Comparison of Polycyclic Aromatic Compounds in Air Measured by Conventional Passive and Passive Dry Deposition Samplers and Contributions from Petcoke and Oil sands Ore

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Section S1 Ore-Air Partitioning Experimental Information

The experimental set-up for measuring ore-air partitioning was based on the apparatus and approach presented in Francisco et al., 2017. Oil sands ore sample (0.490 g) was placed inside a glass tube with 0.5 cm diameter plugged with glass wool on both ends. Zero air passed through the glass tube filled with ore at flow rate of 18.3 cm^3/min and was collected on a PUF over 63.5 h, resulting in total volume of air sampled of 69.7 L. The PUF sample was extracted, processed and analyzed according to the same methodology used for the PAS and PAS-DD samples. The compounds present in the air stream have come to equilibrium with the ore (see equilibrium confirmation described in Francisco et al.) and therefore can be used estimate an ore-air partition coefficient.

Francisco, A. P., Harner, T., Eng, A.: Measurement of polyurethane foam – air partition coefficients for semivolatile organic compounds as a function of temperature: Application to passive air sampler monitoring, Chemosphere, 174, 638-642, 2017.

Table S1 Instrumental and method detection limits of PACs, NPAHs, and OPAHs. Instrument detection limit (IDL) was determined by the lowest analyte concentration that produces a signal greater than three times the signal of the noise. Method detection limit (MDL) is calculated by MDL = Avg of field blanks + 3 × (standard deviation of field blanks)

Compound	Abbreviation	IDL ng	MDL ng
PAHs			
Acenapthylene	ACY	0.479	0.319
Acenaphthene	ACE	1.04	101
Fluorene	FLU	0.307	20.6
Phenanthrene	PHE	0.469	32.3
Anthracene	ANT	0.531	0.354
Fluoranthene	FLA	0.281	4.98
Pyrene	PYR	0.240	7.40
Benz(a)anthracene	BaA	0.354	0.236
Chrysene	CHR	0.325	2.80
Benzo(b)fluoranthene	BbF	0.830	0.553
Benzo(k)fluoranthene	BkF	1.12	0.744
Benzo(a)pyrene	BaP	0.866	0.579
Benzo(e)pyrene	BeP	1.25	34.6
Perylene	PER	0.941	0.627
Indeno(1,2,3-c,d)pyrene	IcdP	0.237	0.158
Dibenz(a,h)anthracene	DahA	0.336	0.224
Benzo(ghi)perylene	BghiP	0.439	0.293
DBT			
Dibenzothiophene	DBT	0.209	0.139
Alk-PAHs			
C1 Naphthalenes	C1-NAP	0.215	64.3
C2 Naphthalenes	C2-NAP	0.324	0.216
C3 Naphthalenes	C3-NAP	0.444	311
C4 Naphthalenes	C4-NAP	0.157	1090
C1 Fluorenes	C1-FLU	0.930	278
C2 Fluorenes	C2-FLU	1.62	582
C3 Fluorenes	C3-FLU	0.342	0.228
C4 Fluorenes	C4-FLU	0.381	0.254
C1 Phenanthrenes/Anthracenes	C1-PHE/ANT	0.754	215
C2 Phenanthrenes/Anthracenes	C2-PHE/ANT	1.60	92.2
C3 Phenanthrenes/Anthracenes	C3-PHE/ANT	0.00100	211
C4 Phenanthrenes/Anthracenes	C4-PHE/ANT	0.394	71.6
Retene	RET	1.30	5.34
C1 Fluoranthenes/Pyrenes	C1-FLA/PYR	0.291	12.9
C2 Fluoranthenes/Pyrenes	C2-FLA/PYR	0.222	97.8
C3 Fluoranthenes/Pyrenes	C3-FLA/PYR	0.309	0.206
C4 Fluoranthenes/Pyrenes	C4-FLA/PYR	0.099	0.066
C1-Benz(a)anthracenes/Chrysenes/Triphenylenes	C1-BaA/CHR/TRI	0.067	0.045
C2-Benz(a)anthracenes/Chrysenes/Triphenylenes	C2-BaA/CHR/TRI	0.406	228
C3-Benz(a)anthracenes/Chrysenes/Triphenylenes	C3-BaA/CHR/TRI	0.375	61.5

