



*Supplement of*

## **Uptake behavior of polycyclic aromatic compounds during field calibrations of the XAD-based passive air sampler across seasons and locations**

**Yuening Li et al.**

*Correspondence to:* Faqiang Zhan (faqiang.zhan@utoronto.ca) and Frank Wania (frank.wania@utoronto.ca)

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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<sub>2</sub>SO<sub>4</sub>. 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  $\mu$ L of extract was injected in splitless mode to a DB-5MS column (J&W Scientific; 60m  $\times$  0.25mm i.d., 0.10  $\mu$ m film thickness) at inlet temperature of 280  $^{\circ}$ C and separated under a temperature program: 70  $^{\circ}$ C for 1 min, 10  $^{\circ}$ C min<sup>-1</sup> to 90  $^{\circ}$ C for 1 min, 4  $^{\circ}$ C min<sup>-1</sup> to 130  $^{\circ}$ C, 5  $^{\circ}$ C min<sup>-1</sup> to 240  $^{\circ}$ C and 4  $^{\circ}$ C min<sup>-1</sup> to 300  $^{\circ}$ C and held for 2 min. The interface connecting the GC with the MSD was set to 310  $^{\circ}$ C, while the ion source and quadrupole temperatures were 230  $^{\circ}$ C and 150  $^{\circ}$ C, respectively. The carrier gas was helium at 1.0 mL min<sup>-1</sup>. 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  $\times$  0.25 mm i.d.  $\times$  0.15  $\mu$ m film thickness) (Anderson et al., 2015). Helium was used as the carrier gas at a flow rate of 2 mL min<sup>-1</sup>, and 2  $\mu$ L of extract was injected in pulsed splitless mode at 300  $^{\circ}$ C. The oven temperature program was as follows: initial oven temperature was 70  $^{\circ}$ C and held for 1 min then raised to 180  $^{\circ}$ C at 50  $^{\circ}$ C min<sup>-1</sup>, raised to 230  $^{\circ}$ C at 3  $^{\circ}$ C min<sup>-1</sup>, held for 6 min and raised to 280  $^{\circ}$ C at 17  $^{\circ}$ C min<sup>-1</sup>, held for 10 min, raised to 298  $^{\circ}$ C at 5  $^{\circ}$ C min<sup>-1</sup>, and raised to 350  $^{\circ}$ C at 14 $^{\circ}$ C min<sup>-1</sup>, and held for 5 min. The ion source and interface temperature were set at 300  $^{\circ}$ C and 290  $^{\circ}$ C, respectively. The precursor and product ions for GC-MS/MS detection are listed in Table S2. For the GFF analysis, the GC oven program was the same as indicated here, but the source, inlet, and interface temperatures were set to 320  $^{\circ}$ C, 340  $^{\circ}$ C, and 320  $^{\circ}$ C, respectively. The quadrupole temperature was maintained at 150  $^{\circ}$ C.

## 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 ( $3 \times 1$  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 >8 hours to remove potential contaminants. All other materials coming in contact with samples or extracts were cleaned and rinsed with solvents three times prior to use. 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, 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 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 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

| <b>Chemicals</b>     | <b>Quantifier ion</b> | <b>Qualifier ion</b> |
|----------------------|-----------------------|----------------------|
| 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

| <b>Chemicals</b>                                    | <b>Abbreviation</b>              | <b>Precursor ion</b> | <b>Product ion</b> | <b>CE (eV)</b> |
|---|----------------------------------|----------------------|--------------------|----------------|
| <b>Spiking Standards</b>                            |                                  |                      |                    |                |
| Fluorene-d <sub>10</sub>                            | FLU-d <sub>10</sub>              | 176.0                | 174.0              | 30             |
|   |                                  | 175.0                | 173.0              | 40             |
| Anthracene-d <sub>10</sub>                          | ANT-d <sub>10</sub>              | 188.0                | 160.0              | 30             |
|   |                                  | 188.0                | 186.0              | 25             |
| Fluoranthene-d <sub>10</sub>                        | FLA-d <sub>10</sub>              | 212.0                | 208.0              | 45             |
|   |                                  | 210.0                | 208.0              | 25             |
| Benz[a]anthracene-d <sub>12</sub>                   | BaA-d <sub>12</sub>              | 240.0                | 236.0              | 45             |
|   |                                  | 240.0                | 212.0              | 35             |
| Benzo[a]pyrene-d <sub>12</sub>                      | BaP-d <sub>12</sub>              | 264.0                | 260.0              | 50             |
|   |                                  | 264.0                | 236.0              | 45             |
| <sup>13</sup> C <sub>6</sub> -Ideno[1,2,3-cd]pyrene | <sup>13</sup> C <sub>6</sub> -IP | 284.0                | 282.0              | 40             |
|   |                                  | 282.0                | 280.0              | 40             |
| Dibenz[a,c]anthracene-d <sub>14</sub>               | DiBacA-d <sub>14</sub>           | 292.0                | 288.0              | 50             |
|   |                                  | 292.0                | 264.0              | 45             |
| 5-Methylchrysene-d <sub>3</sub>                     | 5-MeCHY-d <sub>3</sub>           | 245.0                | 228.0              | 45             |
|   |                                  | 245.0                | 243.0              | 30             |
| 1-Methylnaphthalene-d <sub>10</sub>                 | 1-MeNAP-d <sub>10</sub>          | 152.0                | 122.0              | 40             |
|   |                                  | 150.0                | 122.0              | 25             |
| 2,6-Dimethylnaphthalene-d <sub>12</sub>             | 2,6-DiMeNAP-d <sub>12</sub>      | 168.0                | 166.0              | 25             |
|   |                                  | 168.0                | 150.0              | 20             |
| Coronene-d <sub>12</sub>                            | COR-d <sub>12</sub>              | 311.8                | 308.2              | 60             |
| <b>Injection Standards</b>                          |                                  |                      |                    |                |
| <sup>13</sup> C <sub>6</sub> - Benz[a]anthracene    |                                  | 234.1                | 208.1              | 35             |
|   |                                  | 234.1                | 232.1              | 30             |
| <b>Native Standards</b>                             |                                  |                      |                    |                |
| 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-dimethylphenanthrene   | 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 |

|                       |        |       |       |    |
|-----------------------|--------|-------|-------|----|
| Dibenz[a,c]anthracene | DiBacA | 125.0 | 124.0 | 15 |
|                       |        | 278.0 | 276.0 | 45 |
|                       |        | 276.0 | 274.0 | 45 |
| Benzo[ghi]perylene    | BghiP  | 125.0 | 124.0 | 15 |
|                       |        | 276.0 | 274.0 | 60 |
|                       |        | 276.0 | 275.0 | 35 |
| Anthanthrene          | ANTA   | 138.0 | 137.0 | 15 |
|                       |        | 276.0 | 274.0 | 60 |
|                       |        | 276.0 | 275.0 | 35 |
| Coronene              | COR    | 138.0 | 137.0 | 15 |
|                       |        | 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) |
| <b>Toronto Calibration Study</b>                    |                          |                         |
| Fluorene-d <sub>10</sub>                            | 66.7                     | 81.8                    |
| Anthracene-d <sub>10</sub>                          | 71.7                     | 82.2                    |
| Fluoranthene-d <sub>10</sub>                        | 78.2                     | 82.5                    |
| Benz[a]anthracene-d <sub>12</sub>                   | 92.6                     | 99.2                    |
| Benzo[a]pyrene-d <sub>12</sub>                      | 75.2                     | 67.1                    |
| <sup>13</sup> C <sub>6</sub> -Ideno[1,2,3-cd]pyrene | 85.8                     | 82.4                    |
| Dibenz[a,c]anthracene-d <sub>14</sub>               | 82.8                     | 80.3                    |
| 5-Methylchrysene-d <sub>3</sub>                     | 89.9                     | 97.2                    |
| 1-Methylnaphthalene-d <sub>10</sub>                 | 54.9                     | 75.1                    |
| 2,6-Dimethylnaphthalene-d <sub>12</sub>             | 35.0                     | 59.2                    |
| Coronene-d <sub>12</sub>                            | 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                  | $\log K_{\text{XAD/air}}$<br>(L air g <sup>-1</sup> XAD)<br>at 20 °C <sup>1</sup> | $\Delta U_{\text{XAD/air}}$<br>(kJ/mol) <sup>1</sup> | MDL for<br>PAS<br>(ng/sample) <sup>2</sup> | MDL for<br>AAS<br>(pg/m <sup>3</sup> ) <sup>2</sup> | MDL for<br>PAS<br>(ng/sample) <sup>3</sup> | MDL for<br>AAS<br>(pg/m <sup>3</sup> ) <sup>3</sup> |
|----------------------------|---|--|--|---|--|---|
| 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  |  |   |

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

<sup>2</sup> The MDLs for samples from the experiment conducted in Toronto.

