atmospheric pressure photoionization (APPI) assisted with post column addition of acetone (0.4 mL min^{-1} of 85:15 methanol:acetone v/v; final composition 10% acetone) dopant. PAHs were ionized via postive mode APPI assisted with post column addition of chlorobenzene and 2,4-difluoroanisole (0.4 mL min^{-1} of 84.25:15:0.75 methanol:chlorobenzene:2,4-difluoroanisole v/v; final composition 10% chlorobenzene and 0.5% 2,4-difluoroanisole) dopant. Analyte retention times and triple quadrupole acquisition parameters are available in the supporting information (**Table S10**).

Table S1. DOC and $SUVA_{254}$ values. (Averages N=3)

Sample Composition			DOC (mg/L)		$SUVA_{254}$ (L mg^{-1} cm^{-1})	
Fuel	**Light Type**	**Irradiation Period (days)**	**Average**	**Std. Dev.**	**Average**	**Std. Dev.**
CI Crude Oil	Light	1	4.22	2.764	0.0100	0.005
		4	10.61	2.028	0.0150	0.002
		7	18.84	4.931	0.0168	0.004
		10	20.54	2.319	0.0169	0.001
	Dark	1	0.84	0.067	0.0080	0.002
		4	1.59	0.408	0.0029	0.001
		7	1.67	0.158	0.0024	0.000
		10	1.47	0.291	0.0034	0.002
Diesel	Light	1	6.27	0.521	0.0108	0.001
		4	11.51	0.885	0.0139	0.001
		7	13.49	1.294	0.0137	0.003
		10	14.76	0.993	0.0128	0.000
	Dark	1	0.77	0.209	0.0056	0.002
		4	1.05	0.338	0.0058	0.005
		7	0.98	0.179	0.0045	0.001
		10	0.95	0.124	0.0046	0.000

Table S2. Spectral Indices (RSU). (Averages N=3)

Sample Composition			T		A		M		C		N		FluI		FrI		BIX		HIX	
Fuel	Light Type	Irradiation Period (days)	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
CI Crude Oil	Light	1	1.71	0.36	1.69	0.50	1.34	0.35	0.43	0.11	1.42	0.37	1.21	0.02	1.44	0.02	1.63	0.03	0.58	0.03
		4	2.84	0.19	4.07	0.25	3.22	0.18	1.27	0.56	3.35	0.18	1.22	0.01	1.31	0.02	1.43	0.03	0.68	0.00
		7	1.68	0.34	2.42	0.28	2.05	0.30	0.62	0.06	2.12	0.31	1.20	0.02	1.22	0.03	1.29	0.04	0.69	0.01
		10	1.16	0.28	1.50	0.30	1.33	0.29	0.42	0.10	1.39	0.29	1.18	0.01	1.15	0.04	1.21	0.05	0.66	0.01
	Dark	1	0.14	0.04	0.05	0.01	0.05	0.01	0.02	0.00	0.06	0.02	1.40	0.03	1.57	0.04	1.69	0.05	0.28	0.03
		4	0.24	0.15	0.07	0.02	0.09	0.04	0.02	0.01	0.10	0.05	1.45	0.06	1.62	0.19	1.76	0.17	0.29	0.07
		7	0.14	0.00	0.06	0.00	0.06	0.00	0.02	0.00	0.07	0.01	1.40	0.06	1.69	0.04	1.89	0.07	0.31	0.01
		10	0.13	0.02	0.07	0.01	0.06	0.01	0.02	0.00	0.06	0.01	1.35	0.04	1.69	0.05	1.91	0.13	0.35	0.04
Diesel	Light	1	4.99	0.22	0.66	0.07	1.40	0.07	0.26	0.03	1.43	0.08	1.19	0.02	1.35	0.04	1.37	0.03	0.36	0.02
		4	2.50	0.28	0.52	0.03	0.79	0.08	0.24	0.01	0.84	0.08	1.19	0.01	0.89	0.01	0.90	0.01	0.30	0.02
		7	1.30	0.16	0.34	0.07	0.47	0.08	0.17	0.03	0.49	0.09	1.19	0.02	0.82	0.05	0.82	0.04	0.24	0.05
		10	0.90	0.11	0.25	0.04	0.34	0.05	0.12	0.02	0.36	0.05	1.14	0.02	0.81	0.01	0.83	0.02	0.20	0.01
	Dark	1	0.08	0.02	0.06	0.04	0.03	0.01	0.02	0.01	0.03	0.01	1.48	0.07	1.34	0.35	1.48	0.35	0.30	0.03
		4	0.08	0.02	0.04	0.02	0.02	0.01	0.01	0.00	0.03	0.01	1.35	0.06	1.39	0.20	1.58	0.25	0.24	0.07
		7	0.09	0.02	0.04	0.02	0.03	0.01	0.01	0.00	0.03	0.01	1.41	0.06	1.56	0.16	1.72	0.09	0.23	0.06
		10	0.04	0.04	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01	1.40	0.08	1.14	0.36	1.28	0.29	0.34	0.11

