



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

4 Yuening Li,¹ Faqiang Zhan,^{1,*} Yushan Su,^{1,#} Ying Duan Lei,¹ Chubashini Shunthirasingham,²
5 Zilin Zhou,³ Jonathan P. D. Abbatt,³ Hayley Hung,² Frank Wania^{1,*}

6 ¹*Department of Physical and Environmental Sciences, University of Toronto Scarborough,*
7 *1265 Military Trail, Toronto, Ontario, Canada M1C 1A4*

8 ²*Air Quality Processes Research Section, Environment and Climate Change Canada, 4905*
9 *Dufferin Street, Toronto, Ontario, Canada M3H 5T4*

10 ³*Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario,*
11 *Canada M5S 3H6*

12 [#]*current: Ontario Ministry of the Environment, Conservation and Parks, 125 Resources Road,*
13 *Etobicoke, Ontario, Canada M9P 3V6*

14 ^{*}Corresponding authors: frank.wania@utoronto.ca, faqiang.zhan@utoronto.ca



15 **ABSTRACT**

16 Polycyclic aromatic compounds (PACs) continue to demand attention due to their widespread
17 presence and well-established health implications. Given that incomplete combustion is a
18 major contributor to PACs and inhalation constitutes a crucial human exposure pathway, a
19 comprehensive understanding of the concentrations, spatial distributions, and fates of a broad
20 range of PACs in the atmosphere is important. Passive air samplers (PASs) are a commonly
21 utilized technique for PAC sampling and monitoring. In this study, we present the results from
22 two one-year calibration experiments, one starting in summer and the other in winter, using a
23 passive air sampler equipped with XAD resin as the sorbent (XAD-PAS). Throughout both
24 experiments, PACs were consistently sorbed during the initial six-month period. However, the
25 sorbed amounts for many PACs exhibited a decrease after half a year of deployment. Three
26 hypotheses to explain this phenomenon were explored, including the uptake of atmospheric
27 particles, evaporation from the sorbent, and reactions with photooxidants. All had to be rejected
28 based on the obtained data, additional laboratory experiments and model results. Model
29 simulations were further used to (i) confirm that a loss process must be invoked to explain the
30 observed uptake behaviour and (ii) estimate the kinetics of that loss process for different PACs.
31 Sampling rates (*SRs*) for 28 PACs derived from the linearized uptake curves during the first
32 six months of deployment were comparable to those of other semi-volatile organic compounds
33 obtained during the same calibration experiment, and they also demonstrate a consistent
34 negative correlation with volatility.



35 **1. INTRODUCTION**

36 Approximately 4 million square kilometers of savanna, forest, grassland, and agricultural
37 ecosystems are burnt through both natural and controlled fires annually (Nolan et al., 2022).
38 These fire events have attracted global attention to the release of pollutants, including harmful
39 particles, organic vapors, and greenhouse gases, into the air as well as the related potential
40 health risks. In particular, the production and dispersion of polycyclic aromatic compounds
41 (PACs) in the environment have emerged as significant concerns. PACs comprise organic
42 molecules composed of fused aromatic rings, including unsubstituted polycyclic aromatic
43 hydrocarbons (PAHs), alkylated PAHs (alk-PAHs), and heterocyclic aromatic compounds
44 containing N, O, or S atoms in their structure (Moradi et al., 2022). PACs originate from a
45 multitude of sources, encompassing both natural and human-related activities, many related to
46 the incomplete combustion of organic matter. Natural sources include wild fires (Nolan et al.,
47 2022; Environment Canada and Health Canada, 1994; Nikolaou et al., 1984; Wnorowski et al.,
48 2021), volcanic eruptions (Nikolaou et al., 1984; Programme United Nations Environment,
49 2020), and biogenic processes (Wakeham et al., 1980). Anthropogenic activities contribute
50 substantially to the emissions of PACs into the environment (Environment Canada and Health
51 Canada, 1994), with vehicle emissions (Berthiaume et al., 2021; Muir and Galarneau, 2021),
52 cooking and heating (Shen et al., 2012; Environment Canada and Health Canada, 1994), wood
53 burning (Lima et al., 2005; Xu et al., 2006), industrial processes (Lima et al., 2005; Xu et al.,
54 2006), and tobacco smoke (Holme et al., 2022) releasing numerous PACs into the atmosphere.
55 PAHs have been widely studied due to their ubiquitous presence in the environment and their
56 potential for eliciting adverse health effects, such as allergic potential, carcinogenicity,
57 teratogenicity, and genotoxicity (Rice and Baker, 2007; Boffetta et al., 1997; White, 2002; Kim
58 et al., 2013; Organization, 1998; ATSDR (Agency for Toxic Substances Disease Registry),
59 1995), PAHs are regulated and routinely monitored by numerous agencies and governments
60 across the globe.

61 With past research efforts mainly focused on PAHs, alk-PAHs have only recently started to
62 garner attention from researchers. The addition of alkyl groups alters the physicochemical
63 properties of PAHs, affecting their solubility, volatility, and toxicological properties. Certain
64 alk-PAHs may be more toxic than their non-alkylated counterparts (Golzadeh et al., 2021;
65 Hawthorne et al., 2006; Andersson and Achten, 2015; Grung et al., 2011; Kaisarevic et al.,
66 2009; Pechillips et al., 1979; Sarma et al., 2017), raising concerns about their potential
67 ecological and human health impacts. Whereas alk-PAHs have been identified at elevated



68 concentrations, and in some cases, are even dominant among PACs in air (Wnorowski et al.,
69 2022; Moradi et al., 2022; Jariyasopit et al., 2019) and food (Golzadeh et al., 2021), they have
70 not been widely studied, monitored, and regulated (Moradi et al., 2022). Studies in Canada are
71 particularly limited in number, with some data available for the Greater Toronto Area
72 (Jariyasopit et al., 2019; Moradi et al., 2022) and Athabasca oil sands region (Harner et al.,
73 2013; Jariyasopit et al., 2018; Wnorowski et al., 2021; Mahoney et al., 2023; Cheng et al., 2018;
74 Rauert et al., 2020; Harner et al., 2018; Moradi et al., n.d.; Jariyasopit et al., 2021; Ahad et al.,
75 2021).

76 Because inhalation is a critical human exposure pathway (Carl-Elis et al., 2002; Liu et al.,
77 2007), achieving a comprehensive understanding of PAC concentrations, spatial distribution,
78 and fate in the atmosphere is important. As atmospheric PAC concentrations are related to
79 proximity to emission sources, urban areas, industrial zones, regions with high traffic density,
80 and places close to wildfire typically exhibit elevated PAC concentrations. Atmospheric
81 transport can disperse PACs widely, both while bound to particles and in the gas phase (Muir
82 and Galarneau, 2021; Zhou et al., 2019; Wnorowski et al., 2022; Masclet et al., 2000). Clearly,
83 there is a need for reliable air sampling techniques for a wide range of PACs.

84 Atmospheric PACs can be sampled using active air samplers (AASs) and passive air samplers
85 (PASs). In AASs, pumps are used to pull air through a sampling medium (e.g., a sorbent or/and
86 a filter) to capture atmospheric PACs in the gas or/and particle phase. While accurate sampling
87 volumes are usually easily obtained, the need for a stable electrical power supply and high
88 maintenance requirements and operational expenses limit the geographical scope of AASs,
89 especially in remote areas. Without using pumps, PASs sample and retain chemicals by relying
90 on chemical vapors' diffusing and sorbing to a sorbent. Low cost and maintenance
91 requirements expand their potential spatial applications, e.g., in areas close to wildfire regions.
92 However, obtaining accurate sampling volumes can be challenging. Confidently using a PAS
93 requires quantitative knowledge of the uptake kinetics and of the limits of linear uptake for the
94 targeted compounds, which is typically obtained by calibration studies using co-located AAS
95 and PASs.

96 Sorbents used for sampling PACs in PASs include polyurethane foam (PUF) (Cheng et al.,
97 2013; Domínguez-Morueco et al., 2017; Pozo et al., 2015), polyethylene (PE) (Bartkow et al.,
98 2004; Meierdierks et al., 2021), polydimethyl siloxane (PDMS) (Barthel et al., 2012; Bohlin-
99 Nizzetto et al., 2020), and styrene–divinylbenzene co-polymeric resin (commercial name XAD)
100 (Barthel et al., 2012; Lévy et al., 2018). Calibration studies have been conducted for PACs in



101 PAS based on PE (Meierdierks et al., 2021), PUF (Harner et al., 2013; Bohlin-Nizzetto et al.,
102 2020; Tromp et al., 2019; Holt et al., 2017; Bohlin et al., 2014a; Melymuk et al., 2011), PDMS
103 (Tromp et al., 2019), and XAD(Ellickson et al., 2017; Armitage et al., 2013). However, due to
104 a relative low uptake capacity, some sorbents, such as PE and PDMS, are less widely used in
105 PAS. Even though PUF-PASs are widely used, they have some limitations: (1) the uptake
106 capacity of PUF is too small to sample more volatile PACs within the linear uptake regime
107 during longer deployment periods, which may lead to relatively high uncertainties and
108 difficulties in data interpretation (Li and Wania, 2021; Li et al., 2022). (2) Gas-phase
109 concentrations of PACs, especially of less volatile PACs, may be hard to obtain as the PUF-
110 PAS samples both gaseous and particle-bound PACs (Melymuk et al., 2011), with sampling
111 rates for the latter suffering from high variability and uncertainty (Holt et al., 2017).

112 The significantly greater uptake capacity (Wania and Shunthirasingham, 2020; Hayward et al.,
113 2011) of the XAD-PAS (Wania et al., 2003) results in a demonstrably longer linear uptake
114 period (Wania and Shunthirasingham, 2020; Li et al., 2023a, b) for many semi-volatile organic
115 compounds (SVOCs) compared to other PASs. Moreover, the XAD-PAS's shelter was
116 intentionally designed to mitigate the impact of wind and particle uptake. Although the XAD-
117 PAS has been calibrated for PAC twice (Ellickson et al., 2017; Armitage et al., 2013), these
118 studies only targeted a limited number of PAHs and no alk-PAHs or heterocyclic aromatic
119 compounds. While Armitage et al. (2013) deployed AASs and PASs side-by-side, Ellickson et
120 al. (2017) positioned certain PASs at a considerable distance from the AASs, which could
121 potentially introduce heightened levels of uncertainty into the findings. The current study
122 sought to conduct a “gold standard” calibration for XAD-PAS with the following objectives:
123 (1) evaluate the uptake behaviors of a large number of PACs in XAD-PAS, including PAHs,
124 alk-PAHs, and the heterocyclic aromatic compound dibenzothiophene; (2) determine the linear
125 uptake regimes and obtain experimental sampling rates for these PACs; (3) assess the impact
126 of meteorological conditions and chemical properties on the sampling of these PACs.