<sup>3</sup> 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.

| <b>Chemicals</b>               | <b>MDL (pg/m<sup>3</sup>)</b> |
|--------------------------------|-------------------------------|
| 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                        |
| Benzo[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 |
| <b>Forest site</b>   |  |         |          |          |          |          |          |
| 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      |
| <b>Clearing site</b> |  |         |          |          |          |          |          |
| 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 <sup>3</sup> ) |            |            |             |             |             |             |             |             |             |             |             |
|----------------------------|--|------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                            | 28<br>days   | 56<br>days | 84<br>days | 112<br>days | 140<br>days | 168<br>days | 196<br>days | 224<br>days | 252<br>days | 280<br>days | 308<br>days | 336<br>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 <sup>3</sup> ) |         |          |          |          |          |          |
|----------------------|--|---------|----------|----------|----------|----------|----------|
|                      | 36 days  | 60 days | 120 days | 181 days | 246 days | 323 days | 365 days |
| <b>Forest site</b>   |  |         |          |          |          |          |          |
| Fluoranthene         |  | 46.5    | 30.5     | 28.6     | (139)    | (120)    | (257)    |
| Pyrene               |  | 50.0    | 47.3     | 13.6     | (294)    | (60.5)   | (408)    |
| <b>Clearing site</b> |  |         |          |          |          |          |          |
| 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.

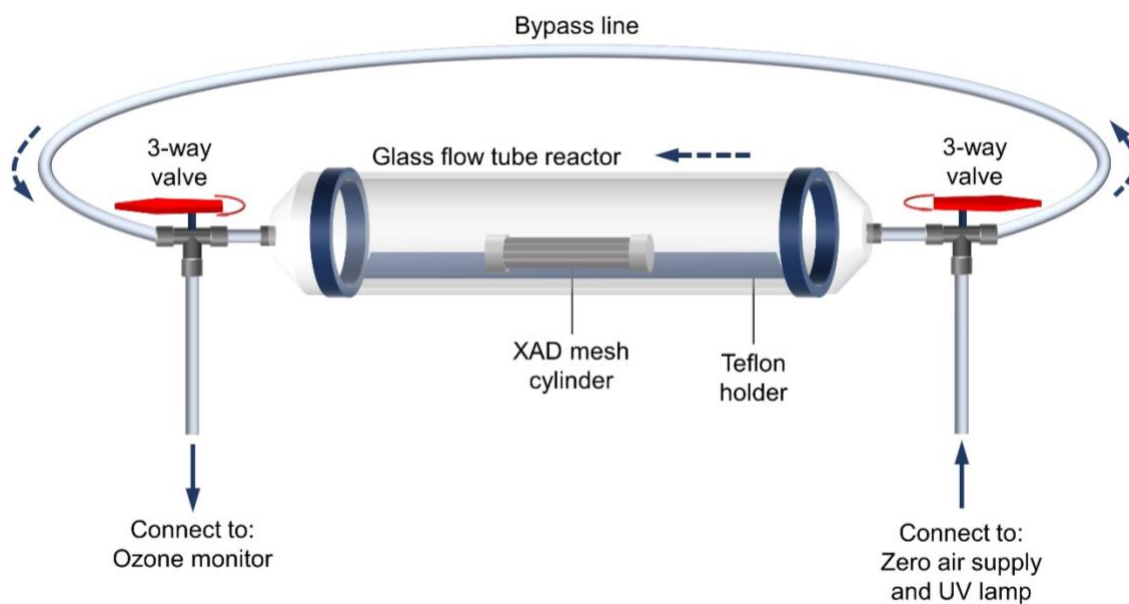
**Table S10.** Sorption rate ( $k_{\text{sorb}}$ ) and degradation constants ( $k_d$ ) of selected PACs obtained by fitting the output of the model by Zhang and Wania to empirically determined uptake curves from the Toronto experiment, assuming the air side boundary thicknesses of 0.01 cm

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

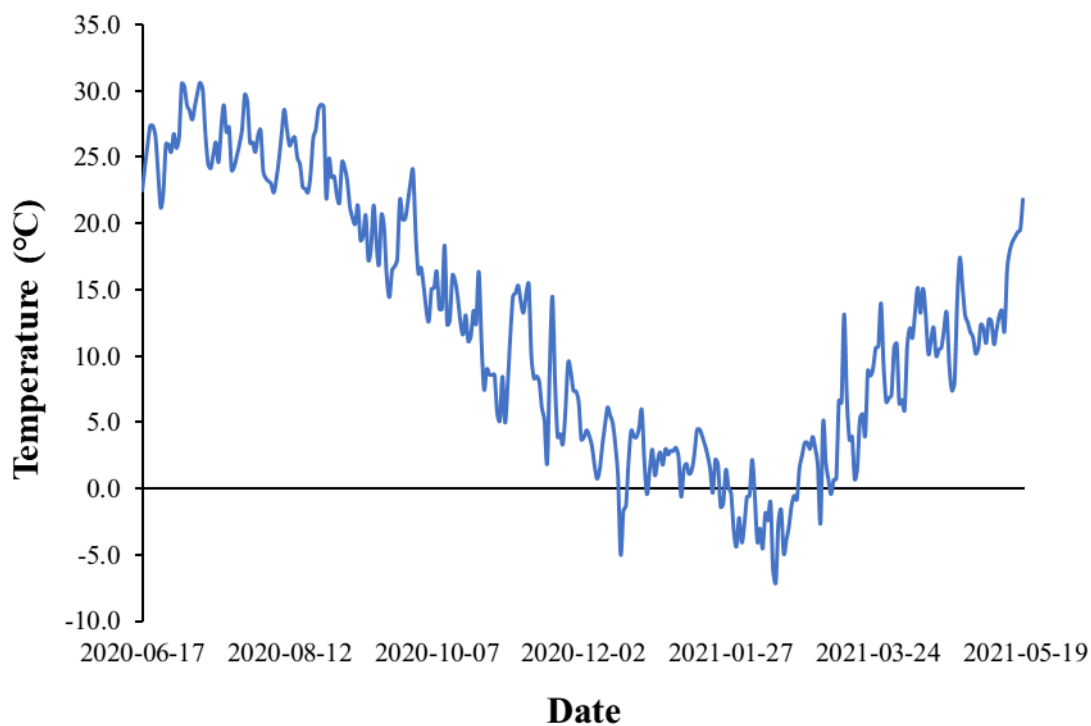


**Table S11.** The actual sampling rates ( $SR_{\text{actual}}$ ) calculated using the simulated uptake amounts of PACs in the first six months from the model by Zhang and Wania and the actual active air sampling data in the Toronto experiment. Chemical specific sorption rates are used, and the degradation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

