Separation of Thia-arenes and Aza-arenes from Polycyclic Aromatics in Snowpack

Samples from the Athabasca Oil Sands Region by GC×GC/ToF-MS

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Supporting Information

Snowpack sample collection and processing	S2
Table S1:	S4
Table S2	S5
Table S3:	S6
Table S4:	S7
Table S5:	S8
Figure S1:.....	S9
Figure S2:.....	S10
Figure S3:.....	S11
Figure S4:.....	S12

Snowpack sample collection and processing

Snowpack samples were collected between late February and early March 2012 at varying distances from the major industrial developments in the Regional Municipality of Wood Buffalo in northern Alberta, Canada. Sampling sites were accessed by helicopter, and snow samples were collected at 50-100 m upwind of landing sites. Composited snowpack profiles were collected into pre-cleaned high density polypropylene buckets using clean techniques and a 10 cm in diameter custom-made stainless steel corer and stainless steel spatulas. All samples were kept frozen until processing at the Environment and Climate Change Canada Centre for Inland Waters (CCIW) facilities in Burlington, ON. Snow buckets were thawed for 2 to 3 days and processed in a clean room (high-efficiency particulate air –HEPA- and carbon filtered air). Melted snow (4-5 L per sample) was filtered by pumping through a 0.7 µm pore size GF/F filter, with 142 mm in diameter and pre-fired at 400 °C, connected to a 30 cm Teflon column (2 cm i.d.) packed with 50 g of pre-cleaned XAD-2 resin. Filters were extracted with a 1:1 hexane-acetone mixture followed by 100% dichloromethane (DCM) using accelerated solvent extraction (ASE), after being packed in a 33 mL extraction cell between two layers of 2.5 g of Hydromatrix (diatomaceous earth sorbent). The methods for extracting GF/F filters on the ASE are as follows (each method was run once for each ASE cell):

Method 1:

Preheat	1 min	Pressure	1500 psi
Heat	5 min	Temp	100 °C
Static	5 min	Solvent A	50% Hexane
Flush	75% of volume	Solvent B	50% Acetone
Purge	60 sec		
Cycles	1		

Method 2:

Preheat	1 min	Pressure	1500 psi
Heat	5 min	Temp	100 °C
Static	5 min	Solvent	100% DCM

Flush	75% of volume
Purge	60 sec
Cycles	1

XAD resin was transferred to an elution column and extracted with 100 mL of acetone at a flow rate of ~10 mL/min, followed by 200 mL of DCM at a flow rate of ~3-5 mL/min. The DCM eluent and ASE extract were back-extracted using 200 mL of a 3% sodium chloride solution and dried using pre-fired sodium sulfate. The combined and concentrated extracts (using TurboVap) were sent for analysis at the Air Quality Research Division (AQRD) Environment and Climate Change Canada laboratory in Ottawa, Ontario, where they were fractionated on silica gel solid phase columns with hexane followed by benzene, following AQRD protocol 3.03/5.1/M (Environment and Climate Change Canada, 2013). The AQRD laboratory in Ottawa maintains third-party accreditation to ISO 17025:2005 international standard's requirements. Polycyclic aromatic hydrocarbons analysis in atmospheric samples is part of the portfolio of air-related accredited methods carried out in this laboratory. The benzene fraction (F2) was analyzed by GC×GC/ToF-MS. Sampling sites designated as AR6 (57.018 N; -111.485 W) and AMS5 (56.969 N; -111.482 W), located near the major developments, were used in this study.

Table S1: LC-50×NSP-35 average and percent relative standard deviation (RSD) for first dimension retention indexes (RIs), first dimension retention time (¹t_R), second dimension retention times (²t_R), total peak area (the sum of the three highest modulated peaks), peak height of the highest modulated peak, and full width at half height (FWHH) of the highest modulated peak, for a standard solution containing 45 PACs at 50 pg µL⁻¹ (n=8).