127 2. METHODS AND MATERIALS

128 **Field Sampling.** The main calibration experiment was conducted in 2020/2021 on the campus
129 of the University of Toronto Scarborough in the eastern suburbs of Toronto (43.7837, -
130 79.1903), with results for other SVOCs reported previously (Li et al., 2023b, a). For
131 comparison, we also present the results of calibration experiments conducted in 2001/2002 in
132 a forest (44.3184, -79.9341) and a nearby clearing (44.3270, -79.9169) site in Borden, Ontario,
133 with air concentrations having been previously reported (Su et al., 2007a, b). The Borden sites



134 are approximately 85 km to the Northwest of the Toronto site. In each study, XAD-PASs were
135 deployed simultaneously ca. 1.5 m above the ground, and AASs, collecting particle and gas
136 phase separately, were placed side by side with the PASs. Both calibration experiments lasted
137 ~1 year, with the Borden experiments starting in November 2001 and the Toronto experiment
138 in June 2020. During the experiments, XAD-PASs were retrieved every four weeks in Toronto
139 and after 36, 60, 120, 181, 246, 323, and 365 days in Borden. Periodical 24-hour-long active
140 air samples in Borden and consecutive week-long active air samples in Toronto were obtained
141 using high-volume active air samplers (HV-AASs) and mid-volume active air samplers (MV-
142 AAS), respectively. Detailed sampling information has been described in previous publications
143 (Su et al., 2007a, b; Li et al., 2023b, a).

144 **Sample Treatment.** Glass fiber filters (GFFs) and PUFs from the Borden experiment were
145 Soxhlet extracted with dichloromethane and petroleum ether, respectively. Extracts were
146 cleaned, fractionated, and concentrated as described previously (Su et al., 2006, 2007a). The
147 XAD from the PASs deployed at Borden was loaded to and extracted in an elution column with
148 250 mL of methanol, followed by 350 mL of dichloromethane. After removing methanol with
149 250 mL of 3% sodium chloride, extracts were concentrated and fractionated using the method
150 described in Wania et al. (2003) The fractionated extracts were solvent exchanged into iso-
151 octane, and finally concentrated to 0.5 mL using nitrogen. More detail on sample treatment is
152 available in earlier publications (Su et al., 2006, 2007a; Wania et al., 2003).

153 For the samples from the Toronto experiment, one XAD-PAS cylinder from each retrieval date,
154 all blank samples, the PUF-XAD-PUF sandwiches, and GFFs were subjected to extraction
155 using an accelerated solvent extractor (Dionex 350). Prior to extraction, labeled standards
156 (Table S2) were spiked onto the samples as surrogates. The extracts were then concentrated
157 using rotary evaporation, water residues were removed using sodium sulfate columns, solvent-
158 exchanged into iso-octane, and further concentrated to 0.1 mL for PAS and 0.5 mL for AAS
159 using nitrogen-blowdown. Prior to instrumental analysis, 2.96 ng and 14.8 ng injection
160 standards (Table S2) were added to PAS and AAS extracts, respectively. Detailed procedures
161 were reported previously (Li et al., 2023b, a).

162 **Instrumental Analysis.** Extracts from the Borden experiment were analysed for 16 PAHs with
163 an Agilent 6890 gas chromatograph (GC) equipped with an Agilent 5973 mass spectrometric
164 (MS) detector using electron ionization in selected ion monitoring mode. In extracts from the
165 Toronto experiment, a total of 22 PAHs, 22 alk-PAHs and dibenzothiophene were analyzed.
166 This analysis were carried out using an Agilent 7890A GC coupled with a 7000A triple



167 quadrupole MS for PAS and PUF/XAD sandwich extracts and an Agilent 8890 GC coupled
168 to with a 7010B MS/MS for the GFF extracts, using electron ionization in multiple reaction
169 monitoring mode. Details on instruments, columns, temperatures, and other parameters are
170 given in the Supporting Information (SI).

171 **Ozone Exposure Experiment.** A laboratory experiment was conducted to examine the
172 potential of PAHs to undergo reactions with ozone while being sorbed to XAD. Approximately
173 150 g of pre-cleaned XAD-2 resin was added to ~300 mL of an acetone solution containing
174 ~3500-5000 ng each of acenaphthene, anthracene, phenanthrene, pyrene, and fluoranthene. To
175 make sure the XAD-resin was well mixed, it was stirred continuously using a clean spatula
176 until all acetone had evaporated (confirmed by repeatedly weighing of the PAC-loaded XAD-
177 resin). ~5.0 g of the spiked XAD resin was added to 10 mesh cylinders (2.0 cm diameter), as
178 used in the XAD-PAS, reducing the amount of resin required by placing a smaller empty mesh
179 cylinder (1.0 cm diameter) in their centre (Zhang et al., 2011). The exact weight of the XAD
180 in each mesh cylinder was recorded and used for data normalization.

181 Five randomly selected spiked mesh cylinders were extracted and analyzed using the same
182 method as for the samples from the Toronto experiment mentioned above in order to investigate
183 the variability of the PAHs in these cylinders. Three mesh cylinders were exposed to 1000 ppb
184 ozone at 0% relative humidity (RH) in a flowtube (Zhou and Abbatt, 2021) (Figure S1), two
185 for 24 hours and one for 72 hours. As a control, two mesh cylinders were exposed to air for 24
186 hours at 0% RH in the same flow tube. Upon retrieval, the five mesh cylinders from the flow
187 tube experiments were extracted and analyzed as before.

188 **Calculation of Sampling Rates (SR).** During the linear uptake phase, the *SR* of a compound
189 in the XAD-PAS is linearly related to the effective sampling volume V_{eff} (m^3):

$$190 \quad V_{eff} = \frac{M_{PAS}}{C_{air}} = SR \cdot t \quad (1)$$

191 where M_{PAS} (ng) is the field blank corrected amount of a PAC sorbed to the XAD-2 resin, and
192 C_{air} is the atmospheric gas phase concentration of the PAC ($ng\ m^{-3}$) averaged over the
193 deployment period t of a sampler (day). C_{air} is derived by averaging the concentrations recorded
194 by the AAS during a PAS's deployment. The *SR* for each compound during the period of linear
195 uptake is then obtained as the slope of the linear regression between V_{eff} and t .

196 **Chemical Properties Compilation.** The logarithm of the equilibrium concentration ratios
197 between XAD-resin and air ($K_{XAD/air}$, $L\ air\ g^{-1}\ XAD$) at 20 °C (Table S4) and the internal



198 energies of phase transfer between XAD and the gas phase $\Delta U_{\text{XAD/air}}$ (J mol^{-1} , Table S4) were
199 calculated using solute descriptors for PACs from the UFZ-LSER database (UFZ-LSER
200 database v 3.2.1 [Internet], 2022) and the poly parameter free energy relationships (ppLFERs)
201 by Hayward et al. (2011) The $\log K_{\text{XAD/air}}$ values at the mean temperatures over the entire
202 deployment period of the Borden and Toronto calibration experiments (7.9 and 12.2°C,
203 respectively) (Table 2) were obtained from $\log K_{\text{XAD/air}}$ at 20 °C and $\Delta U_{\text{XAD/air}}$ using the van't
204 Hoff equation (Atkinson and Curthoys, 1978; Goss, 1996).

205 **Model Simulations.** A mechanistic model developed by Zhang and Wania (2012) was used to
206 simulate the uptake of PACs with different $K_{\text{XAD/air}}$ during the two calibration experiments
207 beginning in different seasons (June and November). This model describes the diffusion of
208 chemicals from the atmospheric gas phase to the sorbent of a PAS and the kinetics of reversible
209 sorption to that sorbent. It has been modified to consider degradation loss of chemical sorbed
210 to the XAD-resin and to incorporate time-variant temperature and atmospheric ozone
211 concentrations. The Levenberg-Marquardt algorithm was used to find the combinations of
212 sorption rate k_{sorb} and degradative loss rate k_d that provide the best fit between predicted and
213 measured uptake curves. The actual temperature measured during the two calibration
214 experiments (Figures S2 and S3) were used in the simulations. Measured ozone concentrations
215 reported for the vicinity of the sampling sites (Figures S4 and S5) were used as input for
216 photooxidant degradation simulations only. The thickness of the stagnant air boundary layer
217 was assumed to be 0.01 cm and the simulated deployment length was 336 days.

218 **3. RESULTS AND DISCUSSION**

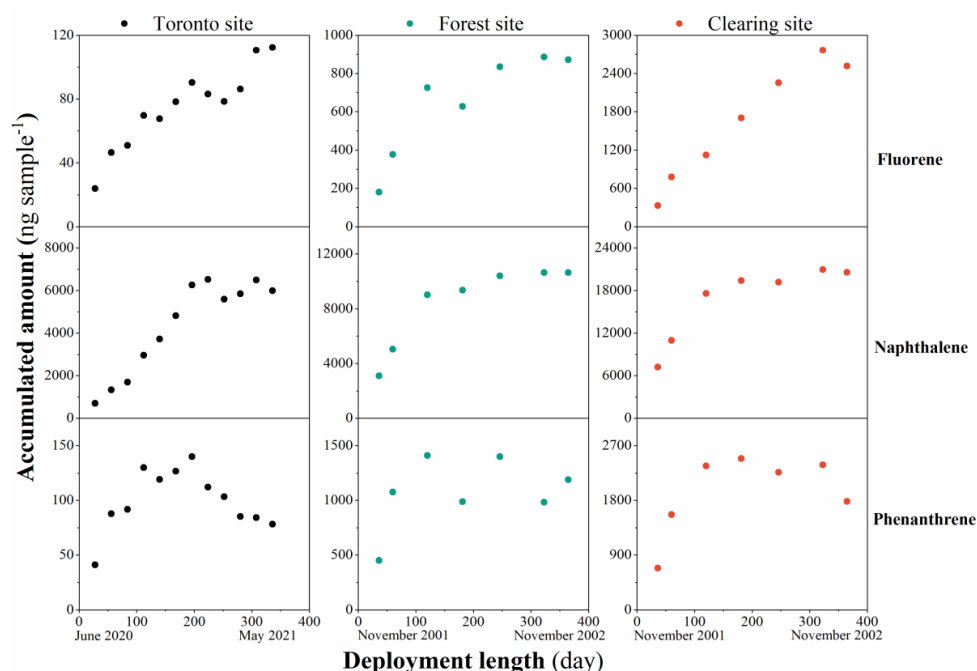
219 **Amounts Accumulated in PASs.** Fifteen PAHs, twelve alk-PAHs and dibenzothiophene were
220 reliably detected in the PAS extracts from the Toronto experiment (Table S6). Seven of these
221 PAHs were also detected in the extracts from the Borden experiment (Table S7). The amounts
222 of fluorene, naphthalene, and phenanthrene accumulated in the PASs are plotted versus
223 deployment length in Figure 1. Plots for the remaining 25 PACs are provided in Figures S6 and
224 S7 in the Supporting Information. These plots reveal that for only five of the 28 PACs in the
225 Toronto experiment, namely, acenaphthylene, fluorene, 1-methylfluorene, chrysene, and
226 benzo[b]fluoranthene, does the amount sorbed to the XAD increase relatively continuously
227 with increasing deployment for the entire length of the experiment. The amounts of the
228 remaining PACs either were largely constant (e.g., naphthalene in Figure 1) or decreased (e.g.,
229 phenanthrene in Figure 1) after approximately six-months of deployment. The observed uptake
230 behaviour was consistent between the three study sites, i.e., was observed in Toronto and the



231 forest and clearing sites in Borden (Figure 1). This behaviour is in contrast to continuous uptake
232 observed for a large number of SVOCs targeted in the same calibration study in Toronto (Li et
233 al., 2023b, a).

