

Supplementary Materials: Assessment and Characterization of Alkylated PAHs in Selected Sites across Canada

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Section S1. Standards and Chemicals

The studied polycyclic aromatic hydrocarbons (PACs), their acronyms and properties are listed in Table S1. PACs targeted in this study include individually analyzed compounds and also determined as analyte groups C1 to C4 alkylated PAHs and DBTs because of their co-elution and the limited chromatographic selectivity for such large numbers of isomers. For example, BTCs comprise summed C1-C4 alkylated series of B[a]A, TRI, CHRY since these compounds co-elute during chromatographic analysis. Designations C1, C2, C3, and C4 refer to the number of carbons in the alkyl side chains for alk-PAHs and DBTs.

NIST Standard Reference Material SRM 1649b (Gaithersburg, MD, USA) was used as a control for evaluating the analytical accuracy of the PACs determined in ambient air. The deuterated surrogates used to estimate recoveries (*d*₈-acenaphthylene, *d*₁₀-acenaphthene, *d*₁₀-fluorene, *d*₁₀-phenanthrene, *d*₁₀-anthracene, *d*₁₀-pyrene, *d*₁₂-benzo[a]anthracene, *d*₁₂-triphenylene, *d*₁₂-chrysene, *d*₁₂-benzo[b]fluoranthene, *d*₁₂-benzo[e]pyrene, *d*₁₂-benzo[a]pyrene, *d*₁₂-perylene, *d*₁₂-indeno[1,2,3-cd]pyrene, *d*₁₄-dibenz[a,h]anthracene, *d*₁₂-benzo[ghi]perylene, and *d*₁₀-fluoranthene as internal standards), with 99 % or greater purity, were obtained from CDN Isotopes (Pointe-Claire, QC, Canada) and CIL (Tewksbury, MA, USA).

Section S2. Additional Sampling Information:

A high volume sampler built by Environment Canada (based on Tisch HiVol sampler) and used in the National Air Pollution Surveillance Program (NAPS) to routinely monitor ambient air quality was deployed at the monitoring study sites. The sampler was fitted with a TSP (PM₃₀ cut off) inlet. A teflon-coated borosilicate glass fiber filter (GFF) (PALL Life Sciences, PALLFLEX Membrane Filters EMFAB TX40HI20-WW, 20.32x25.40cm) was used to collect PM₃₀ associated PACs. Two PUF sorbent plugs (Sure-line Mfg. Inc., 8.26x7.62cm, open-cell grade 1545, pre-cleaned on accelerated solvent extractor (ASE) with dichloromethane/acetone followed by hexane, and dried under vacuum at 50°C) were used to collect volatiles from the GP filtered ambient air.

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Section S3. GC-MS analysis:

Instrumental and acquisition conditions were described elsewhere [1]. Briefly, analysis was carried out on an Agilent 6890GC interfaced directly to an Agilent 5973 MSD. A 1 µL cool on-column injection was set to track the GC oven temperature. The chromatographic separation was performed on a DB-XLB column (30m x0.25mm x0.25µm) with a helium flow of 2.0 mL/min. The initial temperature of the GC oven was 90°C and then, after 1 min, increased to 320°C at a rate 5°C/min and finally held for 10 min for a total run time of 77 min. A minimum of three ions were monitored for all native analytes, two characteristic ions for each of the surrogate analytes and one ion for the internal standard under Selected Ion Monitoring mode.

Section S4. Quality Control:

For quality assurance and quality control, field and laboratory blank samples were prepared following the same procedures as for the samples. Before Soxhlet extraction, each sample (filter and PUF-pair) was spiked with 100 µL recovery surrogates at 10 ng/µL. Prior to GC-MS analysis, all samples were spiked with 100 µL of d₁₀-fluoranthene. A laboratory control sample consisting of a blank filter spiked with surrogate compounds was processed along with each set of field samples. Chromatographic performance was verified daily by confirming chromatographic resolution of mid-level calibration standards that were run daily on GC-MS. All measured concentrations were recovery corrected [1]. Instrument detection limit (IDL) was established when response for characteristic ions exceeded the background noise level by a minimum ratio of 3:1. The analytical MDL was obtained by using data from seven replicate analyses of filter/PUF samples spiked at amounts of 0.02 µg of the standard solution. The standard deviation (SD) obtained from replicate analysis and the Student t-value were used to calculate analytical MDL at 95% confidence level for each analyte ($t(n-1), 0.95 \times \text{SD}$). Summary of IDL, MDL and recovery are provided in Table S3.

Table S1. Properties and Characteristics of Studied Individual and Grouped PACs.

Compound	Abbreviation	Formula	Molecular Weight [g/mol]	Number of Rings	Mp [°C]	Bp [°C]	Ps@25°C [Pa] ¹
Acenaphthylene	AL	C ₁₂ H ₈	152	3	92	280	4.15 x10 ⁰
Acenaphthene	AE	C ₁₂ H ₁₀	154	3	93	279	1.36 x10 ⁰
Fluorene	FL	C ₁₃ H ₁₀	166	3	115	295	6.19 x10 ⁻¹
Anthracene	AN	C ₁₄ H ₁₀	178	3	215	340	6.59 x10 ⁻²
Phenanthrene	PHE	C ₁₄ H ₁₀	178	3	100	340	8.75 x10 ⁻²
2-Methylfluorene	MFL	C ₁₄ H ₁₂	180	3	85	307	1.57 x10 ⁻¹
Pyrene	PY	C ₁₆ H ₁₀	202	4	151	404	1.06 x10 ⁻²
Fluoranthene	FLT	C ₁₆ H ₁₀	202	4	108	384	8.11 x10 ⁻³
Benzo[a]fluorene	B[a]FL	C ₁₇ H ₁₂	216	4	100	339	3.19 x10 ⁻²
1-Methylpyrene	MPY	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Benzo[b]fluorene	B[b]FL	C ₁₇ H ₁₂	216	4	121	370	5.19 x10 ⁻⁴
Benzo[g,h,i]fluoranthene	B[ghi]FL	C ₁₈ H ₁₀	226	5	153	415	4.67 x10 ⁻⁴
Benz[a]anthracene	B[a]A	C ₁₈ H ₁₂	228	4	158	438	1.07 x10 ⁻⁴
Triphenylene	TRI	C ₁₈ H ₁₂	228	4	199	425	1.47 x10 ⁻⁴
Chrysene	CHRY	C ₁₈ H ₁₂	228	4	253	448	1.68 x10 ⁻⁴
Retene	RET	C ₁₈ H ₁₈	234	3	101	390	1.93 x10 ⁻³
7-Methylbenz[a]anthracene	MB[a]A	C ₁₉ H ₁₄	242	4	148	410	6.05 x10 ⁻⁴
Benzo[b]fluoranthene	B[b]FLT	C ₂₀ H ₁₂	252	5	168	443	1.73 x10 ⁻³
Perylene	PER	C ₂₀ H ₁₂	252	5	274	443	2.03 x10 ⁻⁴