Name	RI		¹ t _R		² t _R		*Total Peak Area		**Peak Height		**FWHH	
	average	RSD (%)	average (s)	RSD (%)	average (s)	RSD (%)	average	RSD (%)	average	RSD (%)	average	RSD (%)
IND	146.5	1.26	276.0	0.77	0.84	0.99	60540.7	2.46	8210.8	0.90	0.038	24.7
2,6-metNAP	145.5	0.96	274.7	0.59	1.03	1.03	9413.6	0.96	1107.2	1.41	0.041	0.81
2,7-metNAP	145.5	0.96	274.7	0.59	1.03	1.03	9413.6	0.96	1107.2	1.41	0.041	0.81
ACY	145.0	0.01	274.0	0.00	1.11	0.98	198378.0	0.41	24502.0	1.01	0.040	1.19
ACE	145.0	0.01	274.0	0.00	1.18	0.92	104840.0	4.57	11995.3	1.22	0.041	0.37
2,3-metNAP	148.3	1.47	278.0	0.91	0.94	1.14	2741.5	15.7	413.3	5.94	0.029	3.16
1,5-metNAP	148.3	1.47	278.0	0.91	0.94	1.14	2741.5	15.7	413.3	5.94	0.029	3.16
FL	202.6	0.78	341.0	0.54	1.08	1.47	171941.3	2.64	25257.3	2.27	0.031	0.06
1-metFL	244.8	0.00	390.0	0.00	1.20	0.92	80643.7	2.94	10531.7	4.19	0.035	1.83
DBT	278.8	0.46	429.4	0.35	1.34	0.73	1185.1	11.8	146.0	6.26	0.038	11.3
PH	300.3	0.05	458.0	0.47	1.38	0.94	94363.7	3.51	10877.0	2.13	0.041	1.48
AN	303.4	0.05	502.0	0.43	1.35	0.79	140537.0	5.29	16506.3	1.88	0.039	1.34
1-metDBT	303.4	0.05	502.0	0.43	1.65	0.96	83236.0	2.29	7679.5	1.91	0.050	1.22
ACR	304.3	0.07	515.0	0.55	1.40	0.83	97034.7	5.51	10787.3	3.69	0.041	0.74
PHR	305.6	0.10	534.0	0.80	1.46	0.92	50625.7	1.66	5348.1	2.90	0.044	0.71
4-metDBT	305.8	0.03	537.4	0.28	1.51	0.75	74406.3	2.54	7917.1	3.33	0.044	0.66
2,8-metDBT	306.6	0.05	548.5	0.38	1.85	0.74	75489.0	4.28	6261.7	4.43	0.055	1.92
3,6-metPH	307.6	0.06	562.5	0.46	1.87	0.87	60558.7	2.81	5000.2	1.20	0.055	3.13
1-metPH	308.7	0.05	578.0	0.40	1.62	0.76	58890.3	4.26	5721.3	3.45	0.048	1.34
9-metAN	311.7	0.04	621.0	0.30	1.70	0.58	39480.0	3.77	3682.2	3.29	0.051	1.02
2-metAN	312.8	0.06	637.5	0.40	1.49	0.68	60991.0	1.51	6429.3	2.17	0.044	1.83