234 Theoretically, the amount of a chemical taken up in a PAS should always increase with
235 deployment length (Wania and Shunthirasingham, 2020). A decrease with increasing
236 deployment length might occur if the chemical is degraded while being sorbed or if the rate of
237 evaporation from the sorbent exceeds the rate of uptake. The latter occurs only if a chemical's
238 air concentration decreases or temperature increases after the chemical has reached a state of
239 equilibrium between atmospheric gas phase and sorbent. Equilibrium is more easily established
240 for volatile chemicals, sorbents with low uptake capacity and long deployments. We explored
241 three hypotheses to explain these unexpected decreasing trends in the amounts accumulated in
242 PASs.

243 **Can Uptake of Particle-bound Compounds Explain Decreasing Trends in the Amounts**
244 **Accumulated in PASs?** The first hypothesis posits that the observed uptake behaviour was
245 caused by the potentially inconsistent and unpredictable uptake and accumulation of
246 atmospheric particles in the XAD-PAS. This hypothesis is based on previous studies showing
247 that some PASs do not efficiently block wind from carrying particle-bound substances to the
248 sorbent, as is, e.g., observed in the case of the PUF-PAS with double bowl shelters (Wania and
249 Shunthirasingham, 2020; Chaemfa et al., 2009; Bohlin et al., 2014b; Harner et al., 2013). Even
250 though there is currently no evidence of the uptake of particle-bound SVOCs in the XAD-PAS,
251 if such uptake were to occur, the accumulated amount of a chemical in the XAD-PAS would
252 be the sum of the amount taken up from the gas phase and the amount derived from sampled
253 particle phase. Consequently, the uptake amount could be influenced by the size, type, and
254 concentrations of particles in air and the wind exposure of a PAS during deployment.



255

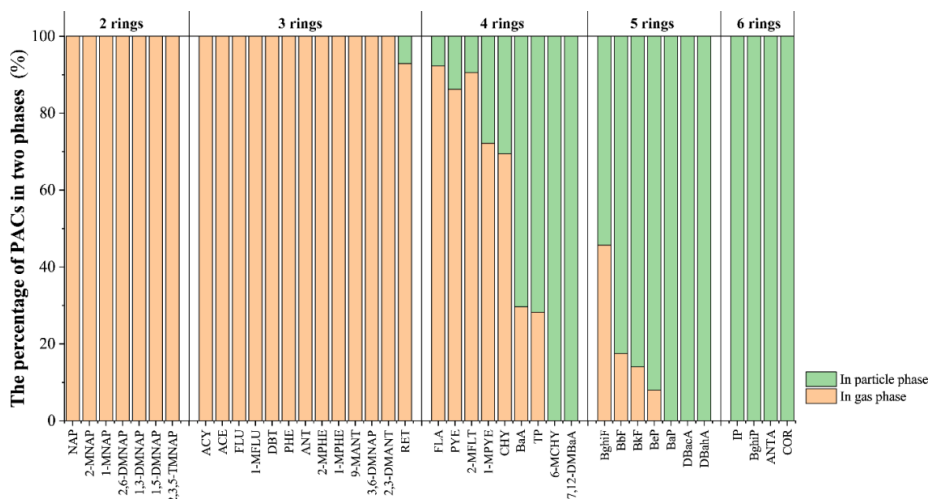
256 **Figure 1:** The amounts of three representative chemicals accumulating in the XAD-PASs throughout
 257 the one-year deployment period. The black, green, and red markers indicate the blank-
 258 corrected measured values at the site in Toronto, and the forest and clearing sites in Borden,
 259 respectively. The deployment month and the month in which the last PAS was retrieved are
 260 also indicated at the bottom part of this figure.

261 Seventeen PAHs and four alk-PAHs were reliably detected in the particles collected on the
 262 GFFs from the AASs in the Toronto experiment. Almost all two- and three-rings PACs were
 263 only detected in the gas phase, some four-rings and five-rings PACs could be detected in both
 264 gas and particle phase, and nine less volatile PACs were only found in the particle phase (Figure
 265 2). This is consistent with previous studies (Lewis and Coutant, 2020; Ravindra et al., 2008;
 266 Terzi and Samara, 2004) indicating less volatile PACs with four or more rings mainly being
 267 associated with atmospheric particles, whereas volatile PACs are mostly in the gas phase.

268 Only PACs with at least four or more fused rings in their structure could be detected with a
 269 high percentage in the particle phase, whereas the chemicals taken up by the XAD-PASs were
 270 primarily more volatile PACs with three or fewer rings. The absence of these relatively volatile
 271 PACs in the particle phase (i.e., levels below the LOD) demonstrates that the variation of their
 272 accumulated amount in XAD-PASs in the second half of the year-long deployment cannot be
 273 associated with the uptake of atmospheric particles. Because concentrations of particle-bound



274 PACs in Ontario are much higher in winter than in summer (Su et al., 2007a), their hypothetical
275 uptake would be expected to occur during the latter half of the Toronto experiment and the first
276 half of the Borden study. However, the same deviations from continuous uptake are apparent
277 in the second half of both experiments (Figure 1).



278

279 **Figure 2:** The average percentages of PACs detected in the particle (green) and gas phase (orange) of
280 the 48 week-long active air samples taken during the Toronto experiment. PACs were
281 grouped based on the number of rings in their structure.

282 In the case of the least volatile PACs with five and six rings that were only detected in the
283 particle phase, their absence in PAS extracts provides further evidence that the XAD-PAS does
284 not take up atmospheric particles. Daly et al. (2007) previously reported that involatile
285 chemicals tend to have levels below the limit of detection in XAD-PAS extracts, which is also
286 consistent with our previous studies indicating that no SVOCs with $\log K_{XAD/air}$ higher than 7.0
287 at 12.2 °C were detected in XAD-PASs (Li et al., 2023b, a). All evidence therefore refutes the
288 first hypothesis that particle uptake may be the cause of the variation in the uptake amounts.

289 **Can a Limited Sorbent Uptake Capacity Explain Decreasing Trends in the Amounts**
290 **Accumulated in PASs?** The second hypothesis is that the uptake capacity for XAD-PAS is
291 too small to prevent some PACs from reaching equilibrium between sorbent and atmospheric
292 gas phase after six months of deployment. A subsequent decrease in sorbed amount could then
293 be attributed to a decrease in air concentration or an increase in temperature, both of which
294 would allow evaporative loss to exceed uptake. Several pieces of evidence do not support this
295 interpretation:



296 During the same calibration experiment in Toronto, we observed highly linear uptake over the
297 entire 48 weeks for SVOCs as volatile as hexachlorobutadiene and monochlorinated biphenyl,
298 with estimated $\log(K_{\text{XAD/air}} / (\text{L air g}^{-1} \text{XAD}))$ values of 2.95 and 3.56 at 20 °C, respectively.
299 Naphthalene, the most volatile of the PACs targeted, has an estimated $\log(K_{\text{XAD/air}} / (\text{L air g}^{-1}$
300 $\text{XAD}))$ of 2.69. It is implausible that some chemicals remain in the linear uptake phase, while
301 chemicals with a very similar or higher affinity for sorbing to XAD from the gas phase would
302 reach equilibrium in the same experiment. Furthermore, there is no indication that the extent
303 of loss of PAC from the PAS during the second half of deployment is related to compound
304 volatility. For example, whereas phenanthrene is less volatile than either naphthalene or
305 fluorene, i.e., has a higher $K_{\text{XAD/air}}$ (Table 2), it was lost from the XAD-PAS to a greater extent
306 than either of these PACs (Figure 1).

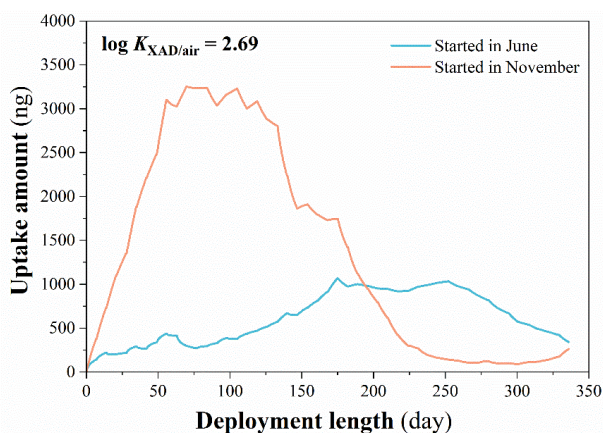
307 The potential for evaporative net loss of a PAC from the XAD-PAS is largest in summer, when
308 PAC air concentrations tend to be lower and temperatures are highest. This implies that this
309 potential for evaporative loss during the second half of a one-year experiment would be higher
310 in the case of the Borden calibrations (starting in November) than in the Toronto experiment
311 (starting in June). Figure 3 displays simulated uptake curves for a compound that is volatile
312 enough to reach equilibrium between XAD and gas phase. Applying the seasonal variability of
313 naphthalene air concentrations and the temperatures measured in Borden and Toronto (Figure
314 S7), the model predicts widely divergent uptake curves for deployments starting in November
315 and June. The loss of sorbed naphthalene occurs earlier during an experiment starting in winter
316 (after ca. 120 days of deployment), and the extent of loss is more pronounced. In contrast, the
317 naphthalene uptake curves observed in the field calibration experiments are remarkably similar
318 (Figure 1). In summary, all evidence indicates that PACs did not reach equilibrium and a
319 limited XAD uptake capacity cannot explain the absence of continuous uptake.

320 **Can Degradative Loss Explain Decreasing Trends in the Amounts Accumulated in PASs?**

321 The third hypothesis posits that reactions of sorbed PACs with photooxidants present in the
322 atmosphere could account for the lack of continuous uptake (Jariyasopit et al., 2015; Melymuk
323 et al., 2017). It is well established that ozone can react with PAHs sorbed to solid phases
324 (Borrowman et al., 2016; Zhou et al., 2019) and atmospheric particles (Van Vaeck and Van
325 Cauwenberghe, 1984; Kasumba and Holmén, 2018). While nitrogen dioxide may also react
326 with some PAHs, either no reactions were found (Grosjean et al., 1983; Pitts et al., 1980), or
327 only negligible percentages of PAHs were observed to react with nitrogen dioxide (Tokiwawa
328 et al., 1981). Even though gaseous and sorbed PAHs can react with OH radicals (Brubaker and



329 Hites, 1998; Atkinson and Arey, 2007; Esteve et al., 2004, 2006; Bedjanian et al., 2010), such
330 reactions are less likely to occur within the dark environment of a XAD-PAS housing.
331 Consequently, we focused solely on the reaction between ozone and PACs.



332

333 **Figure 3:** Predicted uptake curves for a chemical with a $\log (K_{XAD/air} / (L \text{ air } g^{-1} \text{ XAD}))$ value of 2.69 at
334 20 °C during calibration experiments starting in June and November, while assuming air
335 concentration and temperature variability typical for Southern Ontario. The thickness of the
336 stagnant air boundary layer was set to 0.01cm, the sorption rate was set as $3 \times 10^5 \text{ day}^{-1}$ and
337 no degradation was assumed.