C4-Benz(a)anthracenes/Chrysenes/Triphenylenes	C4-BaA/CHR/TRI	0.0000956	0.0000637
Alk-DBTs			
C1-Dibenzothiophenes	C1-DBT	0.293	37.8
C2-Dibenzothiophenes	C2-DBT	0.194	9.71
C3-Dibenzothiophenes	C3-DBT	0.364	23.7
C4-Dibenzothiophenes	C4-DBT	0.404	42.9
NPAHs			
1,4-napthoquinone	NAQ	0.0134	2.64
1-nitronaphthalene	1-NN	0.0284	0.523
1-methyl/2-methyl-5-nitronaphthalene	1M5NN/2M1NN	0.0247	1.08
2-nitronaphthalene	2-NN	0.0428	1.46
2-nitrobiphenyl	2-NBP	0.0268	0.0179
2-methyl-4-nitronaphthalene	2M4NN	0.0199	0.0132
1-methyl-4-nitronaphthalene	1M4NN	0.0215	0.0144
1-methyl-6-nitronaphthalene	1M6NN	0.128	0.0854
3-nitrobiphenyl	3-NBP	0.0418	0.0279
4-nitrobiphenyl	4-NBP	0.165	0.110
1,5-dinitronaphthalene	1,5-DNN	0.0646	0.0430
1,3-dinitronaphthalene	1,3-DNN	0.0391	0.0261
3-nitrobenzofuran	3-NBF	0.101	0.0673
5-nitroacenaphthene	5-NAC	0.0941	0.0627
2-nitrofluorene	2-NFL	0.0370	0.0247
9-nitroanthracene	9-NAN	0.0329	0.0219
1,8-dinitronaphthalene	1,8-DNN	0.0222	0.0148
9-nitrophenanthrene	9-NPH	0.0260	0.0174
2-nitrodibenzothiophene	2-NDBT	0.134	0.0893
3-nitrophenanthrene	3-NPH	0.0860	0.0573
2-nitroanthracene	2-NAN	0.2160	0.144
2-/3-nitrofluoranthene	2-NF/3-NF	0.0211	0.0140
1-nitropyrene	1-NP	0.0167	0.0112
2-nitropyrene	2-NP	0.299	0.199
2,8-dinitrodibenzothiophene	DNDBT	0.236	0.157
7-nitrobenz(a)anthracene	7-NBaA	0.0394	0.0262
1,3-dinitropyrene	1,3-DNP	0.0108	0.00721
1,6-dinitropyrene	1,6-DNP	0.155	0.103
1,8-dinitropyrene	1,8-DNP	0.354	0.236
6-nitrobenzo(a)pyrene	6-NBaP	0.601	0.401
OPAHs			
9-fluorenone	FLO	0.0912	10.9
9,10-anthraquinone	ANQ	0.0334	32.4
2-methyl-9,10-anthraquinone	2MANQ	0.0458	1.75
Benzo(a)fluorenone	BaFL	0.00781	0.976
Benzo(b)fluorenone	BbFL	0.0501	0.639
Benzanthrone	BENZ	0.0359	1.16
Benz(a)anthracene-7,12-dione	BaAD	0.0245	0.636

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Table S2 Air concentrations of parent PAHs, dibenzothiophene (DBT), alk-PAHs, retene (RET), alk-DBTs, NPAHs, and OPAHs measured in the PAS and PAS-DD samples during October to November 2015. An asterisk denotes 2/3 MDL. (N.D. = Non detect)