Table S3. Relative contribution of PARAFAC components (%). (Averages N=3)

Sample Composition			C1		C2		C3		C4		C5		C6	
Fuel	Light Type	Irradiation Period (days)	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
CI Crude Oil	Light	1	42.03	0.89	23.03	1.18	5.03	0.38	16.87	1.27	9.52	0.36	3.52	0.53
		4	48.15	0.16	25.29	0.75	4.51	0.10	9.77	0.22	9.95	0.77	2.33	0.17
		7	49.32	0.49	23.31	0.39	5.10	0.33	7.70	1.12	10.52	0.83	4.06	0.23
		10	48.38	0.46	20.19	0.71	6.85	0.37	6.90	0.27	11.02	0.64	6.66	0.19
	Dark	1	19.56	1.93	10.28	1.98	36.25	6.85	18.68	2.19	6.22	0.45	9.01	9.06
		4	19.36	2.64	10.37	4.20	28.29	7.88	20.16	1.72	5.81	0.83	16.02	14.64
		7	21.62	1.39	12.98	1.24	29.90	5.01	18.48	2.98	5.73	0.71	11.29	7.33
		10	27.03	5.11	11.93	1.57	24.52	1.74	14.25	3.44	6.91	1.06	15.36	2.92
Diesel	Light	1	17.30	0.41	1.42	0.06	33.83	1.06	39.44	1.01	6.29	0.38	1.72	0.23
		4	14.97	0.68	1.28	0.11	52.96	1.68	15.20	0.48	5.45	0.44	10.13	0.30
		7	13.50	3.23	1.61	0.53	56.35	5.15	7.60	2.55	5.06	1.02	15.86	2.17
		10	11.01	1.03	1.64	0.20	58.86	1.84	3.39	0.71	4.15	0.39	20.96	0.95
	Dark	1	22.60	4.31	4.51	0.14	40.36	1.98	6.67	1.76	9.46	2.49	16.40	1.81
		4	18.17	4.66	5.11	0.53	36.06	4.35	9.66	2.24	8.00	1.56	23.00	4.94
		7	19.28	8.19	5.34	0.97	33.78	5.47	12.64	6.74	7.26	1.00	21.71	4.19
		10	19.45	4.92	1.72	2.98	48.72	9.66	10.37	3.70	8.68	2.42	11.07	11.06

Figure S1. Validated six-component PARAFAC model.