338 Specifically, we exposed PAC sorbed to XAD to high concentrations of ozone in a flow tube
339 to probe the possibility of degradative loss. If the reaction rate of the PACs with ozone is
340 assumed to be proportional to the ozone concentration, an exposure to ~1000 ppb of ozone for
341 24 and 72 hour is equivalent to two to four months of continuous exposure to atmospherically
342 relevant ozone levels of ~25 ppb. During the sampling period in Toronto, the ozone
343 concentration measured at an air monitoring station (43.7479, -79.2741) located ca. 8 km from
344 our sampling site ranged from 10 to 50 ppb with an annual average of 26 ppb (Figure S4). The
345 ozone concentration in the vicinity of the Borden site had a similar range (10 to 60 ppb) and
346 mean (27 ppb) (Figure S5).

347 We succeeded in obtaining a consistent loading of PAHs in the XAD-filled mesh cylinders:
348 The amounts of five PAHs on the XAD, when normalized to the net weight of resin in a mesh
349 cylinder, had a relative standard deviation (RSD) between 4.6 and 6.6% (Table 1). Neither
350 extended exposure to ozone in the flow tube nor exposure to air in the control experiment
351 resulted in a significant change ($p > 0.05$) in these amounts of PAHs in the XAD-filled mesh
352 cylinders (Table 1). In other words, the experiments suggest that ozone did not react with the



353 PACs sorbed to XAD resin. Interestingly, we did observe the continuous loss of ozone during
 354 the flow tube experiments (Figure S8). This loss was much larger than when no XAD was
 355 present in the flow tube, i.e., can be attributed to the resin. One potential explanation is that
 356 ozone reacts with the benzene rings in the XAD resin and because of the orders of magnitude
 357 higher abundance of these aromatic structures compared with the sorbed PAHs, this reaction
 358 may protect the sorbed PAHs from being attacked.

359 **Table 1** The amounts of spiked PAHs on XAD resin before and after ozone exposure

The amount of PAHs on XAD resin (ng)					
	Acenaphthene	Anthracene	Phenanthrene	Pyrene	Fluoranthene
Loading Test	60.2 ± 3.1	84.1 ± 5.6	66.9 ± 3.1	120.3 ± 6.6	63.2 ± 3.4
Control Group					
0 ppb O ₃ (1 day)	64.5 ± 1.3	87.1 ± 8.1	68.1 ± 4.8	126.4 ± 2.6	65.5 ± 3.0
Experimental Group					
1000 ppb O ₃ (1 day)	61.7 ± 1.2	84.8 ± 2.5	66.4 ± 2.4	123.8 ± 3.5	64.8 ± 1.9
1000 ppb O ₃ (3 days)	62.5	91.3	68.7	126.9	67.0

360 Further evidence that reactions with photooxidants are not responsible for the loss of PACs
 361 from the XAD-resin is provided again by the expected seasonal variability in the importance
 362 of that process. In both Toronto and Borden, the ozone concentrations are seasonally variable
 363 with higher levels in late summer and early fall and lower levels in winter (Figures S4 and S5).
 364 It thus should affect the second half of a one-year deployment much more strongly in the
 365 Borden experiment than the Toronto experiment. No such difference is apparent. To simulate
 366 the influence of ozone on the uptake amount of a PAC, a model simulation was conducted for
 367 three representative PACs in the Toronto experiment using the model by Zhang and Wania
 368 (2012) modified to allow the sorbed PAC to react with atmospheric ozone. The results from
 369 simulations show that the R^2 values of the best fitting uptake curves for these three PACs
 370 decrease when the actual time-variant ozone concentration is used as an input parameter
 371 (Figure S9). Finally, we note that PAHs that are known to have a higher reactivity with ozone
 372 than others, such as fluorene (Kasumba and Holmén, 2018), anthracene (Kasumba and Holmén,
 373 2018), and benz(a)anthracene (Van Vaecck and Van Cauwenberghe, 1984), do not appear to
 374 show a higher rate of loss from the XAD-PAS when compared to the other PACs. Consequently,
 375 based on these discussions and analyses, we conclude that ozone was not the cause of the
 376 decreasing trend of these PACs in the XAD-PASs.

377 **What Can Explain Decreasing Trends in the Amounts Accumulated in PASs?** After
 378 rejecting all three of our hypotheses, we can formulate a number of constraints on any further
 379 potential explanations. We find that the phenomenon is affecting different PACs to a different



380 extent, but this extent is neither related to the PACs' volatility, e.g., as expressed through the
381 $K_{XAD/air}$, nor to their relative reactivity with photo-oxidants. We further find that the
382 phenomenon appears to be very similar in calibration studies started in early winter and early
383 summer in a region with a strongly seasonal climate. This suggests that the strength of the
384 process causing this phenomenon cannot be strongly affected by season. All three of our
385 hypotheses relied on a seasonally variable process: PAC particle concentrations peak in winter,
386 temperature and therefore evaporative loss potential is highest in summer, and photo-oxidant
387 concentrations and degradative loss potential are also highest in summer.

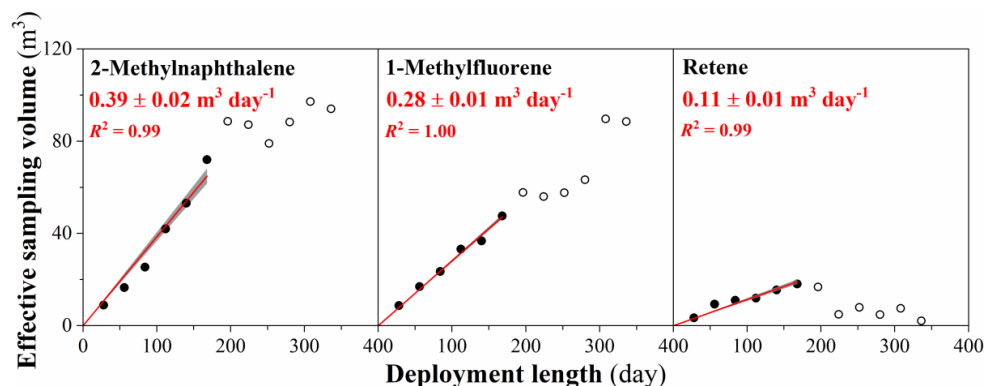
388 We used additional model simulations (Zhang and Wania, 2012) to further shed light on this
389 issue. For 18 PACs we determined the combination of k_{sorb} and k_d values that resulted in the
390 best fit between model-predicted uptake curves and the uptake curves measured during the
391 Toronto experiment ($R^2 > 0.4$). The fits are shown in Figure S10 and the fitted parameters are
392 summarized in Table S10. The k_{sorb} values range between 2,500 and 300,000 day^{-1} , with higher
393 values for more volatile PACs, as had been observed previously.⁶² This range encompasses the
394 range of k_{sorb} values previously estimated for polychlorinated biphenyls (10,000 to 80,000 day^{-1}).⁶² The k_d values range from extremely low values for benzo[b]fluoranthene to 0.073 day^{-1}
395 for triphenylene, the latter corresponding to a half-life on the order of 9 days. For many of the
396 PACs the fitted k_d values indicate a loss process with a half-life ranging from 10 days (2-
397 methylfluoranthene) to 100 days (phenanthrene). We further explored whether it is possible to
398 obtain model results that describe the observation, if it is assumed that the sorbed PACs do not
399 undergo loss. Uptake curves predicted using the k_{sorb} values in Table S10 and a k_d of zero, i.e.,
400 without degradative loss, deviate strongly from the measured ones (Figure 11). In other words,
401 the model cannot find a best fit to the observations without a loss process.
402

403 In summary, the evidence suggests the presence of a process that results in the loss of PACs
404 from the XAD-resin with half-lives on the order of weeks to months. The kinetics of that loss
405 process is different for different PACs, with the k_d values in Table 10 approximating the relative
406 susceptibility of different PACs. We have to concede that we presently do not know the nature
407 of that loss process. Microbial degradation could be a possibility, although reported relative
408 rates of degradation for PAHs (Ghosal et al., 2016) are not consistent with our k_d values, i.e.,
409 PAHs with shorter biodegradation half-lives do not appear to show a higher rate of loss from
410 the XAD-PAS. Microbial degradation is likely to be very complex and potentially related to
411 microbial species and communities, as well as environment conditions. More efforts are needed
412 in future studies to further identify the process leading to the loss of PACs from the resin.



413 **Is It Possible to Still Derive Useful Kinetic Information from the Calibration Experiments?**

414 V_{eff} values calculated using Eq. (1) are provided in Tables S7 and S9. Remarkably, when V_{eff}
415 for 15 PAHs, 12 alk-PAHs and dibenzothiophene from the Toronto calibration experiment are
416 plotted against deployment length, i.e., if we linearize the uptake curves from Figures 1 and S2,
417 almost all of the data show good linearity for the first six months of deployment (most linear
418 regressions have $R^2 > 0.90$ and p values < 0.05 , Table 2). Examples of such plots for 2-
419 methylanthalene, 1-methylfluorene, and retene are shown in Figure 4, with the remainder
420 being compiled in Figure S12. This is also true for fluoranthene and pyrene measured at the
421 clearing site in Borden, but not at the forest site (Figure S13). As only PUF plugs were used in
422 the AASs to sample PAHs from the gas phase in Borden, five light PAHs (i.e., naphthalene,
423 acenaphthylene, acenaphthene, fluorene, and phenanthrene) suffered from breakthrough,
424 yielded unreliable C_{air} and therefore were excluded from the data analysis.



425

426 **Figure 4:** The effective sampling volume of three representative PACs throughout the 48-week
427 deployment period for XAD-PASs in Toronto. The markers indicate field blank-corrected
428 measured values, whereby data points marked with open symbols were excluded from the
429 regression analysis. The red lines indicate linear regressions forced through the origin. The
430 shaded areas represent the uncertainties of the calculated sampling rates obtained from the
431 uncertainties of the slopes of these regressions. Sampling rates in $\text{m}^3 \text{ day}^{-1}$ are obtained from
432 the slope of these regressions.

433 As might be expected from the uptake curves, the V_{eff} for most PACs is leveling-off or
434 decreasing after six months (Figures 3, S11, and S12). Nevertheless, the linear uptake within
435 the first half year of deployment suggests that the XAD-PAS can be used to sample PACs from
436 the gas phase, even the most volatile one (naphthalene), as long as the deployment period does
437 not exceed six months. Experimental sampling rates ($SR_{\text{experimental}}$) for 28 PACs, including 15



438 PAHs, 12 alk-PAHs, and dibenzothiophene, were estimated from the slopes of linear
439 regressions for the data points from the first six months of deployment and ranged from 0.05
440 to $0.53 \text{ m}^3 \text{ day}^{-1}$. Uncertainties of the $SR_{\text{experimental}}$ values in the range of 2 to 15% were estimated
441 from the standard error of the slopes of these linear regressions. For fourteen compounds (2
442 PAHs, 11 alk-PAHs, and dibenzothiophene), these are the first SR s ever reported for the XAD-
443 PAS. The $SR_{\text{experimental}}$ values for fluoranthene and pyrene from the Toronto and Borden
444 experiments are very close, lending support to the reliability of the two experiments. The actual
445 sampling rates (SR_{actual}) for 18 PACs were obtained using the simulated no-degradation uptake
446 amounts in the first six months of deployment (Figure S11) and AAS data in our Toronto
447 experiment based on Eq. (1) (Table S11).