2,3-metDBT	313.5	0.06	646.6	0.43	1.86	0.78	71510.3	1.72	6044.7	2.36	0.055	1.98
CAR	317.1	0.06	699.0	0.40	1.34	0.68	126365.0	2.89	15321.0	1.61	0.039	0.90
2,4,6-metDBT	321.2	0.04	756.9	0.26	1.96	0.63	46060.3	2.27	3604.8	2.28	0.058	2.19
FLT	323.2	0.05	785.5	0.33	1.86	0.52	111692.0	1.81	9228.4	1.92	0.056	0.76
9,10-metAN	324.0	0.03	797.4	0.19	2.08	0.66	34525.3	2.41	2674.9	1.81	0.060	0.92
RET	325.8	0.05	822.0	0.28	2.19	0.62	25894.3	2.56	1856.7	2.29	0.055	27.5
PY	330.5	0.05	890.0	0.24	1.94	0.69	119784.0	3.09	9434.6	3.38	0.059	2.78
1-metPY	350.8	0.06	1180.5	0.25	2.02	0.59	48707.7	1.22	3746.6	2.65	0.058	2.19
BbFL	354.7	0.03	1237.3	0.13	1.75	0.48	19353.7	2.21	1776.2	1.81	0.050	0.89
TRI	378.9	0.05	1583.0	0.18	2.11	0.46	58478.3	4.77	4333.5	1.64	0.062	1.35
BaAN	390.5	0.06	1749.0	0.20	1.82	0.56	45638.7	3.27	4020.3	2.34	0.051	4.24
CHR	400.3	0.03	1893.0	0.15	1.70	0.38	51244.0	5.38	4794.8	3.58	0.049	1.84
6-metCHR	404.7	0.03	1981.5	0.13	1.95	0.50	35653.3	1.94	2878.3	0.74	0.056	2.70
BbFLT	432.8	0.04	2555.7	0.12	1.84	0.59	46202.0	2.83	3933.4	3.77	0.054	3.83
BkFLT	435.9	0.02	2619.1	0.07	1.80	0.48	41914.0	0.94	3652.0	1.60	0.054	0.89
BePY	437.8	0.03	2657.4	0.10	2.02	0.54	42641.0	1.99	3237.6	3.79	0.059	3.13
PER	444.8	0.03	2798.6	0.10	2.02	0.46	29787.7	1.76	2259.3	0.80	0.059	3.27
BaPY	450.5	0.03	2914.0	0.08	1.84	0.50	33268.7	0.64	2800.7	2.12	0.055	4.27
DahA	498.9	0.03	3778.0	0.07	2.47	0.47	11948.7	2.81	686.2	3.02	0.072	26.6
BghiP	500.4	0.02	3804.0	0.06	2.78	0.52	15505.0	15.6	897.2	2.33	0.095	6.54
PIC	526.1	0.02	4263.3	0.05	2.64	0.45	9169.0	24.8	530.7	5.61	0.065	36.9
<i>Avg</i>		0.21		0.32		0.73		4.34		2.68		4.73
<i>Min</i>		0.00		0.00		0.38		0.41		0.74		0.06
<i>Max</i>		1.47		0.91		1.47		24.8		6.26		36.9

