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Field-testing polyethylene passive samplers for the detection of neutral polyfluorinated alkyl substances in air and water

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1 **Running head: Testing passive polyethylene samplers for neutral PFASs**

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3 **Field-Testing Polyethylene Passive Samplers for the Detection of Neutral Polyfluorinated**
4 **Alkyl Substances (PFASs) in Air and Water**

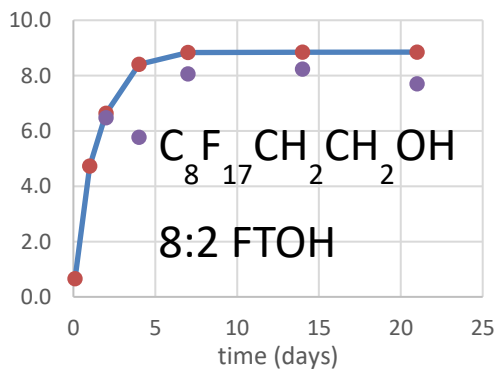
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10
11 Keywords: PFASs, FTOHs, passive sampler, dissolved concentration, gas-phase

12
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14 **Graphical abstract**



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ABSTRACT

19
20 Fluorotelomer alcohols (FTOHs), perfluorooctane-sulfonamidoethanols (FOSEs),
21 perfluorooctane-sulfonamides (FOSAs) and other poly- and perfluorinated alkyl substances
22 (PFASs) are common and ubiquitous by-products of industrial telomerization processes. They
23 can degrade into various perfluorinated carboxylic acids, which are persistent organic
24 contaminants of concern. This study assessed the use of polyethylene (PE) passive samplers as a
25 sampling tool for neutral PFAS precursors during field-deployments in air and water. A wide
26 range of neutral PFASs was detected in PE sheets exposed in waste water treatment effluents in
27 August 2017. Equilibration times for most neutral PFASs was on the order of 1-2 weeks. Based
28 on known sampling rates, the partitioning constants between PE and water, K_{PEw} , were derived.
29 Log K_{PEw} values were mostly in the range of 3 – 4.5, with greatest values for 8:2 FTOH, 10:2
30 FTOH and *n*-ethyl-FOSE. To test the utility of PE for gas-phase compounds, parallel active and
31 passive sampling was performed in ambient air in Providence (RI, USA) in April 2016. Most
32 PFASs equilibrated within 2-7 days. Greatest concentrations in PE samplers were detected for
33 MeFOSE and EtFOSE. Polyethylene-air partitioning constants, log K_{PEa} , were ~ 7-8 for the
34 FTOHs, and approached 9 for *n*-methyl-FOSA and *n*-methyl-FOSE. PE sheets showed promise
35 as a passive sampling approach for neutral PFASs in air and water.

36

INTRODUCTION

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Fluorinated compounds have become distributed across the globe over the past half-century, as increasing industrial production of synthetic organic compounds containing fluorine has led to their introduction into the environment (Key et al. 1997). In general, per- and polyfluorinated alkyl substances (PFASs) repel oil and water, and are considered surfactants. These surfactant properties have been applied to a wide number of commercial and industrial applications including paper, textiles, paints, non-stick cookware, polishes, electronics, and water-repellant clothing (Kissa 1994).

Two key PFASs, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been targeted as persistent organic pollutants (POPs) due to their physicochemical properties, their global distribution, and demonstrated adverse effects in wildlife and humans. Elevated PFOS concentrations have been found present in wildlife tissue at polar sites in both the Arctic and in the Antarctic (Giesy and Kannan 2001; Houde et al. 2006; Houde et al. 2011). PFOS is ionic at ambient pH and has thus a low vapor pressure and high water solubility compared to other POPs (Giesy and Kannan 2002; Krusic et al. 2005), and would not be expected to be transported long distances via the atmosphere. PFASs have been detected in surface waters of the Arctic Ocean in the range of 100 pg/L, indicating long-range transport is occurring (Yamashita et al. 2008; Yeung et al. 2017). Yet ocean transport is not sufficient to explain observed concentrations in the Arctic Ocean, particularly in the surface ocean (Yeung et al. 2017). A secondary atmospheric source of PFOS and PFOA from the degradation of precursor compounds, such as fluorotelomer alcohols (FTOHs), perfluorinated sulfonamidoethanols (FOSEs) and sulfonamides (FOSAs), has been suggested to account for the presence of ionic PFASs in remote regions (Hurley et al. 2004; Wallington et al. 2006).

