Supplement for

Uptake Behavior of Polycyclic Aromatic Compounds during Field Calibrations of the XAD-Based Passive Air Sampler Across Seasons and Locations

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Text S1 Sample Treatment and Analysis

Sample Treatment

Borden Experiment. Samples were extracted using either dichloromethane (DCM) or petroleum ether (PE), concentrated to ~1.0 mL using rotary evaporation and a gentle nitrogen stream, then cleaned and fractionated on a silicic acid/alumina (S/A) column (10 mm I.D.) (Su et al., 2006, 2007). The S/A column was prepared with 3.0 g of silicic acid (3% deactivated) topped with 2.0 g of alumina (6% deactivated) and followed with 1.0 cm of anhydrous Na_2SO_4. The column was cleaned with 30 mL of DCM followed with 30 mL PE. The concentrated extract was gently loaded on the top of the column, and Fraction 1 (F1) was eluted with 50 mL PE, followed by 30 mL of DCM to obtain Fraction 2 (F2). Some low molecular weight PAHs were eluted in F1, while intermediate and heavier PAHs were contained in F2. Both fractions were further evaporated to ~0.5 mL for instrumental analysis. Finally, 100 ng of Mirex was added as an internal standard to all concentrated extracts prior to instrumental analysis.

Toronto Experiment. The detailed extraction method for samples has been described in previous publications (Li et al., 2023b, a).

Instrumental Analysis

Borden Experiment. Instrumental analysis for PAHs was conducted on an Agilent 6890 gas chromatograph equipped with an auto-sampler (Agilent 7683) and a mass spectrometric detector (Agilent 5973 MSD). 2 μL of extract was injected in splitless mode to a DB-5MS column (J&W Scientific; 60m × 0.25mm i.d., 0.10 μm film thickness) at inlet temperature of 280 °C and separated under a temperature program: 70 °C for 1 min, 10 °C min^{-1} to 90 °C for 1 min, 4 °C min^{-1} to 130 °C, 5 °C min^{-1} to 240 °C and 4 °C min^{-1} to 300 °C and held for 2 min. The interface connecting the GC with the MSD was set to 310 °C, while the ion source and quadrupole temperatures were 230 °C and 150 °C, respectively. The carrier gas was helium at 1.0 mL min^{-1}. PAHs were analyzed by electron impact in selected ion monitoring mode. 16 PAHs were quantified and the corresponding ions (target/qualifier) are listed in Table S1.

Toronto Experiment. The PACs were analyzed using GC-MS/MS (Agilent 7000A Triple Quadrupole GC-MS/MS and 8890 GC –MS/MS) in EI mode. PACs congeners were separated by a select PAH column (Agilent J&W Scientific select PAH column, 30 m × 0.25 mm i.d. × 0.15 μm film thickness) (Anderson et al., 2015). Helium was used as the carrier gas at a flow rate of 2 mL min^{-1}, and 2 μL of extract was injected in pulsed splitless mode at 300 °C. The oven temperature program was as follows: initial oven temperature was 70 °C and held for 1 min then raised to 180 °C at 50 ˚C min^{-1}, raised to 230 °C at 3 °C min^{-1}, held for 6 min and raised to 280 °C at 17 ˚C min^{-1}, held for 10 min, raised to 298 °C at 5 °C min^{-1}, and raised to 350 °C at 14°C min^{-1}, and held for 5 min. The ion source and interface temperature were set at 300 °C and 290 °C, respectively. The precursor and product ions for GC-MS/MS detection are listed in Table S2.

Text S2 Quality Assurance and Quality Control

All glassware was machine-washed with detergents and baked at 450 °C in a muffle furnace for over 8 hours to remove potential contaminants. All the other experimental materials coming in contact with

the samples or extracts were cleaned and rinsed with solvents three times before use.

Borden Experiment. Prior to sampling, the GFFs were pre-cleaned by baking at 425 °C overnight (~20 hr) and were wrapped in acetone-rinsed aluminum foil until use; the PUFs were cleaned with a Soxhlet using first acetone (~20 hours) and then petroleum ether (PE) for ~20 hours. The PUFs were further dried under vacuum in a desiccator and finally stored in an acetone-rinsed jar with a Teflon-lined lid. All XAD used in this study was pre-cleaned using the same rigorous procedures described previously: rinsed with Milli-Q water and Soxhlet extracted three times for four days each using methanol, acetonitrile, and dichloromethane (DCM). Furthermore, the cleaned XAD was subject to a wash with sodium hydroxide, DCM, and methanol (Wania et al., 2003), and the sample vial was rinsed three times (3 × 1 mL) with iso-octane. The quantitative results from a large number of field blanks (35 PUFs that had been placed in the sampler, but that had not aspirated any air) were used in the definition of method detection limit (MDL), defined as three times standard deviation of the concentrations in the field blanks. Laboratory procedure blanks and thimbles, collected periodically, were either non-detectable or systematically lower than field blanks. The results from two PAS blanks, collected at the beginning of the PAS deployment, and the MDLs derived from them, are listed in Table S4. Levels of the analytes in six procedural XAD blanks, extracted jointly with the samples, were either non-detectable or below MDL. All reported data are blank corrected provided they exceeded the MDLs. However, no data were adjusted for recovery. Recoveries of 10 ng of mixed native PAHs spiked onto pre-cleaned PUFs ranged from 79.4% to 91.6% with RSDs between 1.4% and 9.8% for PAHs (n = 5). The extraction efficiency was also tested by extracting twice the four XAD samples, which had been exposed in the field for 12 months. None of analytes was found above the MDL in the second extract, indicating complete extraction of the XAD resin.

One-third of back PUF samples, collected during different seasons, were extracted separately in order to test for chemical breakthrough. Fluorene and phenanthrene also exhibited some seasonally variable, but relatively low break-through. Up to 30 and 15 % of the total fluorene and phenanthrene was found in the back PUFs, thus these data were not used for sampling rate calculations.

Toronto Experiment. All glassware was machine-washed with detergents and baked at 450 °C in a muffle furnace for over 8 hours to remove potential contaminants. All the other experimental materials coming in contact with the samples or extracts were cleaned and rinsed with solvents three times prior to use. The glass fiber filters were baked at 450 °C in a muffle furnace for over 8 hours, and PUFs were cleaned three times using methanol, acetone, and hexane, each for a duration of 24 hours with each solvent. All extraction and concentration procedures were conducted in a trace analytical lab. Seven procedure blanks were extracted and analyzed with field blanks and field samples. The amounts of target chemicals in PAS and AAS extracts (M_{PAS} and M_{AAS}, ng) were reduced by the average of the amount detected in field blanks. Quantification was done using an internal standard method relying on the spiked labeled chemicals. Therefore, the reported amounts have been corrected for recovery. The recoveries of surrogates are given in Table S2. The MDLs, provided in Table S3, were calculated as three times the standard deviations of the levels in field blanks if the analytes were detected in blanks (the signal-to-noise ratio (S/N) > 3), otherwise they were calculated as the concentrations at which the S/N is 3.

Table S1. The quantifier and qualifier ions for GC-MS detection for samples from the Borden calibration study

Chemicals	Quantifier ion	Qualifier ion
Naphthalene	128	127
Acenaphthylene	152	151
Acenaphthene	153	154
Fluorene	166	165
Phenanthrene	178	179
Anthracene	178	179
Fluoranthene	202	200
Pyrene	202	200
Benz[a]anthracene	228	226
Chrysene	228	226
Benzo[b]fluoranthene	252	253
Benzo[k]fluoranthene	252	253
Benzo[a]pyrene	252	253
Indeno[123-cd]pyrene	276	274
Dibenz[ah]anthracene	278	276
Benzo[ghi]perylene	276	274
Mirex	272	237

Table S2. The precursor and product ions for GC-MS/MS detection for samples from the Toronto experiment

Chemicals	Abbreviation	Precursor ion	Product ion	CE (eV)
Spiking Standards				
Fluorene-d_{10}	FLU-d_{10}	176.0	174.0	30
		175.0	173.0	40
Anthracene-d_{10}	ANT-d_{10}	188.0	160.0	30
		188.0	186.0	25
Fluoranthene-d_{10}	FLA-d_{10}	212.0	208.0	45
		210.0	208.0	25
Benz[a]anthracene-d_{12}	BaA-d_{12}	240.0	236.0	45
		240.0	212.0	35
Benzo[a]pyrene-d_{12}	BaP-d_{12}	264.0	260.0	50
		264.0	236.0	45
$^{13}C_6$-Ideno[1,2,3-cd]pyrene	$^{13}C_6$-IP	284.0	282.0	40
		282.0	280.0	40
Dibenz[a,c]anthracene-d_{14}	DiBacA-d_{14}	292.0	288.0	50
		292.0	264.0	45
5-Methylchrysene-d_3	5-MeCHY-d_3	245.0	228.0	45
		245.0	243.0	30
1-Methylnapthalene-d_{10}	1-MeNAP-d_{10}	152.0	122.0	40
		150.0	122.0	25
2,6-Dimethylnaphthalene-d_{12}	2,6-DiMeNAP-d_{12}	168.0	166.0	25
		168.0	150.0	20
Coronene-d_{12}	COR-d_{12}	311.8	308.2	60
Injection Standards				
$^{13}C_6$- Benz[a]anthracene		234.1	208.1	35
		234.1	232.1	30
Native Standards				
Naphthalene	NAP	127.9	78.1	25
		126.1	74.0	35
		127.9	102.1	25
2-Methylnaphthalene	2-MeNAP	141.9	115.1	35
		141.9	141.0	25
		140.9	115.0	25
1-Methylnaphthalene	1-MeNAP	141.9	115.1	35
		141.9	141.0	25
		140.9	115.0	25
2,6-Dimethylnaphthalene	2,6-DiMeNAP	156.0	115.1	40
		156.0	141.1	20
		140.9	115.1	20
1,3-Dimethylnaphthalene	1,3-DiMeNAP	156.0	115.1	40
		156.0	141.1	20
		140.9	115.1	20
1,5-Dimethylnaphthalene	1,5-DiMeNAP	156.0	115.1	40
		156.0	141.1	20

		140.9	115.1	20
Acenaphthylene	ACY	152.0	102.0	40
		152.0	126.0	35
		150.0	98.0	40
Acenaphthene	ACE	154.0	152.0	40
		153.0	77.0	45
		153.0	127.0	35
2,3,5-Trimethylnaphthalene	2,3,5-TriMeNAP	170.0	155.1	20
		155.0	128.0	30
Fluorene	FLU	166.0	164.0	45
		166.0	165.0	25
		164.8	163.1	40
1-Methylfluorene	1-MeFLU	180.0	165.1	20
		164.0	163.0	20
Dibenzothiophene	DBT	183.9	139.0	45
		183.9	152.1	25
Phenanthrene	PHE	176.0	150.0	30
		178.0	176.0	35
		178.0	152.1	25
Anthracene	ANT	178.0	176.0	35
		178.0	152.1	25
2-Methylphenanthrene	2-MePHE	192.0	189.0	45
		192.0	191.0	20
		191.0	189.0	30
2-Methylanthracene	1-MePHE	192.0	189.0	45
		192.0	191.0	20
		191.0	189.0	30
1-Methylanthracene	9-MeANT	192.0	189.0	45
		192.0	191.0	20
		191.0	189.0	30
1-Methylphenanthrene	1-MePHE	192.0	189.0	45
		192.0	191.0	20
		191.0	189.0	30
9-Methylanthracene	9-MeANT	192.0	189.0	45
		192.0	190.0	30
		192.0	191.0	20
		191.0	189.0	30
3,6-dimethlylphenanthrene	3,6-DiMeNAP	206.0	191.1	20
		206.0	205.0	15
		191.0	189.0	30
2,3-dimethylanthracene	2,3-DiMeANT	206.0	191.1	20
		210.0	208.0	25
		191.0	189.0	30
Fluoranthene	FLA	202.0	200.0	40
		201.0	200.0	20
		200.0	199.0	25
Pyrene	PYE	202.0	200.0	50
		201.0	200.0	30