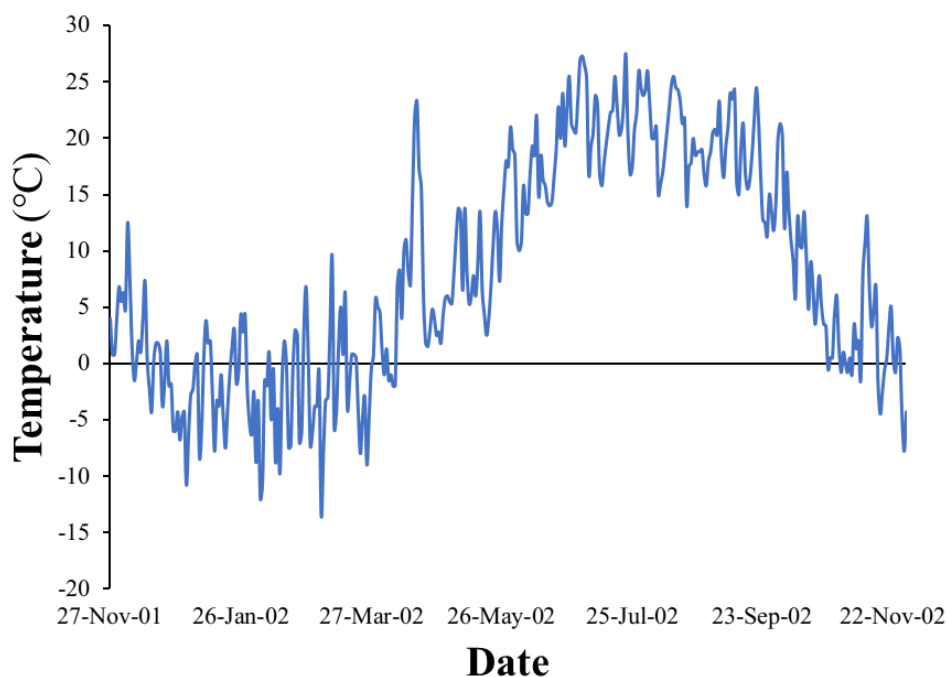
| <b>Chemicals</b>           | <b><math>SR_{\text{actual}}</math> (<math>\text{m}^3 \text{ day}^{-1}</math>)</b> | <b><math>R^2</math></b> |
|----------------------------|---|-------------------------|
| 1-Methylnaphthalene        | 0.69  | 0.90                    |
| 2,6-dimethylnaphthalene    | 0.69  | 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                    |



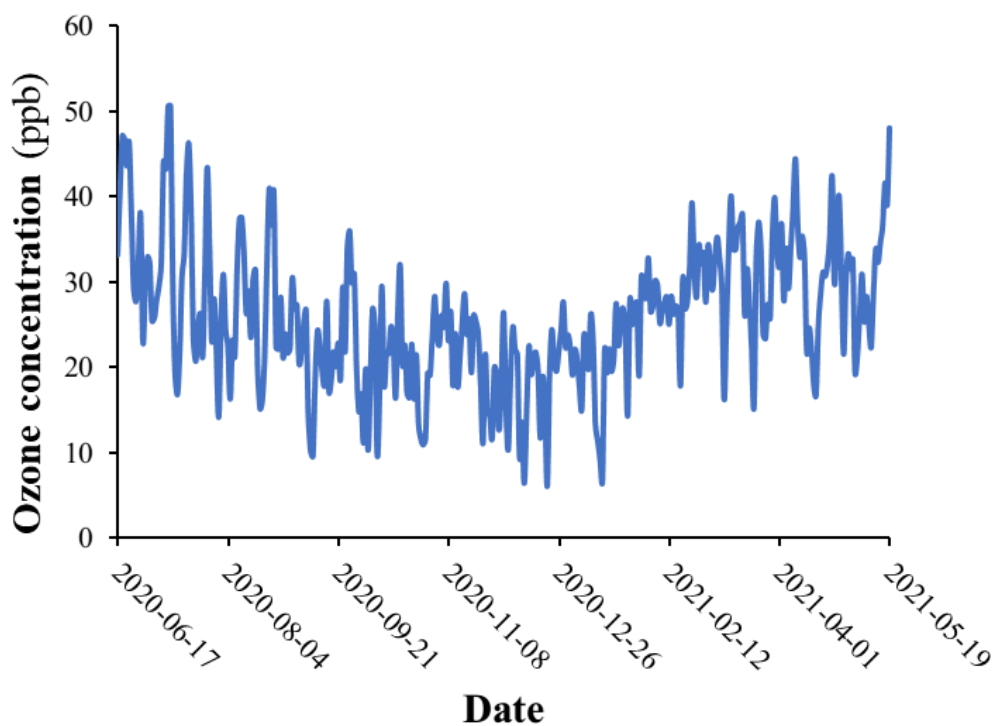
**Figure S1.** Schematic diagram of the experimental setup for the reaction of ozone and PAHs sorbed on a XAD-2 filled mesh cylinder.



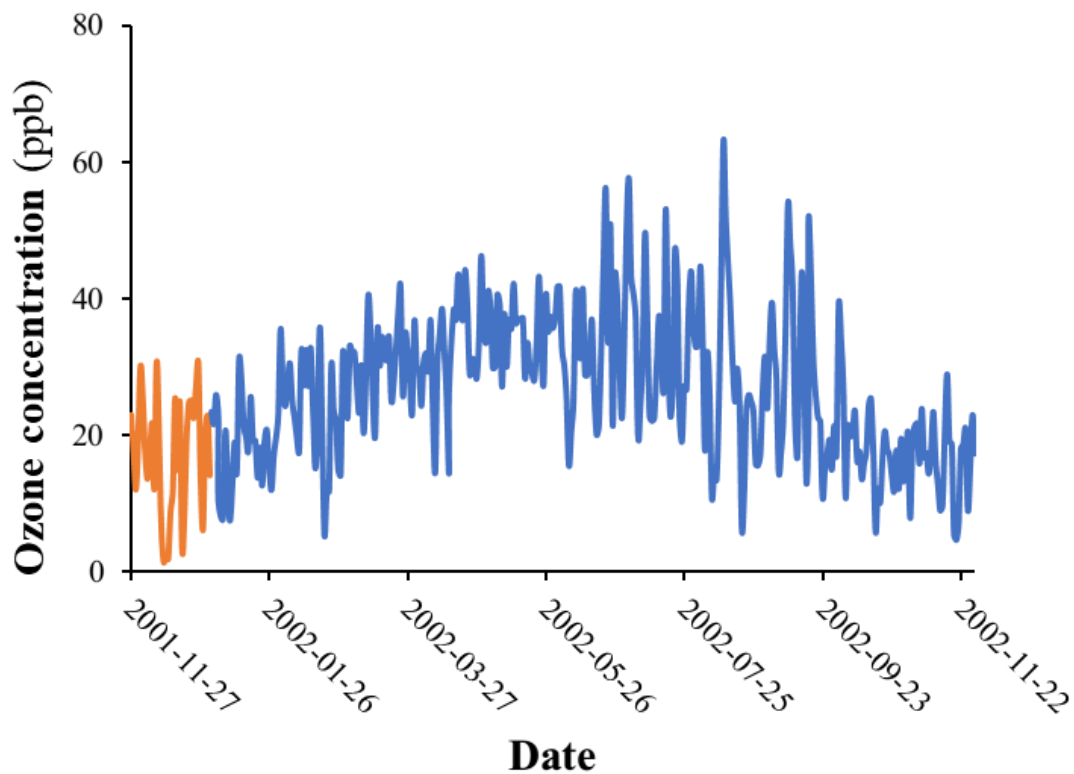
**Figure S2.** Ambient temperature recorded by us using hourly resolution thermometers (ibuttons) during the whole sampling period in the Toronto experiment.