Compound	Abbreviation	Formula	Molecular Weight [g/mol]	Number of Rings	Mp [°C]	Bp [°C]	Ps@25°C [Pa] ¹
Benzo[k]fluoranthene	B[k]FLT	C ₂₀ H ₁₂	252	5	217	480	1.02 x10 ⁻⁵
Benzo[e]pyrene	B[e]P	C ₂₀ H ₁₂	252	5	177	312	2.45 x10 ⁻⁵
Benzo[a]pyrene	B[a]P	C ₂₀ H ₁₂	252	5	176	495	3.99 x10 ⁻⁵
3-Methylcholanthrene	MCH	C ₂₁ H ₁₆	268	5	180	280	1.96 x10 ⁻⁴
Indeno[1,2,3-cd]fluoranthene	IF	C ₂₂ H ₁₂	276	6	160	401	2.53 x10 ⁻³
Anthanthrene	ANT	C ₂₂ H ₁₂	276	6	162	405	8.32 x10 ⁻⁴
Indeno[1,2,3-cd]pyrene	IP	C ₂₂ H ₁₂	276	6	161	404	8.80 x10 ⁻⁴
Benzo[g,h,i]perylene	B[ghi]P	C ₂₂ H ₁₂	276	6	200	486	8.11 x10 ⁻⁶
Benzo[b]chrysene	B[b]C	C ₂₂ H ₁₄	278	5	269	524	3.33 x10 ⁻⁵
Dibenz[a,h]anthracene	D[ah]A	C ₂₂ H ₁₄	278	5	269	524	3.33 x10 ⁻⁵
C1-C4 NAP:							
Naphthalene, 2-methyl-	2M-NAP	C ₁₁ H ₁₀	142	2	34	241	9.08 x10 ⁰
Naphthalene, 1-methyl-	1M-NAP	C ₁₁ H ₁₀	142	2	34	240	11.00 x10 ⁰
Naphthalene, 2-ethyl-	2E-NAP	C ₁₂ H ₁₂	156	2	-7	258	4.21 x10 ⁰
Naphthalene, 1-ethyl-	1E-NAP	C ₁₂ H ₁₂	156	2	-14	259	6.96 x10 ⁰
Naphthalene, 2,6-dimethyl-	26dM-NAP	C ₁₂ H ₁₂	156	2	97	265	3.91 x10 ⁰
Naphthalene, 2,7-dimethyl-	27dM-NAP	C ₁₂ H ₁₂	156	2	97	265	3.91 x10 ⁰
Naphthalene, 1,7-dimethyl-	17dM-NAP	C ₁₂ H ₁₂	156	2	-17	264	1.95 x10 ⁰
Naphthalene, 1,3-dimethyl-	13dM-NAP	C ₁₂ H ₁₂	156	2	-6	263	3.09 x10 ⁰
Naphthalene, 1,6-dimethyl-	16dM-NAP	C ₁₂ H ₁₂	156	2	-17	264	1.95 x10 ⁰
Naphthalene, 1,4-dimethyl-	14dM-NAP	C ₁₂ H ₁₂	156	2	8	268	2.85 x10 ⁰
Naphthalene, 1,5-dimethyl-	15dM-NAP	C ₁₂ H ₁₂	156	2	82	265	2.44 x10 ⁰
Naphthalene, 2,3-dimethyl-	23dM-NAP	C ₁₂ H ₁₂	156	2	105	268	9.07 x10 ⁻¹
Naphthalene, 1,2-dimethyl-	12dM-NAP	C ₁₂ H ₁₂	156	2	2	265	1.69 x10 ⁰
Naphthalene, 1,8-dimethyl-	18dM-NAP	C ₁₂ H ₁₂	156	2	82	265	2.44 x10 ⁰
Naphthalene, 2-ethyl-6-methyl-	2E6M-NAP	C ₁₃ H ₁₄	170	2	49	283	6.45 x10 ⁻¹
Naphthalene, 1,2,6-trimethyl-	126tM-NAP	C ₁₃ H ₁₄	170	2	56	283	6.45 x10 ⁻¹
Naphthalene, 7-isopropyl-1-methyl-	7IP1M-NAP	C ₁₄ H ₁₆	184	2	49	289	4.67 x10 ⁻¹
Naphthalene, 1,2,5,6-tetramethyl-	1256teM-NAP	C ₁₄ H ₁₆	184	2	72	298	2.88 x10 ⁻¹
C1-C4 FL:							
Fluorene, 9-methyl-	9M-FL	C ₁₄ H ₁₂	180	3	46	155	2.21 x10 ⁻¹
Fluorene, 3-methyl-	3M-FL	C ₁₄ H ₁₂	180	3	80	307	1.77 x10 ⁻¹
Fluorene, 2-methyl-	2M-FL	C ₁₄ H ₁₂	180	3	80	307	1.77 x10 ⁻¹
Fluorene, 1-methyl-	1M-FL	C ₁₄ H ₁₂	180	3	85	307	1.57 x10 ⁻¹
Fluorene, 4-methyl-	4M-FL	C ₁₄ H ₁₂	180	3	80	307	1.77 x10 ⁻¹
Fluorene, 9-ethyl-	9E-FL	C ₁₅ H ₁₄	194	3	80	123	1.04 x10 ⁻¹