		200.0	199.0	25
Retene	RET	219.0	203.1	25
		219.0	204.1	15
9,10-Dimethylanthracene	9,10-DiMeANT	206.0	205.0	20
		206.0	191.1	20
		191.0	189.0	20
2-Methylfluoranthene	2-MeFLA	216.0	215.0	25
		215.0	213.0	40
1-Methylpyrene	1-MePYE	216.0	215.0	25
		215.0	213.0	40
		215.0	189.0	30
Benzo(ghi)Fluoranthene	BghiF	226.0	225.0	35
		226.0	224.0	55
Benz[a]anthracene	BaA	228.0	226.0	40
		226.0	224.0	40
		226.0	225.0	25
Triphenylene	TP	228.0	226.0	40
		226.0	225.0	25
Chrysene	CHY	228.0	226.0	40
		226.0	225.0	25
6-Methylchrysene	6-MeCHY	242.0	241.0	20
		241.0	239.0	35
4-Methylchrysene	4-MeCHY	242.0	239.0	55
		242.0	241.0	20
		241.0	239.0	35
2-Ethylchrysene	2-EtCHY	256.0	239.0	55
		256.0	241.0	20
		241.0	239.0	35
Benzo[b]fluoranthene	BbF	252.0	250.0	45
		250.0	248.0	45
7,12-Dimethylbenz[a]anthracene	7,12-DiMeBaA	256.0	241.0	20
		241.0	239.0	35
Benzo[k]fluoranthene	BkF	252.0	250.0	45
		252.0	226.0	30
		250.0	248.0	45
		126.0	113.0	15
Benzo[e]pyrene	BeP	252.0	250.0	45
		252.0	226.0	30
		250.0	248.0	45
		126.0	113.0	15
Benzo[a]pyrene	BaP	252.0	250.0	45
		252.0	226.0	30
		250.0	248.0	45
Indeno[1,2,3-c,d] pyrene	IP	275.9	274.2	45
		273.9	272.1	45
		138.0	137.0	15
Dibenz[a,h]anthracene	DiBahA	278.0	276.0	45
		276.0	274.0	45

		125.0	124.0	15
Dibenz[a,c]anthracene	DiBacA	278.0	276.0	45
		276.0	274.0	45
		125.0	124.0	15
Benzo[ghi]perylene	BghiP	276.0	274.0	60
		276.0	275.0	35
		138.0	137.0	15
Anthanthrene	ANTA	276.0	274.0	60
		276.0	275.0	35
		138.0	137.0	15
Coronene	COR	300.0	298.0	60
		300.0	299.0	40
		298.0	296.0	45

Table S3. Recoveries of spiked surrogates for samples from the Toronto calibration experiment

	Recovery Rates (%)	
	Passive air sample (PAS)	**Active air sample (AAS)**
Toronto Calibration Study		
Fluorene-d_{10}	66.7	81.8
Anthracene-d_{10}	71.7	82.2
Fluoranthene-d_{10}	78.2	82.5
Benz[a]anthracene-d_{12}	92.6	99.2
Benzo[a]pyrene-d_{12}	75.2	67.1
$^{13}C_6$-Ideno[1,2,3-cd]pyrene	85.8	82.4
Dibenz[a,c]anthracene-d_{14}	82.8	80.3
5-Methylchrysene-d_3	89.9	97.2
1-Methylnapthalene-d_{10}	54.9	75.1
2,6-Dimethylnaphthalene-d_{12}	35.0	59.2
Coronene-d_{12}	65.3	72.5

Table S4. The list of reliably detected PACs, their properties, and method detection limits (MDLs) for passive air samples (PASs) and active air samples (AASs)

Chemicals	log $K_{XAD/air}$ (L air g^{-1} XAD) at 20 °C[1]	$\Delta U_{XAD/air}$ (kJ/mol)[1]	MDL for PAS (ng/sample)[2]	MDL for AAS (pg/m^3)[2]	MDL for PAS (ng/sample)[3]	MDL for AAS (pg/m^3)[3]
Naphthalene	2.69	-34	0.41	3.8	22	55
2-Methylnaphthalene	3.06	-35	0.56	5.2		
1-Methylnaphthalene	3.19	-35	0.76	7.0		
2,6-dimethylnaphthalene	3.45	-36	0.68	6.3		
1,3-dimethylnaphthalene	3.57	-36	0.45	4.2		
1,5-dimethylnaphthalene	3.75	-37	0.16	1.5		
Acenaphthylene	3.33	-35	0.064	0.60	23	17
Acenaphthene	3.61	-36	0.074	0.68	12	14
2,3,5-trimethylnaphthalene	4.05	-38	0.10	0.90		
Fluorene	3.97	-37	0.013	0.12	15	5.8
1-Methylfluorene	4.38	-39	0.36	3.3		
Dibenzothiophene	4.35	-38	0.0053	0.052		
Phenanthrene	4.35	-38	0.0075	0.072	12	22
Anthracene	4.22	-37	0.036	0.33	8.3	9.7
2-Methylphenanthrene	4.88	-39	0.0092	0.084		
1-Methylanthracene	4.81	-39	0.014	0.17		
9-Methylanthracene	4.91	-39	0.014	0.13		
Fluoranthene	5.16	-40	0.14	1.3	12	1.9
Pyrene	5.01	-39	0.11	1.0	10	2.4
Retene	5.80	-42	0.038	0.35		
2-methylfluoranthene	5.24	-40	0.21	1.9		
1-Methylpyrene	5.56	-41	0.050	0.46		
Benzo(ghi)Fluoranthene	5.69	-40	0.029	0.27		
Benz[a]anthracene	6.08	-42	0.0089	0.083		
Triphenylene	6.13	-42	0.028	0.34		
Chrysene	6.10	-42	0.023	0.17		
Benzo[b]fluoranthene	7.05	-45	0.042	0.38		
Benzo[k]fluoranthene	7.03	-44	0.018	0.16		

[1] The logarithm of the equilibrium concentration ratios between XAD resin and air ($K_{XAD/air}$, L air g^{-1} XAD) at 20 °C and the internal energies of phase transfer between XAD and air ($\Delta U_{XAD/air}$) were calculated based on poly parameter free energy relationships (ppLFERs) on the UFZ-LSER website.

[2] The MDLs for samples from the experiment conducted in Toronto.

[3] The MDLs for samples from the experiment conducted in Borden.

Table S5. The method detection limits (MDLs) for the PACs in the glass fiber filters from active air sampling in the Toronto calibration experiment.

Chemicals	**MDL (pg/m^3)**
Fluoranthene	0.98
Pyrene	0.00088
Retene	0.011
9,10-dimethylanthracene	0.0043
2-methylfluoranthene	0.011
1-Methylpyrene	0.00058
Benzo(ghi)Fluoranthene	0.0052
Benz[a]anthracene	0.0046
Chrysene	0.13
Triphenylene	0.0070
6-Methylchrysene	1.1
4-Methylchrysene	0.014
6-ethylchrysene	0.00066
Benzo[b]fluoranthene	0.0023
7,12-Dimethylbenz[a]anthracene	0.0016
Benzo[k]fluoranthene	0.0031
Benzo[e]pyrene	0.012
Benzo[a]pyrene	0.0062
Dibenz[a,c]anthracene	0.0032
Indeno[1,2,3-c,d] pyrene	0.0069
Dibenz[a,h]anthracene	0.0061
Benzo[ghi]perylene	1.3
Anthanthrene	0.0021
Coronene	1.5

Table S6. The experimental accumulated amounts of PACs in PASs during the one-year deployment period in Toronto

Chemicals	Accumulated amounts of PACs in PASs (ng)											
	28 days	56 days	84 days	112 days	140 days	168 days	196 days	224 days	252 days	280 days	308 days	336 days
Naphthalene	697	1330	1690	2960	3720	4820	6260	6520	5590	5840	6500	5990
2-Methylnaphthalene	128	262	369	550	628	798	928	863	744	795	833	782
1-Methylnaphthalene	75.9	154	193	118	359	386	353	404	392	279	160	372
2,6-dimethylnaphthalene	66.6	137	227	296	284	280	398	334	339	334	307	277
1,3-dimethylnaphthalene	94.2	227	308	434	327	557	517	480	377	369	315	354
1,5-dimethylnaphthalene	2.26	25.2	46.1	53.1	49.8	57.2	59.3	47.1	37.7	50.7	60.9	52.6
Acenaphthylene	0.444	0.872	0.958	2.47	2.64	3.25	3.96	3.99	3.85	3.81	5.76	6.43
Acenaphthene	6.94	26.1	29.1	37.4	36.8	36.5	30.9	26.3	20.7	16.5	18.0	15.7
2,3,5-trimethylnaphthalene	5.86	12.1	15.5	20.6	18.1	20.1	19.0	14.9	12.8	9.75	9.76	8.41
Fluorene	20.5	40.0	43.8	59.9	58.1	67.4	77.6	71.5	67.5	74.1	95.1	96.6
1-Methylfluorene	3.70	8.17	10.5	13.1	13.2	16.4	19.4	18.5	18.5	19.5	26.5	25.3
Dibenzothiophene	0.668	0.930	0.950	1.27	1.13	1.53	1.20	1.34	0.714	0.342	0.727	0.401
Phenanthrene	41.1	87.7	91.8	130	119	127	140	112	103	85.3	84.3	78.2
Anthracene	0.398	0.736	0.800	1.15	1.00	1.08	0.974	0.737	0.953	0.869	1.26	1.21
2-Methylphenanthrene	2.74	6.46	7.00	9.14	8.16	8.62	9.48	7.18	6.34	4.65	4.64	4.09
1-Methylphenanthrene	1.06	2.43	2.44	3.28	2.79	3.03	3.00	2.31	1.84	1.27	1.41	1.30
9-Methylanthracene	0.0765	0.317	0.443	0.515	0.428	0.515	0.742	0.424	0.445	0.410	0.472	0.251
Fluoranthene	4.70	11.5	12.4	15.9	16.2	19.1	21.5	22.0	15.0	12.6	13.6	14.8
Pyrene	0.471	1.45	1.56	1.62	1.80	2.22	1.97	3.06	1.04	0.853	0.875	2.07
Retene	0.322	0.787	0.923	1.00	1.34	1.68	1.67	0.503	0.786	0.473	0.733	0.210
2-Methylfluoranthene	0.439	1.41	1.58	1.56	1.97	2.34	2.40	2.95	1.79	1.68	1.88	1.96
1-Methylpyrene	N.D.	0.234	0.303	0.297	0.480	0.392	0.269	0.104	0.248	0.668	0.646	0.539
Benzo(ghi)Fluoranthene	0.0213	0.0544	0.0659	0.0709	0.0851	0.131	0.131	0.257	0.0708	0.0476	0.0467	0.174
Benz[a]anthracene	0.0230	0.0628	0.0652	0.0329	0.0820	0.123	0.0689	0.0950	0.138	0.0802	0.0811	0.0843
Triphenylene	0.0704	0.165	0.176	0.177	0.230	0.279	0.276	0.411	0.190	0.131	0.132	0.216
Chrysene	0.0367	0.0900	0.108	0.116	0.154	0.195	0.227	0.295	0.234	0.242	0.336	0.385
Benzo[b]fluoranthene	0.0297	0.0508	0.0493	0.0672	0.0861	0.118	0.114	0.231	0.191	0.130	0.161	0.206
Benzo[k]fluoranthene	N.D.	0.0121	0.00749	0.0130	0.0175	0.0324	0.0275	0.0524	0.0456	0.0243	0.0286	0.0293

N.D. means not detected.