Start	28-Sep-15	28-Sep-15	28-Sep-15	28-Sep-15	29-Sep-15	29-Sep-15	1-Oct-15	1-Oct-15	29-Sep-15	29-Sep-15
Stop	27-Nov-15	27-Nov-15	27-Nov-15	27-Nov-15	26-Nov-15	26-Nov-15	27-Nov-15	27-Nov-15	26-Nov-15	26-Nov-15
Days	59	59	59	59	57	57	56	56	57	57
Site	AMS 5		AMS 14		AMS 13		AMS 6		AMS 9	
	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD
Parent PAHs (ng/m^3)										
ACY	N.D.	0.44	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
ACE	0.23*	0.46	0.23*	0.23*	0.24*	0.43	0.24*	0.37	0.24*	0.56
FLU	0.84	1.70	0.50	0.82	0.34	0.53	0.62	1.5	0.49	0.90
PHE	3.00	7.02	1.34	3.0	0.95	1.72	2.47	6.0	1.5	3.0
ANT	0.17	0.29	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FLA	0.66	1.75	0.32	0.72	0.10	0.21	0.84	1.6	0.18	0.40
PYR	0.88	2.44	0.21	0.48	0.11	0.22	0.71	1.3	0.22	0.49
RET	0.84	2.82	0.71	2.0	0.22	0.55	1.6	4.03	0.31	0.86
BaA	0.061	0.22	0.013	0.015	0.020	0.060	0.041	0.096	0.034	0.10
CHR	0.097	0.42	0.015	0.046	0.030	0.083	0.056	0.15	0.047	0.16
BbF	0.043	0.20	0.0084	0.024	0.010	0.042	0.039	0.16	0.020	0.08
BkF	N.D.	0.037	N.D.	N.D.	N.D.	N.D.		0.046	N.D.	N.D.
BeP	0.078*	0.20	0.078*	0.078*	0.081*	0.081*	0.082*	0.082*	0.081*	0.081*
BaP	0.033	0.16	N.D.	N.D.	N.D.	0.036	N.D.	N.D.	0.027	0.086
PER	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
DahA	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
IcdP	0.024	0.11	0.0035	0.011	0.010	0.020	0.020	0.087	0.010	0.035
BghiP	0.064	0.30	0.0046	0.022	0.020	0.053	0.040	0.14	0.037	0.091
ΣPAHs	6.2	16	2.7	5.5	1.9	3.5	5.2	12	2.9	6.0
DBT	0.55	1.2	0.051	0.11	0.21	0.36	0.16	0.36	0.32	0.65

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Start	28-Sep-15	28-Sep-15	28-Sep-15	28-Sep-15	29-Sep-15	29-Sep-15	1-Oct-15	1-Oct-15	29-Sep-15	29-Sep-15
Stop	27-Nov-15	27-Nov-15	27-Nov-15	27-Nov-15	26-Nov-15	26-Nov-15	27-Nov-15	27-Nov-15	26-Nov-15	26-Nov-15
Days	59	59	59	59	57	57	56	56	57	57
Site	AMS 5		AMS 14		AMS 13		AMS 6		AMS 9	
	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD
Alk-PACs (ng/m^3)										
C1-NAPs	2.33	3.8	0.82	1.3	0.93	1.4	1.4	2.1	1.9	3.6
C2-NAPs	0.51	0.86	0.16	0.21	0.19	0.28	0.20	0.33	0.34	0.76
C3-NAPs	5.30	8.02	1.1	1.7	2.2	4.5	1.9	3.4	3.4	6.0
C4-NAPs	7.25	12.35	2.5*	2.5*	2.6*	7.4	2.6*	2.6*	4.4	9.6
C1-FLUs	2.55	6.09	0.63*	0.63*	1.55	2.6	0.90	1.9	2.3	3.2
C2-FLUs	4.82	12	1.3*	1.3*	2.2	3.6	1.4*	6.0	3.7	3.4
C1-PHEs/ANTs	8.87	22	1.39	3.9	3.8	8.3	4.2	9.9	6.1	13
C2-PHEs/ANTs	4.82	15	0.40	1.3	1.7	4.7	1.6	4.3	2.6	6.3
C3-PHEs/ANTs	2.80	10	0.48*	1.13	0.99	3.7	1.5	3.1	1.6	5.1
C4-PHEs/ANTs	0.61	3.3	0.16*	0.16*	0.17*	1.0	0.22	0.54	0.43	1.5
C1-FLTs/PYRs	0.97	3.3	0.098	0.33	0.21	0.67	0.50	1.1	0.32	1.1
C2-FLTs/PYRs	2.76	10	0.22*	0.82	1.2	3.1	1.2	2.8	1.5	4.5
C1-BTCs	0.073	N.D.	N.D.	N.D.	0.041	0.00010	N.D.	N.D.	0.050	0.18
C2-BTCs	2.87	11	0.52*	0.85	1.3	4.9	1.0	3.2	1.7	5.6
C3-BTCs	0.61	3.1	0.14*	0.14*	0.28	1.2	0.19*	0.83	0.35	1.7
Σalk-PAHs	47	120	10	16	19	47	19	42	31	66
RET	0.84	2.8	0.71	2.0	0.22	0.55	1.6	4.0	0.31	0.86
C1-DBTs	0.29	0.80	0.085*	0.085*	0.088*	0.27	0.090*	0.19	0.20	0.5
C2-DBTs	1.42	4.1	0.077	0.16	0.78	1.8	0.51	1.1	0.98	3.0
C3-DBTs	1.42	5.8	0.48*	0.15	0.96	2.8	0.46	1.4	1.3	3.7
C4-DBTs	0.57	1.9	0.10*	0.10*	0.33	1.1	0.17	0.60	0.44	1.8
Σalk-DBTs	3.7	13	0.31	0.49	2.2	6.0	1.2	3.2	2.9	8.9
ΣPACs	**58**	**150**	**14**	**24**	**24**	**58**	**27**	**61**	**37**	**83**