Compound	Abbreviation	Formula	Molecular Weight [g/mol]	Number of Rings	Mp [°C]	Bp [°C]	Ps@25°C [Pa] ¹
Fluorene, 1,7-dimethyl-	17dM-FL	C ₁₅ H ₁₄	194	3	NA	NA	NA
Fluorene, 9-n-propyl-	9P-FL	C ₁₆ H ₁₆	208	3	89	330	5.13 x10 ⁻²
Fluorene, 9-n-butyl-	9B-FL	C ₁₇ H ₁₈	222	3	99	343	2.65 x10 ⁻²
DBT:							
Dibenzothiophene	DBT	C ₁₂ H ₈ S	184	3	93	318	1.01 x10 ⁻¹
C1-C4 DBT:							
Dibenzothiophene, 4-methyl-	4M-DBT	C ₁₃ H ₁₀ S	198	3	100	331	4.97 x10 ⁻²
Dibenzothiophene, 2-methyl-	2M-DBT	C ₁₃ H ₁₀ S	198	3	100	331	4.97 x10 ⁻²
Dibenzothiophene, 3-methyl-	3M-DBT	C ₁₃ H ₁₀ S	198	3	100	331	4.97 x10 ⁻²
Dibenzothiophene, 1-methyl-	1M-DBT	C ₁₃ H ₁₀ S	198	3	100	331	4.97 x10 ⁻²
Dibenzothiophene, 4,6-dimethyl-	46dM-DBT	C ₁₄ H ₁₂ S	212	3	111	343	2.57 x10 ⁻³
Dibenzothiophene, 2,6-dimethyl-	26dM-DBT	C ₁₄ H ₁₂ S	212	3	111	343	2.57 x10 ⁻³
Dibenzothiophene, 2,8-dimethyl-	28dM-DBT	C ₁₄ H ₁₂ S	212	3	117	357	1.19 x10 ⁻²
Dibenzothiophene, 1,8-dimethyl-	18dM-DBT	C ₁₄ H ₁₂ S	212	3	111	343	2.57 x10 ⁻³
Dibenzothiophene, 2,3-dimethyl-	23dM-DBT	C ₁₄ H ₁₂ S	212	3	111	343	2.57 x10 ⁻³
Dibenzothiophene, 2,4,7-trimethyl-	247tM-DBT	C ₁₅ H ₁₄ S	226	3	122	355	1.36 x10 ⁻²
Dibenzothiophene, 2,3,7-trimethyl-	237tM-DBT	C ₁₅ H ₁₄ S	226	3	NA	NA	NA
Dibenzothiophene, 2,3,8-trimethyl-	238tM-DBT	C ₁₅ H ₁₄ S	226	3	NA	NA	NA
Dibenzothiophene, 4,6-diethyl-	46dE-DBT	C ₁₆ H ₁₆ S	240	3	127	366	7.19 x10 ⁻³
Dibenzothiophene, 2-n-butyl-	2B-DBT	C ₁₆ H ₁₆ S	240	3	NA	NA	NA
C1-C4 PHE/AN:							
Phenanthrene, 3-methyl-	3M-PHE	C ₁₅ H ₁₂	192	3	58	157	1.76 x10 ⁻²
Phenanthrene, 2-methyl-	2M-PHE	C ₁₅ H ₁₂	192	3	58	157	1.76 x10 ⁻²
Anthracene, 2-methyl-	2M-AN	C ₁₅ H ₁₂	192	3	209	340	4.71 x10 ⁻²
Phenanthrene, 4-methyl-	4M-PHE	C ₁₅ H ₁₂	192	3	123	340	1.87 x10 ⁻²
Phenanthrene, 9-methyl	9M-PHE	C ₁₅ H ₁₂	192	3	94	340	3.08 x10 ⁻²
Anthracene, 1-methyl	1M-AN	C ₁₅ H ₁₂	192	3	86	200	NA
Phenanthrene, 1-methyl-	1M-PHE	C ₁₅ H ₁₂	192	3	123	340	1.87 x10 ⁻²
Anthracene, 9-methyl-	9M-AN	C ₁₅ H ₁₂	192	3	82	196	1.93 x10 ⁻²
Phenanthrene, 2,7-dimethyl-	27dM-PHE	C ₁₆ H ₁₄	206	3	145	351	1.63 x10 ⁻²
Phenanthrene, 1,6-dimethyl-	16dM-PHE	C ₁₆ H ₁₄	206	3	109	351	1.63 x10 ⁻²
Phenanthrene, 1,7-dimethyl-	17dM-PHE	C ₁₆ H ₁₄	206	3	109	351	1.63 x10 ⁻²
Phenanthrene, 1,2-dimethyl-	12dM-PHE	C ₁₆ H ₁₄	206	3	109	351	1.63 x10 ⁻²

Compound	Abbreviation	Formula	Molecular Weight [g/mol]	Number of Rings	Mp [°C]	Bp [°C]	Ps@25°C [Pa] ¹
Anthracene, 9,10-dimethyl-	910dM-AN	C ₁₆ H ₁₄	206	3	183	351	1.63 x10 ⁻²
Phenanthrene, 9-n-propyl-	9P-PHE	C ₁₇ H ₁₆	220	3	112	363	8.59 x10 ⁻³
Phenanthrene, 1,2,6-trimethyl-	126tM-PHE	C ₁₇ H ₁₆	220	3	NA	NA	NA
Phenanthrene, 1,9-dimethyl-7-ethyl-	19dM-7E-PHE	C ₁₈ H ₁₈	234	3	NA	NA	NA
Phenanthrene, 1,9-dimethyl-5-ethyl -	19dM-5E-PHE	C ₁₈ H ₁₈	234	3	NA	NA	NA
Phenanthrene, 1,2,6,9-tetramethyl-	1269teM-PHE	C ₁₈ H ₁₈	234	3	NA	NA	NA
C1-C4 FLT/PY:							
Fluoranthene, 2-methyl-	2M-FLT	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Fluoranthene, 8-methyl-	8M-FLT	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Fluoranthene, 7-methyl-	7M-FLT	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Fluoranthene, 1-methyl-	1M-FLT	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Fluoranthene, 3-methyl-	3M-FLT	C ₁₇ H ₁₂	216	4	105	333	4.35 x10 ⁻²
Pyrene, 2-methyl-	2M-PY	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Pyrene, 4-methyl-	4M-PY	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Pyrene, 1-methyl-	1M-PY	C ₁₇ H ₁₂	216	4	132	383	2.79 x10 ⁻³
Fluoranthene, 3-ethyl-	3E-FLT	C ₁₈ H ₁₄	230	4	141	395	1.47 x10 ⁻³
Pyrene, 4,5-dimethyl-	45dM-PY	C ₁₈ H ₁₄	230	4	NA	NA	NA
Pyrene, 1-n-propyl-	1P-PY	C ₁₉ H ₁₆	244	4	149	407	7.63 x10 ⁻⁴
Pyrene, 1-n-butyl-	1B-PY	C ₂₀ H ₁₈	258	4	157	418	3.97 x10 ⁻⁴
C1-C4 BTC:							
Chrysene, 2-methyl-	2M-CHRY	C ₁₉ H ₁₄	242	4	148	411	6.05 x10 ⁻⁴
Chrysene, 4-methyl-	4M-CHRY	C ₁₉ H ₁₄	242	4	256	411	6.05 x10 ⁻⁴
Chrysene, 1-methyl-	1M-CHRY	C ₁₉ H ₁₄	242	4	256	411	6.05 x10 ⁻⁴
Triphenylene, 2-methyl-	2M-TRI	C ₁₉ H ₁₄	242	4	148	411	6.05 x10 ⁻⁴
Benz[a]anthracene, 6,8-dimethyl-	68dM-BaA	C ₂₀ H ₁₆	256	4	154	422	3.15 x10 ⁻⁴
Benz[a]anthracene, 3,9-dimethyl-	39dM-BaA	C ₂₀ H ₁₆	256	4	154	422	3.15 x10 ⁻⁴
Benz[a]anthracene, 7,12-dimethyl-	712dM-BaA	C ₂₀ H ₁₆	256	4	122	422	3.15 x10 ⁻⁴
Chrysene, 6-n-propyl-	6P-CHRY	C ₂₁ H ₁₈	270	4	NA	NA	NA
Chrysene, 1,3,6-trimethyl-	136tM-CHRY	C ₂₁ H ₁₈	270	4	NA	NA	NA
Chrysene, 6-n-butyl-	6B-CHRY	C ₂₂ H ₂₀	284	4	NA	NA	NA

¹Values from Chemspider (<http://www.chemspider.com>, 2015), calculated with US Environmental Protection Agency's EPISuite™; NA – not available.

Table S2. PACs grouping.