* Based on the summation of the three highest modulated peaks

** Based on the highest modulated peak

Table S2: LC-50×NSP-35 average first dimension retention indexes (RIs), first dimension retention time (1t_R), second dimension retention times (2t_R), first dimension resolution (1R), second dimension resolution (2R) and 2D resolution (R_{2D}) for a standard solution containing 45 PACs at 50 pg μL^{-1} ($n=8$). Instrument detection limits in pg μL^{-1} (IDLs) are also shown.

Name	RI	1t_R (s)	2t_R (s)	1R	2R	R_{2D}	IDLs (pg μL^{-1})
NAP	n.d.	n.d.	n.d.	-	-	-	
1-metNAP	n.d.	n.d.	n.d.	-	-	-	
2-metNAP	n.d.	n.d.	n.d.	-	-	-	
ACY	145.0	274.0	1.11	0.00	1.65	1.65	0.5
ACE	145.0	274.0	1.18	0.03	3.69	3.69	1.0
2,6-metNAP	145.5	274.7	1.03	0.00	0.00	0.00	10.0
2,7-metNAP	145.5	274.7	1.03	0.07	0.12	0.14	10.0
IND	146.5	276.0	0.84	0.10	0.04	0.11	0.5
2,3-metNAP	148.3	278.0	0.94	0.00	0.00	0.00	10.0
1,5-metNAP	148.3	278.0	0.94	3.50	0.06	3.50	10.0
FL	200.0	341.0	1.08	3.06	3.61	4.73	0.5
1-metFL	244.8	390.0	1.20	2.46	3.99	4.69	0.5
DBT	278.8	429.4	1.34	1.79	0.95	2.02	10.0
PH	300.0	458.0	1.38	2.75	0.66	2.83	0.5
AN	303.4	502.0	1.35	0.00	6.63	6.63	0.5
1-metDBT	303.4	502.0	1.65	0.81	5.46	5.52	0.5
ACR	304.3	515.0	1.40	1.19	1.36	1.81	0.5
PHR	305.6	534.0	1.46	0.21	1.24	1.26	0.5
4-metDBT	305.8	537.4	1.51	0.69	6.77	6.80	1.0
2,8-metDBT	306.6	548.5	1.85	0.88	0.42	0.97	0.5
3,6-metPH	307.6	562.5	1.87	0.97	4.71	4.81	0.5
1-metPH	308.7	578.0	1.62	2.69	1.50	3.08	1.0
9-metAN	311.7	621.0	1.70	1.03	4.48	4.60	0.5
2-metAN	312.8	637.5	1.49	0.57	7.52	7.54	0.5
2,3-metDBT	313.5	646.6	1.86	3.28	11.1	11.6	1.0
CAR	317.1	699.0	1.34	3.62	12.9	13.4	0.5
2,4,6-metDBT	321.2	756.9	1.96	1.79	1.81	2.54	1.0
FLT	323.2	785.5	1.86	0.75	3.77	3.84	0.5
9,10-metAN	324.0	797.4	2.08	1.54	2.01	2.53	1.0
RET	325.8	822.0	2.19	4.25	4.35	6.08	1.0
PY	330.5	890.0	1.94	18.2	1.21	18.2	0.5
1-metPY	350.8	1180.5	2.02	3.55	4.83	6.00	0.5
BbFL	354.7	1237.3	1.75	21.6	6.31	22.5	10.0
TRI	378.9	1583.0	2.11	10.4	5.00	11.5	0.5
BaAN	390.5	1749.0	1.82	9.00	2.43	9.32	0.5
CHR	400.0	1893.0	1.70	5.53	4.70	7.26	0.5
6-metCHR	404.7	1981.5	1.95	31.9	2.03	32.0	0.5
BbFLT	432.8	2555.7	1.84	3.17	0.67	3.24	1.0
BkFLT	435.9	2619.1	1.80	1.91	3.82	4.27	1.0
BePY	437.8	2657.4	2.02	7.06	0.05	7.06	1.0
PER	444.8	2798.6	2.02	5.77	3.27	6.63	1.0
BaPY	450.0	2914.0	1.84	43.2	10.0	44.4	1.0
DahA	498.9	3778.0	2.47	1.30	3.71	3.93	10.0
BghiP	500.0	3804.0	2.78	23.0	1.69	23.0	10.0
PIC	526.1	4263.3	2.64	-	-	-	10.0
				<i>avg</i>	<i>5.45</i>	<i>3.43</i>	<i>7.45</i>
				<i>min</i>	<i>0.00</i>	<i>0.00</i>	<i>0.50</i>
				<i>max</i>	<i>43.20</i>	<i>12.92</i>	<i>44.35</i>

Table S3: LC-50×NSP-35 and SLB-IL60×Rxi-17 analysis of two snow samples (AR6 and AMS5) collected near main industrial developments in the oil sands region of Alberta. Only tentatively identified peaks (similarities >70% with NIST 2011 or Wiley v.9 libraries, S/N>50:1) are shown, and classified into unsubstituted PAHs (unPAHs), alkylated PAHs (aPAHs), aza-arenes, thia-arenes or others.

PACs	LC-50 × NSP-35		SLB-IL60 × Rxi-17	
	AR6	AMS5	AR6	AMS5
unPAHs	103	87	108	45
aPAHs	243	195	174	185
aza-arenes	171	152	219	104
thia-arenes	166	145	145	87
Other	790	741	667	522
Total	1473	1320	1313	943

Table S4: SLB-IL60×Rxi-17 average and percent relative standard deviation (RSD) for first dimension retention indexes (RIs), first dimension retention time (¹t_R), second dimension retention times (²t_R), total peak area (the sum of the three highest modulated peaks), peak height of the highest modulated peak, and full width at half height (FWHH) of the highest modulated peak, for a standard solution containing 45 PACs at 50 pg µL⁻¹ (n=8).