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Start	28-Sep-15	28-Sep-15	28-Sep-15	28-Sep-15	29-Sep-15	29-Sep-15	1-Oct-15	1-Oct-15	29-Sep-15	29-Sep-15
Stop	27-Nov-15	27-Nov-15	27-Nov-15	27-Nov-15	26-Nov-15	26-Nov-15	27-Nov-15	27-Nov-15	26-Nov-15	26-Nov-15
Days	59	59	59	59	57	57	56	56	57	57
Site	AMS 5		AMS 14		AMS 13		AMS 6		AMS 9	
	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD	PAS	PAS-DD
NPAHs and OPAHs (pg/m^3)										
NAQ	28	44	12	14	6.2*	6.2*	32	28	6.2*	9.6
1-NN	30	18	1.2*	1.2*	1.2*	N.D.	6.5	3.2	3.6	N.D.
1M5NN/2M1NN	50	34	3.9	9.7	8.1	12	14	20	11	25
2-NN	15	18	3.3*	3.3*	3.4*	N.D.	4.7*	6.0	3.4*	N.D.
FLO	397	940	390	620	110	230	540	1100	180	440
1M4NN	29	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
4-NBP	29	79	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	15	41
ANQ	130	210	73*	73*	76*	76*	97	220	76*	76*
MANQ	28	33	7.8	10.	4.1*	4.1*	21	18.51	4.1*	10.
9-NAN	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.4	N.D.	N.D.	7.5
2-NDBT	N.D.	22	N.D.	N.D.	N.D.	9.6	N.D.	N.D.	N.D.	14
BaFL	15	75	8.3	21	5.8	20	23	84	6.00	34
BbFL	10	30	4.9	4.7	3.1	6.9	12	18	3.7	12
BENZ	13	26	8.8	8.4	2.7*	2.7*	24	21	2.7*	8.4
BaAD	4.3	N.D.	1.4*	4.0	1.5*	4.2	5.5	16	1.5	N.D.
ΣNPAHs+OPAHs	**770**	**1,500**	**520**	**770**	**230**	**370**	**783**	**1,500**	**310**	**640**

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Table S3 PAC, NPAH, and OPAH concentrations in the fluid, delayed petcoke and oil sands ore particles. An asterisk denotes 2/3 MDL. (N.D. = Non detect; n/a = not available)