Group Name	PACs
Unsubstituted PAHs:	
VOL (Volatile PAHs)	AL, AE, FL, PHE, AN
SVOL (Semi-volatile PAHs)	FLT, PY, B[a]A, CHRY
PM (Particle-bound PAHs)	B[b]FLT, B[k]FLT, B[a]P, D[ah]A, B[ghi]P
Alkylated PAHs and DBTs:	

G1 (VOL-alk-PAHs)	C1–C4 NAP, C1–C4 FL, DBT
G2 (SVOL-alk-PAHs)	RET, C1–C4 DBT, C1–C4 PHE/AN
G3 (PM-alk-PAHs)	C1–C4 FLT/PY, C1–C4 BTC

Table S3. Method performance parameters.

Compound	IDL [ng/μL]	MDL [ng/m ³]	Recovery [%]
Acenaphthylene	0.0005	0.002	74
Acenaphthene	0.0002	0.007	76
Fluorene	0.0002	0.010	79
Anthracene	0.001	0.003	77
Phenanthrene	0.0008	0.015	87
2-Methylfluorene	0.001	0.009	89
Pyrene	0.0005	0.008	94
Fluoranthene	0.0004	0.004	94
Benzo[a]fluorene	0.0007	0.002	94
1-Methylpyrene	0.0005	0.003	94
Benzo[b]fluorene	0.0006	0.002	94
Benzo[g,h,i]fluoranthene	0.0009	0.002	94
Benz[a]anthracene	0.001	0.003	108
Triphenylene	0.0008	0.003	91
Chrysene	0.0009	0.003	92
7-Methylbenz[a]anthracene	0.002	0.002	94
Benzo[b]fluoranthene	0.002	0.002	101
Perylene	0.003	0.003	94
Benzo[k]fluoranthene	0.003	0.003	99
Benzo[e]pyrene	0.002	0.002	99
Benzo[a]pyrene	0.003	0.003	98
3-Methylcholanthrene	0.005	0.007	98
Indeno[1,2,3-cd]fluoranthene	0.003	0.003	98
Anthanthrene	0.004	0.009	98
Indeno[1,2,3-cd]pyrene	0.003	0.005	107
Benzo[g,h,i]perylene	0.002	0.003	103
Benzo[b]chrysene	0.004	0.004	103
Dibenz[a,h]anthracene	0.003	0.003	107
C1–C4 NAP:			
Naphthalene, 2-methyl-	0.0002	0.051	70
Naphthalene, 1-methyl-	0.0002	0.031	70
Naphthalene, 2-ethyl-	0.001	0.008	70
Naphthalene, 1-ethyl-	0.001	0.004	70
Naphthalene, 2,6-dimethyl-	0.001	0.018	70
Naphthalene, 2,7-dimethyl-	0.001	0.018	70
Naphthalene, 1,7-dimethyl-	0.001	0.009	70
Naphthalene, 1,3-dimethyl-	0.001	0.011	70
Naphthalene, 1,6-dimethyl-	0.001	0.012	70
Naphthalene, 1,4-dimethyl-	0.001	0.003	70
Naphthalene, 1,5-dimethyl-	0.001	0.01	70
Naphthalene, 2,3-dimethyl-	0.001	0.01	70
Naphthalene, 1,2-dimethyl-	0.001	0.006	70
Naphthalene, 1,8-dimethyl-	0.001	0.002	70
Naphthalene, 2-ethyl-6-methyl-	0.001	0.009	70
Naphthalene, 1,2,6-trimethyl-	0.001	0.005	70
Naphthalene, 7-isopropyl-1-methyl-	0.0005	0.002	70
Naphthalene, 1,2,5,6-tetramethyl-	0.0005	0.003	70

Compound	IDL [ng/μL]	MDL [ng/m ³]	Recovery [%]
C1-C4 FL:			
Fluorene, 9-methyl-	0.001	0.003	79
Fluorene, 3-methyl-	0.001	0.003	79
Fluorene, 2-methyl-	0.001	0.005	79
Fluorene, 1-methyl-	0.001	0.004	79
Fluorene, 4-methyl-	0.001	0.003	79
Fluorene, 9-ethyl-	0.001	0.002	79
Fluorene, 1,7-dimethyl-	0.001	0.004	79
Fluorene, 9-n-propyl-	0.002	0.002	79
Fluorene, 9-n-butyl-	0.002	0.002	79
DBT:			
Dibenzothiophene	0.002	0.002	64
C1-C4 DBT:			
Dibenzothiophene, 4-methyl-	0.001	0.002	64
Dibenzothiophene, 2-methyl-	0.001	0.000	64
Dibenzothiophene, 3-methyl-	0.001	0.001	64
Dibenzothiophene, 1-methyl-	0.001	0.001	64
Dibenzothiophene, 4,6-dimethyl-	0.001	0.002	64
Dibenzothiophene, 2,6-dimethyl-	0.001	0.001	64
Dibenzothiophene, 2,8-dimethyl-	0.001	0.001	64
Dibenzothiophene, 1,8-dimethyl-	0.001	0.002	64
Dibenzothiophene, 2,3-dimethyl-	0.002	0.002	64
Dibenzothiophene, 2,4,7-trimethyl-	0.002	0.002	64
Dibenzothiophene, 2,3,7-trimethyl-	0.002	0.002	64
Dibenzothiophene, 2,3,8-trimethyl-	0.002	0.002	64
Dibenzothiophene, 4,6-diethyl-	0.0005	0.001	64
Dibenzothiophene, 2-n-butyl-	0.001	0.001	64
C1-C4 PHE/ANT:			
Phenanthrene, 3-methyl-	0.001	0.007	87
Phenanthrene, 2-methyl-	0.001	0.006	87
Anthracene, 2-methyl-	0.002	0.003	87
Phenanthrene, 4-methyl-	0.001	0.003	87
Phenanthrene, 9-methyl	0.002	0.006	87
Anthracene, 1-methyl	0.002	0.006	87
Phenanthrene, 1-methyl-	0.001	0.005	87
Anthracene, 9-methyl-	0.001	0.003	87
Phenanthrene, 2,7-dimethyl-	0.005	0.005	87
Phenanthrene, 1,6-dimethyl-	0.002	0.004	87
Phenanthrene, 1,7-dimethyl-	0.005	0.005	87
Phenanthrene, 1,2-dimethyl-	0.002	0.002	87
Anthracene, 9,10-dimethyl-	0.002	0.002	87
Phenanthrene, 9-n-propyl-	0.001	0.002	87
Phenanthrene, 1,2,6-trimethyl-	0.001	0.003	87
Retene	0.001	0.016	94
Phenanthrene, 1,9-dimethyl-7-ethyl-	0.002	0.003	87
Phenanthrene, 1,9-dimethyl-5-ethyl -	0.002	0.002	87
Phenanthrene, 1,2,6,9-tetramethyl-	0.002	0.003	87
C1-C4 FLT/PY:			
Fluoranthene, 2-methyl-	0.0005	0.005	94
Fluoranthene, 8-methyl-	0.0005	0.005	94
Fluoranthene, 7-methyl-	0.0005	0.003	94
Fluoranthene, 1-methyl-	0.0005	0.002	94