60 Hydroxyl radical attack on these precursors is very slow and atmospheric lifetimes range from
61 10-20 days for FTOHs of varying carbon length and from 20-50 days for selected FOSAs (Stock
62 et al. 2004; Piekarz et al. 2007). The estimated atmospheric residence time for 8:2 FTOH is
63 greater than 50 days (Wania 2007). A 10-50 day lifetime is sufficient to allow for hemispheric
64 transport to the Arctic from primary source regions (Ellis et al. 2004; Wallington et al. 2006).

65 The majority of studies that observe FTOHs and PFASs in the environment utilize active
66 sampling methods (Jahnke, Huber, et al. 2007; Ahrens, Shoeib, Harner, Lane, et al. 2011; Liu et
67 al. 2013). These methods typically require a large amount of sample media to be collected (e.g.
68 air, water, etc.) to quantify the low (pg range) environmental concentrations that are found. For
69 these experimental set-ups, a large volume of media is pulled through a filter and adsorbent on
70 which the POPs collect over time. Active sampling is expensive and time consuming, prohibiting
71 the widespread monitoring of these compounds.

72 In recent years, a variety of passive sampling techniques have been developed to measure many
73 POPs in the environment (Harner et al. 2006; Jahnke, Ahrens, et al. 2007; Lohmann et al. 2012).
74 Several studies have relied on passive sampling for the detection of neutral, volatile PFASs. In
75 particular polyurethane foam (PUF) discs, often sorbent-impregnated, have been used repeatedly
76 (Genualdi et al. 2010; Kim et al. 2012; Ahrens et al. 2013; Wang et al. 2018), but also, activated
77 carbon felts (S Oono et al. 2008; Liu et al. 2013), and semi-permeable membrane devices
78 (SPMDs) (Fiedler et al. 2010). In contrast, the use of single phase polymers, such as silicone-
79 rubber based samplers or polyethylene sheets (PE) has not been explored for neutral, volatile
80 PFASs.

81

82 PE sampling devices accumulate organic contaminants through diffusion. Due to its
83 reliance on diffusion, PE samplers inherently select only for gaseous compounds in the air and
84 dissolved compounds in the water (Adams et al. 2007). In comparison to many active and
85 passive methods, PE sheets are best at accumulating hydrophobic organic contaminants, cost
86 little, and are easy to handle and use (Lohmann et al. 2012). In addition, the ability to measure
87 both aqueous and atmospheric concentrations at sampling sites provides insight into the transport
88 processes that control a compound's movement through the environment and the quantification
89 of air-water fluxes (Morgan and Lohmann 2008; Khairy et al. 2014; McDonough et al. 2014).
90 The passive uptake of a water or air contaminant by a passive samplers is a well characterized
91 process (Vrana et al. 2001; Bartkow et al. 2005):

$$N_s = C_t K_{PEw} m_s \left[1 - \exp\left(-\frac{R_s t}{K_{PEw} m_s}\right) \right] \quad (1)$$

92 where

93 N_s is the amount of pollutant absorbed (pg);

94 R_s is sampling rate (L/day);

95 t is exposure time (day);

96 m_s is the passive sampler mass (kg);

97 K_{PEw} is the PE-water partitioning constant (L/kg); and

98 C_t is the ambient concentration (pg/L).

99 Initially, the uptake is linear, simply a function of the sampling rate (R_s) and ambient
100 concentration, C_t . As the exposure time increases, the target compounds in the sampler approach
101 equilibrium, and the amount absorbed can be expressed by the PE-water (K_{PEw}) or PE-air
102 partitioning coefficient (K_{PEa}):

$$N_s = C_w K_{PEw} m_s \text{ or } = C_a K_{PEa} m_s \quad (2)$$

103 where

104 C_w and C_a are the ambient dissolved or gas-phase concentrations (pg/L).

105

106 The uptake stage is dependent on the magnitude of K_{PEw} or K_{PEa} , and environmental mass
107 transfer coefficients.