Name	RI		¹ t _R		² t _R		*Total Peak Area		**Peak Height		**FWHH	
	average	RSD (%)	average (s)	RSD (%)	average (s)	RSD (%)	average	RSD (%)	average	RSD (%)	average	RSD (%)
NAP	200.0	0.00	748.0	0.00	1.42	0.26	144002.7	1.06	15928.0	3.39	0.041	2.32
2-metNAP	215.2	0.10	898.3	0.24	1.50	0.49	44740.7	10.1	5130.7	10.4	0.040	2.76
1-metNAP	216.2	0.00	908.0	0.00	1.61	0.37	39228.0	6.56	4030.5	5.81	0.044	2.46
2,6-metNAP	229.7	0.10	1041.7	0.21	1.54	0.36	31071.3	10.7	3363.5	10.0	0.042	2.08
2,7-metNAP	229.7	0.10	1041.7	0.21	1.54	0.36	31071.3	10.7	3363.5	10.0	0.042	2.08
1,5-metNAP	231.2	0.00	1056.0	0.00	1.80	0.38	23041.0	12.3	2133.5	6.94	0.049	6.71
2,3-metNAP	236.9	0.00	1112.0	0.00	1.56	0.27	25670.7	8.71	2865.7	7.97	0.042	3.05
ACY	239.3	0.00	1136.0	0.00	1.90	0.31	33222.3	9.60	3016.1	7.86	0.052	3.57
ACE	252.2	0.00	1264.0	0.00	1.45	0.24	62083.0	8.05	7512.3	5.03	0.037	2.58
FL	259.9	0.00	1340.0	0.00	1.69	0.35	23724.7	10.3	2485.5	9.18	0.044	0.73
IND	271.5	0.08	1454.7	0.14	0.91	0.44	29539.3	10.3	6017.1	10.4	0.022	1.81
1-metFL	274.9	0.00	1488.0	0.00	1.72	0.40	9267.3	19.2	931.0	20.8	0.045	2.85
DBT	289.9	0.00	1636.0	0.00	1.69	0.46	189.9	42.8	28.0	29.4	0.033	25.2
PH	300.0	0.00	1736.0	0.00	1.51	3.32	19274.0	7.32	2152.4	7.81	0.041	0.97
AN	301.0	0.00	1744.0	0.00	1.53	0.36	17200.3	31.8	2007.8	29.2	0.040	2.88
1-metDBT	302.2	0.09	1753.6	0.12	1.89	0.77	11416.3	10.4	1079.4	11.1	0.051	3.63
3-metDBT	302.8	0.08	1758.7	0.12	1.72	0.66	9860.5	19.0	1024.3	17.2	0.044	9.32
ACR	307.4	0.08	1797.3	0.11	1.53	0.26	11571.3	3.68	1369.4	1.07	0.039	5.73
PHR	311.7	0.00	1832.0	0.00	1.53	0.39	5524.7	13.0	664.6	16.2	0.038	6.39
2-metAN	315.4	0.08	1862.7	0.11	1.55	0.65	7912.2	21.9	901.0	19.0	0.042	2.86
1-metPH	316.0	0.00	1868.0	0.00	1.64	0.47	8843.1	10.8	905.0	7.29	0.046	1.75
2,8-metDBT	317.4	0.06	1879.3	0.09	1.69	0.47	10974.3	9.47	1099.8	8.30	0.046	4.81