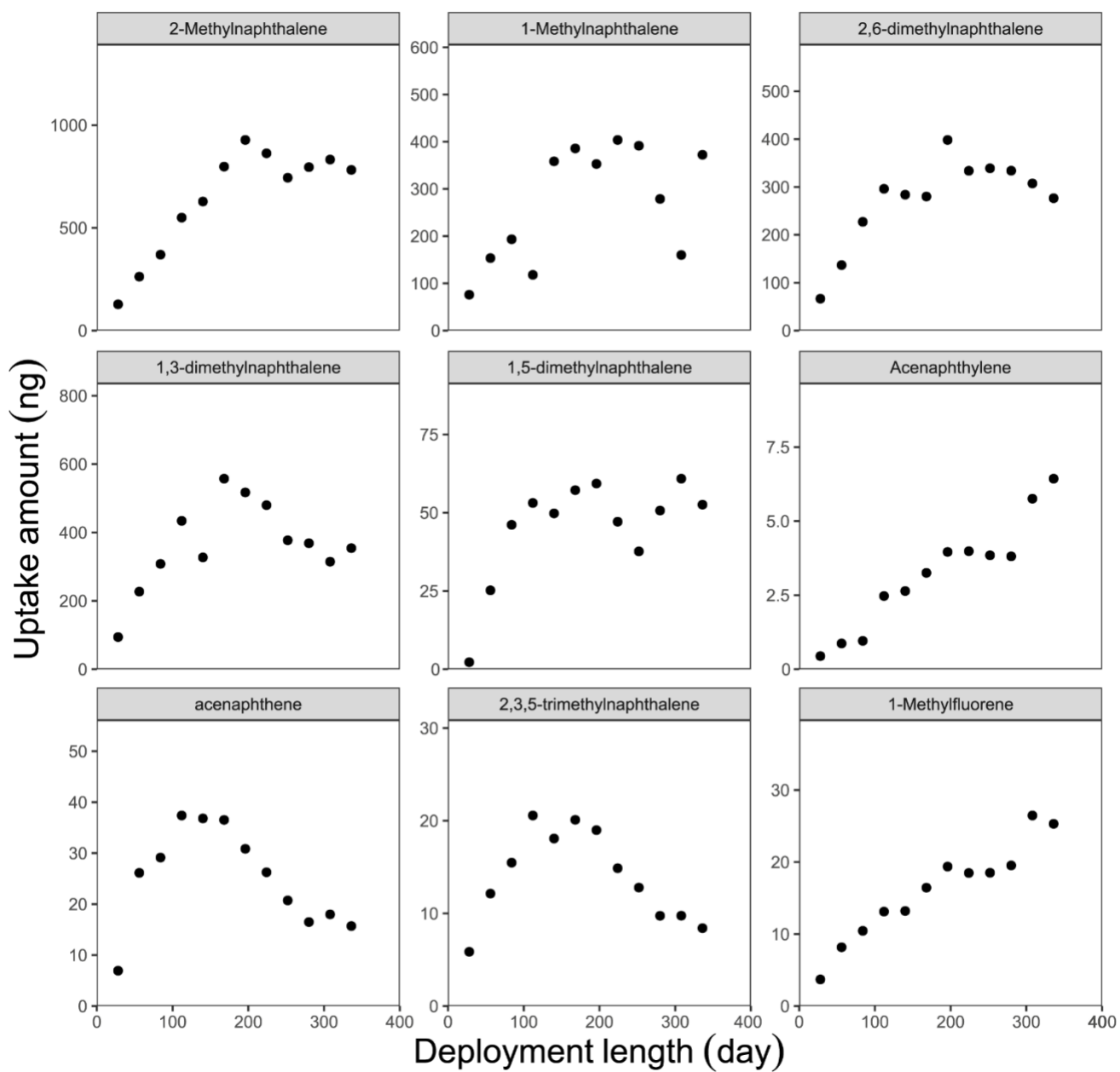
**Figure S3** Ambient temperature recorded at Shanty Bay station (44.40, -79.63) which is the closest weather station with available temperature data to the sampling sites during Borden experiment.



**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.

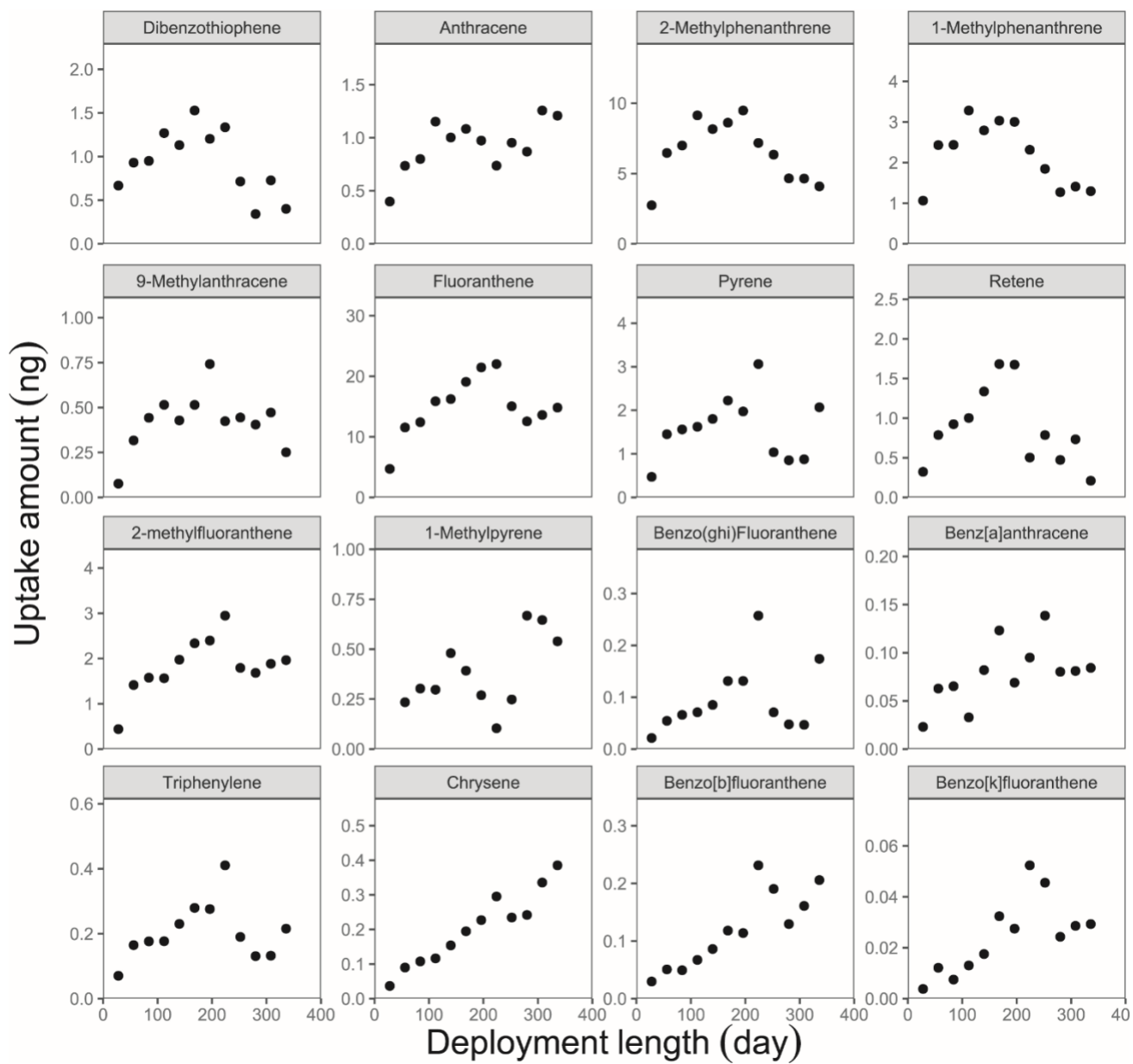
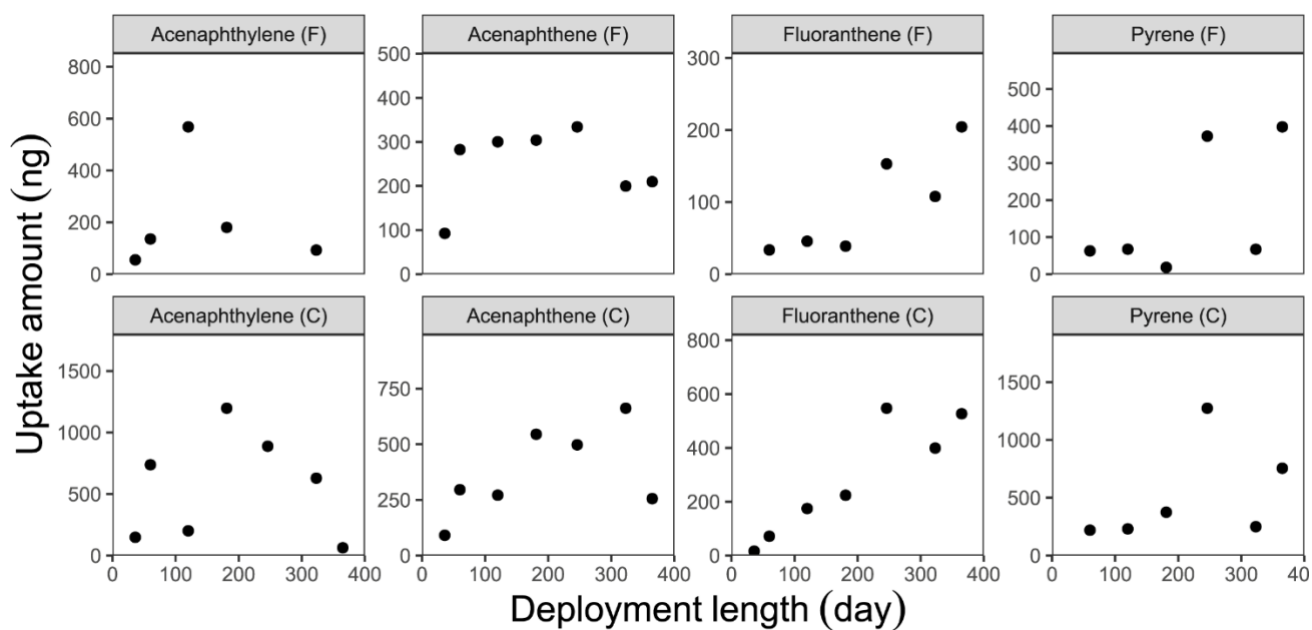
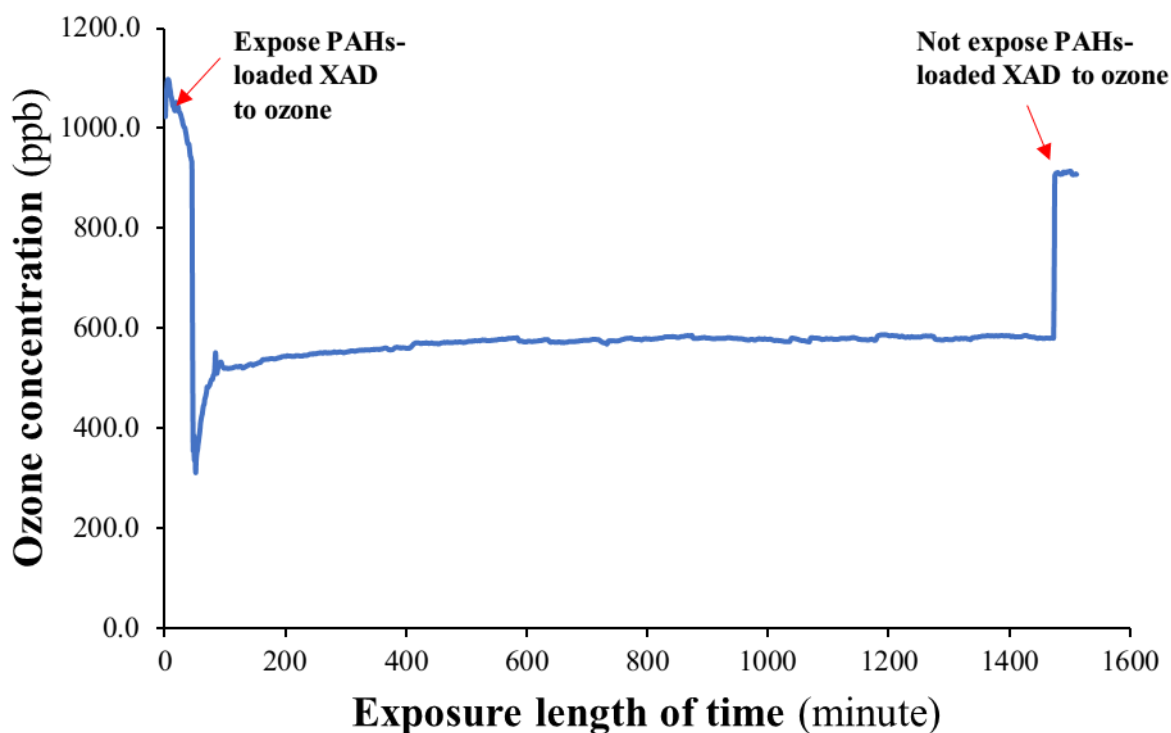