Compound	IDL [ng/ μ L]	MDL [ng/m ³]	Recovery [%]
Fluoranthene, 3-methyl-	0.001	0.002	94
Pyrene, 2-methyl-	0.001	0.002	94
Pyrene, 4-methyl-	0.001	0.002	94
Pyrene, 1-methyl-	0.001	0.002	94
Fluoranthene, 3-ethyl-	0.001	0.003	94
Pyrene, 4,5-dimethyl-	0.001	0.002	94
Pyrene, 1-n-propyl-	0.001	0.002	94
Pyrene, 1-n-butyl-	0.002	0.003	94
C1-C4 BTC:			
Chrysene, 2-methyl-	0.001	0.003	94
Chrysene, 4-methyl-	0.001	0.003	94
Chrysene, 1-methyl-	0.001	0.002	94
Triphenylene, 2-methyl-	0.001	0.003	97
Benz[a]anthracene, 6,8-dimethyl-	0.002	0.002	99
Benz[a]anthracene, 3,9-dimethyl-	0.002	0.002	99
Benz[a]anthracene, 7,12-dimethyl-	0.005	0.005	99
Chrysene, 6-n-propyl-	0.002	0.002	94
Chrysene, 1,3,6-trimethyl-	0.005	0.005	94
Chrysene, 6-n-butyl-	0.005	0.005	94

Table S4. Total (GP + PM) PAC concentrations (ng/m³) measured at the Montréal site during the study period (2015-2016).

Compound ^a	Min	Max	Mean ± SD	Median
4,AL	0.02	5.2	0.76±1.1	0.27
AE	0.14	4.8	0.93±0.91	0.56
FL	0.28	5.2	1.8±1.3	1.4
AN	0.05	1.9	0.24±0.32	0.14
PHE	0.96	12	4.6±2.8	3.7
MFL	0.06	2.3	0.53±0.46	0.37
PY	0.18	3.8	0.78±0.67	0.62
FLT	0.27	5.4	1.2±0.89	0.98
B[a]FL	0.01	0.25	0.04±0.05	0.02
MPY	0.01	0.16	0.03±0.03	0.02
B[b]FL	0.01	0.19	0.03±0.04	0.02
B[ghi]FL	0.02	0.51	0.09±0.11	0.05
B[a]A	0.01	0.45	0.07±0.08	0.03
TRI	0.01	0.19	0.05±0.04	0.04
CHRY	0.03	0.73	0.15±0.16	0.07
RET	0.07	1.4	0.37±0.27	0.29
MB[a]A	<MDL	0.01	<MDL	<MDL
B[b]FLT	0.02	0.96	0.17±0.20	0.09
PER	<MDL	0.22	0.01±0.03	0.005
B[k]FLT	0.01	0.31	0.05±0.06	0.03
B[e]P	<MDL	0.48	0.07±0.08	0.04
B[a]P	0.01	0.50	0.06±0.09	0.02
MCH	<MDL	0.04	<MDL	<MDL
IF	<MDL	0.05	<MDL	<MDL
ANT	<MDL	0.60	0.03±0.09	<MDL
IP	0.01	0.48	0.08±0.09	0.06
B[ghi]P	<MDL	0.66	0.08±0.10	0.05

Compound ^a	Min	Max	Mean ± SD	Median
B[b]C	<MDL	0.05	<MDL	<MDL
D[ah]A	<MDL	0.58	0.3±0.09	<MDL
C1-NAP	0.19	13	2.6±2.9	1.4
C2-NAP	0.31	17	3.3±3.5	2.0
C3-NAP	0.65	17	3.8±3.3	2.9
C4-NAP	0.27	9.6	2.2±1.7	1.6
C1-FL	0.16	4.8	1.2±0.98	0.94
C2-FL	0.13	4.4	1.5±0.97	1.3
C3-FL	0.14	7.9	2.7±1.9	2.5
C4-FL	0.04	1.8	0.69±0.48	0.69
DBT	0.01	0.63	0.16±0.16	0.10
C1-DBT	0.01	1.1	0.21±0.24	0.10
C2-DBT	0.01	1.5	0.29±0.32	0.15
C3-DBT	0.01	0.90	0.17±0.19	0.09
C4-DBT	<MDL	0.36	0.07±0.08	0.04
C1-PHE/AN	0.14	3.9	1.4±0.90	1.2
C2-PHE/AN	0.06	2.2	0.99±0.67	0.93
C3-PHE/AN	0.03	1.4	0.44±0.31	0.40
C4-PHE/AN	0.04	0.99	0.27±0.18	0.24
C1-FLT/PY	0.05	1.3	0.22±0.23	0.15
C2-FLT/PY	0.03	1.1	0.16±0.20	0.10
C3-FLT/PY	0.02	1.2	0.12±0.19	0.07
C4-FLT/PY	<MDL	0.52	0.05±0.07	0.03
C1-BTC	0.03	0.79	0.10±0.13	0.06
C2-BTC	0.01	0.59	0.06±0.09	0.04
C3-BTC	0.01	0.05	0.07±0.08	0.05
C4-BTC	0.01	0.68	0.06±0.10	0.04

<MDL – below MDL; ^aPAHs and alk-PAHs sorted with increasing molecular weight; ^bvalues below MDL were replaced by (½ × MDL) for reporting purposes; (N=54).

Table S5. Total (GP + PM) PAC concentrations (ng/m³) measured at the Toronto site during the study period (2015–2016).