108 The overarching goal for this research was the field-testing of PE as a simple sampling technique
109 for the monitoring of neutral PFASs. In particular, our goals were to (i) determine whether PE
110 passive samplers enrich PFASs in air and water sufficiently for detection; (ii) estimate PE-water
111 and PE-air partitioning coefficients, and compare them to predicted values; and (iii) discuss if
112 and how PE samplers can be used for the quantification of volatile, neutral PFASs.

113

114

MATERIALS AND METHODS

115 *Target compounds*

116 This study targeted 9 individual neutral PFASs, specifically fluorotelomer alcohols
117 (FTOHs), fluorotelomer acrylates (FTAcrs), perfluorinated sulfonamidoethanols (FOSEs) and
118 sulfonamides (FOSAs), ranging in molecular weight from 364 - 619 g/mol (Table 1). Native and
119 mass-labeled surrogate standards ($^{13}\text{C}_{12-6:2}$ FTOH, $^{13}\text{C}_{12-8:2}$ FTOH, $^{13}\text{C}_{12-10:2}$ FTOH,
120 MeFOSA-d₃, and MeFOSE-d₇) were purchased from Wellington Laboratories (Guelph, Ontario,
121 Canada).

122 A master solution containing the PFAS surrogates was mixed at 1000 ng/ml in 8:2:1
123 hexane:DCM:methanol, of which 25 μl (at 50 ng/mL) were added prior to extraction.

124 *Instrumental analysis*

125 All samples were analyzed using gas chromatography/mass spectrometry (GC/MS) on an
126 Agilent 7890B chromatograph coupled with an Agilent 5977A MSD operating in positive
127 chemical ionization (PCI) mode using selected-ion-monitoring (SIM). The ion source was held at
128 300 °C while the transfer line was held at 250 °C. Aliquots of 2 µL were injected via an
129 autosampler. A splitless intake (270 °C) led into a polar Supelcowax 10 column (60 m, internal
130 diameter 10 µm). Gas flow of the helium carrier gas was held at 1.5 mL/min. The oven-
131 temperature program was derived based on a published method (Xie et al. 2013), and optimized
132 for shorter run times. The program was as follows: 50 °C for 2 min, 3 °C/min to 70 °C, 10 °C to
133 130 °C, 20 °C/min to 220 °C, 120 °C/in to 275 °C hold for 5 minutes, -10 °C/min to 270 °C hold
134 for 10 minutes.

135 *Polyethylene passive samplers*

136 The passive samplers used in this research consisted of low-density polyethylene (PE), 25
137 µm (1 mil) in thickness, of around 0.9 g each for air (~ 10 cm x 40 cm), and ~ 1.6 g for WWTP
138 deployments (~ 15 cm x 45 cm). The PE was manufactured by a commercial sheeting company
139 (Covalence Plastics, IN., Minneapolis, MN, USA). PE samplers were cleaned by sequential
140 extractions using acetone, dichloromethane, and twice hexane for 24 hours per solvent.

141 Sample processing and analysis took place in a clean lab at the University of Rhode
142 Island (URI). All glassware was rinsed with acetone, hexane, and DCM (~10 mL each) and then
143 baked for at least 8 hours at 450 °C. XAD (Sigma-Aldrich) and XAD sandwiched between 2
144 PUF plugs (8 cm length x 9 cm diameter, Tisch Environmental, Cleves, OH, USA) sandwiches
145 were extracted in a Soxhlet apparatus using ~150 mL of hexane for 24 hours.

146 PEs were extracted in individual 60 mL amber vials using ~55 mL of hexane for 24 hours.
147 Extracts were concentrated first on a Rotovap to a few mL and then under a mild nitrogen stream
148 to ~200 μ L. After which, 40 ng p-terphenyl- d_{14} was added as an injection standard.

149 *Field deployments*

150 Aqueous deployments of PE samplers were performed in September of 2016 at
151 the South Kingston Waste Water Treatment Plant (WWTP), Narragansett, RI, USA. Ambient
152 temperatures ranged from 22 – 24 $^{\circ}$ C; water flow was around 2 million gallons per day (~ 3,800
153 m^3 /day) (see SI Table 2). PE passive samplers were submerged in the effluent outflow of the
154 WWTP (Figure S1) for 1, 2, 4, 7, 14, and 21 days; at which time 3 sheets each were collected,
155 plus a field blank. Prior to extraction, each PE sheet was wiped with Kimwipes to remove the
156 biofouling. Active sampling using a pump filtered ~ 20 L per day through a filter-PUF plug
157 combination. The PUF plugs were Soxhlet extracted, followed by a silica gel column clean-up,
158 but poor chromatography prevented the quantification of PFASs in these samples.

