Trace Analysis of Semivolatile Compounds in Marine Sediment Using the Agilent 7000 Triple Quadrupole GC/MS

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Background

Each year, the Corps of Engineers' Portland District (CENWP) dredges 3 to 5 million cubic yards of sediment at the mouth of the Columbia River (MCR) to maintain the 6-mile long, deep-draft, navigation entrance channel. The MCR dredged material is placed at two US Environmental Protection Agency (EPA) designated Ocean Dredged Material Disposal Site (ODMDS) locations. Management of dredged material and ODMDS is a shared responsibility of the EPA and the US Army Corps of Engineers (USACE) under the Clean Water Act (CWA) and the Marine Protection, Research, and Sanctuaries Act (MPRSA).

Columbia River

The ODMDS projects have been supported at the Region 10 Lab since 2009. The first semivolatile (SV) method, which used GC-MS, was challenged to meet all reporting limit requirements. This was improved in 2013 with new GC/MS-SIM method, and further improved in 2014 with this GC/MS/MS method, which now has additional sensitivity and improved robustness.

Typically a lower quantitation limit is achieved by increasing the amount extracted then concentrating that extract. For marine sediments, increasing the extraction amount also increases the interferences and cleanup requirements. The EPA Region 10 has developed an efficient GC/MS/MS method for the analysis of 37 SV compounds in marine sediment. This method requires no cleanup or sample concentration and met the project reporting requirements of 10 ug/kg for most compounds.

Extraction Procedure

- Add 10-12 g sediment to a clear 40-mL VOA vial
- Add 1-2 g of Hydromatrix® to the sample and shake. If the sample has high moisture content, additional Hydromatrix® may be necessary to obtain a flowable mixture – see Figure 1
- Add surrogate
- Add 10 mL dichloromethane and 10 mL acetone to each sample
- Place samples in sonic bath for 30 minutes.
- Store samples for 12 or more hours then sonicate a second time for an additional 30 minutes
- Centrifuge samples at 1600 rpm for 15 minutes
- Transfer 5 mL sample extract into a centrifuge tube and solvent exchange to dichloromethane
- Transfer 1 mL sample extract into autosampler vial and spike with internal standard

Figure 1

Instrumentation

GC Conditions

Analytical Column	J&W DB-5MS, 30m x 0.25m x0.25µm
Column Flow	1.2 mL/min constant
Initial Temperature	50 hold 0.7 min
Rate 1	20 °C/min
Final Temperature	320 °C hold 3 min
Total Time	17.45 min

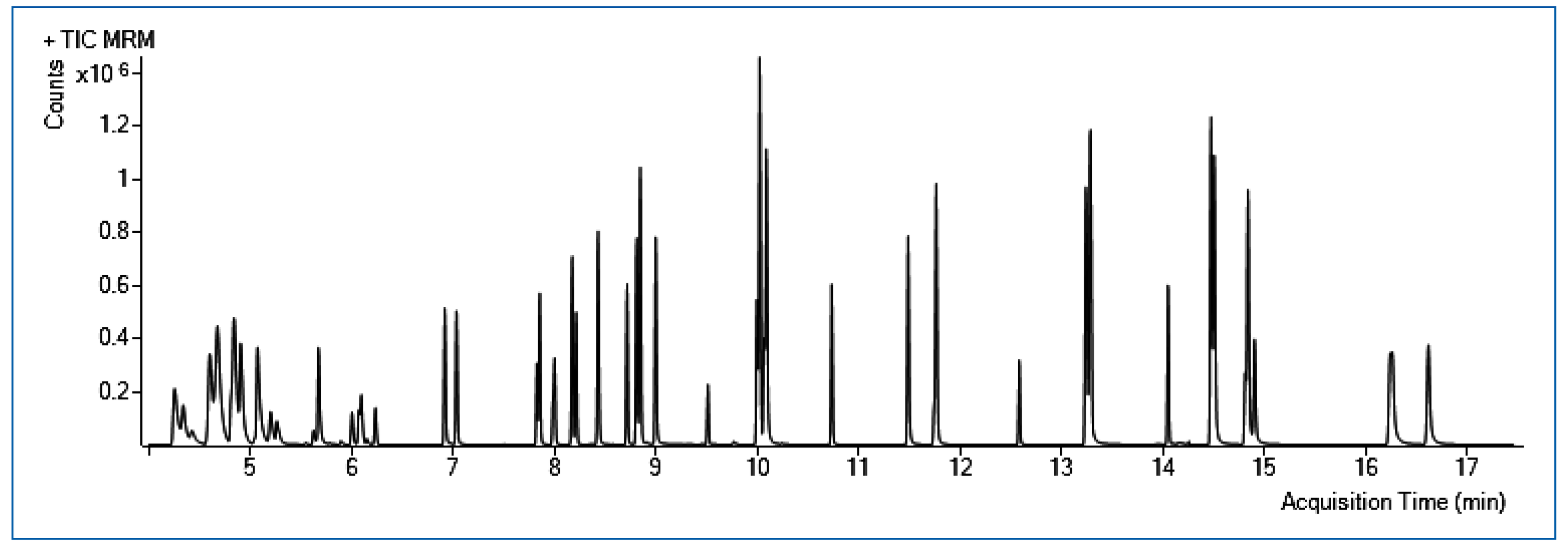
Injection Temp	280 °C
Liner	Single Taper Gooseneck w/Wool 4 mm x 6.5 mm x 78.5 mm
Injection Volume	1 µL (dichloromethane)
Injection Type	Pulsed Splitless
Pulse Pressure	30 psi (1 min)