Compound ^a	Min	Max	Mean ± SD	Median
AL	0.06	10	0.92±1.5	0.51
AE	0.30	6.7	2.1±1.5	1.7
FL	1.4	13	4.3±2.5	3.4
AN	0.19	1.9	0.72±0.37	0.66
PHE	3.2	39	11±7.7	8.6
MFL	0.53	4.1	1.5±0.76	1.3
PY	0.77	4.1	1.9±0.78	1.7
FLT	0.83	7.1	2.6±1.4	2.2
B[a]FL	0.03	0.25	0.07±0.03	0.06
MPY	0.08	0.78	0.16±0.09	0.14
B[b]FL	0.02	0.16	0.04±0.02	0.03
B[ghi]FL	0.08	0.78	0.16±0.09	0.14
B[a]A	0.04	0.74	0.13±0.09	0.11
TRI	0.04	0.29	0.08±0.03	0.07
CHRY	0.07	0.96	0.20±0.12	0.17
RET	0.18	1.4	0.51±0.26	0.46
MB[a]A	<MDL	<MDL	<MDL	<MDL
B[b]FLT	0.06	1.2	0.23±0.15	0.21
PER	<MDL	0.14	0.02±0.02	0.02
B[k]FLT	0.02	0.44	0.08±0.06	0.07
B[e]P	0.04	0.71	0.15±0.09	0.14
B[a]P	0.03	0.71	0.11±0.09	0.09
MCH	<MDL	<MDL	<MDL	<MDL
IF	<MDL	0.07	<MDL	<MDL
ANT	<MDL	0.16	0.03±0.02	0.02
IP	0.04	0.79	0.15±0.10	0.15
B[ghi]P	0.07	1.1	0.23±0.14	0.19
B[b]C	<MDL	0.04	<MDL	<MDL
D[ah]A	<MDL	0.08	0.02±0.01	0.01
C1-NAP	0.08	26	3.8±4.2	2.7
C2-NAP	0.05	30	6.3±5.7	5.1
C3-NAP	0.04	47	10±8.7	8.6
C4-NAP	0.03	23	8.7±4.5	8.0
C1-FL	0.01	11	4.0±2.2	3.5
C2-FL	0.04	16	6.2±3.8	5.7
C3-FL	0.12	40	11±8.3	10
C4-FL	0.04	12	3.3±2.5	2.8
DBT	0.01	1.7	0.47±0.39	0.42
C1-DBT	0.01	1.4	0.40±0.32	0.36
C2-DBT	0.01	2.1	0.62±0.49	0.53
C3-DBT	0.01	1.3	0.41±0.31	0.31
C4-DBT	0.01	0.69	0.20±0.15	0.16
C1-PHE/AN	0.05	8.1	3.5±1.8	3.3
C2-PHE/AN	0.05	6.4	2.7±1.4	2.4
C3-PHE/AN	0.04	3.6	1.5±0.80	1.4
C4-PHE/AN	0.03	1.5	0.71±0.33	0.67
C1-FLT/PY	0.01	1.5	0.52±0.23	0.49
C2-FLT/PY	0.02	1.3	0.49±0.21	0.49
C3-FLT/PY	0.03	1.2	0.47±0.20	0.48
C4-FLT/PY	0.02	0.61	0.26±0.11	0.23

Compound ^a	Min	Max	Mean ± SD	Median
C1-BTC	0.02	0.72	0.27±0.11	0.26
C2-BTC	0.01	0.47	0.28±0.11	0.28
C3-BTC	0.02	0.69	0.38±0.15	0.38
C4-BTC	0.01	0.69	0.37±0.16	0.37

<MDL – below MDL; ^aPAHs and alk-PAHs sorted with increasing molecular weight; values below MDL were replaced by ($\frac{1}{2} \times \text{MDL}$) for reporting purposes; (N=52).

Table S6. Total (GP + PM) PAC concentrations (ng/m³) measured at the Hamilton site during the study period (2015-2016).

	Min	Max	Mean ± SD	Median
AL	0.02	7.6	1.2±1.9	0.33
AE	0.15	4.6	1.2±1.0	0.93
FL	0.79	28	3.9±4.8	1.9
AN	0.05	8.8	0.81±1.3	0.28
PHE	1.51	70	12±13	9.1
MFL	0.25	3.5	0.89±0.66	0.68
PY	0.31	16	2.7±3.3	1.3
FLT	0.48	31	4.5±5.6	2.5
B[a]FL	0.01	1.9	0.22±0.35	0.06
MPY	0.01	0.41	0.06±0.07	0.04
B[b]FL	0.01	1.6	0.16±0.28	0.03
B[ghi]FL	0.016	1.1	0.19±0.23	0.09
B[a]A	0.021	2.7	0.38±0.54	0.11
TRI	0.024	1.6	0.18±0.24	0.08
CHRY	0.037	5.2	0.63±0.93	0.22
RET	0.067	1.2	0.34±0.24	0.29
MB[a]A	<MDL	0.006	<MDL	<MDL
B[b]FLT	0.030	7.5	0.08±1.3	0.28
PER	<MDL	0.67	0.09±0.13	0.029
B[k]FLT	0.012	2.2	0.27±0.40	0.09
B[e]P	<MDL	3.7	0.41±0.67	0.13
B[a]P	0.011	2.4	0.31±0.44	0.11
MCH	<MDL	0.084	<MDL	<MDL
IF	<MDL	0.15	0.02±0.03	0.01
ANT	<MDL	0.82	0.08±0.14	0.02
IP	<MDL	3.8	0.43±0.69	0.14
B[ghi]P	<MDL	3.3	0.39±0.61	0.14
B[b]C	<MDL	0.21	0.03±0.04	0.01
D[ah]A	<MDL	0.79	0.08±0.14	0.03
C1-NAP	0.21	27	2.9±3.9	1.8
C2-NAP	0.66	21	3.6±3.3	2.8
C3-NAP	1.6	22	5.5±3.6	4.6
C4-NAP	1.5	12	4.6±2.1	4.1
C1-FL	0.77	7.5	2.1±1.3	1.8
C2-FL	0.68	6.7	2.5±1.3	2.4
C3-FL	0.91	15	4.7±3.0	4.3
C4-FL	0.19	5.6	1.3±1.0	1.2
DBT	0.01	1.9	0.42±0.42	0.28
C1-DBT	<MDL	2.3	0.34±0.37	0.25
C2-DBT	<MDL	5.4	0.48±0.76	0.36
C3-DBT	<MDL	6.9	0.34±0.95	0.19
C4-DBT	<MDL	5.7	0.20±0.78	0.08
C1-PHE/AN	0.43	13	2.9±2.5	2.5
C2-PHE/AN	0.21	7.4	1.9±1.6	1.6
C3-PHE/AN	0.09	10	1.0±1.4	0.78

	Min	Max	Mean ± SD	Median
C4-PHE/AN	0.06	5.8	0.49±0.79	0.36
C1-FLT/PY	0.07	3.7	0.61±0.72	0.29
C2-FLT/PY	0.04	3.9	0.53±0.78	0.23
C3-FLT/PY	0.05	5.2	0.39±0.76	0.14
C4-FLT/PY	0.02	1.9	0.17±0.28	0.07
C1-BTC	0.05	2.2	0.37±0.47	0.14
C2-BTC	0.02	2.2	0.21±0.34	0.08
C3-BTC	0.02	2.1	0.21±0.31	0.10
C4-BTC	0.13	8.4	0.98±1.4	0.41

<MDL – below MDL; ^a PAHs and alk-PAHs sorted with increasing molecular weight; ^b values below MDL were replaced by ($\frac{1}{2} \times \text{MDL}$) for reporting purposes; (N=52).

Table S7. Total (GP + PM) PAC concentrations (ng/m³) measured at the Simcoe site during the study period (2015–2016).