Table S7. The experimental accumulated amounts of PACs in PASs during the one-year deployment period at the forest and clearing sites in the Borden experiment.

Chemicals	Accumulated amounts of PAHs in PASs (ng)						
	36 days	60 days	120 days	181 days	246 days	323 days	365 days
Forest site							
Naphthalene	3100	5040	9020	9360	10400	10600	10600
Acenaphthylene	55.3	136	568	180	N.D.	93.0	N.D.
Acenaphthene	92.6	283	300	304	334	200	210
Fluorene	180	377	725	628	833	886	872
Phenanthrene	450	1080	1410	989	1400	982	1190
Fluoranthene	N.D.	34.0	46.0	39.0	153	108	204
Pyrene	N.D.	62.9	67.4	18.4	373	67.2	398
Clearing site							
Naphthalene	7220	11000	17600	19400	19200	21000	20600
Acenaphthylene	148	738	201	1200	889	629	63.1
Acenaphthene	91.1	296	271	545	498	662	256
Fluorene	332	777	1120	1700	2250	2760	2510
Phenanthrene	684	1560	2360	2490	2260	2380	1790
Fluoranthene	16.3	71.6	175	224	547	399	527
Pyrene	N.D.	219	231	375	1274	250	755

N.D. means not detected.

Table S8. The experimental effective sampling volumes of PACs during the twelve four-week sampling periods for PASs from the Toronto calibration experiment

Chemicals	Effective sampling volumes of XAD-based passive air samplers during the first six sampling periods (m^3)											
	28 days	56 days	84 days	112 days	140 days	168 days	196 days	224 days	252 days	280 days	308 days	336 days
Naphthalene	12.9	20.6	28.7	55.0	75.7	103	(147)	(168)	(157)	(177)	(212)	(207)
2-Methylnaphthalene	8.95	16.5	25.4	42.0	53.1	72.0	(88.6)	(87.1)	(79.1)	(88.3)	(97.2)	(94.1)
1-Methylnaphthalene	8.49	15.3	21.1	14.2	47.6	54.2	(52.5)	(63.5)	(65.2)	(48.5)	(29.4)	(70.7)
2,6-dimethylnaphthalene	7.24	13.3	23.5	34.3	36.3	37.7	(56.7)	(49.6)	(53.1)	(54.4)	(52.8)	(49.0)
1,3-dimethylnaphthalene	8.35	18.4	26.4	42.1	35.3	63.9	(62.9)	(61.5)	(51.4)	(52.8)	(47.7)	(55.6)
1,5-dimethylnaphthalene	2.19	21.9	43.9	57.6	61.0	74.8	(85.7)	(73.4)	(64.2)	(93.0)	(121)	(110)
Acenaphthylene	5.70	12.1	14.7	39.7	46.7	59.1	(74.7)	(81.4)	(84.4)	(91.6)	(148)	(174)
Acenaphthene	4.17	15.2	19.2	28.8	33.3	37.4	(35.3)	(33.2)	(28.8)	(24.8)	(28.9)	(26.4)
2,3,5-trimethylnaphthalene	8.34	15.8	21.1	31.4	30.4	35.5	(34.9)	(28.3)	(25.4)	(20.4)	(21.6)	(19.5)
Fluorene	7.95	14.5	18.6	29.8	33.5	42.4	(52.8)	(51.8)	(52.3)	(60.4)	(81.5)	(85.1)
1-Methylfluorene	8.72	17.0	23.5	33.2	36.8	47.6	(57.8)	(56.0)	(57.6)	(63.3)	(89.7)	(88.5)
Dibenzothiophene	3.58	4.31	4.89	7.52	7.76	11.6	(10.1)	(12.3)	(7.25)	(3.71)	(8.31)	(4.78)
Phenanthrene	4.53	9.17	10.9	17.7	18.6	21.4	(26.0)	(22.7)	(22.6)	(20.0)	(21.1)	(20.6)
Anthracene	15.1	25.4	25.6	37.9	33.7	36.3	(31.3)	(24.1)	(32.2)	(30.3)	(46.2)	(46.4)
2-Methylphenanthrene	3.83	8.51	10.1	15.0	15.2	17.4	(20.7)	(16.7)	(15.8)	(12.4)	(13.2)	(12.1)
1-Methylphenanthrene	5.59	12.1	13.1	19.9	18.8	21.4	(22.1)	(17.7)	(14.7)	(10.6)	(12.3)	(11.7)
9-Methylanthracene	6.82	29.3	41.8	55.6	52.2	67.7	(92.5)	(50.2)	(51.8)	(47.3)	(55.5)	(29.4)
Fluoranthene	6.58	16.4	19.8	28.6	33.0	40.4	(46.6)	(49.3)	(34.8)	(29.9)	(34.0)	(38.5)
Pyrene	2.98	8.97	10.5	11.4	13.6	16.7	(14.7)	(23.0)	(7.94)	(6.45)	(6.91)	(16.9)
Retene	3.44	9.36	11.0	12.0	15.5	18.2	(16.8)	(4.92)	(7.92)	(4.82)	(7.50)	(2.16)
2-Methylfluoranthene	5.74	17.7	21.4	22.1	29.1	33.4	(31.9)	(381)	(23.3)	(22.3)	(25.8)	(27.6)
1-Methylpyrene		34.9	43.6	42.7	65.8	50.6	(31.7)	(11.7)	(28.8)	(76.2)	(74.7)	(63.1)
Benzo(ghi)Fluoranthene	3.55	8.86	11.1	11.0	12.5	17.1	(14.3)	(26.1)	(7.24)	(4.64)	(4.67)	(17.9)
Benz[a]anthracene	4.75	11.0	11.7	5.4	13.3	19.3	(11.8)	(17.5)	(28.8)	(17.6)	(18.7)	(20.0)
Triphenylene	7.91	17.1	18.8	17.1	21.9	24.1	(22.1)	(32.2)	(15.8)	(10.8)	(11.1)	(18.4)
Chrysene	9.91	26.4	34.4	36.7	50.3	60.7	(27.1)	(34.9)	(28.9)	(29.7)	(42.0)	(48.9)
Benzo[b]fluoranthene	2.27	3.63	4.06	5.33	7.39	10.2	(10.7)	(23.1)	(21.1)	(14.9)	(19.1)	(23.8)
Benzo[k]fluoranthene	1.14	3.62	2.57	4.40	6.41	12.0	(10.7)	(21.1)	(20.3)	(11.2)	(13.3)	(12.8)

The numbers in round brackets are not used for sampling rate calculation.

Table S9. The experimental effective sampling volumes of PAHs during the first ca. six-month sampling periods for PASs from the Borden calibration experiment

Chemicals	Effective sampling volumes of XAD-based passive air samplers during the first six sampling periods (m^3)						
	36 days	60 days	120 days	181 days	246 days	323 days	365 days
Forest site							
Fluoranthene		46.5	30.5	28.6	(139)	(120)	(257)
Pyrene		50.0	47.3	13.6	(294)	(60.5)	(408)
Clearing site							
Fluoranthene	6.60	18.3	41.1	69.0	(220)	(196)	(294)
Pyrene		26.3	34.0	77.1	(331)	(80.4)	(282)

The numbers in round brackets are not used for sampling rate calculation.

Table S10. Sorption rate (k_{sorb}) and degradation constants (k_d) of selected PACs obtained by fitting the output of the model by Zhang and Wania to empirically determined uptake curves from the Toronto experiment, assuming the air side boundary thicknesses of 0.01 cm

Chemicals	k_{sorb} (day^{-1})	k_d (day^{-1})	R^2
1-Methylnaphthalene	3.10×10^5	0.023	0.40
2,6-dimethylnaphthalene	1.28×10^5	0.032	0.61
1,3-dimethylnaphthalene	5.60×10^4	0.014	0.45
1,5-dimethylnaphthalene	6.26×10^4	8.5×10^{-4}	0.45
Acenaphthene	3.70×10^4	0.014	0.45
2,3,5-trimethylnaphthalene	5.98×10^4	0.044	0.42
Fluorene	1.46×10^4	1.1×10^{-4}	0.89
1-Methylfluorene	1.76×10^4	7.4×10^{-4}	0.92
Dibenzothiophene	4.12×10^3	0.0089	0.44
Phenanthrene	1.01×10^4	0.0076	0.77
2-methylphenanthrene	9.86×10^3	0.012	0.73
1-methylphenanthrene	2.24×10^4	0.030	0.50
Fluoranthene	2.81×10^4	0.015	0.50
2-methylfluoranthene	5.88×10^4	0.059	0.61
Triphenylene	4.46×10^4	0.073	0.44
Chrysene	6.61×10^3	8.8×10^{-4}	0.92
Benzo[b]fluoranthene	2.50×10^3	2.9×10^{-7}	0.73
Benzo[k]fluoranthene	2.55×10^3	0.0020	0.50

Table S11. The actual sampling rates (SR_{actual}) calculated using the simulated uptake amounts of PACs in the first six months from the model by Zhang and Wania and the actual active air sampling data in the Toronto experiment. Chemical specific sorption rates are used, and the degradation rates are set as zero in simulations.