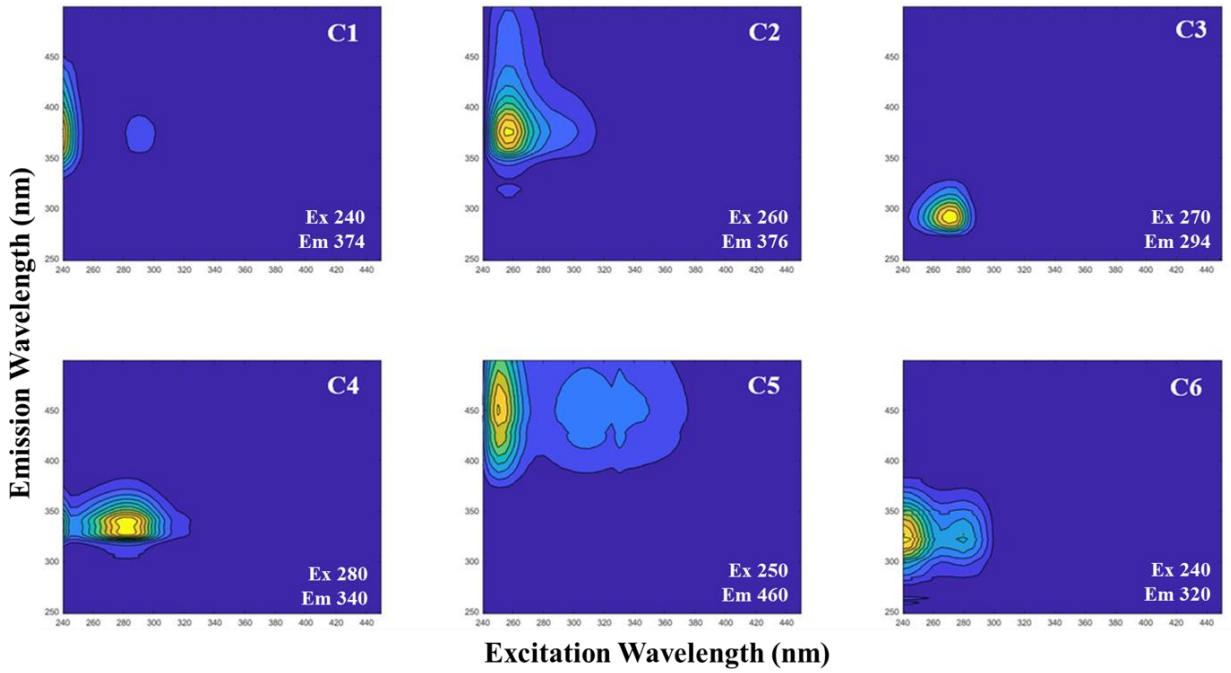

Table S4. Molecular classification (%), averages masses, and NOSC. (Averages N=3)

Sample Composition			CA		Aromatic		ULO		UHO		Aliphatic		Naphthenic Acids		NOSC		Average Mass	
Fuel	Light Type	Irradiation Period (days)	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
CI Crude Oil	Light	4	4.89	0.17	11.32	0.37	46.63	3.95	6.65	0.35	28.72	3.99	1.79	0.17	-0.75	0.06	395.26	8.96
		7	4.31	0.82	10.79	0.92	47.23	2.05	6.90	0.87	28.83	1.98	1.93	0.38	-0.78	0.06	407.46	23.00
		10	4.23	0.70	10.60	0.70	46.47	1.79	8.81	0.77	28.10	1.33	1.78	0.35	-0.72	0.04	426.22	10.97
	Dark	10	2.93	0.10	6.03	0.91	30.11	0.94	19.18	1.48	39.80	0.75	1.95	0.10	-0.66	0.07	329.85	3.95
Diesel	Light	4	3.07	0.30	9.46	0.96	46.73	1.22	7.00	1.04	31.77	3.30	1.96	0.10	-0.71	0.04	403.07	6.68
		7	2.98	0.86	8.80	1.24	48.53	0.61	6.63	0.97	31.18	2.74	1.88	0.16	-0.72	0.00	413.17	20.49
		10	2.56	0.13	8.15	0.08	48.61	2.05	7.06	0.24	31.68	1.98	1.93	0.16	-0.73	0.01	436.11	9.35
	Dark	10	2.46	0.22	4.38	0.34	24.17	0.43	21.21	2.03	46.11	1.81	1.66	0.13	-0.63	0.07	341.66	7.96

Table S5. Molecular classifications of unique features in each treatment group. (Averages N=3)

Sample Composition			Unique Features (#)	CA (%)		Aromatic (%)		ULO (%)		UHO (%)		Aliphatic (%)	
Fuel	Light Type	Irradiation Period (days)		Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
CI Crude Oil	Light	4	2483	3.63	0.47	15.94	2.17	54.31	4.37	1.33	0.33	24.73	7.24
		7	2492	3.08	0.76	11.90	4.30	48.01	15.10	1.75	0.40	35.26	20.38
		10	2484	3.25	0.29	12.22	0.41	52.77	5.58	3.54	0.88	28.25	5.90
	Dark	10	1010	3.08	0.95	7.94	3.13	15.17	1.83	16.33	7.13	57.48	6.34
Diesel	Light	4	1986	1.12	0.21	12.94	1.70	65.14	4.95	1.57	0.46	19.21	6.24
		7	2090	0.97	0.66	10.39	0.76	60.93	13.81	1.86	0.42	25.94	12.64
		10	2293	0.67	0.05	9.93	0.49	64.69	4.07	2.42	0.17	22.33	4.81
	Dark	10	1722	2.07	0.15	2.82	1.00	16.30	1.55	26.85	5.48	51.96	4.69

Figure S2. Compositional contour plot representing relationship between carbon number, z family, and relative abundance (within naphthenic acid classification).