448 The $SR_{\text{experimental}}$ values in this study are lower than those reported for PAHs previously
449 (Armitage et al., 2013; Ellickson et al., 2017). The $SR_{\text{experimental}}$ values for various SVOCs
450 obtained from the same Toronto calibration experiment were also lower than those reported in
451 other literature (Li et al., 2023b, a). The difference between the $SR_{\text{experimental}}$ values calculated
452 in our study and those previously reported may be caused by the difference in ambient wind
453 speed (1.7 , ~ 4.0 , and $\sim 8.0 \text{ m} \cdot \text{s}^{-1}$ during our study, the study of Armitage et al. (2013), and the
454 study of Ellickson et al. (2017), respectively) and possibly also in the rates of degradative loss.
455 Other reasons for the relatively higher SR s in the study of Ellickson et al. (2017) may be due
456 to (1) break-through losses for more volatile PAHs during the high-volume AAS; (2) failure to
457 sample episodes of elevated air concentration when only sampling episodically with the AASs;
458 and (3) lower air concentrations at active air sampling sites than those at passive air sampling
459 sites.

460 The reliability of $SR_{\text{experimental}}$ and SR_{actual} values for PACs presented here is supported by them
461 falling within a similar range as those for other SVOCs from the same calibration experiment
462 (Li et al., 2023b, a). Also, the SR s for PACs exhibit a consistent negative correlation with \log
463 $K_{\text{XAD/air}}$, mirroring the pattern observed for other SVOCs (Figure 5). However, the $SR_{\text{experimental}}$
464 for PACs are relatively lower than those of the PCBs and other SVOCs with similar $K_{\text{XAD/air}}$
465 values, presumably due to the degradative loss, whereas the SR_{actual} for PACs have a
466 relationship with $K_{\text{XAD/air}}$ that is very similar to that of the PCBs (Figure 5). A linear regression
467 with the $\log (K_{\text{XAD/air}} / (\text{L air g}^{-1} \text{ XAD}))$ at $12.2 \text{ }^\circ\text{C}$ yields the following relationship:

$$468 \quad SR_{\text{experimental}} (\text{m}^3 \text{ day}^{-1}) = -0.06(\pm 0.02) \log (K_{\text{XAD/air}} / \text{L g}^{-1}) + 0.55(\pm 0.08) \quad (2)$$

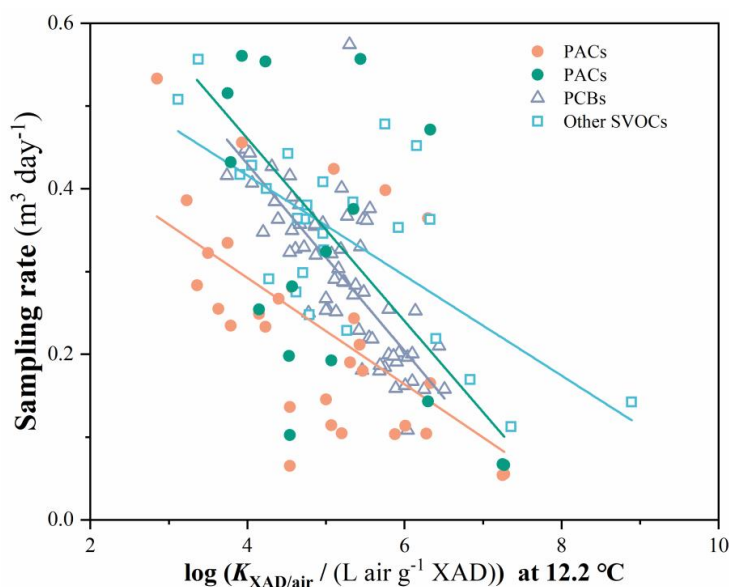
$$469 \quad n = 30, p < 0.0005, R^2 = 0.35$$



470 $SR_{\text{actual}} (m^3 \text{ day}^{-1}) = -0.11(\pm 0.03) \log (K_{\text{XAD/air}}/L \text{ g}^{-1}) + 0.90(\pm 0.17)$ (3)

471 $n = 18, p < 0.0005, R^2 = 0.40$

472 Going forward, we recommend deployment periods for the XAD-PAS to be kept shorter than
473 6 months, if PACs are among the targeted SVOCs. We suggest that for such shorter
474 deployments, the $SR_{\text{experimental}}$ reported in Table 2 can be used. For PACs not included in Table
475 2, their $SR_{\text{experimental}}$ and SR_{actual} can be estimated using a predicted $K_{\text{XAD/Air}}$ value and Eqs. (2)
476 and (3). A quantitative interpretation of PAC levels in XAD-PAS deployed for periods longer
477 than half a year may be compromised by the variable degradation loss of PACs from the XAD-
478 resin. This applies retroactively also to studies that have reported PAH levels in XAD-PAS
479 deployed for one year; they should be considered to be semi-quantitative only (Daly et al., 2007;
480 Lévy et al., 2018; Choi et al., 2009; Westgate et al., 2010; Abdul Hussain et al., 2019;
481 Schummer et al., 2014; Schrlau et al., 2011).



482

483 **Figure 5:** The increase of the sampling rates of 120 chemicals with an increase in volatility. The
484 markers in different colors indicate sampling rates of different chemical groups, and the lines
485 in different colors indicate linear regressions between the sampling rate and $\log K_{\text{XAD/air}}$ at
486 12.2 °C for different chemical groups. The dark green dots and line indicate the simulated
487 sampling rates for PACs without degradation and linear regression for these PACs.



Table 2 Passive Sampling Rates ($\text{m}^3 \text{d}^{-1}$) of PACs Determined in Our Study and Reported in Literature

Chemicals	Abbreviation	$\log K_{\text{XAD/air}}$ (L air g^{-1} XAD) at 7.9 °C	$\log K_{\text{XAD/air}}$ (L air g^{-1} XAD) at 12.2 °C	$SR_{\text{experimental}}$ in our study	R^2	SR in literature
Two rings						
Naphthalene	NAP	2.95	2.85	0.53 ± 0.04	0.97	1.23 (Armitage et al., 2013) 1.10 (Ellickson et al., 2017), 0.75 (Ellickson et al., 2017)
2-Methylnaphthalene	2-MeNAP	3.33	3.23	0.39 ± 0.02	0.99	
1-Methylnaphthalene	1-MeNAP	3.46	3.36	0.28 ± 0.03	0.93	
2,6-dimethylnaphthalene	2,6-DiMeNAP	3.73	3.63	0.25 ± 0.01	0.99	
1,3-dimethylnaphthalene	1,3-DiMeNAP	3.85	3.75	0.33 ± 0.02	0.97	
1,5-dimethylnaphthalene	1,5-DiMeNAP	4.03	3.93	0.46 ± 0.02	0.99	
2,3,5-trimethylnaphthalene	2,3,5-TriMeNAP	4.34	4.23	0.23 ± 0.01	0.98	
Three rings						
Acenaphthylene	ACY	3.60	3.50	0.32 ± 0.03	0.97	1.26 (Armitage et al., 2013), 0.60 (Ellickson et al., 2017), 0.48 (Ellickson et al., 2017)
Acenaphthene	ACE	3.89	3.79	0.23 ± 0.01	0.99	1.05 (Armitage et al., 2013), 0.65 (Ellickson et al., 2017), 0.60 (Ellickson et al., 2017)
Fluorene	FLU	4.26	4.15	0.25 ± 0.01	1.00	
1-Methylfluorene	1-MeFLU	4.68	4.57	0.28 ± 0.01	1.00	
Dibenzothiophene	DBT	4.64	4.54	0.06 ± 0.00	0.98	
Phenanthrene	PHE	4.64	4.54	0.14 ± 0.01	0.99	0.95 (Armitage et al., 2013), 0.55



Anthracene	ANT	4.50	4.40	0.27 ± 0.03	0.94	(Ellickson et al., 2017), 0.70 (Ellickson et al., 2017)
2-Methylphenanthrene	2-MePHE	5.18	5.07	0.11 ± 0.01	0.99	0.35 (Ellickson et al., 2017), 0.25 (Ellickson et al., 2017)
1-Methylphenanthrene	1-MePHE	5.11	5.00	0.15 ± 0.01	0.97	
9-Methylanthracene	9-MeANT	5.21	5.10	0.42 ± 0.03	0.98	
Retene	RET	6.12	6.01	0.11 ± 0.01	0.99	0.37 (Ellickson et al., 2017), 0.25 (Ellickson et al., 2017)
Four rings						
Fluoranthene	FLA	5.47	5.36	0.24 ± 0.01, 0.18 ± 0.01*	1.00, 0.99*	0.80 (Armitage et al., 2013), 0.44 (Ellickson et al., 2017), 0.50 (Ellickson et al., 2017)
Pyrene	PYE	5.31	5.20	0.10 ± 0.01, 0.19 ± 0.02*	0.98, 0.97*	0.74 (Armitage et al., 2013)
2-Methylfluoranthene	2-MeFLT	5.55	5.43	0.21 ± 0.01	0.98	
1-Methylpyrene	1-MePYE	5.87	5.76	0.40 ± 0.05	0.95	
Benz[<i>a</i>]anthracene	BaA	6.40	6.28	0.10 ± 0.02	0.90	0.50 (Ellickson et al., 2017), 0.10 (Ellickson et al., 2017)
Triphenylene	TP	6.45	6.33	0.17 ± 0.02	0.94	0.25 (Ellickson et al., 2017)
Chrysene	CHY	6.42	6.30	0.36 ± 0.01	0.99	0.89 (Armitage et al., 2013), 0.35 (Ellickson et al., 2017), 0.14



		(Ellickson et al., 2017)	
Five rings			
Benzo(ghi)fluoranthene	BghiF	6.00	5.88
Benzo[b]fluoranthene	BbF	7.39	7.27
Benzo[k]fluoranthene	BkF	7.37	7.25
		0.10 ± 0.01	0.97
		0.06 ± 0.00	0.99
		0.05 ± 0.01	0.93

* Data for the clearing site from the Borden experiment. The originally calculated sampling rates are for the long version XAD-PAS, i.e., the length of XAD-2 mesh cylinders is 20 cm; thus, in this table, they were converted to the sampling rates of short version XAD-PAS (10 cm length) by dividing by two (Zhang et al., 2012).



491 **Acknowledgement**

492 We are grateful to Rudy Boonstra for logistical help during field work in Toronto, and Bondi
493 Gevao for help sampling in Borden. Financial support from a Grant and Contribution
494 Agreement (GCXE20S008) with Environment and Climate Change Canada and a Connaught
495 scholarship to YL is gratefully acknowledged. The work at Borden was supported by a grant
496 from the Canadian Foundation for Climate and Atmospheric Sciences (CFCAS).

497 **Code/Data availability**

498 All data generated for this project are contained in the supplement.

499 **Author contribution**

500 YL and FZ performed measurements and analyzed samples from the Toronto experiment, YS
501 performed measurements and analyzed samples from the Borden experiment, both under the
502 supervision of YDL. CS analysed the atmospheric particle samples. YL performed the ozone
503 flow tube experiment with guidance by ZZ and JPDA. YL and FZ performed the model
504 simulations and YL interpreted the data and wrote the manuscript under guidance by FW. HH
505 coordinated the project. All authors reviewed the manuscript.