Chemicals	$\boldsymbol{SR_{actual}}$ **(m^3 day^{-1})**	$\boldsymbol{R^2}$
1-Methylnaphthalene	0.69	0.90
2,6-dimethylnaphthalene	0.69	0.99
1,3-dimethylnaphthalene	0.52	1.00
1,5-dimethylnaphthalene	0.56	1.00
Acenaphthene	0.43	1.00
2,3,5-trimethylnaphthalene	0.55	1.00
Fluorene	0.25	1.00
1-Methylfluorene	0.28	1.00
Dibenzothiophene	0.10	1.00
Phenanthrene	0.20	1.00
2-methylphenanthrene	0.19	1.00
1-methylphenanthrene	0.32	1.00
Fluoranthene	0.38	1.00
2-methylfluoranthene	0.56	1.00
Triphenylene	0.47	1.00
Chrysene	0.14	1.00
Benzo[b]fluoranthene	0.07	1.00
Benzo[k]fluoranthene	0.07	1.00

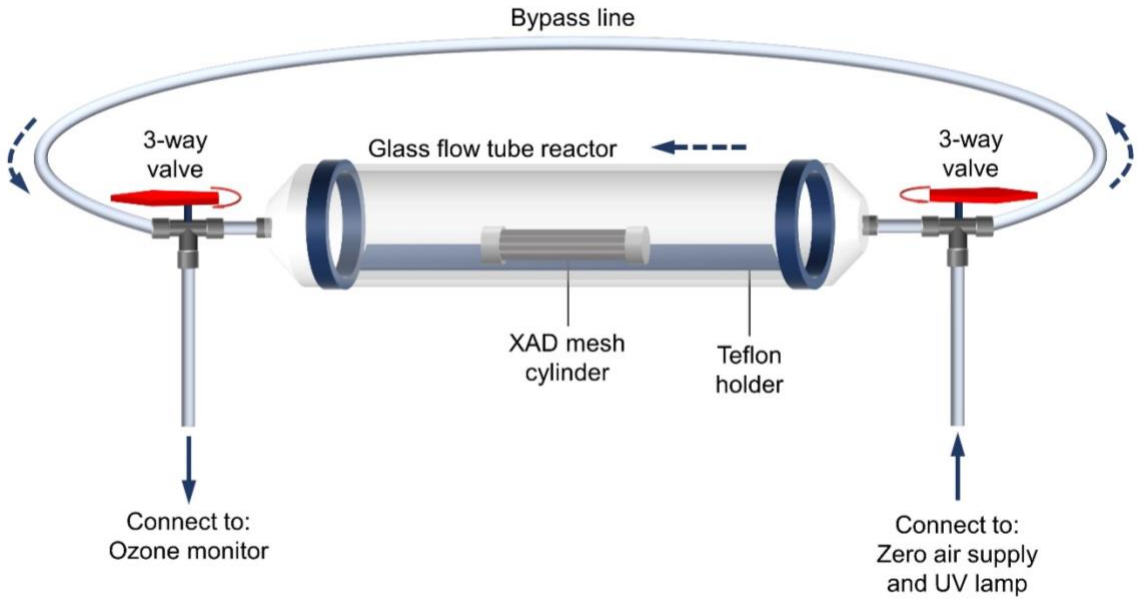

Figure S1. Schematic diagram of the experimental setup for the reaction of ozone and PAHs sorbed on a XAD-2 filled mesh cylinder.

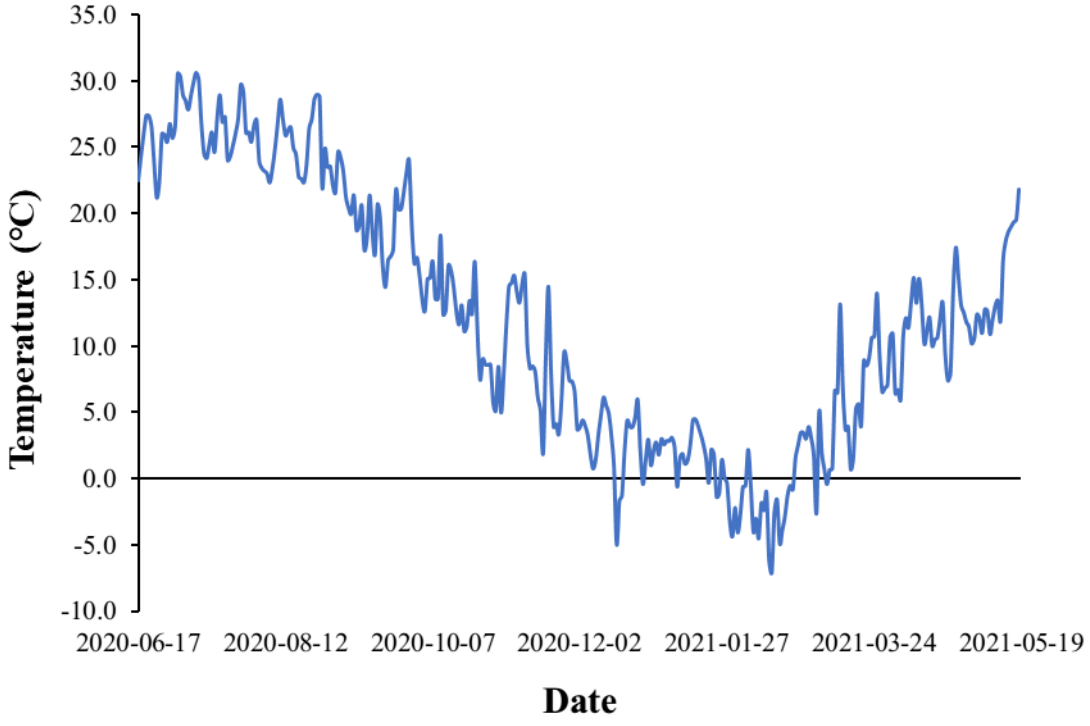

Figure S2. Ambient temperature recorded by us using hourly resolution thermometers (ibuttons) during the whole sampling period in the Toronto experiment.

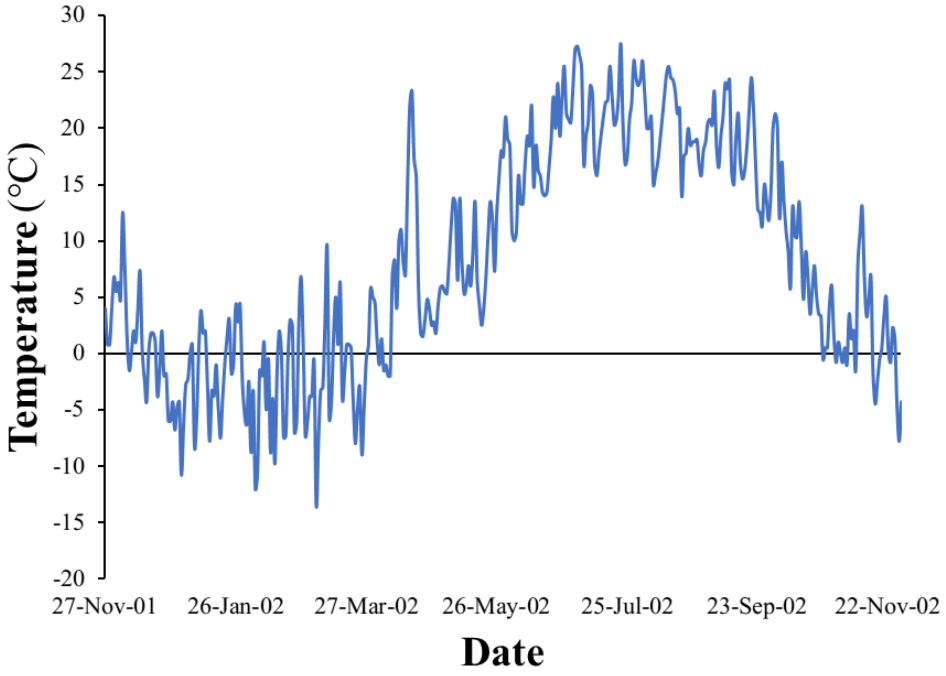

Figure S3 Ambient temperature recorded at Shanty Bay station (44.40, -79.63) which is the closest weather station with available temperature data to the sampling sites during Borden experiment.

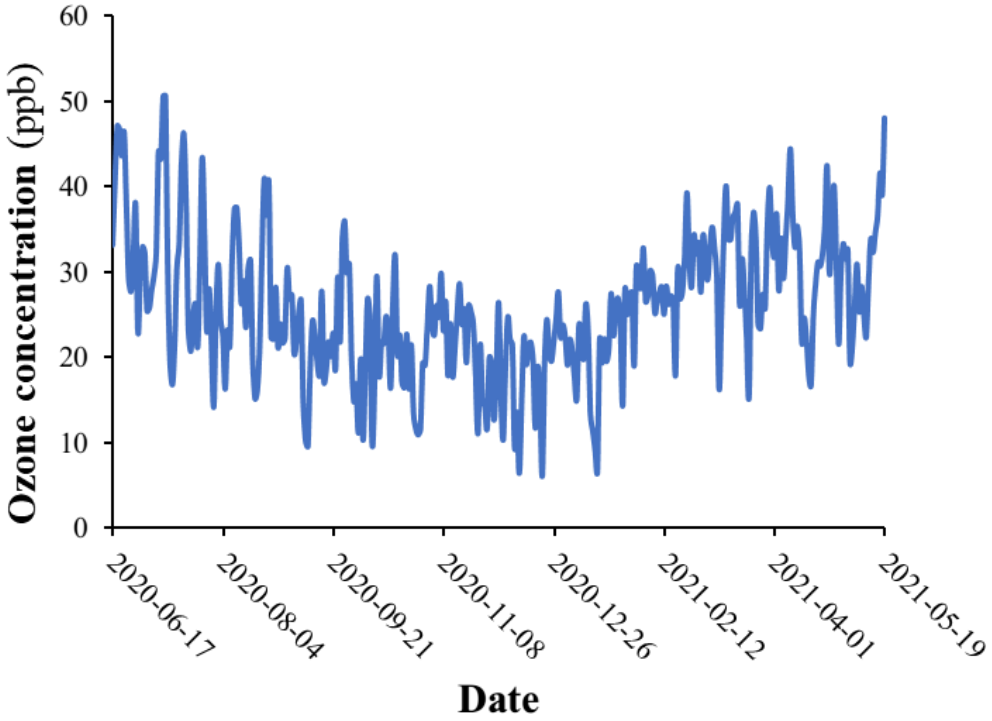

Figure S4. The concentration of ozone obtained from the Toronto East Station (33003) (43.75, -79.27), which is ca. 8 km away from our sampling site during the deployment period of Toronto calibration experiment.

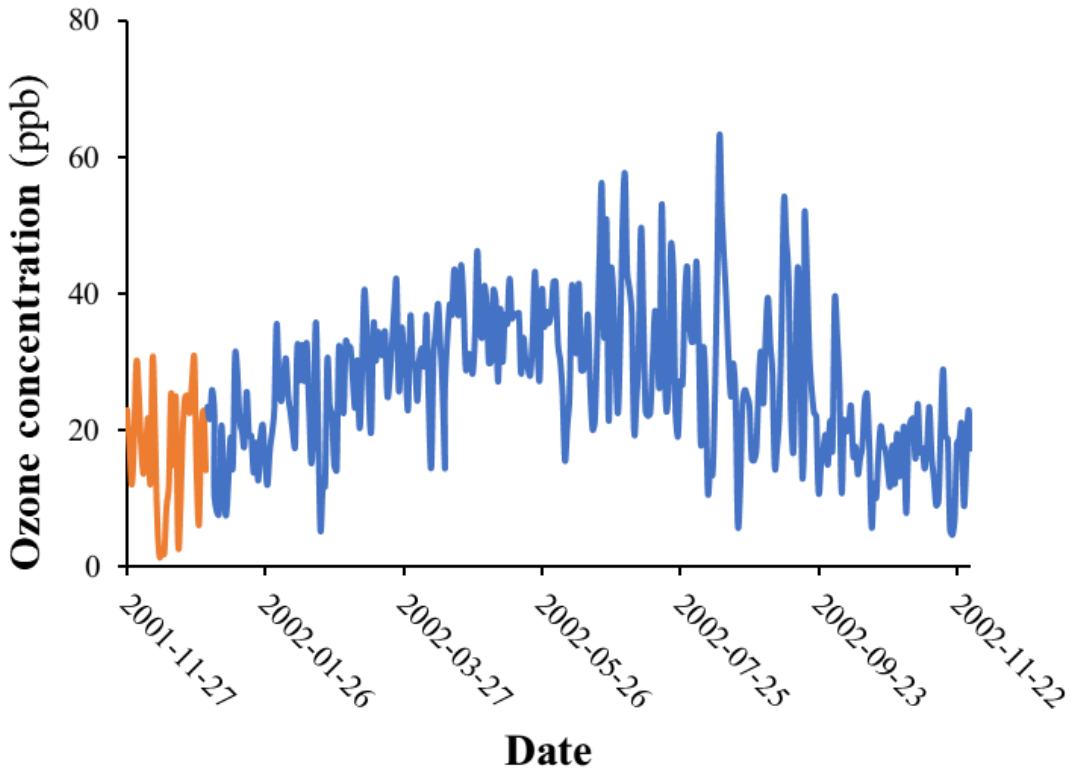

Figure S5. The concentration of ozone obtained from the Barrie Station (47045) (44.38, -79.70), which is ca. 20 km away from our sampling site during the deployment period of Borden calibration experiment. As there are no ozone data for the deployment period from November 27 to December 31, 2001, the ozone concentration from the same period in 2002 (orange line) are used.