159 Sampling rates (R_s) for aqueous PE-samplers were derived based on loss of performance
160 reference compounds (PRCs) (Booij et al. 2002). Three deuterated PAHs (fluorene- d_{10} , pyrene-
161 d_{10} and benzo(a)pyrene- d_{12}) were used as PRCs; average PRC losses were 97% for fluorene- d_{10} ,
162 61% for pyrene- d_{10} and 2% for benzo(a)pyrene- d_{12} . Sampling rates (R_s) were calculated as
163 detailed in previous studies (Carrie A McDonough et al. 2016). In the WWTP deployments
164 performed here, R_s averaged 28.1 ± 4.4 L/day.

165 Air sampling site was performed at an active monitoring site for the RI Department of
166 Environmental Management in eastern Providence, (RI, USA) in April 2016. A pump-operated
167 high volume air sampler (TE-PNY-1123, Tisch Environmental, USA) was deployed on the roof
168 of a 4-storey building using two PUF plugs with XAD sandwiched in-between to collect targets

169 PFASs (Figure S3). Passive air samplers were co-located and deployed on top of the roof at a
170 height of 1 meter. Each passive sampler consisted of a PE sheet placed inside an inverted, pre-
171 cleaned stainless steel bowl (Figure S4). The PE sheet was oven onto a stainless steel wire,
172 which was used to fasten the sheet to the rope holding the stainless steel in-place. Passive PE
173 sheets were deployed for 2, 4, 8, 16 and 32 days. Active air samples were sampled continuously
174 for 48 hours each during the 32 day experiment. Temperatures averaged 13-19 °C; wind speed
175 varied from 7-12 m/s (see SI Table 3). The average high-volume sampling rate was 24 m³/hour
176 (based on flow measurements at the beginning and end of each sample). Passively and actively
177 collected sample media, plus field blanks, were wrapped in baked aluminum foil, placed in an
178 airtight bag and stored in a cooler surround with ice packs during transport. Samples were
179 transported to the URI Bay Campus and placed in a 0 °C refrigerator until analysis.

180 *Quality control*

181 A 5-point standard calibration curve for the native compounds and surrogate compounds
182 was created and used to derive relative response factors (linear, non-weighted regression, r^2
183 ranged from 0.94-0.99). Results were recovery-corrected to the nearest surrogate standard (6:2
184 FTOH-d₄ for 6:2 FTOH, 8:2 FTOH-d₄ for 8:2 FTOH, 10:2 FTOH-d₄ for 10:2 FTOH, MeFOSA-
185 d₃ for MeFOSA and EtFOSA, and MeFOSE-d₇ for MeFOSE and EtFOSE). Recoveries of the
186 surrogate standards were 80 ±48% for ¹³C₁₂-6:2 FTOH, 72 ±23% for ¹³C₁₂-8:2 FTOH, 75 ±32%
187 for ¹³C₁₂-10:2 FTOH, 88 ±29% for MeFOSA-d₃, and 87 ±32% for MeFOSE-d₇. Recoveries
188 tended to be greater for active sampling media (PUFs: 70-123%; PEs: 27-121%).

189 *Detection limits*

190 Instrumental detection limits (IDLs) based on the least detectable amount on the GC were
191 ≤ 30 pg on column (except for 6:2 and 8:2 FTOHs with 100 and 400 pg, see SI Table 1).

192 Average blank values were below 0.1 ng/g PE, except for MeFOSA (0.4 ng/g PE) and EtFOSA
193 (0.1 ng/g PE) in the WWTP field blanks. PFAS amounts in samples exceeded blanks typically by
194 at least 10-fold, so results were not blank-corrected. Method detection limits (MDLs) for PE
195 samplers based on mean field blank concentrations + 3 standard deviations (n=10) were around
196 0.1 ng/g PE, except for MeFOSA (0.8 ng/g PE) and EtFOSA (0.3 ng/g PE) (Table 1). Five PUF-
197 XAD blanks were run to determine blank concentrations (Table 1) and derive MDLs, ranging
198 from 0.1 – 4.6 ng/sample.