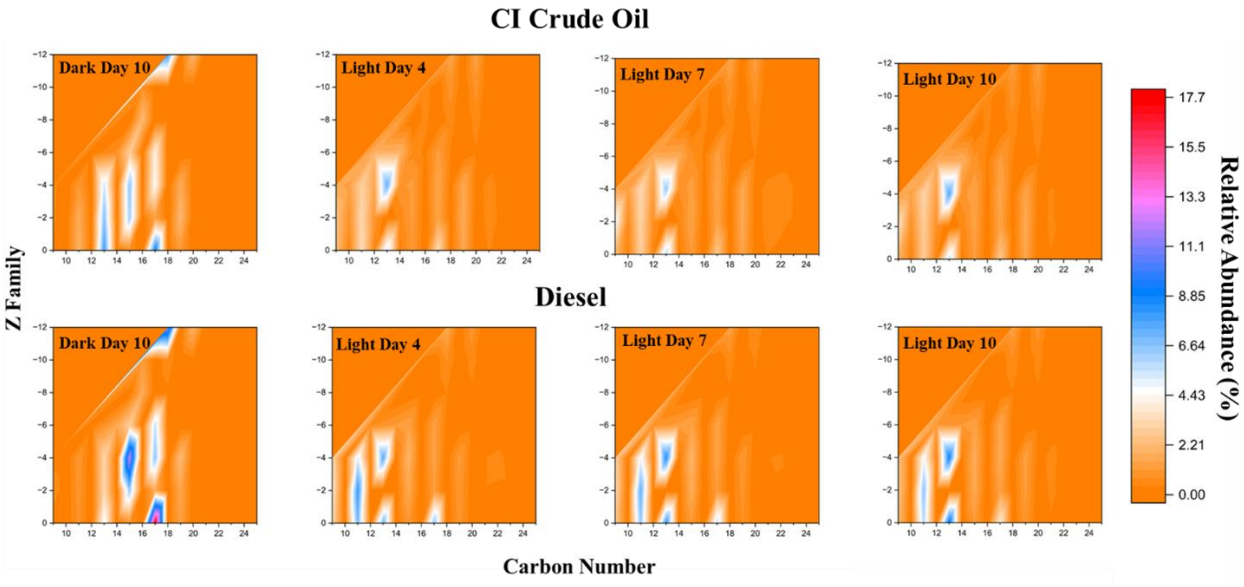

Table S6. oxyPAH and PAH concentration (µg/L). (Averages N=3) ND = Not Detected

Sample Composition			Oxy-PAH				PAH																			
			Phenanthrequinone		1,4-Anthraquinone		Naphthalene		1-Methylnaphthalene		2-Methylnaphthalene		Acenaphthene		Fluorene		Phenanthrene		2,6-Dimethylnaphthalene		Anthracene		2,3,6-Trimethylnaphthalene		Pyrene		1-Methylpyrene	
Fuel	Light Type	Irradiation Period (days)	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
CI Crude Oil	Light	1	ND	–	ND	–	2.42	2.28	17.12	4.76	16.14	4.58	ND	–	0.80	0.03	1.50	0.09	0.70	0.24	0.10	0.18	0.31	0.15	0.08	0.01	0.28	0.04
		4	ND	–	0.14	0.12	0.36	0.32	7.39	4.86	6.74	4.57	ND	–	0.45	0.09	1.73	0.14	0.54	0.29	0.00	0.00	0.09	0.15	0.08	0.02	0.25	0.00
		7	0.11	0.10	0.21	0.01	ND	–	1.07	0.51	1.24	0.33	ND	–	0.18	0.16	1.41	0.03	ND	–	0.23	0.40	ND	–	0.11	0.05	0.23	0.02
		10	0.13	0.11	0.19	0.16	ND	–	0.33	0.33	0.61	0.22	ND	–	0.97	0.04	1.02	0.31	ND	–	0.00	0.00	ND	–	ND	–	ND	–
Diesel	Light	1	ND	–	ND	–	15.49	19.01	60.44	62.49	125.15	136.23	1.96	1.26	1.56	0.97	0.75	0.41	15.17	11.73	ND	–	12.70	6.86	0.07	0.07	ND	–
		4	ND	–	ND	–	8.58	0.97	0.18	0.16	0.70	0.12	0.06	0.11	0.54	0.27	0.31	0.18	0.50	0.31	ND	–	0.91	0.62	0.04	0.06	0.08	0.13
		7	ND	–	ND	–	28.62	44.45	0.14	0.23	0.40	0.10	ND	–	ND	–	0.09	0.08	ND	–	ND	–	ND	–	ND	–	0.06	0.11
		10	ND	–	ND	–	4.17	1.56	0.09	0.16	0.33	0.04	ND	–	ND	–	0.00	0.00	ND	–	ND	–	ND	–	0.04	0.07	0.00	0.00