9-metAN	319.4	0.00	1896.0	0.00	1.72	0.47	5594.0	19.1	588.8	19.8	0.044	8.92
2,3-metDBT	324.1	0.08	1934.0	0.11	1.74	0.74	9559.1	9.54	973.3	8.97	0.044	2.20
3,6-metPH	327.1	0.07	1959.2	0.09	1.66	4.31	8567.9	8.89	993.4	4.70	0.039	7.69
2,4,6-met DBT	327.5	0.08	1962.4	0.11	1.90	0.63	5841.2	23.4	534.6	16.9	0.043	18.8
9,10-metAN	336.1	0.07	2033.3	0.10	1.95	0.71	4307.0	14.6	412.9	11.2	0.047	6.22
RET	338.9	0.00	2056.0	0.00	1.86	0.65	3255.1	30.6	294.9	32.8	0.052	1.31
FLT	348.4	0.07	2134.7	0.10	1.50	0.71	17118.0	8.81	2009.0	8.29	0.038	1.60
PY	354.7	0.07	2186.7	0.09	1.60	0.60	19306.7	11.5	2182.7	10.9	0.041	1.85
BbFL	359.7	0.00	2228.0	0.00	1.70	0.44	2753.2	16.9	304.5	16.4	0.044	4.80
CAR	361.7	0.06	2245.1	0.09	1.02	0.35	19756.0	4.84	3705.6	3.92	0.024	1.41
1-metPY	370.2	0.07	2314.7	0.09	1.67	0.67	7094.2	18.7	780.8	17.0	0.041	5.59
BaAN	399.0	0.00	2552.0	0.00	1.61	0.64	7577.9	16.1	853.7	16.0	0.041	0.93
CHR	400.0	0.00	2560.0	0.00	1.66	0.40	10244.7	36.2	1120.2	33.5	0.041	5.51
TRI	401.0	0.00	2568.0	0.00	1.64	0.42	6708.7	15.1	727.9	19.5	0.041	1.63
6-metCHR	412.1	0.06	2658.7	0.08	1.73	0.50	5819.4	20.6	599.2	22.0	0.045	2.35
BbFLT	440.7	0.00	2892.0	0.00	1.68	1.55	8300.4	25.1	917.7	22.0	0.042	6.40
BkFLT	441.9	0.06	2902.0	0.08	1.67	1.69	7484.1	19.6	804.0	11.9	0.042	7.39
BePY	449.5	0.00	2964.0	0.00	1.86	1.90	8339.5	36.4	744.4	25.4	0.049	13.5
BaPY	450.0	0.00	2968.0	0.00	1.89	2.03	5371.3	6.93	497.8	5.01	0.050	4.63
PER	453.4	0.00	3008.0	0.00	1.97	2.22	5002.6	17.2	474.4	13.8	0.048	3.57
DahA	485.6	0.04	3381.6	0.06	2.77	2.15	2162.0	20.6	175.3	21.7	0.043	35.6
PIC	489.9	0.03	3431.2	0.05	3.00	2.16	2309.0	39.3	152.3	40.0	0.058	38.1
BghiP	499.8	0.06	3545.6	0.10	3.20	2.16	2727.3	34.0	186.9	36.5	0.036	17.0
<i>Avg</i>		0.04		0.06		0.89		16.48		15.0		6.52
<i>Min</i>		0.00		0.00		0.24		1.06		1.07		0.73
<i>Max</i>		0.10		0.24		4.31		42.8		40.0		38.1