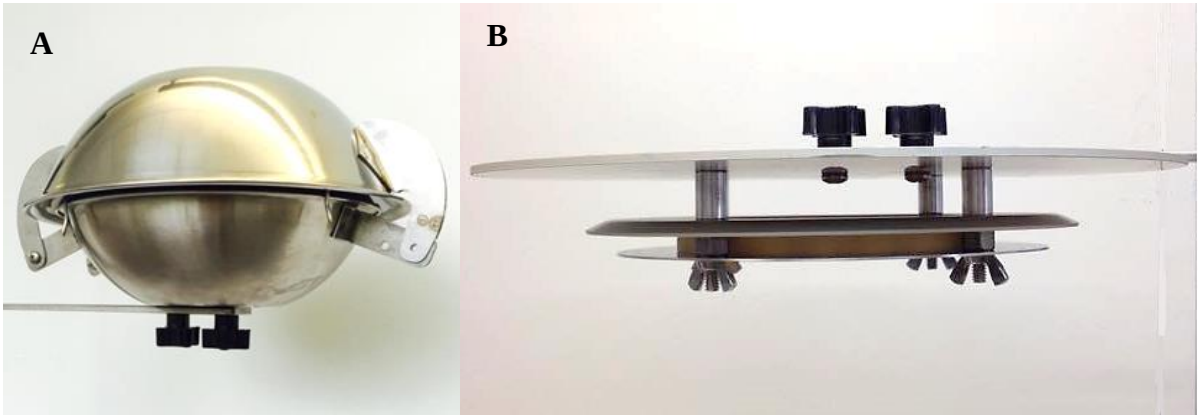
Compounds	Fluid Petcoke (n=2)		Delayed Petcoke (n=3)		Oil Sands Ore (n=3)	
	Avg ng/mg	Stdev	Avg ng/mg	Stdev	Avg ng/mg	Stdev
NAP	0.0603	0.00337	0.317	0.0620	0.0378	0.0646
ACY	N.D.	n/a	0.00224	0.00388	N.D.	n/a
ACE	0.00139*	n/a	0.0101	0.00264	2.36	0.226
FLU	0.0150	0.0000551	0.0669	0.0152	3.38	0.410
PHE	0.242	0.0124	1.23	0.265	11.2	0.270
ANT	0.0970	0.00218	0.518	0.0955	N.D.	n/a
FLA	0.0856	0.00360	0.464	0.100	0.811	0.0502
PYR	0.379	0.0176	1.99	0.369	2.04	0.405
BaA	0.498	0.00981	2.54	0.431	N.D.	n/a
CHR	0.714	0.0216	3.76	0.689	1.38	0.0513
BbF	0.161	0.00734	0.873	0.156	0.579	0.0284
BkF	0.0403	0.00289	0.223	0.034	N.D.	n/a
BeP	0.321	0.0173	1.68	0.287	0.758	0.0634
BaP	0.463	0.00404	2.36	0.364	N.D.	n/a
PER	0.0377	0.00260	0.245	0.054	0.801	0.0872
IcdP	0.162	0.0104	0.875	0.143	0.104	0.00137
DahA	0.129	0.00832	0.690	0.108	0.177	0.00889
BghiP	0.204	0.0102	1.217	0.148	0.255	0.0128
Parent PAHs	**3.61**	**0.114**	**19.1**	**3.18**	**23.9**	**0.72**
DBT	**0.184**	**0.00280**	**0.872**	**0.131**	**0.514**	**0.156**
C1-NAP	0.200	0.00623	1.14	0.175	0.000693*	n/a
C2-NAP	0.0158	0.00466	0.122	0.0217	N.D.	n/a
C3-NAP	0.228	0.0843	0.866	0.077	52.2	12.8
C4-NAP	0.000209*	n/a	0.163	0.207	105	13.8
C1-FLU	0.273	0.0558	0.00310*	n/a	16.6	1.73
C2-FLU	0.000322*	n/a	0.350	0.303	38.6	1.32
C1-PHE/ANT	1.40	0.155	7.59	3.03	35.5	1.98
C2-PHE/ANT	1.18	0.046	6.32	1.25	82.0	3.57
C3-PHE/ANT	0.756	0.054	3.73	0.713	90.8	16.9
C4-PHE/ANT	0.243	0.0274	1.22	0.253	33.8	6.71
C1-FLA/PYR	1.00	0.168	5.23	1.14	18.5	4.83
C2-FLA/PYR	1.50	0.0116	7.74	1.37	36.5	11.0
C4-FLA/PYR	0.102	0.00745	0.540	0.113	N.D.	n/a
C1-BTC	0.281	0.0287	1.63	0.249	1.56	0.0686
C2-BTC	3.02	0.0910	14.9	2.23	16.7	0.148
C3-BTC	0.541	0.0446	2.79	0.448	11.7	0.417
Alk-PAHs	**10.7**	**0.134**	**54.3**	**5.15**	**540**	**11.1**
RET	**0.00134***	**n/a**	**0.00335***	**n/a**	**6.38**	**1.32**
C1-DBT	0.130	0.00033	0.630	0.0982	4.09	1.36
C2-DBT	0.690	0.00366	3.59	0.528	18.7	6.28