Table S7. Retention time, recoveries, and instrument parameters for oxyPAH method.

Name	Transition	Type	RT (min)	Recovery (%) (N=6)	
				Average	Std. Dev.
1-Naphthol	143.1 -> 115.1	Target	19.8	73.8	12.4
2-Naphthol	143.1 -> 115.1	Target	20.6	72.5	12.2
Phenanthrenequinone	208.1 -> 208.1	Target	22.3	69.3	13.6
Anthraquinone	208.1 -> 208.1	Target	26.9	24.8	7.7
1,4-Anthraquinone	208.1 -> 208.1	Target	30.4	79.5	13.7
1-Hydroxy-9,10-Anthraquinone	224.1 -> 224.1	Target	35.6	79.2	14.9
1,4-Chrysenequinone	258.1 -> 258.1	Target	46.0	5.8	1.8
5,12-Naphthacenequinone	258.1 -> 258.1	Target	47.4	88.4	15.2
Benzanthraquinone	258.1 -> 258.1	Target	50.8	81.9	16.5

Table S8. oxyPAH gradient parameters.

Pump 1 (Column Mobile Phase)					Pump 2 (Post Column Ionization Additives)				
Time (min)	A (%)	B (%)	Flow (mL/min)	Max Pressure Limit (bar)	Time (min)	A (%)	B (%)	Flow (mL/min)	Max Pressure Limit (bar)
0.00	20.0	80.0	0.200	400.00	**0.00**	100.0	0.0	0.000	400.00
1.00	20.0	80.0	0.200	400.00	**18.99**	100.0	0.0	0.000	400.00
20.00	60.0	40.0	0.200	400.00	**19.00**	100.0	0.0	0.400	400.00
33.00	71.0	29.0	0.200	400.00	**59.99**	100.0	0.0	0.400	400.00
36.00	75.0	25.0	0.200	400.00	**60.00**	100.0	0.0	0.000	400.00
46.00	75.0	25.0	0.200	400.00					
56.00	90.0	10.0	0.200	400.00					
60.00	90.0	10.0	0.200	400.00					
60.01	20.0	80.0	0.400	400.00					
65.00	20.0	80.0	0.400	400.00					
65.01	20.0	80.0	0.200	400.00					

Table S9. PAH gradient parameters.

Pump 1 (Column Mobile Phase)					Pump 2 (Post Column Ionization Additives)				
Time (min)	**A (%)**	**B (%)**	**Flow (mL/min)**	**Max Pressure Limit (bar)**	**Time (min)**	**A (%)**	**B (%)**	**Flow (mL/min)**	**Max Pressure Limit (bar)**
0.00	40.0	60.0	0.200	400.00	**0.00**	0.0	100.0	0.000	400.00
1.00	40.0	60.0	0.200	400.00	**9.99**	0.0	100.0	0.000	400.00
5.00	60.0	40.0	0.200	400.00	**10.00**	0.0	100.0	0.400	400.00
65.00	100.0	0.0	0.200	400.00	**70.00**	0.0	100.0	0.400	400.00
70.00	100.0	0.0	0.200	400.00	**70.10**	0.0	100.0	0.400	400.00
70.10	40.0	60.0	0.400	400.00					

Table S10. Retention time and instrument parameters for PAH method.