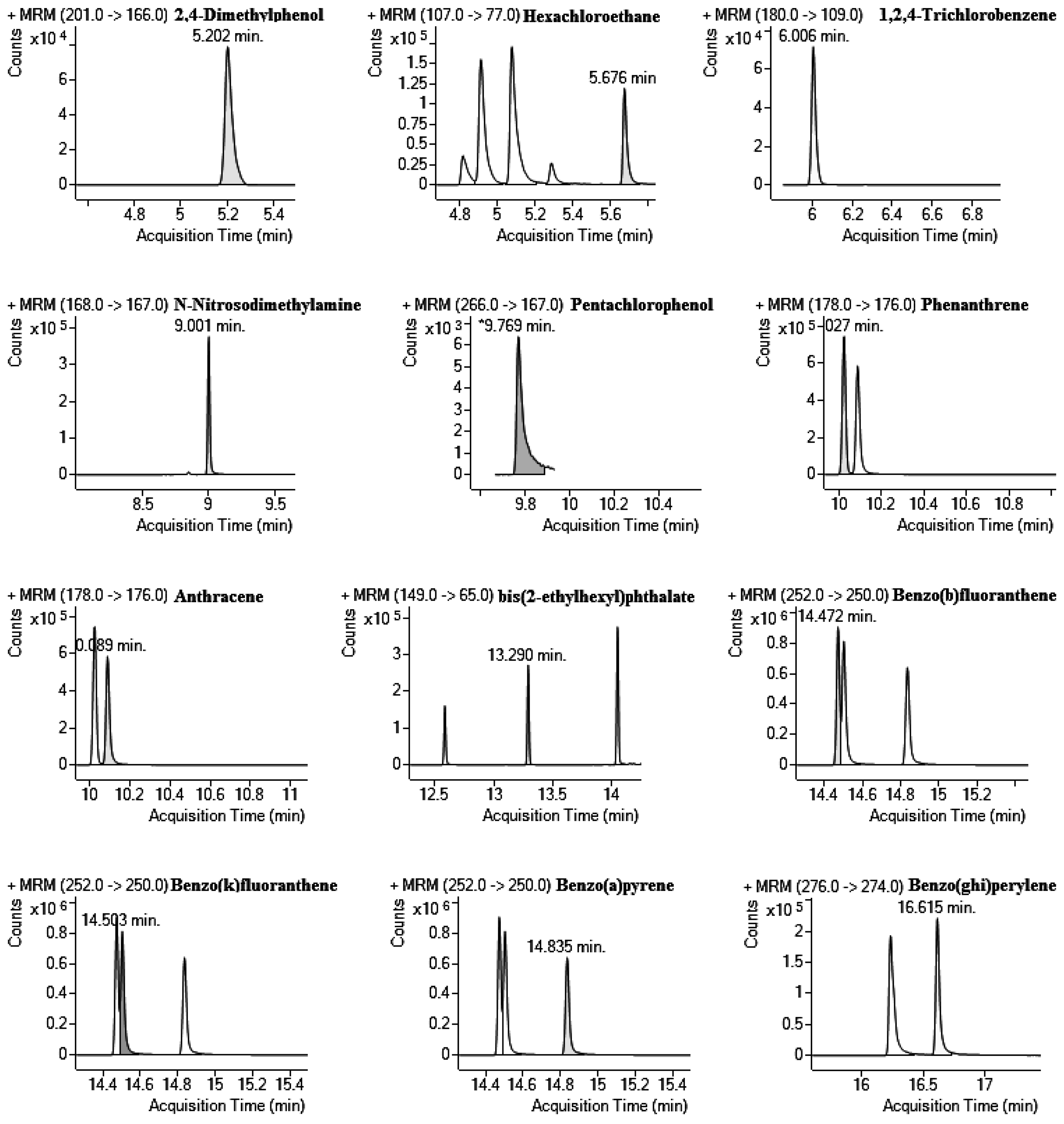
MS/MS Conditions

Source Temperature	350°C
Ionization	EI

Time Segments	min, Dwell
Window 1	4.00, 35
Window 2	4.55, 10
Window 3	5.50, 40
Window 4	5.85, 20
Window 5	7.40, 15
Window 6	8.65, 20
Window 7	9.66, 50
Window 8	9.93, 25
Window 9	11.10, 40
Window 10	12.10, 15
Window 11	14.26, 25
Window 12	15.50, 30