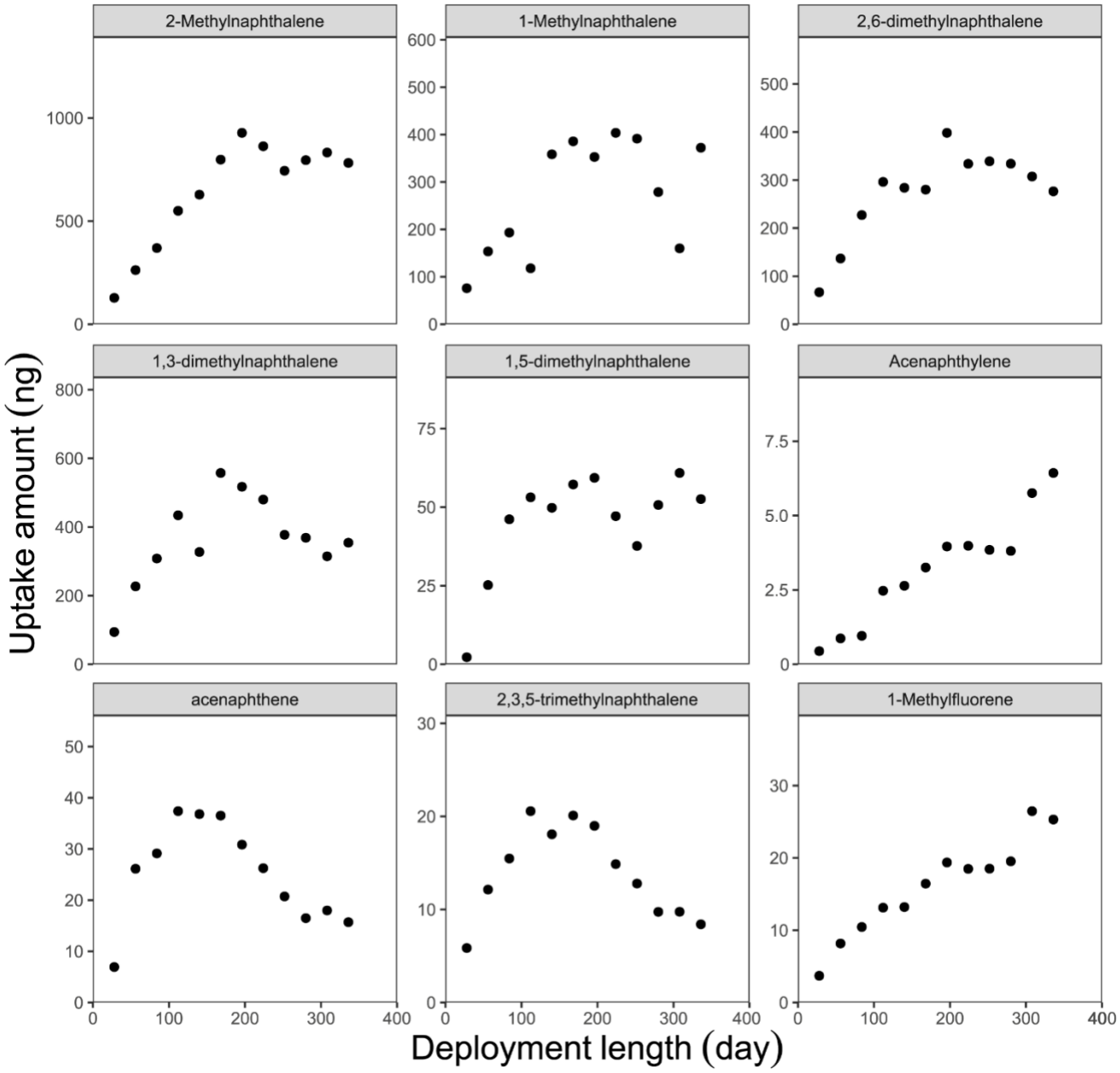

Figure S6. The uptake amount of 25 PACs throughout the 48-week deployment period in Toronto. The black markers indicate the field blank-corrected measured values.

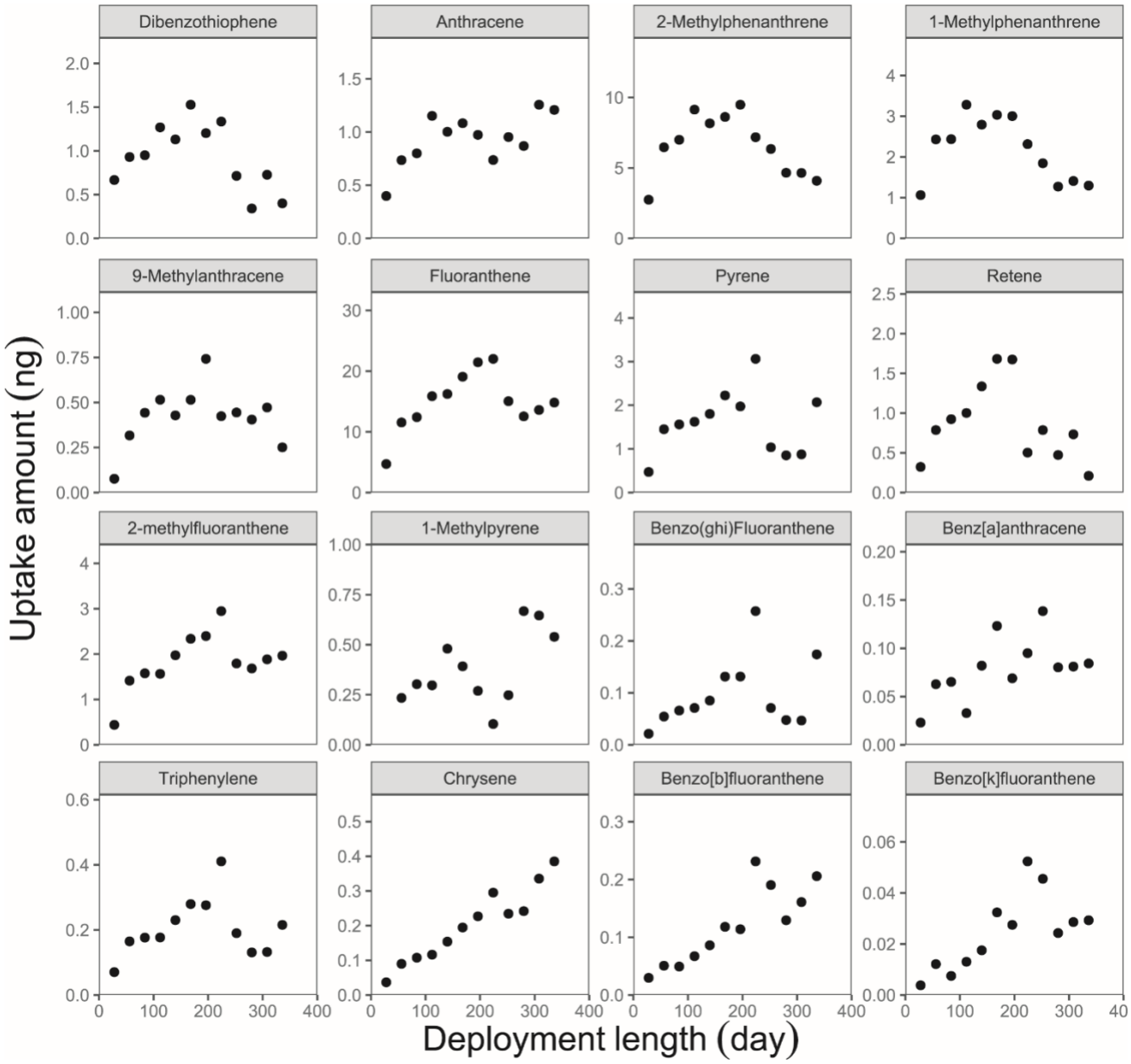

Figure S6. Continued

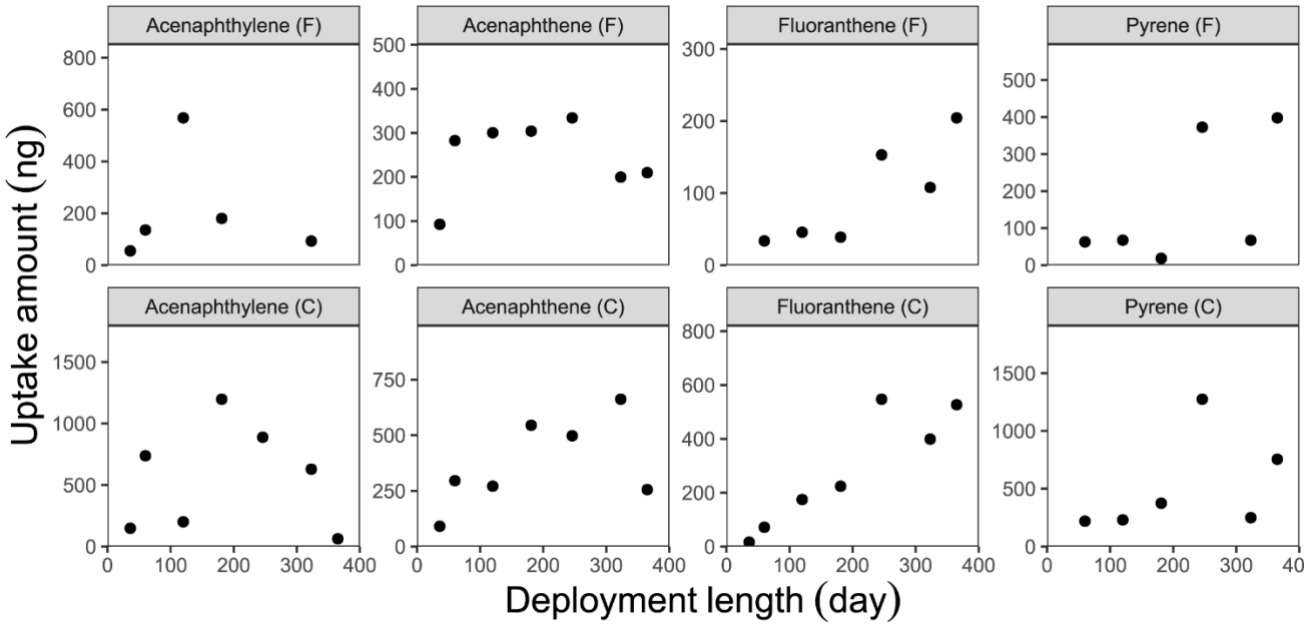

Figure S7. The uptake amount of four PACs at a forest site (F) and a clearing site (C) in Borden, Ontario throughout the one-year deployment. The black markers indicate the field blank-corrected measured values.