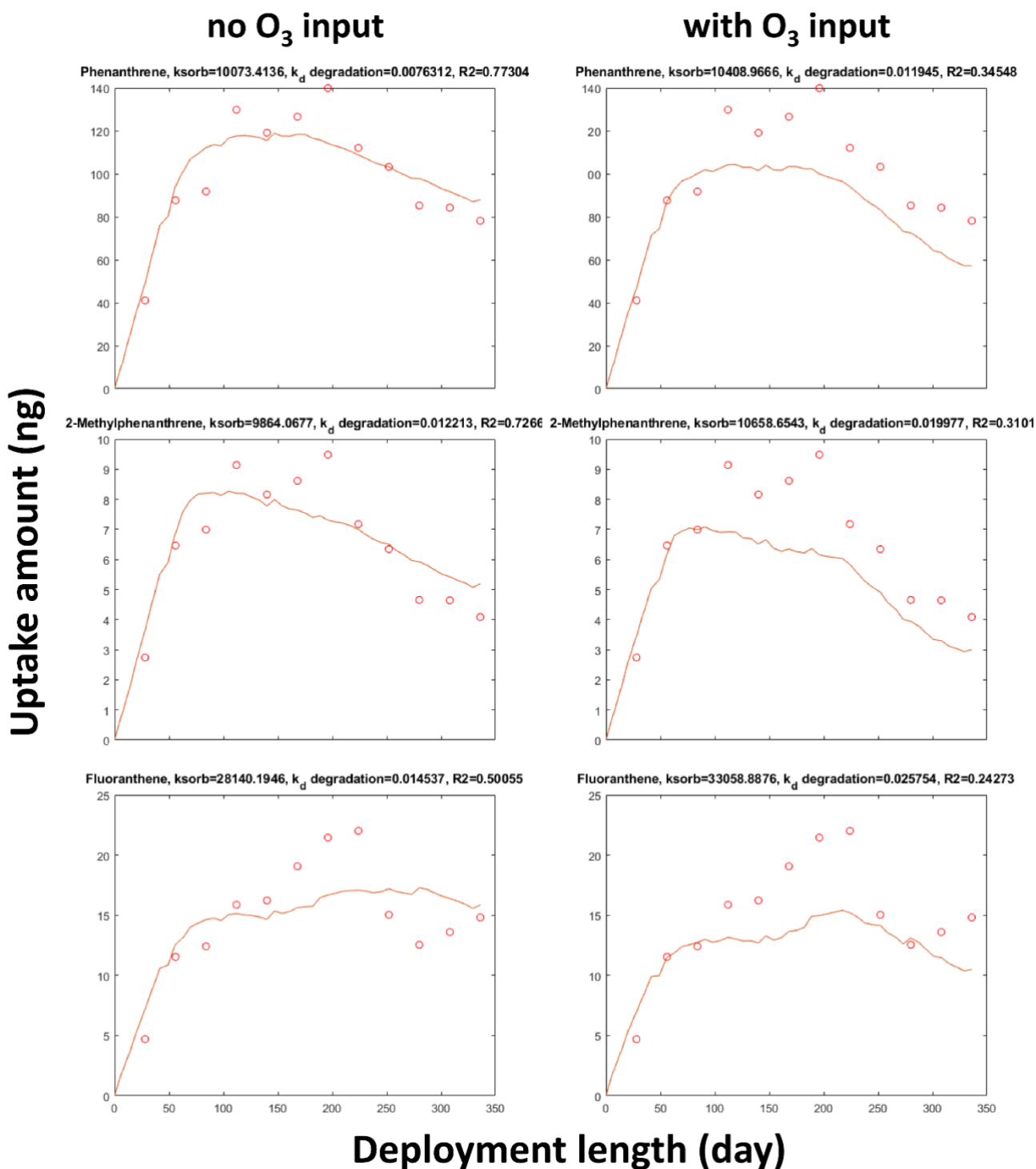
Figure S6. Continued



**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.

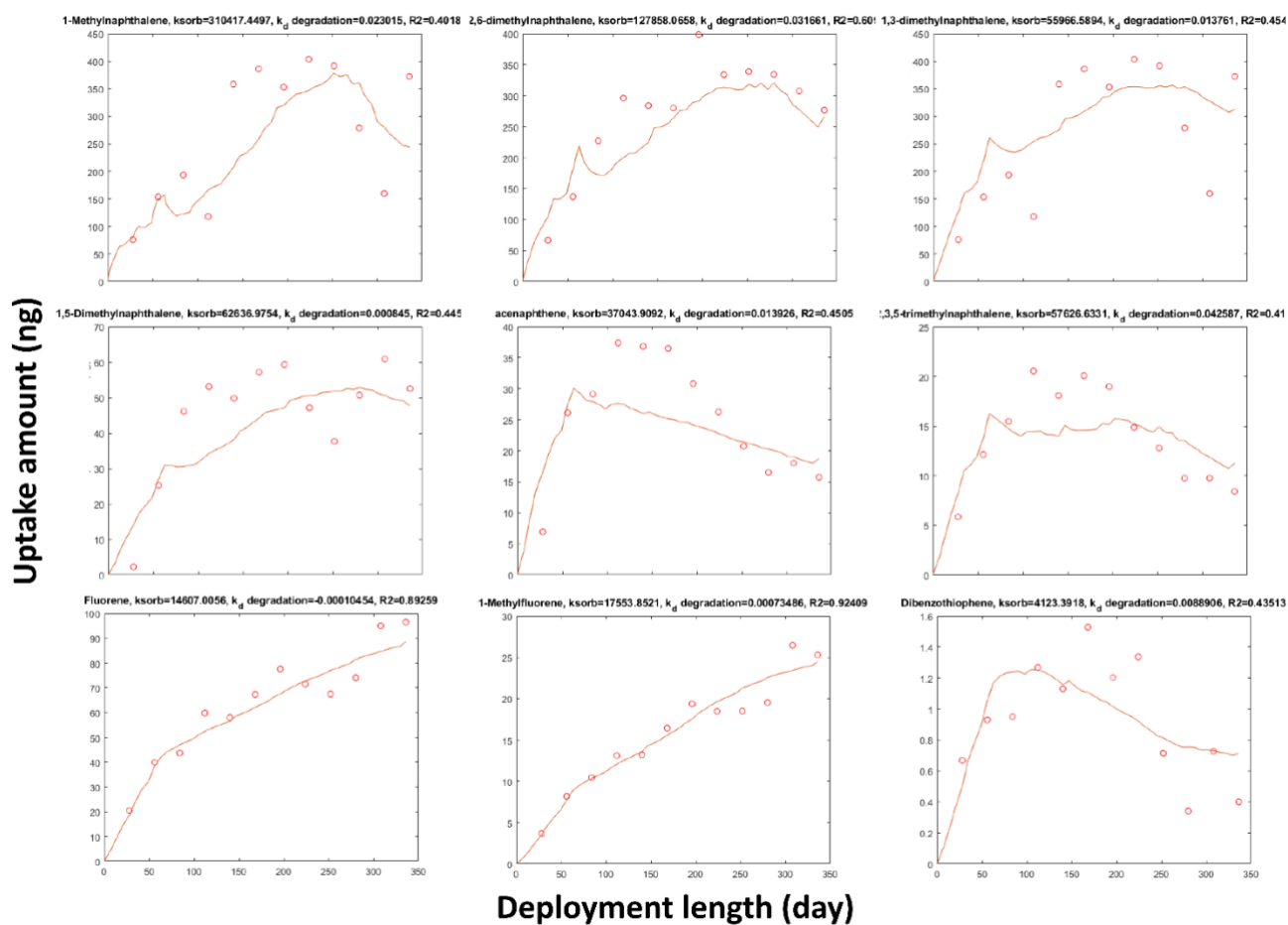


**Figure S8.** The decrease of ozone concentration