Example Chromatograms, 100 pg/uL

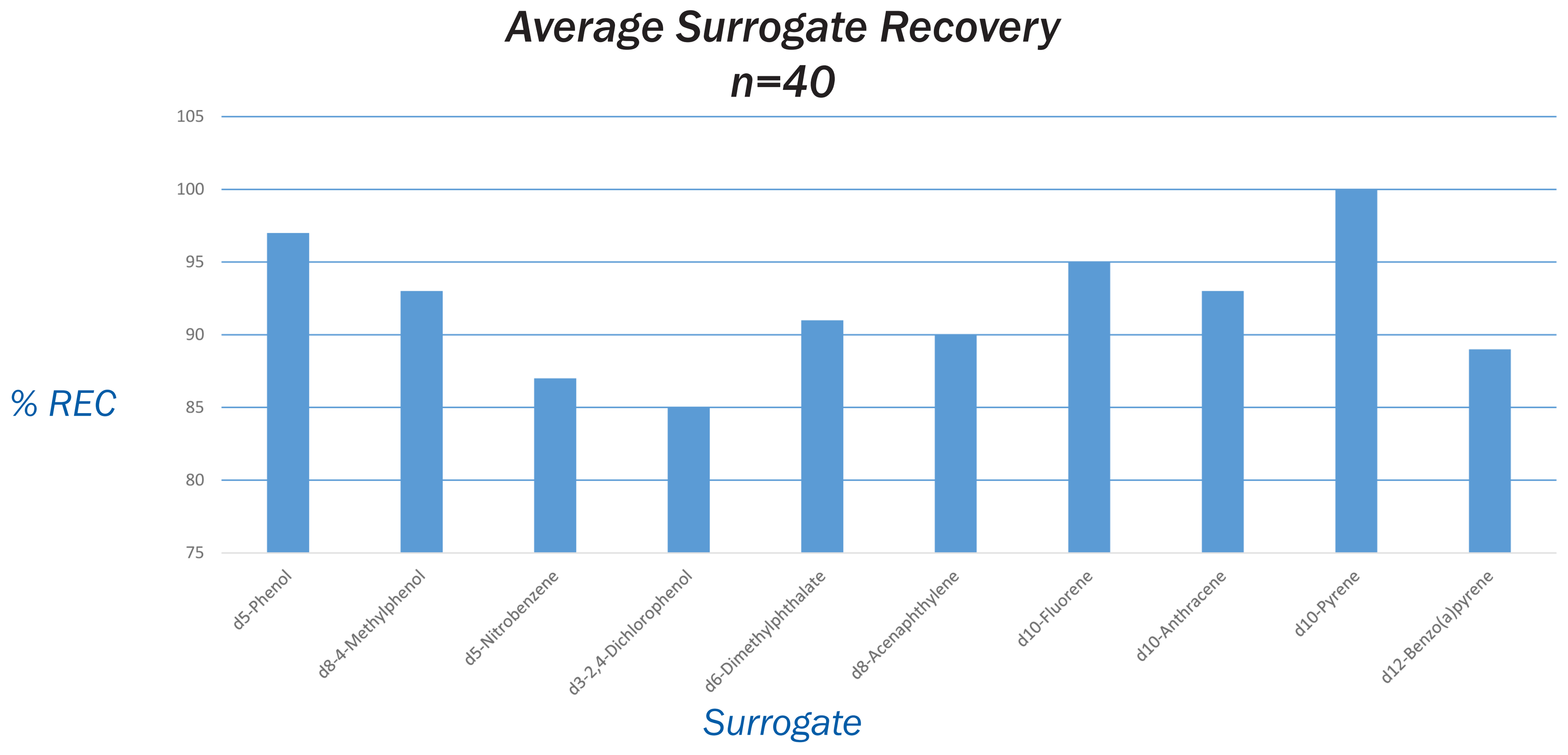




Detection Limits Compared to Reporting Levels

Name	RT (min)	CAS #	Transition Quant. Ion	MDL (ug/kg)	RL (ug/kg)	PRQL (ug/kg)	Matrix Spikes n=4	
							Avg %REC	%RSD
Phenol	4.27	108-95-2	94.0 -> 66.0	0.92	4.9	20	98	6.50
1,4-Dichlorobenzene	4.68	106-46-7	146.0 -> 75.0	0.68	2.5	20	94	3.61
1,2-Dichlorobenzene	4.84	95-50-1	146.0 -> 75.0	0.87	12	20	93	5.45
Benzyl Alcohol	4.82	100-51-6	108.0 -> 79.0	0.69	2.5	50	120	3.46
2-Methylphenol	4.91	95-48-7	108.0 -> 79.0	1.97	2.5	20	96	4.67
4-Methylphenol	5.08	106-44-5	108.0 -> 107.0	0.37	2.5	20	107	3.97
Hexachloroethane	5.20	67-72-1	201.0 -> 166.0	0.47	2.5	20	89	2.87
2,4-Dimethylphenol	5.68	105-67-9	107.0 -> 77.0	0.62	2.5	20	103	5.35
1,2,4-Trichlorobenzene	6.01	120-82-1	180.0 -> 109.0	0.66	2.5	20	92	2.91
Naphthalene	6.10	91-20-3	128.0 -> 102.0	0.62	2.5	20	91	2.30
Hexachlorobutadiene	6.24	87-68-3	225.0 -> 190.0	0.59	2.5	20	87	3.09
2-Methylnaphthalene	6.92	91-57-6	141.0 -> 115.0	0.58	2.5	20	98	2.40
Acenaphthylene	8.01	208-96-8	152.0 -> 151.0	0.55	4.9	20	93	2.75
Acenaphthene	8.22	83-32-9	154.0 -> 152.0	0.54	4.9	20	94	2.65
Dibenzofuran	8.43	132-64-9	168.0 -> 139.0	0.45	2.5	20	99	2.92
Dimethylphthalate	7.86	131-11-3	163.0 -> 77.0	0.56	2.5	20	99	2.74
Diethylphthalate	8.72	84-66-2	149.0 -> 65.0	1.87	12	20	116	2.82
Fluorene	8.85	86-73-7	166.0 -> 165.0	0.54	2.5	20	100	3.19
n-Nitrosodiphenylamine	9.00	86-30-6	168.0 -> 167.0	0.89	4.9	20	99	3.14