Compounds	Fluid Petcoke (n=2)		Delayed Petcoke (n=3)		Oil Sands Ore (n=3)	
	Avg ng/mg, Stdev		Avg ng/mg, Stdev		Avg ng/mg, Stdev	
C3-DBT	1.26	0.127	6.25	0.817	62.9	28.3
C4-DBT	0.0902	0.00644	0.584	0.163	29.8	14.3
Alk-DBTs	**2.17**	**0.130**	**11.1**	**1.60**	**115**	**49.6**
ΣPACs	**16.7**	**0.381**	**85.3**	**10.0**	**686**	**58.2**
	Avg ng/g	**Stdev**	**Avg ng/g**	**Stdev**	**Avg ng/g**	**Stdev**
1-NN	0.129	0.045	0.0300*	n/a	0.0549*	n/a
2-NN	0.288	0.259	0.264*	n/a	0.560*	n/a
1M4NN	N.D.	n/a	N.D.	n/a	2.17	0.350
1,3-DNN	N.D.	n/a	N.D.	n/a	11.9	5.30
3-NBP	0.145	0.205	N.D.	n/a	N.D.	n/a
4-NBP	N.D.	n/a	26.1	0.769	228	41.7
2-NDBT	N.D.	n/a	2.36	0.024	24.9	1.66
3-NPHE	N.D.	n/a	N.D.	n/a	12.4	2.0
2-NP	N.D.	n/a	41.0	1.42	N.D.	n/a
1,6-DNP	1.35	0.139	N.D.	n/a	52.1	5.6
6-NBaP	N.D.	n/a	138	24.9	N.D.	n/a
ΣNPAHs	**1.91**	**0.237**	**208**	**26.4**	**332**	**48.9**
1,4-NAQ	3.11	0.679	3.40	0.389	0.00990*	n/a
FLO	13.0	3.50	37.9	3.23	113	6.33
ANQ	30.5	31.7	88.5	63.6	57.0	23.1
MANQ	14.2	0.0185	144	113	N.D.	n/a
BaFLU	0.300	0.087	177	16.4	29.4	2.83
BbFLU	0.164	0.049	86.8	7.53	N.D.	n/a
BENZ	0.126	0.178	11.4	1.09	2.08	1.97
BaAD	0.152	0.020	87.3	62.0	N.D.	n/a
ΣOPAHs	**61.5**	**36.2**	**637**	**260**	**202**	**26.4**

41

42

Figure S1 Conventional PAS (A) and PAS-DD (B)* samplers.



* Eng, A.; Harner, T.; Pozo, K., A prototype passive air sampler for measuring dry deposition of polycyclic aromatic hydrocarbons. *Environmental Science & Technology Letters* **2013,** *1*, (1), 77-81.

Figure S2 PAC and Alk-PAC compositions of PAS samples (A) and PAS-DD (B) samples at five sampling sites. Concentrations measured by PAS-DD sampler were expressed as ng/m^3 (1st y-axis) for comparison with PAS sampler, using the PAS sampler air volume, corrected for reduced exposure surface of the PAS-DD sampler. Fluxes derived from the PAS-DD were expressed in µg/(m^2·day) (2nd y-axis).