Compound Name	Transition	Type	ISTD Compound Name	Surrogate Compound Name	RT (min)	Recovery (%) (N=6)	
						Average	Std. Dev.
Naphthalene d8	136.0 -> 108.0	Surrogate	Acenapthylene d8		15.8		
Naphthalene	128.0 -> 102.0	Target	Acenapthylene d8	Napthalene d8	16.2		
Acenapthylene d8	160.0 -> 132.0	ISTD			18.0		
Acenaphthylene	152.0 -> 126.0	Target	Acenapthylene d8	Napthalene d8	18.5		
1-Methyl Naphthalene d10	152.0 -> 122.0	ISTD			19.9		
1-Methyl Naphthalene	142.0 -> 115.0	Target	1-Methyl Naphthalene d10	Acenapthene d10	20.5	96.3	7.8
2-Methyl Naphthalene	142.0 -> 115.0	Target	1-Methyl Naphthalene d10	Acenapthene d10	21.2	125.4	26.0
Acenaphthene d10	164.0 -> 162.0	Surrogate	1-Methyl Naphthalene d10		22.1		
Acenaphthene	154.0 -> 153.0	Target	1-Methyl Naphthalene d10	Acenapthene d10	22.7	100.5	5.0
Fluorene d10	176.0 -> 174.0	ISTD			24.0		
Fluorene	166.0 -> 165.0	Target	Fluorene d10	Phenanthrene d10	24.6	95.8	4.8
Phenanthrene d10	188.0 -> 184.0	Surrogate	Fluorene d10		26.0		
9-methyl-9H-fluorene	180.1 -> 165.2	Target	Fluorene d10	Phenanthrene d10	26.6	89.7	6.9
Phenanthrene	178.0 -> 176.0	Target	Fluorene d10	Phenanthrene d10	27.0	97.3	14.9
2,6-Dimethylnaphthalene	156.0 -> 115.0	Target	Fluorene d10	Phenanthrene d10	28.2		
Anthracene	178.0 -> 176.0	Target	Fluorene d10	Phenanthrene d10	30.0	94.2	5.3
Fluoranthene	202.0 -> 200.0	Target	Chrysene d12	Pyrene d10	33.1		
2,3,6-Trimethylnaphthalene	170.2 -> 155.1	Target	Chrysene d12	Pyrene d10	33.4		
Pyrene d10	212.0 -> 208.0	Surrogate	Chrysene d12		33.9		
9-methylanthracene	192.2 -> 191.1	Target	Chrysene d12	Pyrene d10	34.2	89.8	3.3
Pyrene	202.0 -> 200.0	Target	Chrysene d12	Pyrene d10	34.9	115.7	10.5
9,10-Dimethylanthracene	206.2 -> 191.1	Target	Chrysene d12	Benz(a)anthracene d10	38.8		
1-Methylpyrene	216.2 -> 215.2	Target	Chrysene d12	Benz(a)anthracene d10	42.3		
Benz(a)anthracene d10	240.0 -> 236.0	Surrogate	Chrysene d12		43.3		
Benz(a)anthracene	228.0 -> 226.0	Target	Chrysene d12	Benz(a)anthracene d10	44.5	95.5	5.0
Chrysene d12	240.0 -> 236.0	ISTD			44.9		
Chrysene	228.0 -> 226.0	Target	Chrysene d12	Benz(a)anthracene d10	46.3	99.3	6.0
Perylene d12	264.0 -> 260.0	Surrogate	Chrysene d12		50.1		
Benzo(a)pyrene	252.0 -> 250.0	Target	Benzo(a)pyrene d12	Perylene d12	52.0		
Benzo(a)pyrene d12	264.0 -> 260.0	ISTD			55.1		
Benzo(b)fluoranthene	252.0 -> 250.0	Target	Benzo(a)pyrene d12	Perylene d12	56.3	96.2	3.0
Benzo(k)fluoranthene	252.0 -> 250.0	Target	Benzo(a)pyrene d12	Perylene d12	56.4	96.7	4.6
Benzo(ghi)perylene	276.0 -> 274.0	Target	Benzo(a)pyrene d12	Perylene d12	61.3	93.7	5.8
Dibenzo(ah)anthracene	278.0 -> 276.0	Target	Benzo(a)pyrene d12	Perylene d12	64.0	96.1	7.9
Indenopyrene	276.0 -> 274.0	Target	Benzo(a)pyrene d12	Perylene d12	64.2	96.2	7.0

1