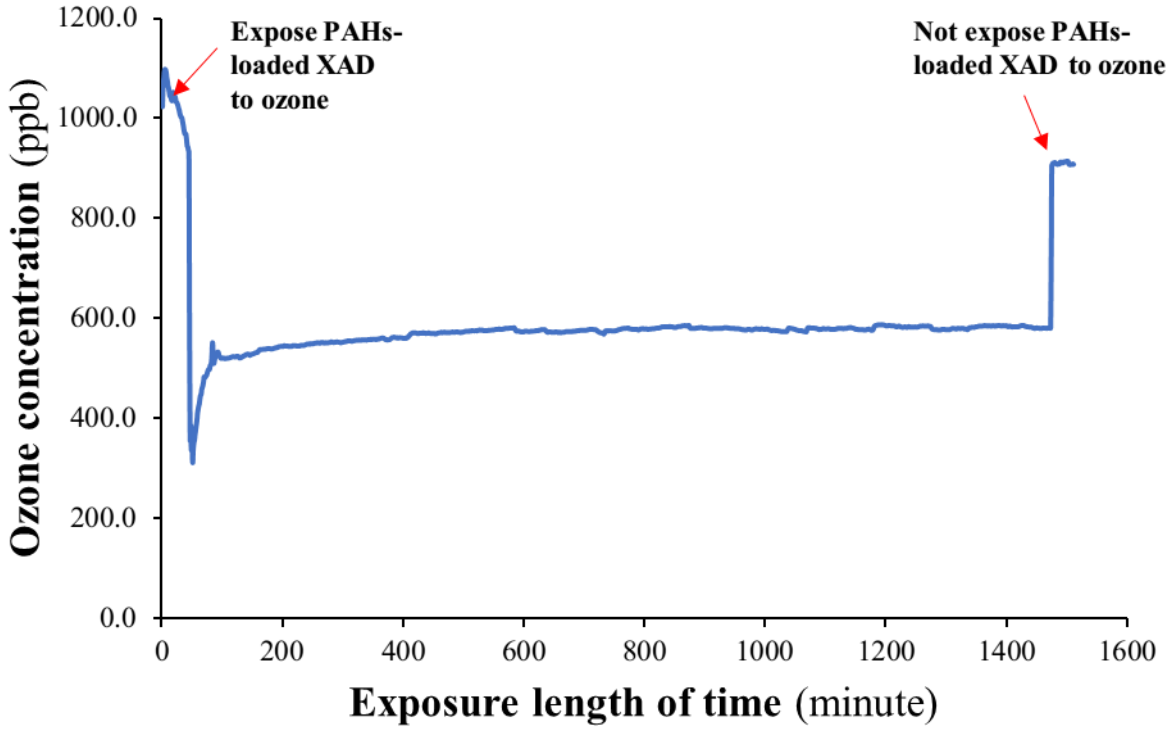

Figure S8. The decrease of ozone concentration in the flow tube in the presence of a PAH-loaded XAD-filled mesh cylinder.

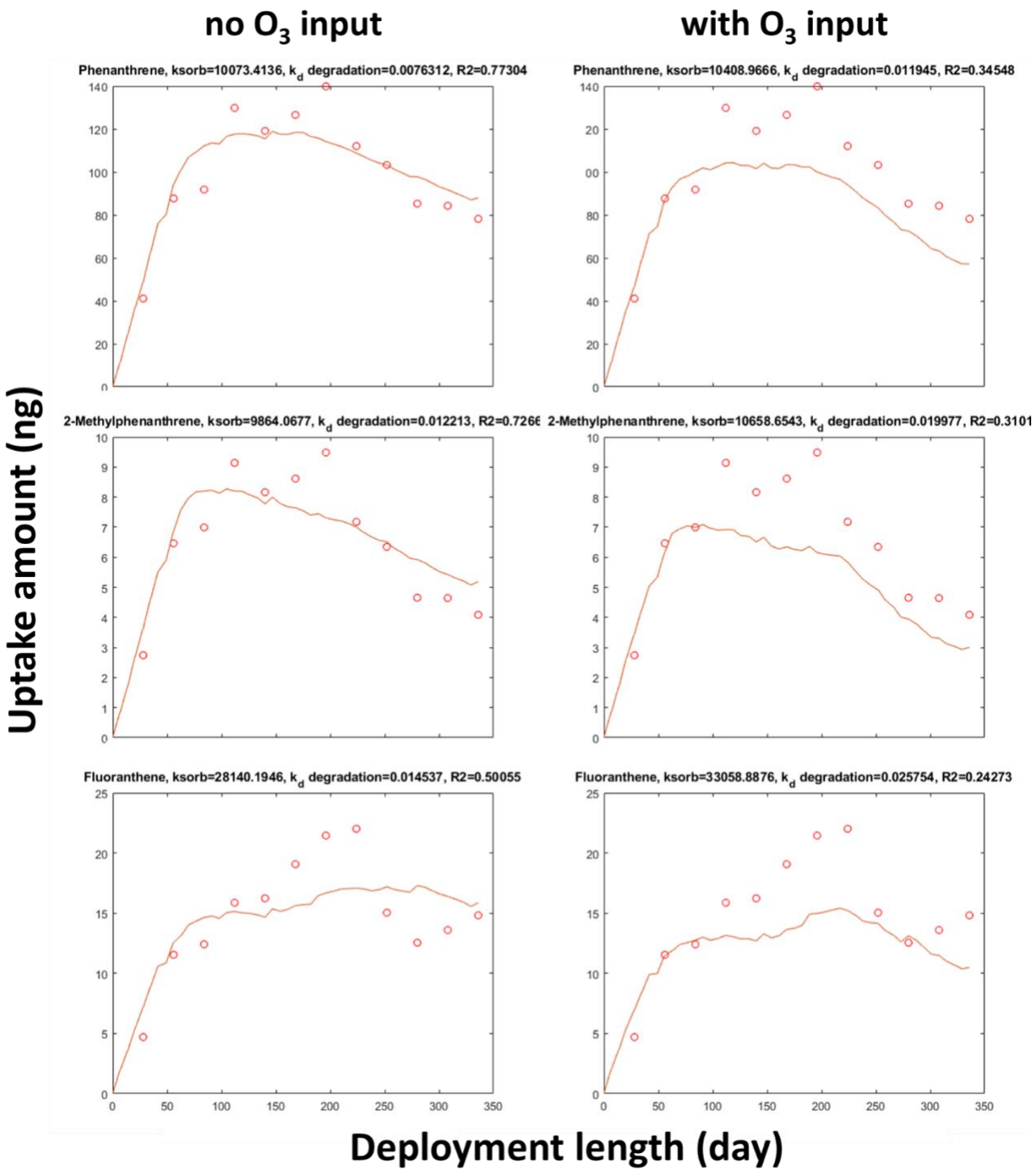

Figure S9. The best fit for the uptake amounts of three representative PACs in the Toronto experiment with ozone concentration considered (right part) and not considered (left part). The red markers indicate the field blank-corrected measured values, and the red lines indicate the best fitting curves for the measured values.

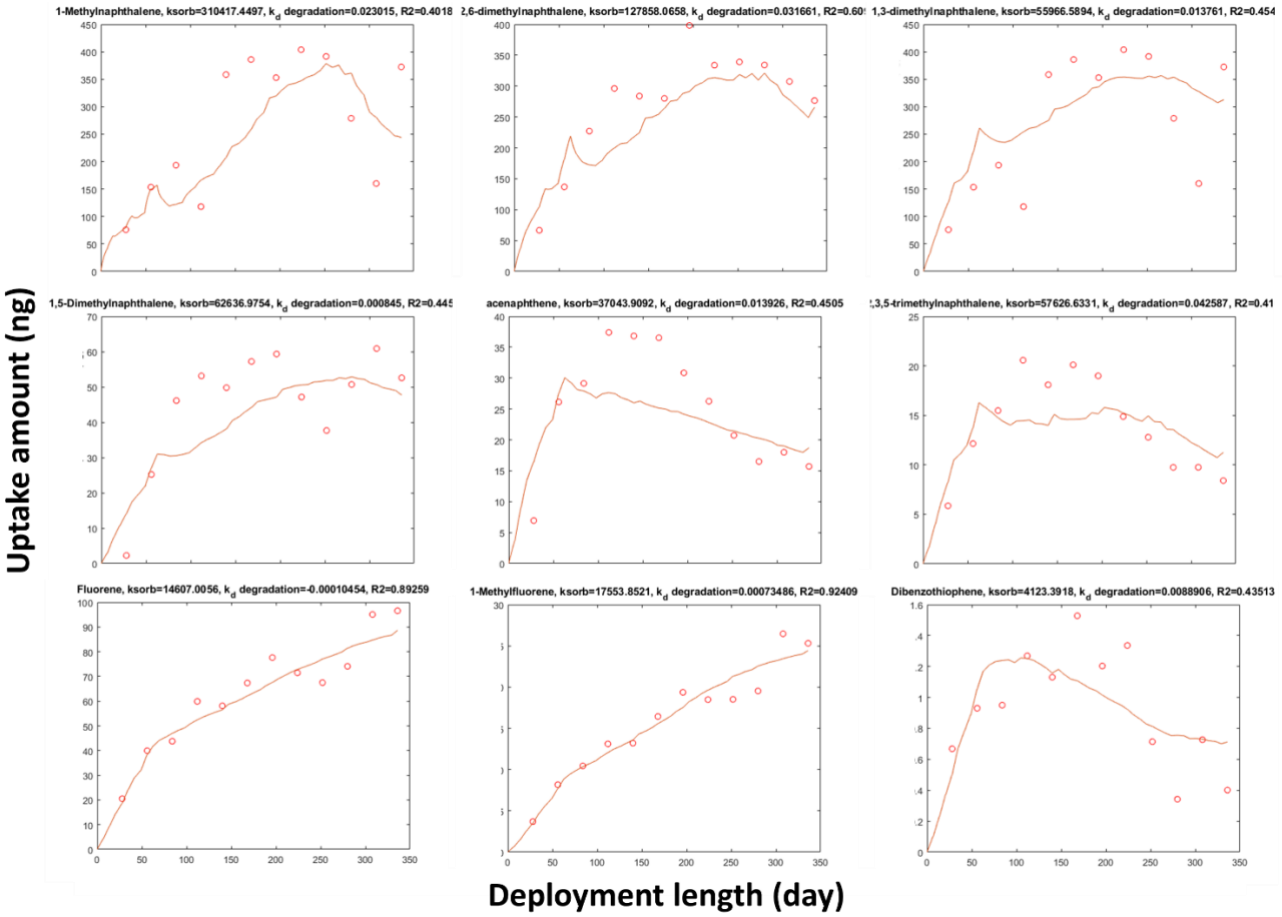

Figure S10. The best fit for the uptake amounts of 18 PACs in the Toronto experiment. The red markers indicate the field blank-corrected measured values, and the red lines indicate the best fitting curves for the measured values.