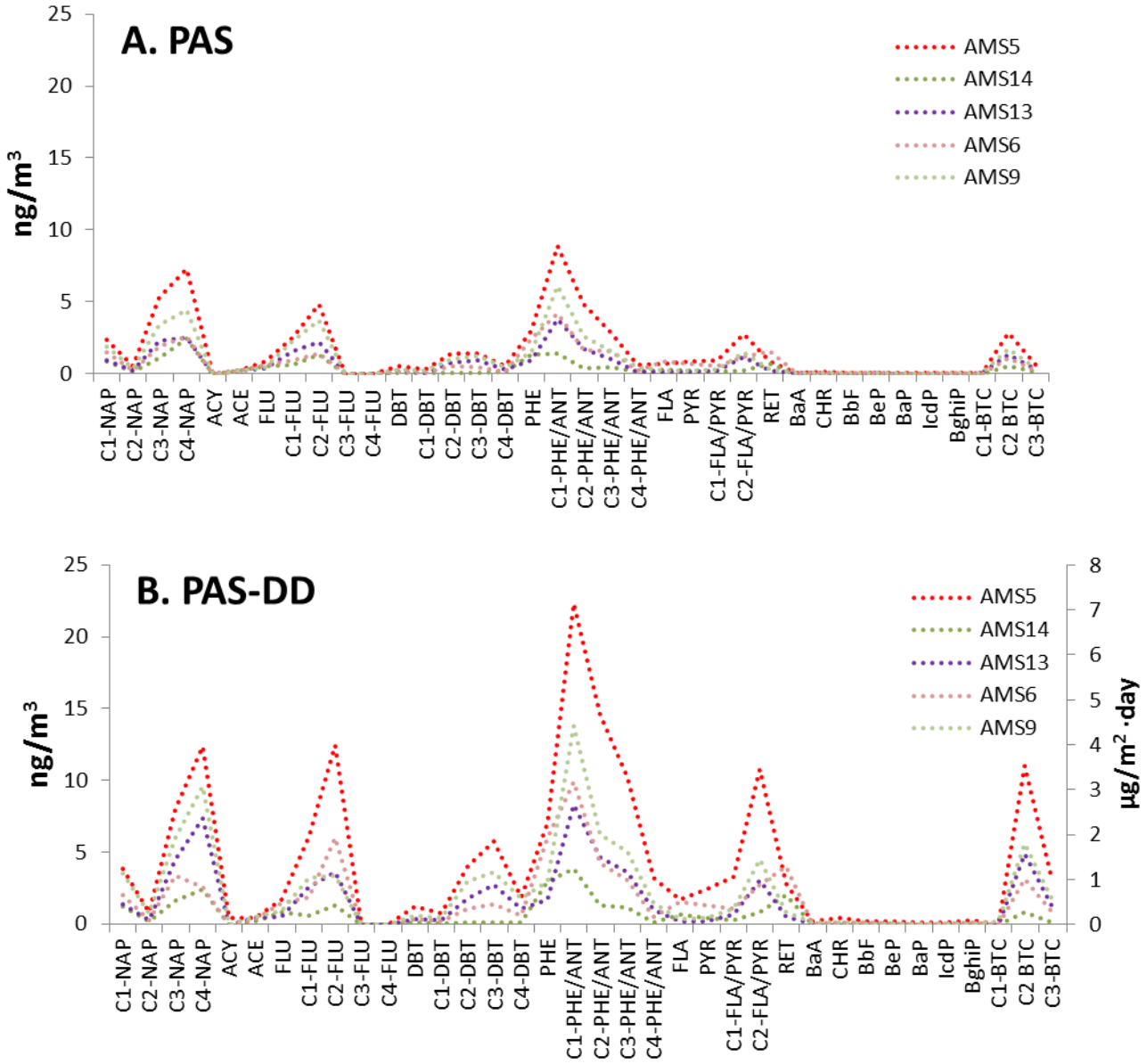


Figure S3 Enhancement ratios for NPAHs and OPAHs during October to November 2015.

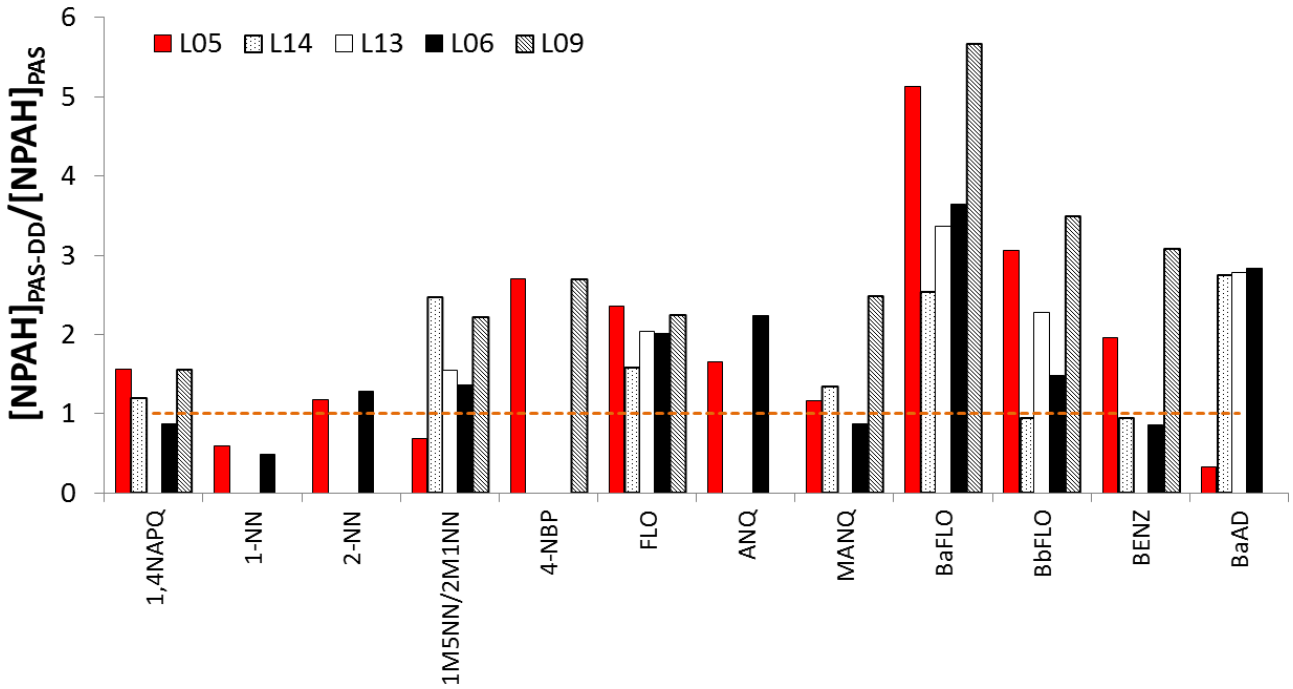


Figure S4 Average PAC compositions (individual concentrations normalized to total PACs) and standard deviations of the PAS, PAS-DD fluid petcoke, delayed petcoke, and oil sands ore samples.