199 *Uncertainty of K_{PEW} values*

200 The uncertainty of the K_{PEW} values represents the analytical uncertainty from the
201 replicates at each time point and the reliance of R_s values derived from d-PAHs. There is a
202 systemic deviation of a R_s values for specific compounds, with decreasing R_s for increasing
203 molecular weight (MW) or molar volume (V_m) (e.g., (Lohmann et al. 2012). All neutral PFASs
204 considered here possess larger MW and V_m than the d-PAHs used as PRCs. Relative to d-
205 pyrene, R_s values of neutral PFASs are lower by an average of 39% (see SI Table 4).

206

207 **RESULTS AND DISCUSSION**

208 *Passive sampling of PFASs in WWTP effluent*

209 All of the target compounds were detected in the PE passive samplers, at concentrations
210 well above those in blank samplers, except 10:2 FTAc. The compound detected in the highest
211 concentration throughout the field study was MeFOSA, with the PEs accumulating an average of
212 140 ng/g PE (Figure 1, SI Table 5), followed by 8:2 FTAc and 10:2 FTOH at around 30 ng/g
213 PE. Other PFASs were at or below 10 ng/g PE.

214 The time-curve of compound uptake by PE samplers displayed increasing concentrations
215 from day 2 to day 21, by 2 to 5-fold, in-line with expectations of accumulation profiles in passive
216 samplers. The notable exception was 8:2 FTOH, which displayed no significant change in
217 concentrations during the deployment period. The measured uptake of 10:2 FTOH followed the
218 theoretical uptake quite well and approached equilibrium (Figure 1). Uptake curves for MeFOSE
219 and EtFOSE showed that they reached equilibrium within the PE samplers within a week (Figure
220 1).

221 We experienced problems with determining concentrations from concurrent active
222 sampling of WWTP effluents using PUF plugs (collecting 20 L), with residual water and
223 residues resulting in poor chromatography. The equilibrium partitioning constants between PE
224 and water, K_{PEW} , were thus determined using a different approach. Knowing the sampling rate of
225 the PE sheets from the loss of PRCs, we thus estimated the two remaining unknowns, K_{PEW} and
226 C_w , in Microsoft Excel with the Solver using the least square difference between model curve
227 and measurements. This approach estimated K_{PEW} , as it is solely responsible for the shape of the
228 uptake curve (the C_w term only affects the maximum concentration accumulated in the sampler,
229 but not the curvature of the modeled uptake curve). Two approaches were used – an unweighed
230 least square regression (LSR) for each sampling time between measured and modeled PE-
231 concentrations, and a weighed LSR approach where the difference between measured and
232 modeled was normalized to the average PE concentrations to give more weight to the initial data
233 points. To account for the discrepancy between the use of d-PAHs as PRCs, and the higher
234 molecular weights of the neutral PFASs, deduced R_s values were reduced by 39% (see SI Table
235 8).

236 Derived log K_{PEW} for FTOHs increased from 2.7-3.5 (6:2), 4.3-4.4 (8:2) to 4.5-4.7 (10:2
237 FTOH) (Table 2). These results imply an average increase of around 0.7 in log K_{PEW} per C_2F_4
238 unit. Log K_{PEW} increased from 3.5-3.9 for MeFOSA to 4.1-4.4 for EtFOSA, and from 3.0-3.7 for
239 MeFOSE to 3.1-4.2 for EtFOSE (Table 2). Addition of a CH_2 -unit (Me to Et-FOSA or-FOSE)
240 increased log K_{PEW} by 0.44 units on average, similar to reported increases of log K_{PEW} by 0.4-0.5
241 for each additional alkyl carbon (Choi et al. 2013; Reitsma et al. 2013). Derived values of K_{PEW}
242 were 4.3 – 4.8 for 8:2FtAcr (Table 2). The uncertainties of the K_{PEW} values derived (mostly 0.1
243 log units) here stem from the analytical uncertainty (average 36%).