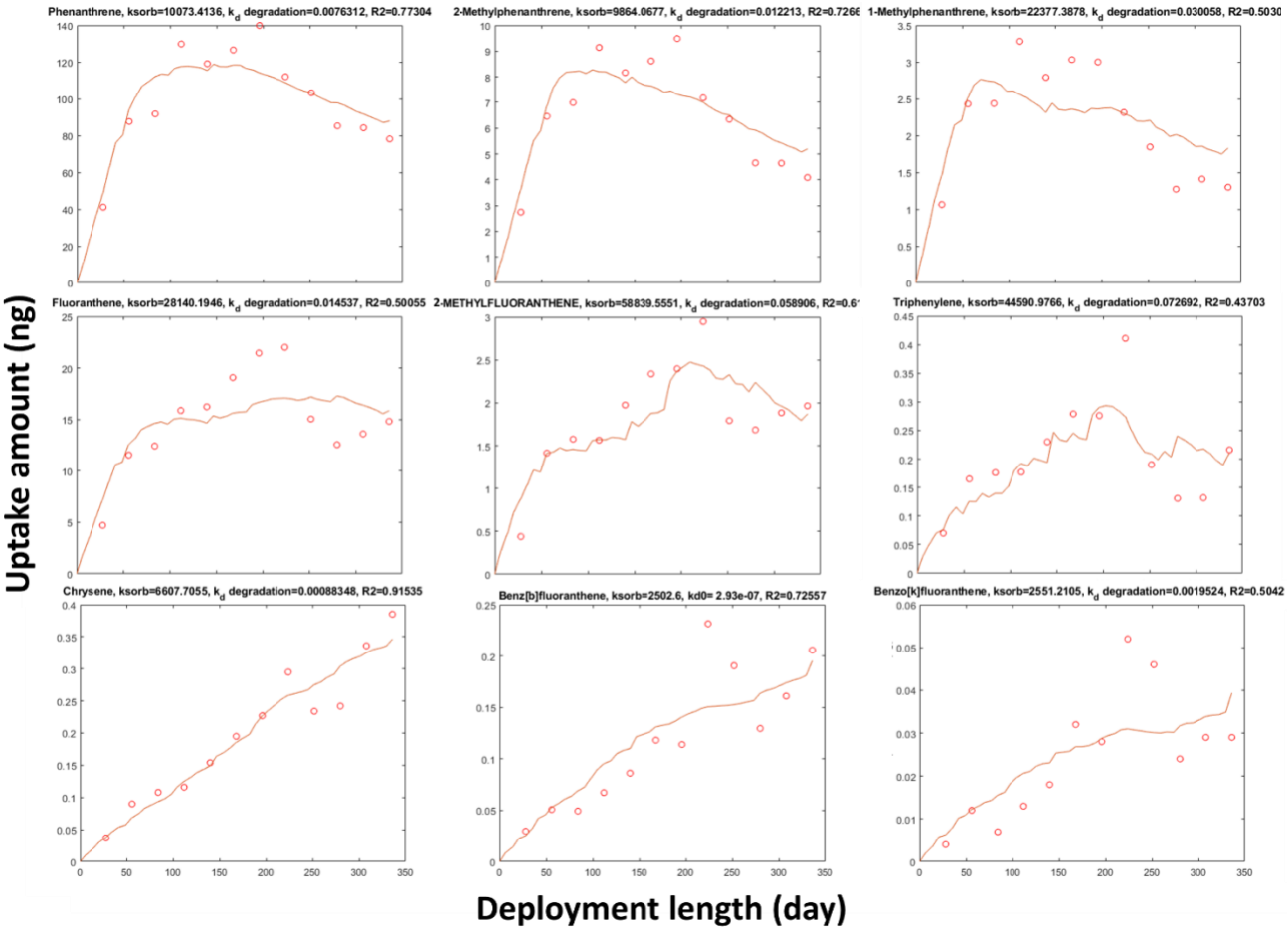

Figure S10. Continued

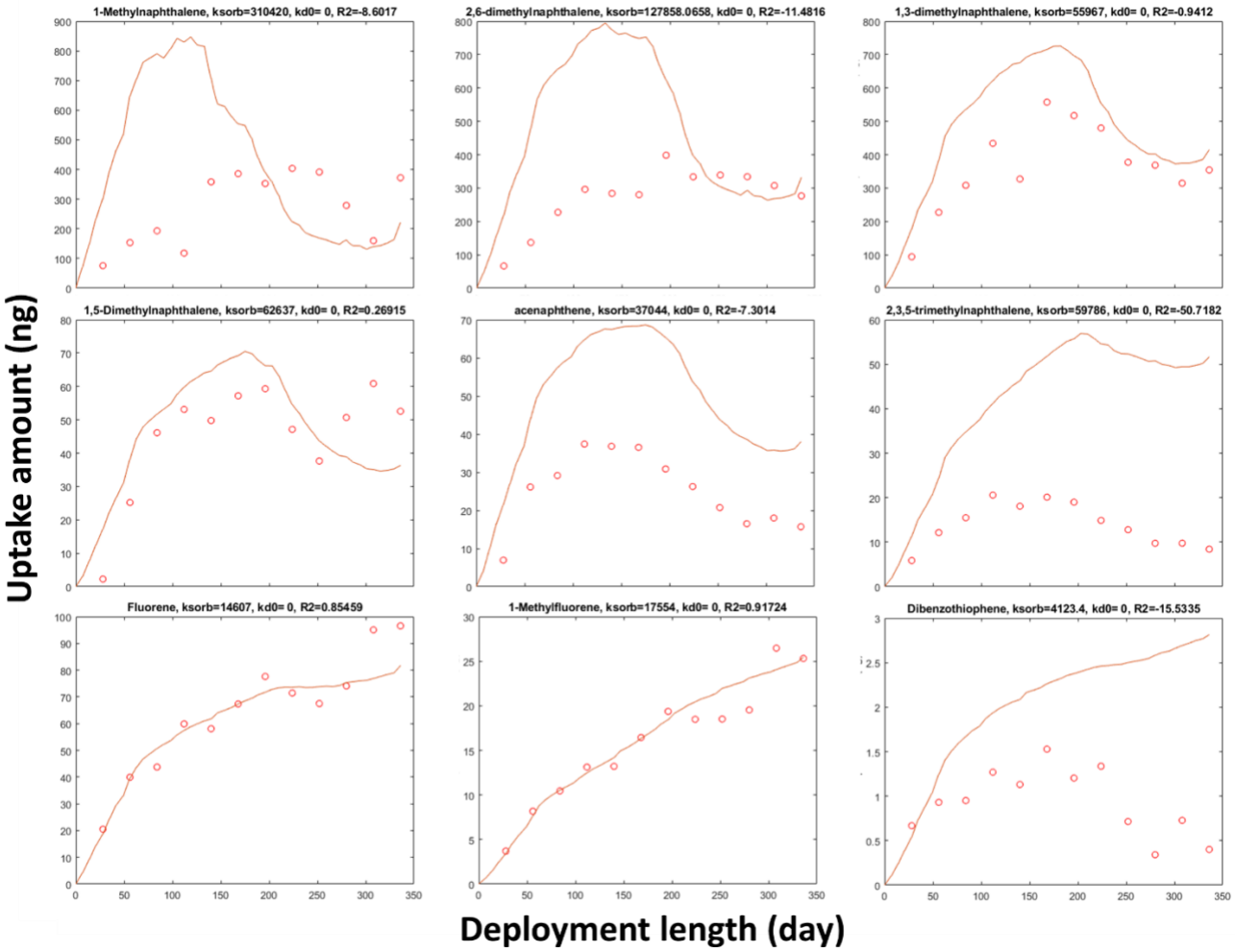

Figure S11. The simulated uptake amounts for 18 PACs in the Toronto experiment with the degradation rate set as zero. The red markers indicate the field blank-corrected measured values, and the red lines indicate the simulated curves.