in the flow tube in the presence of a PAH-loaded XAD-filled mesh cylinder.



**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.

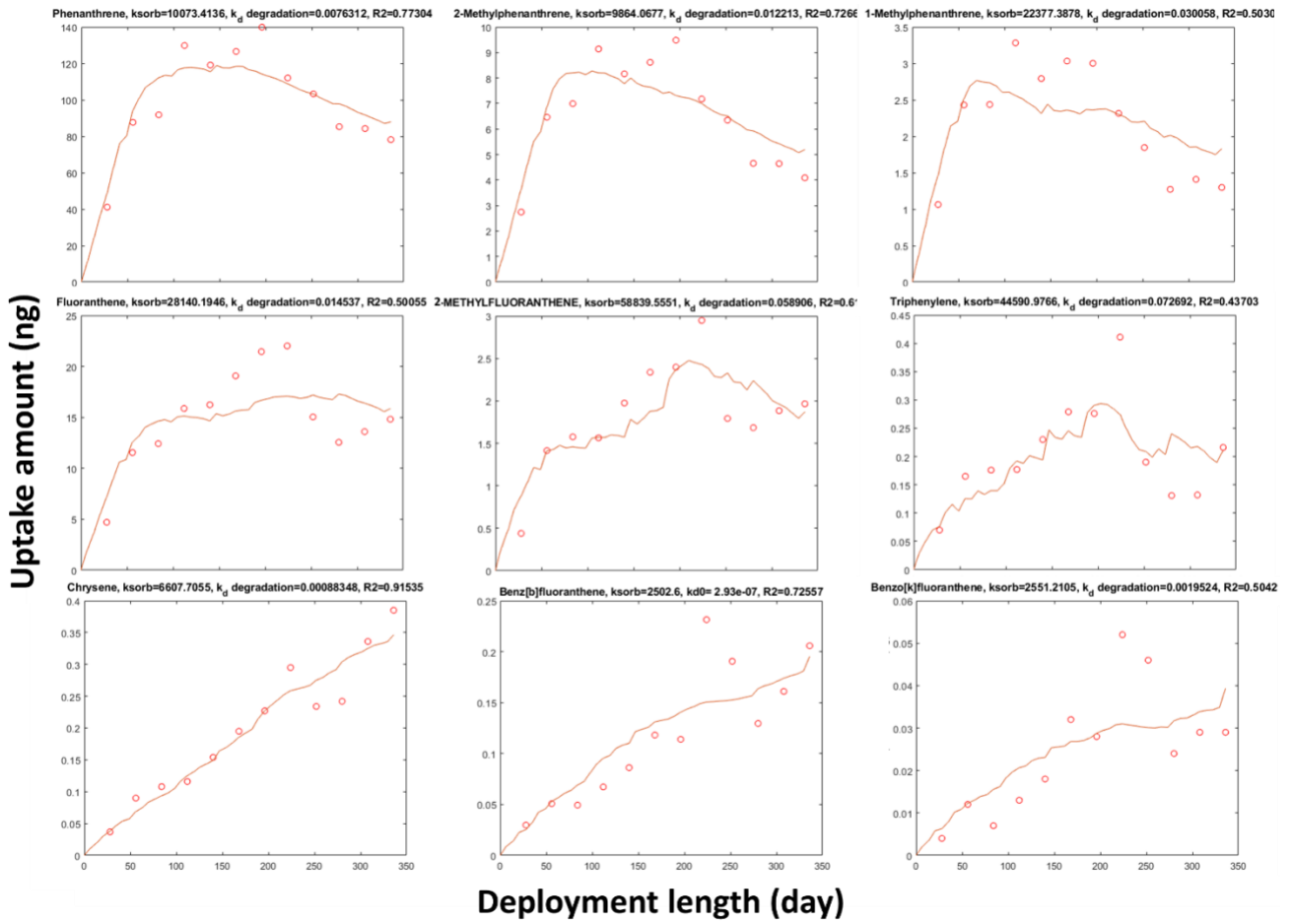
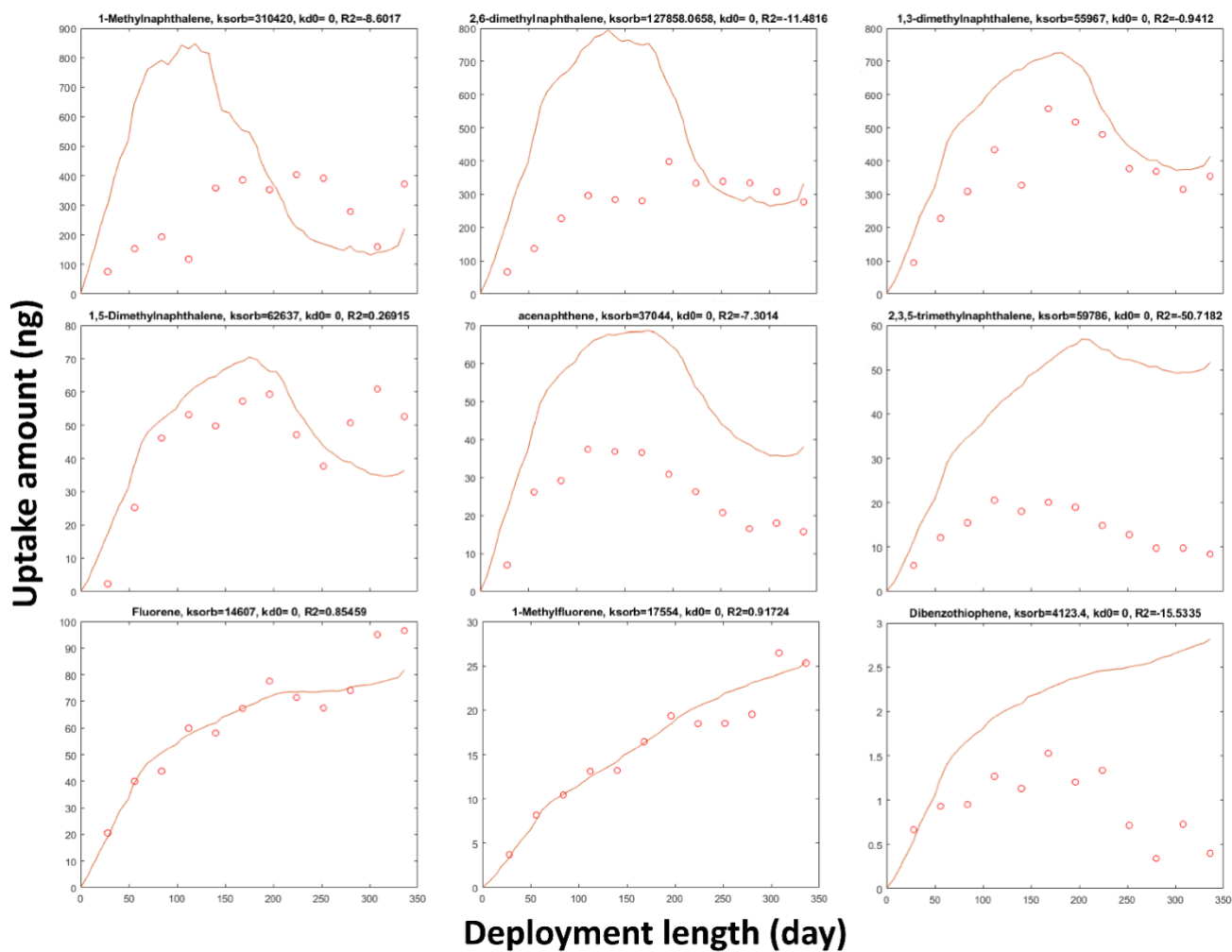