244 For comparison, K_{PEW} values were predicted for the FTOHs based on hexadecane-water
245 partitioning using poly-parameter-linear free energy relationships (LFERs) (Endo and Goss
246 2014a; Endo and Goss 2014b). Predicted K_{PEW} values varied much more than our field-derived
247 data; there is no information available for the other neutral PFASs as far as we know. In a
248 previous comparison of measured versus pp-LFER predicted K_{PEW} values for polar compounds,
249 the prediction via pp-LFER was not as good as other modeling approaches (Hale et al. 2010;
250 Sacks and Lohmann 2011).

251 Our study is the first to report detectable aqueous concentrations of MeFOSA, EtFOSA,
252 8:2 FTacr, MeFOSE, and EtFOSE in a passive sampler deployed in a WWTP outflow. We
253 derived dissolved concentrations for our study site based on the K_{PEW} values above. Dissolved
254 concentrations were at or below 1 ng/L for most compounds. Greater concentrations were
255 derived for 6:2 FTOH (1-3 ng/L) and MeFOSA (14-30 ng/L).

256 There are only a few studies that have reported values for FTOH concentrations in
257 WWTP water effluent (Table 3). The concentrations reported in Duachy et al. 2017 were
258 measured in the WWTP of a fluoropolymer-production plant and as such reflect significantly

259 higher concentrations than would be expected for a residential WWTP. Mahmoud et al. 2009
260 reported aqueous concentrations similar to what was found in this study. Several studies
261 attempted to measure the concentrations of MeFOSA and EtFOSA in WWTP effluent, but in all
262 cases were below detection limits (Ma and Shih 2010; Arvaniti et al. 2012; Stasinakis et al.
263 2013). For FTOHs, 8:2 FTAc and MeFOSA, dissolved concentrations derived here were in the
264 range previously reported from other locations around the world, while we found no data to
265 compare to for MeFOSE and EtFOSE (Table 3).

266

267 *Neutral PFASs from active air sampling*

268 Gas-phase concentrations of volatile PFASs in Providence were dominated by the
269 FTOHs, each around 10 pg/m³, followed by MeFOSE and EtFOSE at around 1-2 pg/m³.
270 MeFOSA was detected mostly below 1 pg/m³, while EtFOSA was < IDL throughout. Traces of
271 the 10:2 FtAc were detected, close to the IDL at around 0.1 pg/m³, with 8:2 FtAc always < IDL
272 (Table 3). Within the FTOHs, 8:2 FTOH displayed greatest average concentrations (16 pg/m³),
273 followed by 6:2 FTOH (11 pg/m³) and 10:2 FTOH (9.9 pg/m³). FTOHs varied in their
274 concentrations by an order of magnitude across the study, but they all exhibit minimum values
275 during the middle of the sampling period. The relative abundances of the FTOHs varied
276 throughout the sampling campaign, though 8:2 FTOH was always more abundant than 10:2
277 FTOH, but the ratio of 6:2 to 8:2 FTOH varied from 2:1 to 1:3.

278 The atmospheric concentrations found in eastern Providence (RI, USA) for FTOHs using
279 active sampling tended to be lower than several other urban studies (SI Table 7) by a wide range.
280 Concentrations from Providence were lower by a factor of 2 compared to 2006 results for
281 Toronto (Canada), but 5-20 times lower than 2005 results from Manchester (UK). The

282 relationship between the various FTOHs, 6:2 : 8:2 : 10:2, differed in this study compared to
283 others. In Providence (RI, USA) the concentrations of all three FTOHs targeted were very
284 similar, while 8:2 FTOH was significantly more prevalent in other studies (Shoeib et al. 2006;
285 Barber et al. 2007; Jahnke, Ahrens, et al. 2007; S. Oono et al. 2008). One possible explanation
286 for the difference in ratios is the addition of PFOS and PFOA to Annex B of the Stockholm
287 convention on persistent organic pollutants in 2009. Already as part of U.S. EPA's stewardship
288 initiative (U.S. EPA), production of C-8 fluorochemicals was phased out, likely causing a
289 decrease in environmental concentrations of 8:2 FTOH. The production method of
290 fluoropolymers has changed since 2009 with increased use of other non-C-8 length compounds,
291 predominantly C-6, C-10, and C-12 fluorocarbons. This change is reflected in the elevated 6:2
292 and 10:2 FTOH concentrations in relation to the 8:2 FTOH in this study and others (Ahrens et al.
293 2012; Wang et al. 2014).