* Based on the summation of the three highest modulated peaks for all PACs

** Based on the highest modulated peak

Table S5: SLB-IL60×Rxi-17 average first dimension retention indexes (RIs), first dimension retention time (1t_R), second dimension retention times (2t_R), first dimension resolution (1R), second dimension resolution (2R) and 2D resolution (R_{2D}) for a standard solution containing 45 PACs at 50 pg μL^{-1} ($n=8$). Instrument detection limits in pg μL^{-1} (IDLs) are also shown.

Name	RI	¹ t _R (s)	² t _R (s)	¹ R	² R	R _{2D}	IDLs (pg μL ⁻¹)
NAP	200.0	748.0	1.42	9.39	1.86	9.57	0.5
2-metNAP	215.2	898.3	1.50	0.61	2.58	2.65	0.5
1-metNAP	216.2	908.0	1.61	8.36	1.61	8.51	0.5
2,6-metNAP	229.7	1041.7	1.54	0.00	0.00	0.00	0.5
2,7-metNAP	229.7	1041.7	1.54	0.89	5.76	5.83	0.5
1,5-metNAP	231.2	1056.0	1.80	3.50	5.32	6.37	1.0
2,3-metNAP	236.9	1112.0	1.56	1.50	7.22	7.38	1.0
ACE	239.3	1136.0	1.90	8.00	10.0	12.8	1.0
ACY	252.2	1264.0	1.45	4.75	6.03	7.67	0.5
FL	259.9	1340.0	1.69	7.17	23.7	24.7	1.0
IND	271.5	1454.7	0.91	2.08	24.1	24.2	1.0
1-metFL	274.9	1488.0	1.72	9.25	0.81	9.29	1.0
DBT	289.9	1636.0	1.69	6.25	4.85	7.91	10.0
PH	300.0	1736.0	1.51	0.50	0.54	0.73	0.5
AN	301.0	1744.0	1.53	0.60	7.84	7.87	0.5
1-metDBT	302.2	1753.6	1.89	0.32	3.46	3.47	5.0
3-metDBT	302.8	1758.7	1.72	2.42	4.67	5.26	1.0
ACR	307.4	1797.3	1.53	2.17	0.14	2.17	1.0
PHR	311.7	1832.0	1.53	1.92	0.37	1.95	5.0
2-metAN	315.4	1862.7	1.55	0.33	2.13	2.16	1.0
1-metPH	316.0	1868.0	1.64	0.71	0.97	1.20	5.0
2,8-metDBT	317.4	1879.3	1.69	1.04	0.73	1.27	1.0
9-metAN	319.4	1896.0	1.72	2.38	0.38	2.41	5.0
2,3-metDBT	324.1	1934.0	1.74	1.58	1.76	2.36	1.0
3,6-metPH	327.1	1959.2	1.66	0.20	5.84	5.85	1.0
2,4,6-metDBT	327.5	1962.4	1.90	4.43	1.15	4.58	5.0
9,10-metAN	336.1	2033.3	1.95	1.42	1.96	2.42	1.0
RET	338.9	2056.0	1.86	4.92	7.78	9.20	1.0
FLT	348.4	2134.7	1.50	3.25	2.39	4.03	1.0
PY	354.7	2186.7	1.60	2.58	2.33	3.48	1.0
BbFL	359.7	2228.0	1.70	1.07	19.9	19.9	10.0
CAR	361.7	2245.1	1.02	4.35	19.8	20.3	0.5
1-metPY	370.2	2314.7	1.67	14.8	1.46	14.9	1.0
BaAN	399.0	2552.0	1.61	0.50	1.22	1.32	1.0
CHR	400.0	2560.0	1.66	0.50	0.49	0.70	1.0
TRI	401.0	2568.0	1.64	5.67	1.97	6.00	1.0
6-metCHR	412.1	2658.7	1.73	13.0	1.10	13.0	1.0
BbFLT	440.7	2892.0	1.68	0.50	0.12	0.51	1.0
BkFLT	441.9	2902.0	1.67	3.10	4.03	5.08	1.0
BePY	449.5	2964.0	1.86	0.20	0.70	0.73	1.0
BaPY	450.0	2968.0	1.89	2.00	1.69	2.62	5.0
PER	453.4	3008.0	1.97	18.7	17.4	25.5	10.0
DahA	485.6	3381.6	2.77	2.48	4.72	5.33	10.0
PIC	489.9	3431.2	3.00	5.72	4.14	7.06	10.0
BghiP	500.0	3545.6	3.20				10.0
			avg	3.75	4.93	7.05	2.47
			min	0.00	0.00	0.00	0.50
			max	18.7	24.1	25.5	10.0

Figure S1: Mass spectra of C4-PH/ANs and co-eluting thia-arenes. a) Retene, b) C4-PH, c) C1-phenanthro[4,5-*b,c,d*]thiophenes, d) phenanthro[4,3-*b*]thiophene. MS taken from NIST MS Search 2.0.

Figure S2: a) 2D-Chromatogram of snowpack sample AR6 using Rtx-5ms×Rxi-17 showing C2-BCT and co-eluting aza-arenes. Mass spectra for all compounds identified and NIST library similarities are also provided: b) C2-BCTs, c) dibenzo[*a,c*]phenazine, d) dibenzo[*b,def*]carbazole, e) 2,6-diphenylpyridine. MS taken from NIST MS Search 2.0.

Figure S3: a) 2D-Chromatogram of snowpack sample AR6 using LC-50×NSP-35 showing C2-BCT and co-eluting aza-arenes. Mass spectra for all compounds identified and NIST library similarities are also provided: b) C2-BCTs, c) dibenzo[*a,c*]phenazine, d) dibenzo[*b,def*]carbazole, e) 2,6-diphenylpyridine. MS taken from NIST MS Search 2.0.

Figure S4: a) 2D-Chromatogram of snowpack sample AR6 using SLB-IL60×Rxi-17 showing C2-BCT and co-eluting aza-arenes. Mass spectra for all compounds identified and NIST library similarities are also provided: b) C2-BCTs, c) dibenzo[a,c]phenazine, d) dibenzo[b,def]carbazole, e) 2,6-diphenylpyridine. MS taken from NIST MS Search 2.0.

** Library similarity of <50% can be explained by a co-eluting aza-arene in the lower section of the 2D-chromatogram