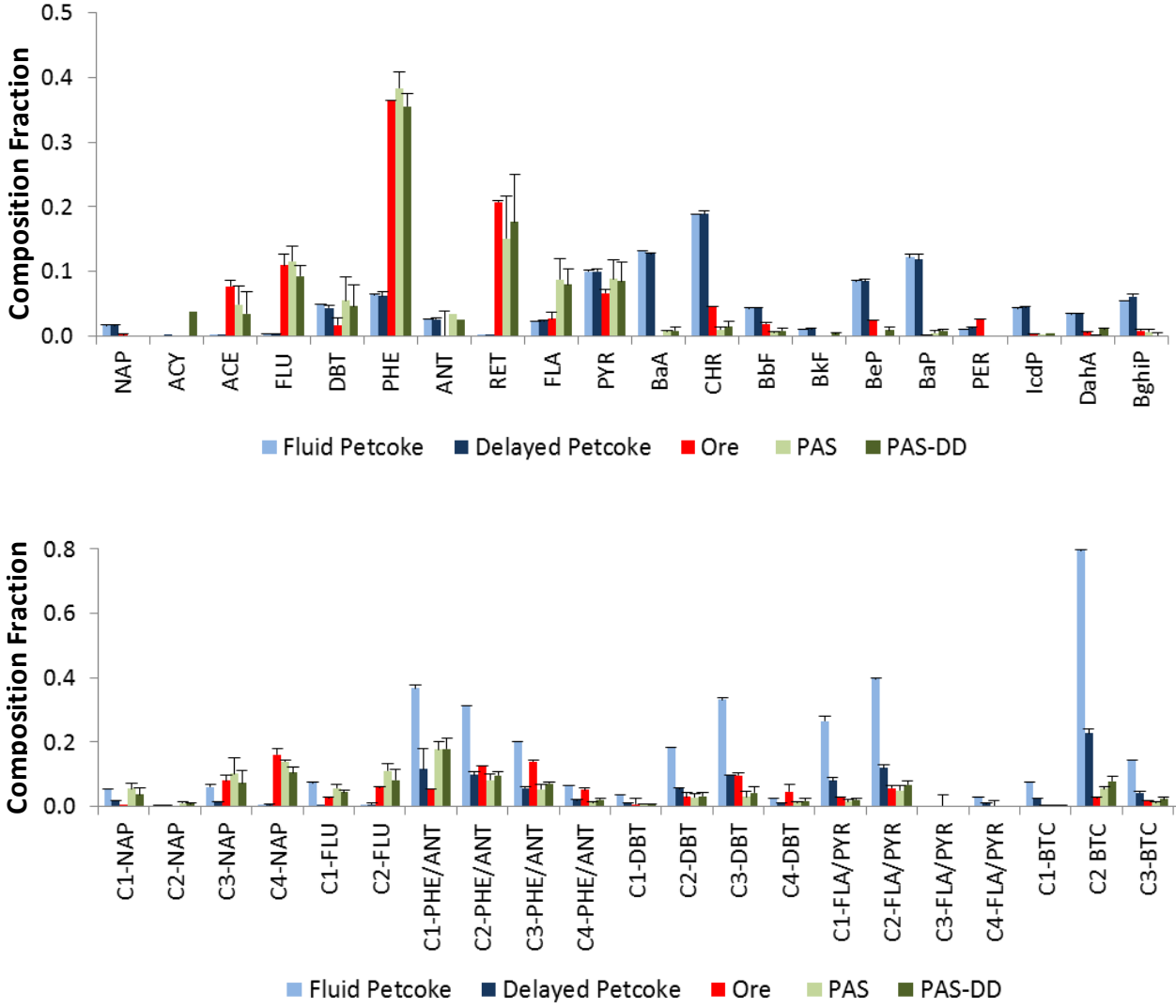


Figure S5 Composition of 4-6 ring PAHs (individual concentrations normalized to total 4-6ring PAHs) and 4-6 ring alk-PAHs (individual concentrations normalized to total 4-6ring alk-PAHs) for the fluid petcoke, delayed petcoke, oil sands ore, and passive air samples.