Hexachlorobenzene	9.51	118-74-1	284.0 -> 214.0	0.46	2.5	20	92	2.43
Pentachlorophenol	9.77	87-86-5	266.0 -> 167.0	1.99	25	100	103	8.92
Phenanthrene	10.03	85-01-8	178.0 -> 176.0	0.43	2.5	20	97	2.29
Anthracene	10.09	120-12-7	178.0 -> 176.0	0.37	2.5	20	104	2.71
di-n-Butylphthalate	10.74	84-74-2	149.0 -> 65.0	1.96	12	20	140	1.75
Fluoranthene	11.49	206-44-0	202.0 -> 201.0	0.44	2.5	20	110	2.08
Pyrene	11.77	129-00-0	202.0 -> 201.0	0.64	2.5	20	95	3.34
Butylbenzylphthalate	12.59	85-68-7	149.0 -> 65.0	0.73	4.9	20	147	2.68
Benzo(a)anthracene	13.24	56-55-3	228.0 -> 226.0	0.31	4.9	20	110	2.24
Chrysene	13.28	218-01-9	228.0 -> 226.0	0.51	2.5	20	87	2.04
bis(2-ethylhexyl)phthalate	13.29	117-81-7	149.0 -> 65.0	1.94	4.9	100	122	2.86
di-n-Octylphthalate	14.05	117-84-0	149.0 -> 65.0	0.29	4.9	20	118	3.19
Benzo(b)fluoranthene	14.48	205-99-2	252.0 -> 250.0	0.38	4.9	20	103	1.60
Benzo(k)fluoranthene	14.51	207-08-9	252.0 -> 250.0	0.55	2.5	20	94	1.25
Benzo(a)pyrene	14.84	50-32-8	252.0 -> 250.0	0.31	4.9	20	94	1.88
Indeno(1,2,3-cd)pyrene	16.24	193-39-5	276.0 -> 274.0	0.47	4.9	20	114	2.23
Dibenz(ah)anthracene	16.26	53-70-3	278.0 -> 276.0	0.55	12	20	118	2.33
Benzo(ghi)perylene	16.62	191-24-2	276.0 -> 274.0	0.57	2.5	20	109	1.78

MDL-Method Detection Level based on 10g sample 100% Solids
PRQL-Project Required Quantitation Limits
RL-Reporting Limits based on 10g sample and 75% Solids



- Average surrogate recovery calculated from all 36 samples and 4 matrix spikes
- All surrogates ranged from 71 - 110% recovery