506 **Competing interests**

507 The authors declare no competing interests.

508 **References**

- 509 Abdul Hussain, B., Westgate, J. N., Hayward, S. J., Shunthirasingham, C., Brown, T. N., Hung, H., Lei,
510 Y. D., and Wania, F.: Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in soils and
511 atmosphere of Western Canadian mountains: The role of source proximity, precipitation, forest cover
512 and mountain cold-trapping, *Atmos. Environ.* **X**, 1, 100004, <https://doi.org/https://doi.org/10.1016/j.aeaoa.2018.100004>, 2019.
- 514 Ahad, J. M. E., Pakdel, H., Labarre, T., Cooke, C. A., Gammon, P. R., and Savard, M. M.: Isotopic
515 analyses fingerprint sources of polycyclic aromatic compound-bearing dust in athabasca oil sands
516 region snowpack, *Environ. Sci. Technol.*, **55**, 5887–5897, <https://doi.org/10.1021/acs.est.0c08339>,
517 2021.
- 518 Andersson, J. T. and Achten, C.: Time to say goodbye to the 16 EPA PAHs? Toward an up-to-date use
519 of PACs for environmental purposes, *Polycycl. Aromat. Compd.*, **35**, 330–354,
520 <https://doi.org/10.1080/10406638.2014.991042>, 2015.
- 521 Armitage, J. M., Hayward, S. J., and Wania, F.: Modeling the uptake of neutral organic chemicals on
522 XAD passive air samplers under variable temperatures, external wind speeds and ambient air
523 concentrations (PAS-SIM), *Environ. Sci. Technol.*, **47**, 13546–13554,
524 <https://doi.org/10.1021/es402978a>, 2013.
- 525 Atkinson, D. and Curthoys, G.: The determination of heats of adsorption by gas-solid chromatography,
526 *J. Chem. Educ.*, **55**, 564–566, <https://doi.org/10.1021/ed055p564>, 1978.
- 527 Atkinson, R. and Arey, J.: Mechanisms of the gas-phase reactions of aromatic hydrocarbons and pahas



- 528 with OH and NO₃ radicals, *Polycycl. Aromat. Compd.*, 27, 15–40,
529 <https://doi.org/10.1080/10406630601134243>, 2007.
- 530 ATSDR (Agency for Toxic Substances Disease Registry): Toxicological profile for polycyclic aromatic
531 hydrocarbons, US Government Printing Office, 1995.
- 532 Barthel, P., Thuens, S., Shunthirasingham, C., Westgate, J. N., Wania, F., and Radke, M.: Application
533 of XAD-resin based passive air samplers to assess local (roadside) and regional patterns of persistent
534 organic pollutants, *Environ. Pollut.*, 166, 218–225,
535 <https://doi.org/https://doi.org/10.1016/j.envpol.2012.03.026>, 2012.
- 536 Bartkow, M. E., Hawker, D. W., Kennedy, K. E., and Müller, J. F.: Characterizing Uptake Kinetics of
537 PAHs from the Air Using Polyethylene-Based Passive Air Samplers of Multiple Surface Area-to-
538 Volume Ratios, *Environ. Sci. Technol.*, 38, 2701–2706, <https://doi.org/10.1021/es0348849>, 2004.
- 539 Bedjanian, Y., Nguyen, M. L., and Le Bras, G.: Kinetics of the reactions of soot surface-bound
540 polycyclic aromatic hydrocarbons with the OH radicals, *Atmos. Environ.*, 44, 1754–1760,
541 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2010.02.007>, 2010.
- 542 Berthiaume, A., Galarneau, E., and Marson, G.: Polycyclic aromatic compounds (PACs) in the
543 Canadian environment: Sources and emissions, *Environ. Pollut.*, 269, 116008,
544 <https://doi.org/https://doi.org/10.1016/j.envpol.2020.116008>, 2021.
- 545 Boffetta, P., Jourenkova, N., and Gustavsson, P.: Cancer risk from occupational and environmental
546 exposure to polycyclic aromatic hydrocarbons, *Cancer Causes Control*, 8, 444–472, 1997.
- 547 Bohlin-Nizzetto, P., Melymuk, L., White, K. B., Kalina, J., Madadi, V. O., Adu-Kumi, S., Prokeš, R.,
548 Příbylová, P., and Klánová, J.: Field- and model-based calibration of polyurethane foam passive air
549 samplers in different climate regions highlights differences in sampler uptake performance, *Atmos.*
550 *Environ.*, 238, <https://doi.org/10.1016/j.atmosenv.2020.117742>, 2020.
- 551 Bohlin, P., Audy, O., Škrdlíková, L., Kukučka, P., Vojta, Š., Příbylová, P., Prokeš, R., Čupr, P., and
552 Klánová, J.: Evaluation and guidelines for using polyurethane foam (PUF) passive air samplers in
553 double-dome chambers to assess semi-volatile organic compounds (SVOCs) in non-industrial indoor
554 environments, *Environ. Sci. Process. Impacts*, 16, 2617–2626, 2014a.
- 555 Bohlin, P., Audy, O., Škrdlíková, L., Kukučka, P., Příbylová, P., Prokeš, R., Vojta, Š., and Klánová, J.:
556 Outdoor passive air monitoring of semi volatile organic compounds (SVOCs): a critical evaluation of
557 performance and limitations of polyurethane foam (PUF) disks, *Environ. Sci. Process. Impacts*, 16,
558 433–444, <https://doi.org/10.1039/C3EM00644A>, 2014b.
- 559 Borrowman, C. K., Zhou, S., Burrow, T. E., and Abbatt, J. P. D.: Formation of environmentally
560 persistent free radicals from the heterogeneous reaction of ozone and polycyclic aromatic compounds,
561 *Phys. Chem. Chem. Phys.*, 18, 205–212, <https://doi.org/10.1039/c5cp05606c>, 2016.
- 562 Brubaker, W. W. and Hites, R. A.: OH Reaction Kinetics of Polycyclic Aromatic Hydrocarbons and
563 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, *J. Phys. Chem. A*, 102, 915–921,
564 <https://doi.org/10.1021/jp9721199>, 1998.
- 565 Carl-Elis, B., Per, G., Annika, H., Bengt, J., Christer, J., Titus, K., Agneta, R., Margareta, T., Katarina,
566 V., and Roger, W.: Cancer risk assessment, indicators, and guidelines for polycyclic aromatic
567 hydrocarbons in the ambient air., *Environ. Health Perspect.*, 110, 451–488,
568 <https://doi.org/10.1289/ehp.110-1241197>, 2002.
- 569 Chaemfa, C., Wild, E., Davison, B., Barber, J. L., and Jones, K. C.: A study of aerosol entrapment and
570 the influence of wind speed, chamber design and foam density on polyurethane foam passive air
571 samplers used for persistent organic pollutants, *J. Environ. Monit.*, 11, 1135–1139, 2009.
- 572 Cheng, H., Deng, Z., Chakraborty, P., Liu, D., Zhang, R., Xu, Y., Luo, C., Zhang, G., and Li, J.: A
573 comparison study of atmospheric polycyclic aromatic hydrocarbons in three Indian cities using PUF
574 disk passive air samplers, *Atmos. Environ.*, 73, 16–21,
575 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2013.03.001>, 2013.



- 576 Cheng, I., Wen, D., Zhang, L., Wu, Z., Qiu, X., Yang, F., and Harner, T.: Deposition mapping of
577 polycyclic aromatic compounds in the oil sands region of Alberta, Canada and linkages to ecosystem
578 impacts, *Environ. Sci. Technol.*, 52, 12456–12464, 2018.
- 579 Choi, S.-D., Shunthirasingham, C., Daly, G. L., Xiao, H., Lei, Y. D., and Wania, F.: Levels of polycyclic
580 aromatic hydrocarbons in Canadian mountain air and soil are controlled by proximity to roads, *Environ.*
581 *Pollut.*, 157, 3199–3206, <https://doi.org/https://doi.org/10.1016/j.envpol.2009.05.032>, 2009.
- 582 Daly, G. L., Lei, Y. D., Castillo, L. E., Muir, D. C. G., and Wania, F.: Polycyclic aromatic hydrocarbons
583 in Costa Rican air and soil: A tropical/temperate comparison, *Atmos. Environ.*, 41, 7339–7350,
584 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2007.05.014>, 2007.
- 585 Domínguez-Morueco, N., Augusto, S., Trabalón, L., Pocurull, E., Borrull, F., Schuhmacher, M.,
586 Domingo, J. L., and Nadal, M.: Monitoring PAHs in the petrochemical area of Tarragona County, Spain:
587 comparing passive air samplers with lichen transplants, *Environ. Sci. Pollut. Res.*, 24, 11890–11900,
588 <https://doi.org/10.1007/s11356-015-5612-2>, 2017.
- 589 Ellickson, K. M., McMahon, C. M., Herbrandson, C., Krause, M. J., Schmitt, C. M., Lippert, C. J., and
590 Pratt, G. C.: Analysis of polycyclic aromatic hydrocarbons (PAHs) in air using passive sampling
591 calibrated with active measurements, *Environ. Pollut.*, 231, 487–496,
592 <https://doi.org/10.1016/j.envpol.2017.08.049>, 2017.
- 593 Environment Canada and Health Canada: Canadian Environmental Protection Act Polycyclic
594 AromaticHydrocarbons-Priority Substances List Ssessment Repor, Ottawa, Ontario, 1–68 pp., 1994.
- 595 Esteve, W., Budzinski, H., and Villenave, E.: Relative rate constants for the heterogeneous reactions of
596 OH, NO₂ and NO radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles.
597 Part 1: PAHs adsorbed on 1–2µm calibrated graphite particles, *Atmos. Environ.*, 38, 6063–6072,
598 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2004.05.059>, 2004.
- 599 Esteve, W., Budzinski, H., and Villenave, E.: Relative rate constants for the heterogeneous reactions of
600 NO₂ and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part
601 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a, *Atmos. Environ.*, 40, 201–211,
602 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2005.07.053>, 2006.
- 603 Ghosal, D., Ghosh, S., Dutta, T. K., and Ahn, Y.: Current state of knowledge in microbial degradation
604 of polycyclic aromatic hydrocarbons (PAHs): A review., *Front. Microbiol.*, 7, 1369,
605 <https://doi.org/10.3389/fmicb.2016.01369>, 2016.
- 606 Golzadeh, N., Barst, B. D., Baker, J. M., Auger, J. C., and McKinney, M. A.: Alkylated polycyclic
607 aromatic hydrocarbons are the largest contributor to polycyclic aromatic compound concentrations in
608 traditional foods of the Bigstone Cree Nation in Alberta, Canada, *Environ. Pollut.*, 275, 116625,
609 <https://doi.org/https://doi.org/10.1016/j.envpol.2021.116625>, 2021.
- 610 Goss, K. U.: Adsorption of VOCs from the gas phase to different minerals and a mineral mixture,
611 *Environ. Sci. Technol.*, 30, 2135–2142, <https://doi.org/10.1021/es950508f>, 1996.
- 612 Grosjean, D., Fung, K., and Harrison, J.: Interactions of polycyclic aromatic hydrocarbons with
613 atmospheric pollutants, *Environ. Sci. Technol.*, 17, 673–679, <https://doi.org/10.1021/es00117a010>,
614 1983.
- 615 Grung, M., Næs, K., Fogelberg, O., Nilsen, A. J., Brack, W., Lübcke-von Varel, U., and Thomas, K. V.:
616 Effects-directed analysis of sediments from polluted marine sites in Norway, *J. Toxicol. Environ. Heal.*
617 *Part A*, 74, 439–454, <https://doi.org/10.1080/15287394.2011.550555>, 2011.
- 618 Harner, T., Su, K., Genualdi, S., Karpowicz, J., Ahrens, L., Mihele, C., Schuster, J., Charland, J.-P. P.,
619 and Narayan, J.: Calibration and application of PUF disk passive air samplers for tracking polycyclic
620 aromatic compounds (PACs), *Atmos. Environ.*, 75, 123–128,
621 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2013.04.012>, 2013.
- 622 Harner, T., Rauert, C., Muir, D., Schuster, J. K., Hsu, Y.-M., Zhang, L., Marson, G., Watson, J. G.,
623 Ahad, J., and Cho, S.: Air synthesis review: polycyclic aromatic compounds in the oil sands region,