Figure S10. Continued



**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.

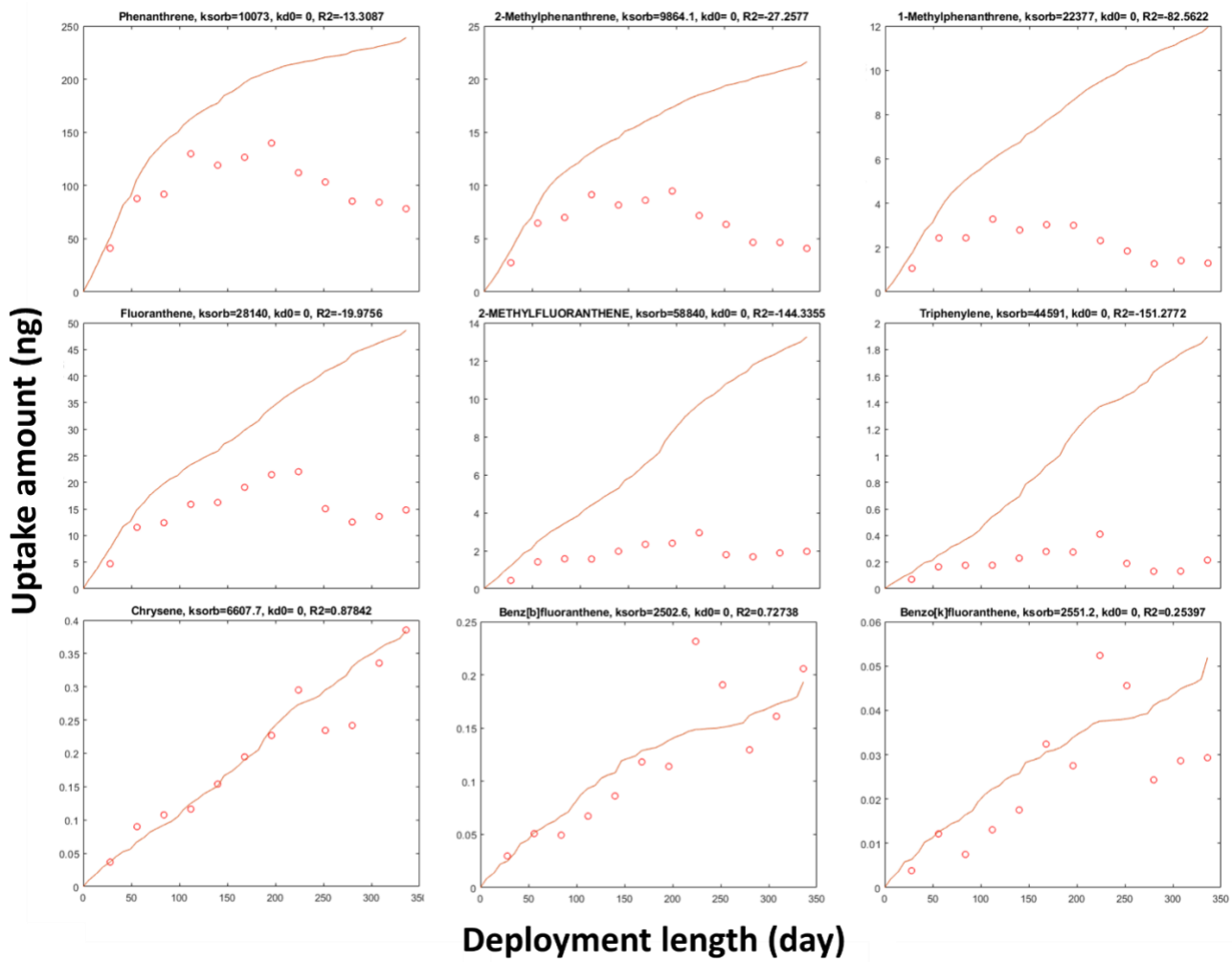
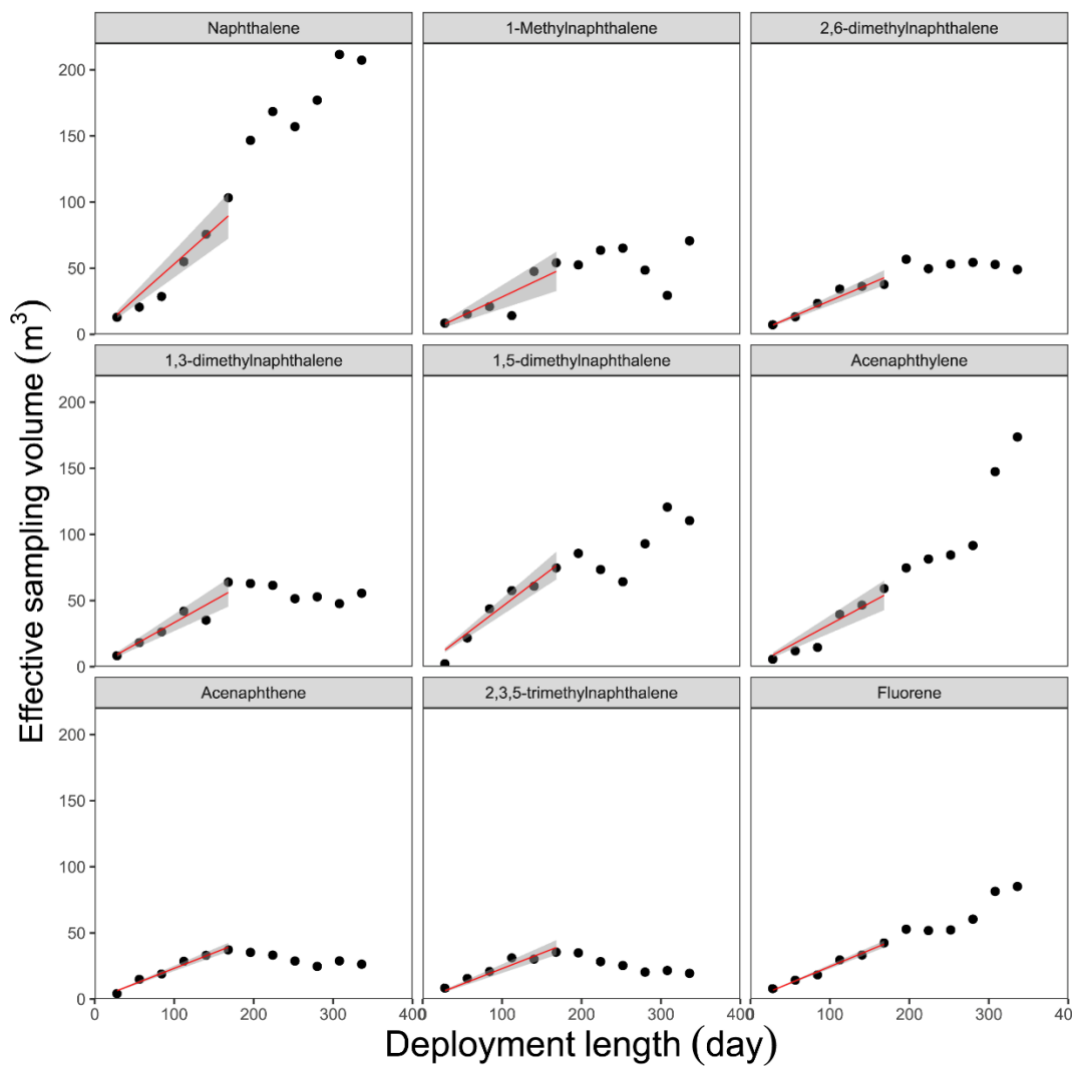