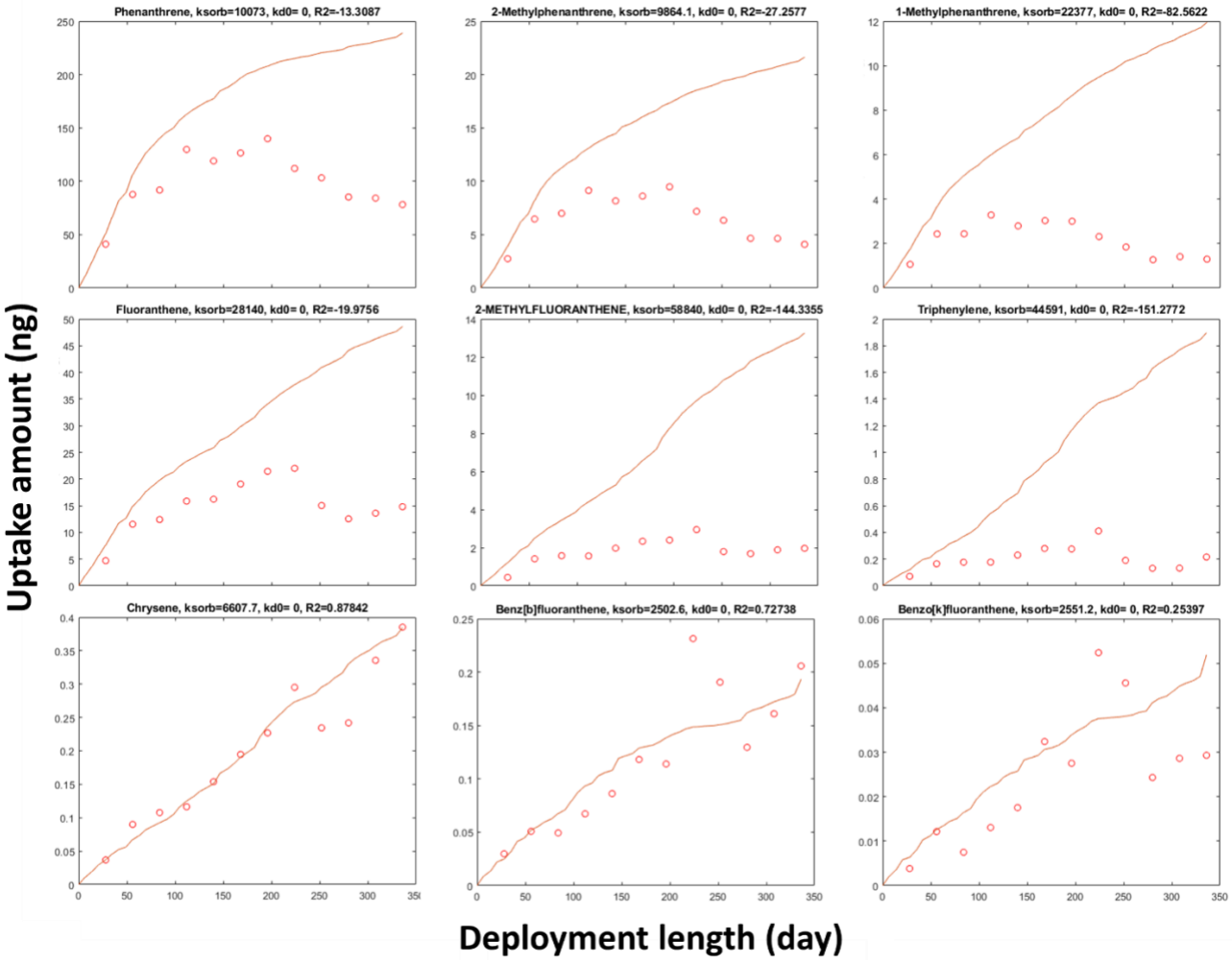

Figure S11. Continued

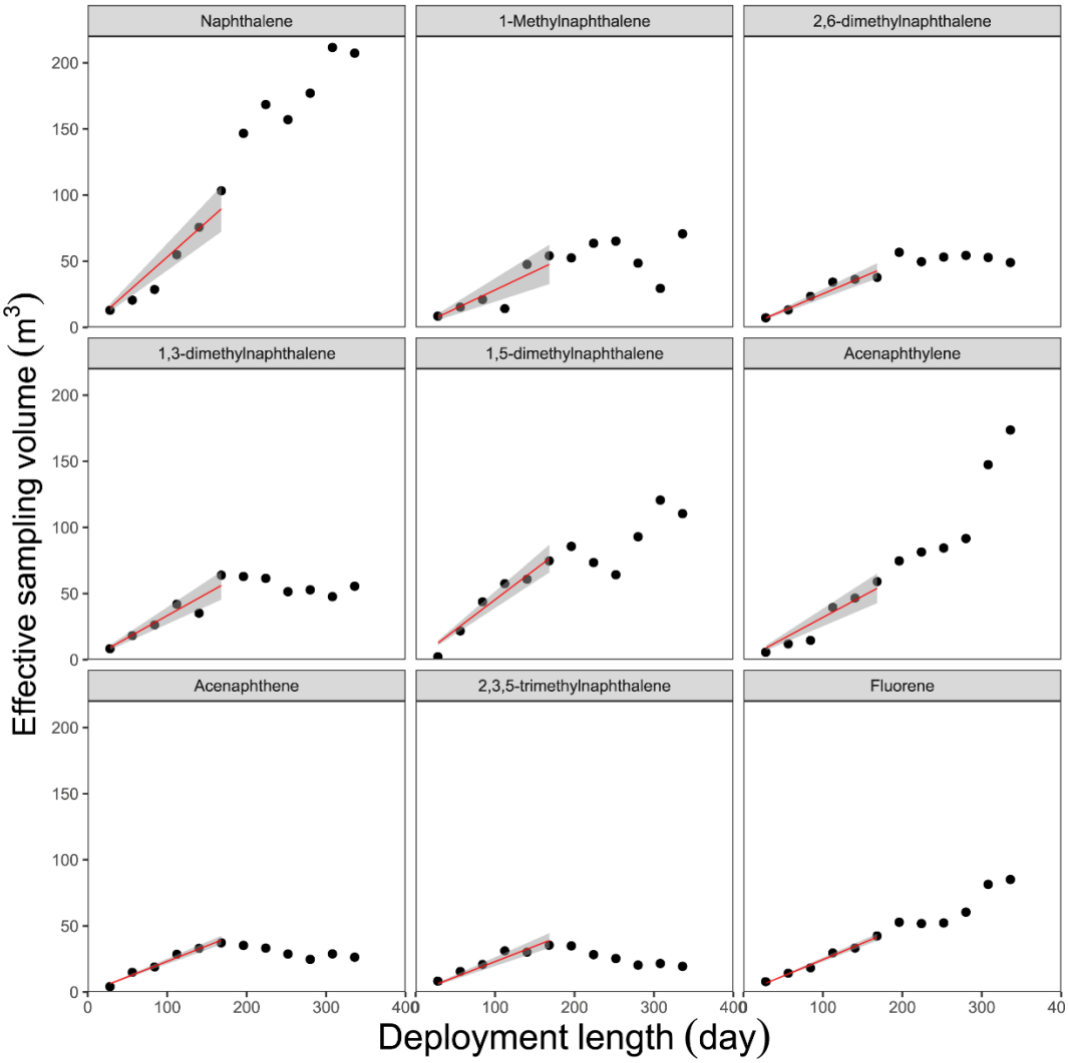

Figure S12. The effective sampling volume of 25 PACs throughout the 48-week deployment period for samples from Toronto. The black markers indicate the field blank-corrected measured values, and the red lines indicate linear regressions forced through the origin based on the data points from the first 168 days. The shading areas represent the 95% intervals of linear regressions.

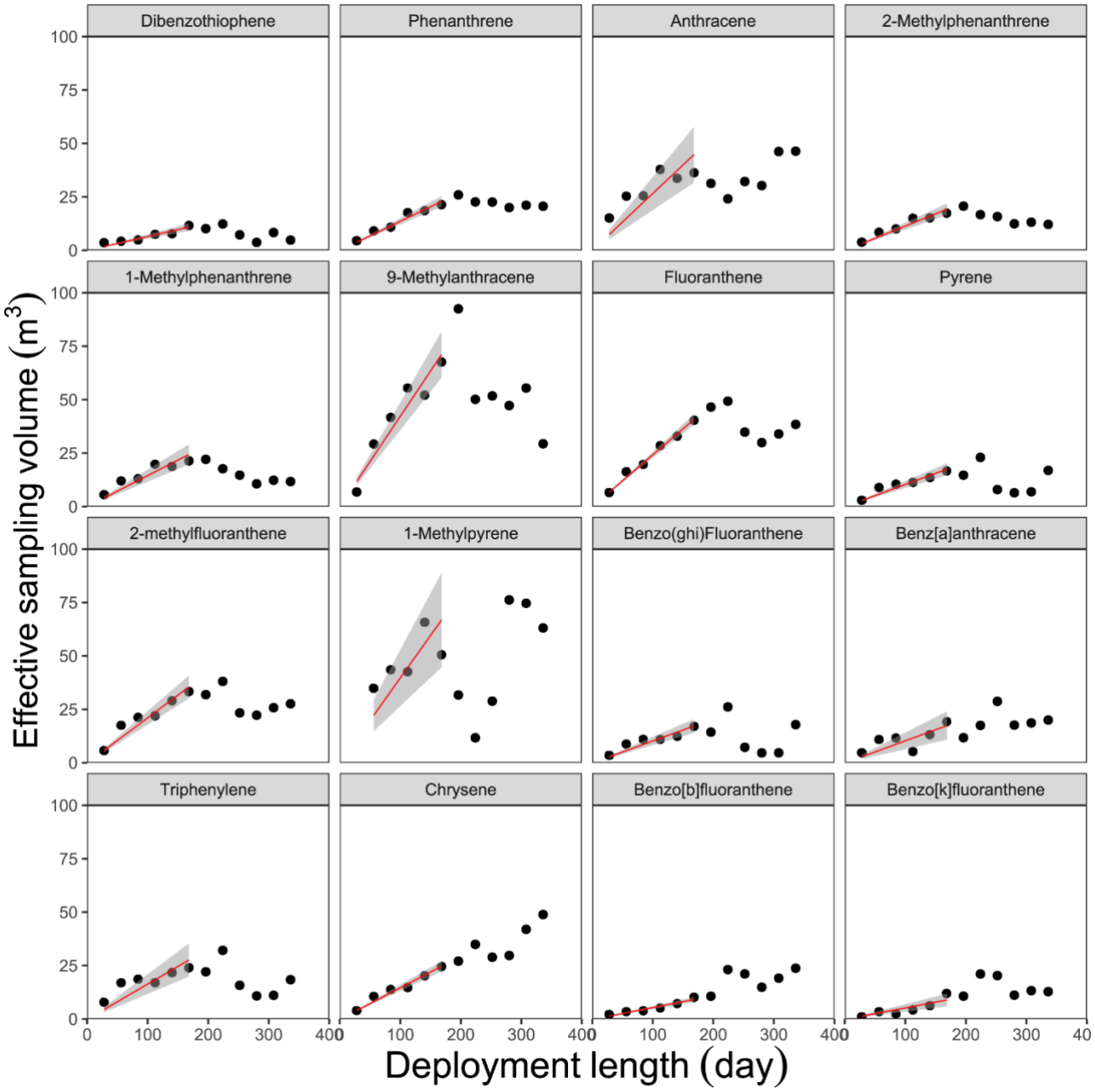

Figure S12. Continued

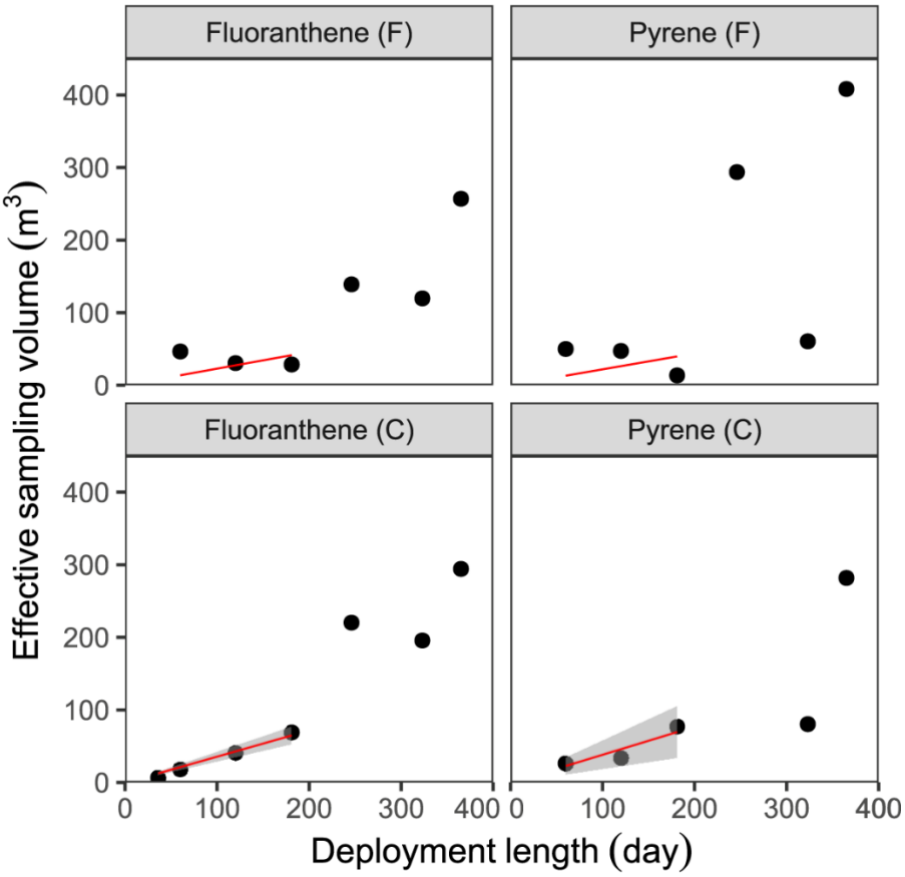

Figure S13. The effective sampling volume of two PACs throughout the one-year deployment period for samples from a forest site (F) and a clearing site (C) in Borden, Ontario. The black markers indicate the field blank-corrected measured values, and the red lines indicate linear regressions forced through the origin based on the data points from the first 183 days. The shading areas represent the 95% intervals.

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