- 624 Environ. Rev., 26, 430–468, 2018.
- 625 Hawthorne, S. B., Miller, D. J., and Kreitinger, J. P.: Measurement of total polycyclic aromatic
626 hydrocarbon concentrations in sediments and toxic units used for estimating risk to benthic
627 invertebrates at manufactured gas plant sites, Environ. Toxicol. Chem., 25, 287–296,
628 <https://doi.org/https://doi.org/10.1897/05-111R.1>, 2006.
- 629 Hayward, S. J., Lei, Y. D., and Wania, F.: Sorption of a diverse set of organic chemical vapors onto
630 XAD-2 resin: Measurement, prediction and implications for air sampling, Atmos. Environ., 45, 296–
631 302, <https://doi.org/10.1016/j.atmosenv.2010.10.028>, 2011.
- 632 Holme, J. A., Valen, H., Brinchmann, B. C., Vist, G. E., Grimsrud, T. K., Becher, R., Holme, A. M.,
633 Øvrevik, J., and Alexander, J.: Polycyclic aromatic hydrocarbons (PAHs) may explain the paradoxical
634 effects of cigarette use on preeclampsia (PE), Toxicology, 473, 153206,
635 <https://doi.org/https://doi.org/10.1016/j.tox.2022.153206>, 2022.
- 636 Holt, E., Bohlin-Nizzetto, P., Borůvková, J., Harner, T., Kalina, J., Melymuk, L., and Klánová, J.: Using
637 long-term air monitoring of semi-volatile organic compounds to evaluate the uncertainty in
638 polyurethane-disk passive sampler-derived air concentrations, Environ. Pollut., 220, 1100–1111,
639 <https://doi.org/10.1016/j.envpol.2016.11.030>, 2017.
- 640 Jariyasopit, N., Liu, Y., Liggio, J., and Harner, T.: Stability of polycyclic aromatic compounds in
641 polyurethane foam-type passive air samplers upon O₃ exposure, Atmos. Environ., 120, 200–204,
642 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2015.08.088>, 2015.
- 643 Jariyasopit, N., Zhang, Y., Martin, J. W., and Harner, T.: Comparison of polycyclic aromatic
644 compounds in air measured by conventional passive air samplers and passive dry deposition samplers
645 and contributions from petcoke and oil sands ore, Atmos. Chem. Phys., 18, 9161–9171,
646 <https://doi.org/10.5194/acp-18-9161-2018>, 2018.
- 647 Jariyasopit, N., Tung, P., Su, K., Halappanavar, S., Evans, G. J., Su, Y., Khoomrung, S., and Harner,
648 T.: Polycyclic aromatic compounds in urban air and associated inhalation cancer risks: A case study
649 targeting distinct source sectors, Environ. Pollut., 252, 1882–1891,
650 <https://doi.org/https://doi.org/10.1016/j.envpol.2019.06.015>, 2019.
- 651 Jariyasopit, N., Harner, T., Shin, C., and Park, R.: The effects of plume episodes on PAC profiles in the
652 athabasca oil sands region, Environ. Pollut., 282, 117014,
653 <https://doi.org/https://doi.org/10.1016/j.envpol.2021.117014>, 2021.
- 654 Kaisarevic, S., Varel, U. L., Orcic, D., Streck, G., Schulze, T., Pogrnic, K., Teodorovic, I., Brack, W.,
655 and Kovacevic, R.: Effect-directed analysis of contaminated sediment from the wastewater canal in
656 Pancevo industrial area, Serbia, Chemosphere, 77, 907–913,
657 <https://doi.org/https://doi.org/10.1016/j.chemosphere.2009.08.042>, 2009.
- 658 Kasumba, J. and Holmén, B. A.: Heterogeneous ozonation reactions of PAHs and fatty acid methyl
659 esters in biodiesel particulate matter, Atmos. Environ., 175, 15–24,
660 <https://doi.org/10.1016/j.atmosenv.2017.11.051>, 2018.
- 661 Kim, K. H., Jahan, S. A., Kabir, E., and Brown, R. J. C.: A review of airborne polycyclic aromatic
662 hydrocarbons (PAHs) and their human health effects, Environ. Int., 60, 71–80,
663 <https://doi.org/10.1016/j.envint.2013.07.019>, 2013.
- 664 Lévy, M., Al-Alam, J., Ridacker, C., Massemin, S., and Millet, M.: Use of XAD®-2 passive air
665 samplers for monitoring environmental trends of PAHs, PCBs and pesticides in three different sites in
666 Strasbourg and its vicinity (east of France), Atmos. Environ., 195, 12–23,
667 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2018.09.052>, 2018.
- 668 Lewis, R. G. and Coutant, R. W.: Determination of phase-distributed polycyclic aromatic hydrocarbons
669 in air by grease-coated denuders, in: Gas and Particle Phase Measurements of Atmospheric Organic
670 Compounds, CRC Press, 201–231, 2020.
- 671 Li, Y. and Wania, F.: Partitioning between polyurethane foam and the gas phase: Data compilation,



- 672 uncertainty estimation and implications for air sampling, *Environ. Sci. Process. Impacts*, 23, 723–734,
673 <https://doi.org/10.1039/d1em00036e>, 2021.
- 674 Li, Y., Armitage, J. M., and Wania, F.: Graphical tools for the planning and interpretation of
675 polyurethane foam based passive air sampling campaigns, *Environ. Sci. Process. Impacts*, 24, 414–425,
676 2022.
- 677 Li, Y., Zhan, F., Lei, Y. D., Shunthirasingham, C., Hung, H., and Wania, F.: Field calibration and PAS-
678 SIM model evaluation of the XAD-based passive air samplers for semi-volatile organic compounds,
679 *Environ. Sci. Technol.*, 57, 9224–9233, <https://doi.org/10.1021/acs.est.3c00809>, 2023a.
- 680 Li, Y., Zhan, F., Shunthirasingham, C., Lei, Y. D., Hung, H., and Wania, F.: Unbiased passive sampling
681 of all polychlorinated biphenyls congeners from air, *Environ. Sci. Technol. Lett.*, 10, 565–572,
682 <https://doi.org/10.1021/acs.estlett.3c00271>, 2023b.
- 683 Lima, A. L. C., Farrington, J. W., and Reddy, C. M.: Combustion-derived polycyclic aromatic
684 hydrocarbons in the environment—a review, *Environ. forensics*, 6, 109–131,
685 <https://doi.org/10.1080/15275920590952739>, 2005.
- 686 Liu, Y. N., Tao, S., Dou, H., Zhang, T. W., Zhang, X. L., and Dawson, R.: Exposure of traffic police to
687 Polycyclic aromatic hydrocarbons in Beijing, China, *Chemosphere*, 66, 1922–1928,
688 <https://doi.org/https://doi.org/10.1016/j.chemosphere.2006.07.076>, 2007.
- 689 Mahoney, C., Montgomery, J., Connor, S., and Cobbaert, D.: Oil sands wetland ecosystem monitoring
690 program indicators in Alberta, Canada: Transitioning from pilot to long-term monitoring, *Water*, 15,
691 1914, 2023.
- 692 Masclet, P., Hoyau, V., Jaffrezo, J. L., and Cachier, H.: Polycyclic aromatic hydrocarbon deposition on
693 the ice sheet of Greenland. Part I: superficial snow, *Atmos. Environ.*, 34, 3195–3207,
694 [https://doi.org/https://doi.org/10.1016/S1352-2310\(99\)00196-X](https://doi.org/https://doi.org/10.1016/S1352-2310(99)00196-X), 2000.
- 695 Meierdierks, J., Zarfl, C., Beckingham, B., and Grathwohl, P.: Unique calibration of passive air
696 sampling for field monitoring of PAHs with polyethylene thin films across seasons and locations,
697 *Environ. Sci. Atmos.*, 1, 253–266, 2021.
- 698 Melymuk, L., Robson, M., Helm, P. A., and Diamond, M. L.: Evaluation of passive air sampler
699 calibrations: Selection of sampling rates and implications for the measurement of persistent organic
700 pollutants in air, *Atmos. Environ.*, 45, 1867–1875, <https://doi.org/10.1016/j.atmosenv.2011.01.011>,
701 2011.
- 702 Melymuk, L., Bohlin-Nizzetto, P., Prokeš, R., Kukučka, P., Příbylová, P., Vojta, Š., Kohoutek, J.,
703 Lammel, G., and Klánová, J.: Uncertainties in monitoring of SVOCs in air caused by within-sampler
704 degradation during active and passive air sampling, *Atmos. Environ.*, 167, 553–565,
705 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2017.08.038>, 2017.
- 706 Moradi, M., Hung, H., Li, J., Park, R., Shin, C., Alexandrou, N., Iqbal, M. A., Takhar, M., Chan, A.,
707 and Brook, J. R.: Assessment of alkylated and unsubstituted polycyclic aromatic hydrocarbons in air in
708 urban and semi-urban areas in Toronto, Canada, *Environ. Sci. Technol.*, 56, 2959–2967,
709 <https://doi.org/10.1021/acs.est.1c04299>, 2022.
- 710 Moradi, M., Eng, A., Staebler, R., and Harner, T.: Atmospheric emissions estimation of polycyclic
711 aromatic compounds from an oil sands tailings pond using passive air samplers, Available SSRN
712 4535613, n.d.
- 713 Muir, D. C. G. and Galarneau, E.: Polycyclic aromatic compounds (PACs) in the Canadian environment:
714 Links to global change, *Environ. Pollut.*, 273, 116425, <https://doi.org/10.1016/j.envpol.2021.116425>,
715 2021.
- 716 Nikolaou, K., Masclet, P., and Mouvier, G.: Sources and chemical reactivity of polynuclear aromatic
717 hydrocarbons in the atmosphere — A critical review, *Sci. Total Environ.*, 32, 103–132,
718 [https://doi.org/https://doi.org/10.1016/0048-9697\(84\)90125-6](https://doi.org/https://doi.org/10.1016/0048-9697(84)90125-6), 1984.
- 719 Nolan, R. H., Anderson, L. O., Poulter, B., and Varner, J. M.: Increasing threat of wildfires: the year