Compound ^a	Min	Max	Mean ± SD	Median
AL	0.01	2.1	0.14±0.30	0.06
AE	0.03	0.85	0.26±0.19	0.23
FL	0.25	3.9	1.3±0.79	1.2
AN	0.02	1.1	0.23±0.26	0.09
PHE	0.46	20	3.3±3.6	2.1
MFL	0.05	1.2	0.45±0.35	0.24
PY	0.08	5.3	0.51±0.76	0.34
FLT	0.14	8.5	0.79±1.2	0.54
B[a]FL	0.01	0.36	0.03±0.05	0.02
MPY	0.01	0.12	0.03±0.03	0.02
B[b]FL	0.01	0.25	0.02±0.03	0.01
B[ghi]FL	0.01	0.35	0.04±0.05	0.02
B[a]A	0.01	0.64	0.04±0.08	0.02
TRI	0.01	0.31	0.04±0.04	0.03
CHRY	0.02	1.0	0.09±0.14	0.06
RET	0.06	1.6	0.35±0.27	0.27
MB[a]A	<MDL	0.01	<MDL	<MDL
B[b]FLT	0.01	1.3	0.10±0.17	0.06
PER	<MDL	0.12	0.01±0.02	<MDL
B[k]FLT	<MDL	0.40	0.03±0.06	0.02
B[e]P	<MDL	0.64	0.05±0.09	0.03
B[a]P	<MDL	0.43	0.04±0.06	0.02
MCH	<MDL	0.01	<MDL	<MDL
IF	<MDL	0.04	<MDL	<MDL
ANT	<MDL	0.16	0.01±0.03	<MDL
IP	<MDL	0.68	0.05±0.09	0.03
B[ghi]P	<MDL	0.62	0.05±0.09	0.03
B[b]C	<MDL	0.06	<MDL	<MDL
D[ah]A	<MDL	0.13	0.01±0.02	<MDL
C1-NAP	0.16	4.1	0.99±0.75	0.86
C2-NAP	0.27	5.6	1.4±0.99	1.3
C3-NAP	0.49	8.6	2.4±1.8	1.7
C4-NAP	0.39	7.1	2.1±1.8	1.3
C1-FL	0.23	3.0	1.1±0.78	0.89
C2-FL	0.18	5.1	1.7±1.5	0.84

Compound ^a	Min	Max	Mean ± SD	Median
C3-FL	0.27	12	3.9±3.9	1.6
C4-FL	0.07	4.4	1.2±1.3	0.48
DBT	0.01	0.99	0.13±0.18	0.08
C1-DBT	<MDL	0.91	0.13±0.17	0.05
C2-DBT	<MDL	1.3	0.24±0.28	0.10
C3-DBT	0.01	0.89	0.13±0.17	0.06
C4-DBT	<MDL	0.38	0.06±0.08	0.02
C1-PHE/AN	0.14	4.9	1.3±1.2	0.71
C2-PHE/AN	0.07	3.8	1.1±1.1	0.54
C3-PHE/AN	0.03	2.0	0.58±0.59	0.29
C4-PHE/AN	0.04	0.83	0.31±0.21	0.24
C1-FLT/PY	0.03	0.86	0.19±0.16	0.13
C2-FLT/PY	0.02	0.71	0.16±0.15	0.09
C3-FLT/PY	0.01	0.49	0.09±0.08	0.07
C4-FLT/PY	<MDL	0.20	0.03±0.03	0.03
C1-BTC	0.02	0.41	0.06±0.05	0.05
C2-BTC	0.01	0.22	0.03±0.03	0.03
C3-BTC	0.01	0.22	0.04±0.03	0.03
C4-BTC	0.01	0.23	0.03±0.03	0.02

<MDL—below MDL ^a PAHs and alk-PAHs sorted with increasing molecular weight;
^b values below MDL were replaced by ($\frac{1}{2} \times \text{MDL}$) for reporting purposes; (N=54).

Table S8. Total (GP + PM) PAC concentrations (ng/m³) measured at the Edmonton site during the study period (2015-2016).

Compound ^a	Min	Max	Mean ± SD	Median
AL	0.02	3.3	0.69±0.79	0.39
AE	0.04	1.4	0.44±0.29	0.35
FL	0.26	3.1	1.1±0.58	0.93
AN	0.04	0.34	0.13±0.07	0.11
PHE	0.82	5.2	2.4±1.2	1.9
MFL	0.12	1.4	0.40±0.25	0.32
PY	0.16	1.3	0.52±0.28	0.43
FLT	0.19	1.3	0.55±0.29	0.42
B[a]FL	0.01	0.06	0.02±0.02	0.02
MPY	0.01	0.06	0.02±0.14	0.02
B[b]FL	<MDL ^b	0.04	0.01±0.01	0.01
B[ghi]FL	0.01	0.23	0.07±0.05	0.05
B[a]A	0.01	0.17	0.04±0.03	0.03
TRI	<MDL	0.14	0.04±0.03	0.03
CHRY	0.01	0.42	0.090±0.08	0.06
RET	0.12	6.0	0.80±1.1	0.45
MB[a]A	<MDL	<MDL	<MDL	<MDL
B[b]FLT	0.01	1.3	0.10±0.18	0.06
PER	<MDL	<MDL	<MDL	<MDL
B[k]FLT	<MDL	0.12	0.03±0.03	0.02
B[e]P	<MDL	0.19	0.06±0.05	0.04
B[a]P	<MDL	0.08	0.02±0.02	0.02
MCH	<MDL	<MDL	<MDL	<MDL
IF	<MDL	0.02	0.01±0.01	<MDL
ANT	<MDL	0.02	0.01±0.01	<MDL
IP	<MDL	0.24	0.06±0.05	0.04
B[ghi]P	<MDL	0.28	0.08±0.06	0.06
B[b]C	<MDL	0.01	<MDL	<MDL
D[ah]A	<MDL	0.02	<MDL	<MDL
C1-NAP	0.22	21	3.3±4.1	1.9
C2-NAP	0.27	19	3.5±3.7	2.4
C3-NAP	0.46	15	4.4±3.4	3.1
C4-NAP	0.51	6.8	2.3±1.4	1.9
C1-FL	0.28	2.7	0.94±0.54	0.83
C2-FL	0.41	2.7	1.2±0.63	1.1
C3-FL	0.80	6.3	2.4±1.3	2.1
C4-FL	0.19	1.6	0.69±0.35	0.64
DBT	0.01	0.48	0.09±0.09	0.06
C1-DBT	0.01	1.2	0.17±0.24	0.08
C2-DBT	0.03	1.3	0.20±0.26	0.10
C3-DBT	0.02	0.69	0.12±0.13	0.07
C4-DBT	0.01	0.31	0.06±0.06	0.04
C1-PHE/AN	0.29	2.6	0.96±0.60	0.78
C2-PHE/AN	0.21	2.4	0.85±0.56	0.71
C3-PHE/AN	0.09	1.4	0.550±0.34	0.43
C4-PHE/AN	0.07	2.3	0.45±0.44	0.29
C1-FLT/PY	0.05	0.36	0.14±0.08	0.11
C2-FLT/PY	0.05	0.39	0.15±0.08	0.12
C3-FLT/PY	0.04	0.36	0.15±0.08	0.12
C4-FLT/PY	0.01	0.19	0.07±0.05	0.06

Compound ^a	Min	Max	Mean ± SD	Median
C1-BTC	0.02	0.30	0.09±0.06	0.07
C2-BTC	0.02	0.22	0.08±0.05	0.07
C3-BTC	0.02	0.27	0.09±0.05	0.08
C4-BTC	0.01	0.30	0.08±0.05	0.08

<MDL—below MDL; ^a PAHs and alk-PAHs sorted with increasing molecular weight; ^b values below MDL were replaced by ($\frac{1}{2} \times \text{MDL}$) for reporting purposes; (N=50).