Figure S11. Continued



**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.

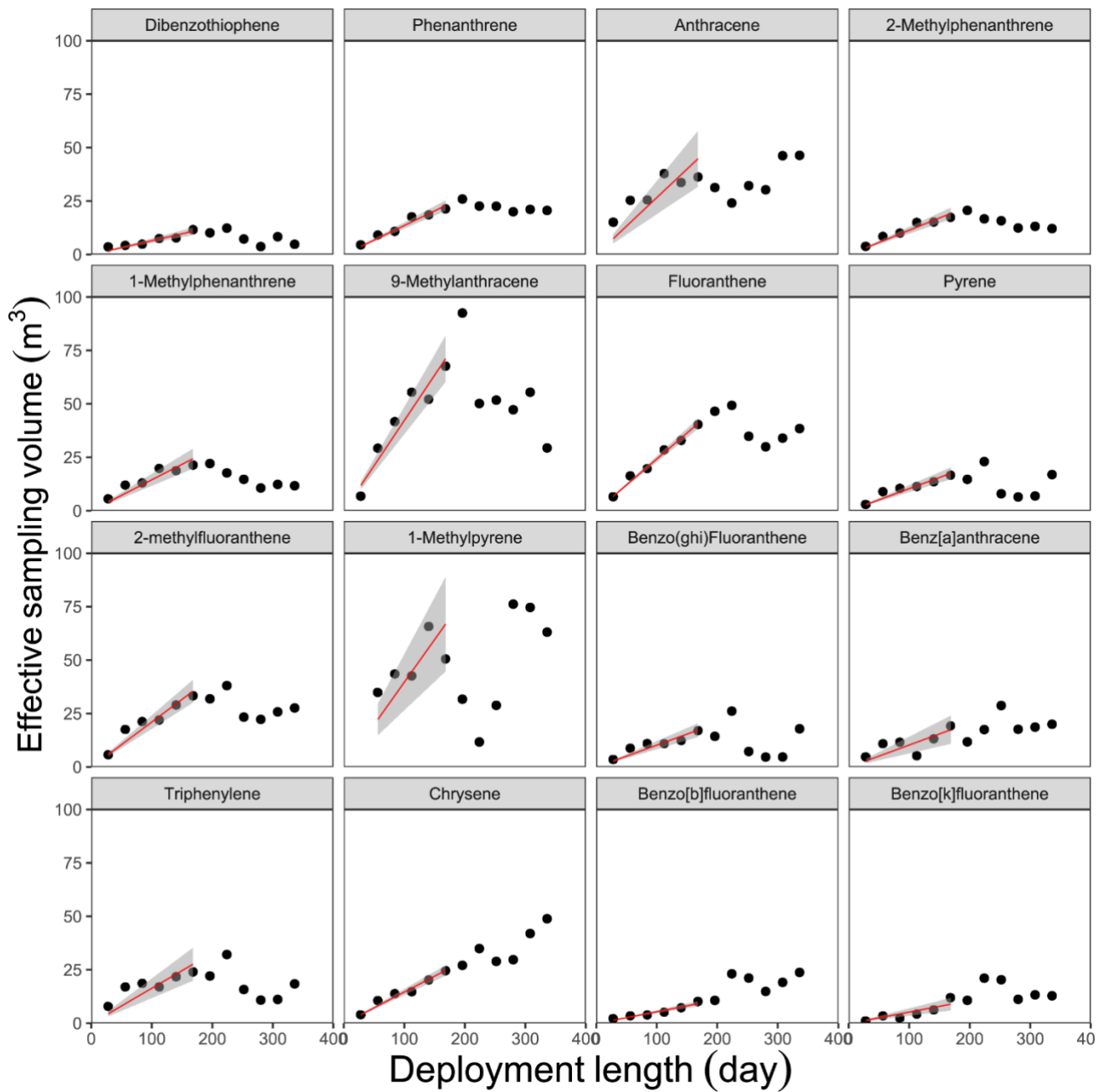
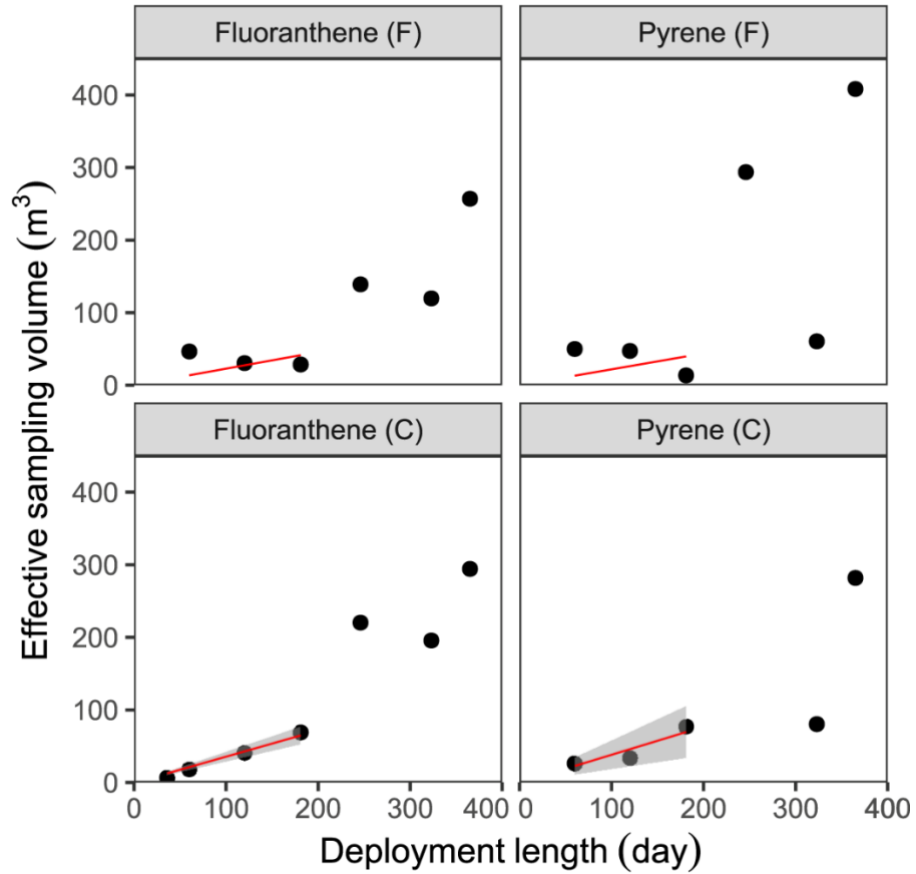


Figure S12. Continued



**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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