- 720 2020 in perspective: A Global Ecology and Biogeography special issue, *Glob. Ecol. Biogeogr.*, 31,
721 1898–1905, <https://doi.org/https://doi.org/10.1111/geb.13588>, 2022.
- 722 Organization, W. H.: Polycyclic aromatic hydrocarbons, selected non-heterocyclic, *Environ. Heal.*
723 *Criteria*, 202, 1998.
- 724 Pechillips, D. H., Grover, P. L., and Sims, P.: A quantitative determination of the covalent binding of a
725 series of polycyclic hydrocarbons to dna in mouse skin, *Int. J. Cancer*, 23, 201–208,
726 <https://doi.org/https://doi.org/10.1002/ijc.2910230211>, 1979.
- 727 Pitts, J. N., Lokensgard, D. M., Ripley, P. S., Van Cauwenberghe, K. A., Van Vaeck, L., Shaffer, S. D.,
728 Thill, A. J., and Belsler, W. L.: “Atmospheric” Epoxidation of benzo[a]pyrene by ozone: Formation
729 of the metabolite benzo[a]pyrene-4,5-oxide, *Science* (80-.), 210, 1347–1349,
730 <https://doi.org/10.1126/science.210.4476.1347>, 1980.
- 731 Pozo, K., Estellano, V. H., Harner, T., Diaz-Robles, L., Cereceda-Balic, F., Etcharren, P., Pozo, K.,
732 Vidal, V., Guerrero, F., and Vergara-Fernández, A.: Assessing polycyclic aromatic hydrocarbons
733 (PAHs) using passive air sampling in the atmosphere of one of the most wood-smoke-polluted cities in
734 Chile: The case study of Temuco, *Chemosphere*, 134, 475–481,
735 <https://doi.org/https://doi.org/10.1016/j.chemosphere.2015.04.077>, 2015.
- 736 Programme United Nations Environment: Polycyclic aromatic hydrocarbons (PAHs) - Assessment
737 report on issues of concern, 1–2 pp., 2020.
- 738 Rauert, C., Harner, T., Ahad, J. M. E., and Percy, K. E.: Using tree cores to evaluate historic atmospheric
739 concentrations and trends of polycyclic aromatic compounds in the Oil Sands region of Alberta, Canada,
740 *Sci. Total Environ.*, 739, 139996, 2020.
- 741 Ravindra, K., Wauters, E., and Van Grieken, R.: Variation in particulate PAHs levels and their relation
742 with the transboundary movement of the air masses, *Sci. Total Environ.*, 396, 100–110,
743 <https://doi.org/https://doi.org/10.1016/j.scitotenv.2008.02.018>, 2008.
- 744 Rice, H. R. and Baker, B. A.: Workplace hazards to women’s reproductive health., *Minn. Med.*, 90, 44–
745 47, 2007.
- 746 Sarma, S. N., Blais, J. M., and Chan, H. M.: Neurotoxicity of alkylated polycyclic aromatic compounds
747 in human neuroblastoma cells, *J. Toxicol. Environ. Heal. Part A*, 80, 285–300,
748 <https://doi.org/10.1080/15287394.2017.1314840>, 2017.
- 749 Schrlau, J. E., Geiser, L., Hageman, K. J., Landers, D. H., and Simonich, S. M.: Comparison of lichen,
750 conifer needles, passive air sampling devices, and snowpack as passive sampling media to measure
751 semi-volatile organic compounds in remote atmospheres, *Environ. Sci. Technol.*, 45, 10354–10361,
752 <https://doi.org/10.1021/es202418f>, 2011.
- 753 Schummer, C., Appenzeller, B. M., and Millet, M.: Monitoring of polycyclic aromatic hydrocarbons
754 (PAHs) in the atmosphere of southern Luxembourg using XAD-2 resin-based passive samplers,
755 *Environ. Sci. Pollut. Res.*, 21, 2098–2107, <https://doi.org/10.1007/s11356-013-2106-y>, 2014.
- 756 Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., Li, W., Shen, H., Huang, Y., Yang, Y.,
757 Wang, W., Wang, X., and Simonich, S. L. M.: Retene emission from residential solid fuels in china and
758 evaluation of retene as a unique marker for soft wood combustion, *Environ. Sci. Technol.*, 46, 4666–
759 4672, <https://doi.org/10.1021/es300144m>, 2012.
- 760 Su, Y., Lei, Y. D., Wania, F., Shoeib, M., and Harner, T.: Regressing gas/particle partitioning data for
761 polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, 40, 3558–3564, 2006.
- 762 Su, Y., Wania, F., Harner, T., and Lei, Y. D.: Deposition of polybrominated diphenyl ethers,
763 polychlorinated biphenyls, and polycyclic aromatic hydrocarbons to a boreal deciduous forest, *Environ.*
764 *Sci. Technol.*, 41, 534–540, <https://doi.org/10.1021/es0622047>, 2007a.
- 765 Su, Y., Wania, F., Ying, D. L., Harner, T., and Shoeib, M.: Temperature dependence of the air
766 concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in a forest and a
767 clearing, *Environ. Sci. Technol.*, 41, 4655–4661, <https://doi.org/10.1021/es070334p>, 2007b.



- 768 Terzi, E. and Samara, C.: Gas-particle partitioning of polycyclic aromatic hydrocarbons in urban,
769 adjacent coastal, and continental background sites of western Greece, *Environ. Sci. Technol.*, 38, 4973–
770 4978, <https://doi.org/10.1021/es040042d>, 2004.
- 771 Tokiwa, H., Nakagawa, R., Morita, K., and Ohnishi, Y.: Mutagenicity of nitro derivatives induced by
772 exposure of aromatic compounds to nitrogen dioxide, *Mutat. Res. Mutagen. Relat. Subj.*, 85, 195–205,
773 [https://doi.org/https://doi.org/10.1016/0165-1161\(81\)90036-4](https://doi.org/https://doi.org/10.1016/0165-1161(81)90036-4), 1981.
- 774 Tromp, P. C., Beeltje, H., Okeme, J. O., Vermeulen, R., Pronk, A., and Diamond, M. L.: Calibration of
775 polydimethylsiloxane and polyurethane foam passive air samplers for measuring semi volatile organic
776 compounds using a novel exposure chamber design, *Chemosphere*, 227, 435–443,
777 <https://doi.org/10.1016/j.chemosphere.2019.04.043>, 2019.
- 778 UFZ-LSER database v 3.2.1 [Internet]: <http://www.ufz.de/lserd>, last access: 13 July 2022.
- 779 Van Vaeck, L. and Van Cauwenberghe, K.: Conversion of polycyclic aromatic hydrocarbons on diesel
780 particulate matter upon exposure to ppm levels of ozone, *Atmos. Environ.*, 18, 323–328,
781 [https://doi.org/https://doi.org/10.1016/0004-6981\(84\)90106-9](https://doi.org/https://doi.org/10.1016/0004-6981(84)90106-9), 1984.
- 782 Wakeham, S. G., Schaffner, C., and Giger, W.: Poly cyclic aromatic hydrocarbons in recent lake
783 sediments—II. Compounds derived from biogenic precursors during early diagenesis, *Geochim.*
784 *Cosmochim. Acta*, 44, 415–429, [https://doi.org/https://doi.org/10.1016/0016-7037\(80\)90041-1](https://doi.org/https://doi.org/10.1016/0016-7037(80)90041-1), 1980.
- 785 Wania, F. and Shunthirasingham, C.: Passive air sampling for semi-volatile organic chemicals, *Environ.*
786 *Sci. Process. Impacts*, 22, 1925–2002, <https://doi.org/10.1039/d0em00194e>, 2020.
- 787 Wania, F., Shen, L., Lei, Y. D., Teixeira, C., and Muir, D. C. G.: Development and calibration of a
788 resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere,
789 *Environ. Sci. Technol.*, 37, 1352–1359, 2003.
- 790 Westgate, J. N., Shunthirasingham, C., Oyiliagu, C. E., von Waldow, H., and Wania, F.: Three methods
791 for quantifying proximity of air sampling sites to spatially resolved emissions of semi-volatile organic
792 contaminants, *Atmos. Environ.*, 44, 4380–4387,
793 <https://doi.org/https://doi.org/10.1016/j.atmosenv.2010.07.051>, 2010.
- 794 White, P. A.: The genotoxicity of priority polycyclic aromatic hydrocarbons in complex mixtures,
795 *Mutat. Res. Toxicol. Environ. Mutagen.*, 515, 85–98, 2002.
- 796 Wnorowski, A., Aklilu, Y., Harner, T., Schuster, J., and Charland, J.-P.: Polycyclic aromatic
797 compounds in ambient air in the surface minable area of Athabasca oil sands in Alberta (Canada),
798 *Atmos. Environ.*, 244, 117897, <https://doi.org/https://doi.org/10.1016/j.atmosenv.2020.117897>, 2021.
- 799 Wnorowski, A., Harnish, D., Jiang, Y., Celo, V., Dabek-Zlotorzynska, E., and Charland, J. P.:
800 Assessment and characterization of alkylated pahs in selected sites across Canada, *Atmosphere (Basel)*,
801 13, <https://doi.org/10.3390/atmos13081320>, 2022.
- 802 Xu, S., Liu, W., and Tao, S.: Emission of polycyclic aromatic hydrocarbons in China, *Environ. Sci.*
803 *Technol.*, 40, 702–708, 2006.
- 804 Zhang, X. and Wania, F.: Modeling the uptake of semivolatile organic compounds by passive air
805 samplers: importance of mass transfer processes within the porous sampling media, *Environ. Sci.*
806 *Technol.*, 9563–9570, 2012.
- 807 Zhang, X., Tsurukawa, M., Nakano, T., Lei, Y. D., and Wania, F.: Sampling medium side resistance to
808 uptake of semivolatile organic compounds in passive air samplers, *Environ. Sci. Technol.*, 45, 10509–
809 10515, <https://doi.org/10.1021/es2032373>, 2011.
- 810 Zhang, X., Wong, C., Lei, Y. D., and Wania, F.: Influence of sampler configuration on the uptake
811 kinetics of a passive air sampler, *Environ. Sci. Technol.*, 45, 397–403, 2012.
- 812 Zhou, S., Hwang, B. C. H., Lakey, P. S. J., Zuend, A., Abbatt, J. P. D., and Shiraiwa, M.: Multiphase
813 reactivity of polycyclic aromatic hydrocarbons is driven by phase separation and diffusion limitations,
814 *Proc. Natl. Acad. Sci. U. S. A.*, 116, 11658–11663, <https://doi.org/10.1073/pnas.1902517116>, 2019.

<https://doi.org/10.5194/egusphere-2023-2202>

Preprint. Discussion started: 19 October 2023

© Author(s) 2023. CC BY 4.0 License.



815 Zhou, Z. and Abbatt, J. P. D.: Formation of gas-phase hydrogen peroxide via multiphase ozonolysis of
816 unsaturated lipids, *Environ. Sci. Technol. Lett.*, 8, 114–120, <https://doi.org/10.1021/acs.estlett.0c00757>,
817 2021.
818