Table S9. Total (GP + PM) PAC concentrations (ng/m³) measured at the AMS 11 site during the study period (2015-2016) (Wnorowski et al., 2021).

Compound ^a	Min	Max	Mean ± SD	Median
AL	0.01	8.5	0.39±1.3	0.06
AE	0.06	2.9	0.79±0.66	0.57
FL	0.17	7.7	1.0±1.1	0.73
AN	0.02	2.7	0.57±0.61	0.33
PHE	0.65	20	3.7±3.2	2.8
MFL	0.15	3.9	0.98±0.64	0.84
PY	0.13	6.8	1.2±1.4	0.68
FLT	0.08	1.9	0.46±0.44	0.32
B[a]FL	0.01	1.8	0.25±0.38	0.10
MPY	0.01	1.9	0.28±0.39	0.12
B[b]FL	<MDL	0.83	0.10±0.16	0.04
B[ghi]FL	0.01	0.49	0.07±0.11	0.02
B[a]A	0.02	9.1	1.2±1.9	0.35
TRI	<MDL	3.4	0.23±0.51	0.08
CHRY	0.01	9.5	1.1±1.7	0.43
RET	0.08	88	4.3±17.	0.39
MB[a]A	<MDL	0.08	<MDL	<MDL
B[b]FLT	<MDL	3.8	0.49±0.75	0.14
PER	<MDL	0.80	0.11±0.18	0.04
B[k]FLT	<MDL	1.1	0.13±0.20	0.04
B[e]P	0.01	8.6	1.1±1.8	0.36
B[a]P	0.01	9.8	1.2±2.1	0.34
MCH	<MDL	0.34	0.03±0.06	0.02
IF	0.01	0.07	0.02±0.01	0.02
ANT	0.01	0.83	0.10±0.18	0.03
IP	<MDL	2.3	0.29±0.48	0.08
B[ghi]P	0.01	7.9	1.0±1.7	0.28
B[b]C	0.01	3.5	0.42±0.74	0.11
D[ah]A	<MDL	3.4	0.42±0.73	0.10
C1-NAP	0.16	44	4.4±8.8	1.7
C2-NAP	0.41	58	6.6±8.9	3.9
C3-NAP	1.5	59	12±10	11
C4-NAP	2.6	35	12±8.0	10
C1-FL	0.59	14	3.3±2.2	2.8
C2-FL	1.0	19	5.8±3.4	5.2
C3-FL	2.1	34	12±7.9	11
C4-FL	0.49	9.3	3.5±2.2	3.1
DBT	0.07	4.4	1.1±1.0	0.77
C1-DBT	0.22	15	3.3±3.3	2.2
C2-DBT	0.36	26	5.2±5.6	3.5
C3-DBT	0.25	22	3.9±4.7	2.3

Compound ^a	Min	Max	Mean ± SD	Median
C4-DBT	0.15	11	2.1±2.5	1.3
C1-PHE/AN	0.62	21	5.4±4.4	3.8
C2-PHE/AN	0.75	23	5.8±5.1	4.1
C3-PHE/AN	0.57	15	3.8±3.6	2.6
C4-PHE/AN	0.28	33	3.3±6.4	1.6
C1-FLT/PY	0.08	13	1.8±2.8	0.69
C2-FLT/PY	0.08	28	4.1±6.3	1.3
C3-FLT/PY	0.08	45	6.2±9.9	1.8
C4-FLT/PY	0.01	32	4.3±6.8	1.3
C1-BTC	0.02	53	7.1±11	2.1
C2-BTC	0.01	43	6.0±9.7	1.7
C3-BTC	0.01	29	4.0±6.3	1.2
C4-BTC	0.01	19	2.8±4.4	0.98

<MDL—below MDL; ^a PAHs and alk-PAHs sorted with increasing molecular weight;
^b values below MDL were replaced by (½ x MDL) for reporting purposes; (N=54).

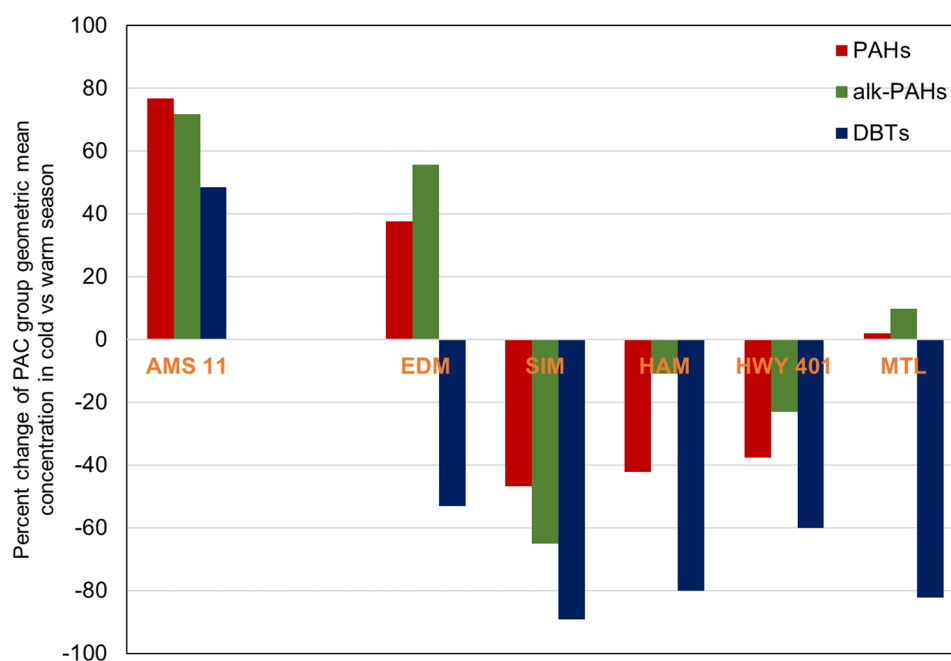


Figure S1. Unsubstituted PAH, alk-PAH and DBT concentration changes at cold (October-March) versus warm (April-September) season by site for 2015-2016 period. Note, the data for the AMS11 site is reported for comparison [2].

References

1. Wnorowski, A., Tardif M., Harnish D., Poole G. & Chiu C.H.. Correction of analytical results for recovery: Determination of PAHs in ambient air, soil, and diesel emission control samples by isotope dilution gas chromatography-mass spectrometry, *Polycyclic Aromatic Compounds*, 2006, 26, 313–329, DOI: 10.1080/10406630601028171.
2. Wnorowski, A., Aklilu, Y. A., Harner, T., Schuster, J., & Charland, J. P. Polycyclic aromatic compounds in ambient air in the surface minable area of Athabasca oil sands in Alberta (Canada). *Atmos. Environ.* 2021, 244, 117897..