294 Concentrations of MeFOSE and EtFOSE in Providence were similar to those previously
295 reported for Toronto (Canada), while we detected much smaller concentrations for MeFOSA and
296 EtFOSA (Table 4). There was no data for comparison for the ambient concentration of 10:2
297 FtAcr (8:2 FTAc was < IDL).

298

299 *Passive sampling of gas-phase PFASs*

300 In contrast to active sampling results, all targeted PFASs were present in the passive
301 samplers (Table S2). Greatest concentrations in PE samplers were detected for MeFOSE and
302 EtFOSE, with mean concentrations greater than 1 ng/g PE, while all other PFASs were < 1 ng/g
303 PE. PE-based FTOH-concentrations were dominated by the 10:2 FTOH and 6:2 FTOH, which

304 were around 0.5 ng/g PE, same as for MeFOSA. Other volatile PFASs were around 0.2 ng/g PE,
305 including the FT Acr, EtFOSA and 8:2 FTOH (SI Table 6).

306 The time-curve of compound uptake by PE samplers for all three FTOHs, MeFOSE,
307 MeFOSA and EtFOSA, displayed relatively constant concentrations during the field study (Table
308 4). In contrast, PE-based concentrations of EtFOSA, 8:2 FTAc and 10:2 FTAc increased by 2-
309 3-fold during the deployment. These uptake profiles imply somewhat low affinities of gaseous
310 PFASs for PE samplers, in-line with results predicted by pp-LFERs (Endo and Goss 2014b).

311

312 *PE – air partitioning constants*

313 The partitioning of neutral PFAS between PE and air (K_{PEa}) was derived as the ratio of passive
314 sampler concentrations to active sampling concentrations sampled over the same time period:

$$K_{PEa} = C_a / C_{PE} \quad (3);$$

315 average concentrations of C_{PE} and C_a were used for each sampling period (Table 5). Log K_{PEa}
316 were around 7-8 for the FTOHs, and closer to 9 for MeFOSA, Et/MeFOSE and 10:2 FTAc. As
317 opposed to K_{PEw} values, no consistent trend appeared with increasing molecular weight for
318 FTOHs.

319 The comparison with K_{PEa} values predicted by pp-LFER showed good agreement only for 10:2
320 FTOH (K_{PEa} from pp-LFER prediction 8.0; measured 7.7 ± 0.4); the field-derived values were
321 greater than model-predicted values for the other FTOHs. The pp-LFER-approach might be
322 biased in predicting much greater differences in K_{PEa} values (strictly speaking, the prediction is
323 for K_{hda} , but hexadecane is arguable an ideal proxy for the interactions provided by polyethylene
324 chains). The field-derived values probably lack precision. As neutral PFASs are also surfactants,

325 there might be contribution included in the field measurements of surface adsorption that is not
326 considered by the pp-LFER predictions.

327

328 *Passive sampler-based water-air gradients*

329 The ratio of target compound concentrations (at equilibrium) in the same passive sampler matrix
330 between water and air was used to derive water to air gradients (chemical activity gradients), and
331 corresponding gaseous air-water exchange fluxes (Liu et al. 2016; Carrie A. McDonough et al.
332 2016). As ratios were based on PFASs that had equilibrated (day 28 for WWTP effluents, days
333 16 and 32 for air PEs), the ratios are not influenced by R_s or K_{PE} values. Instead, the PEs
334 functioned as sensors of the PFASs relative chemical activities (Morgan and Lohmann 2008;
335 Gobas et al. 2018). We should note that aqueous and atmospheric sampling were carried out ca
336 50 km apart, and for different seasons. Atmospheric concentrations are arguably greater in a
337 major town than around a small town's WWTP, so the gradient derived here will be more
338 conservative. Despite these uncertainties, water-based concentrations of neutral PFASs in PE
339 samplers exceeded those in the gas-phase for most compounds (SI Table 9), indicating net
340 volatilization. Exceptions were Me- and EtFOSE, for which gradients were not significantly
341 different from equilibrium. In our case, there is strong evidence that most of the investigated
342 PFASs are subject to strong volatilization from the WWTP effluent, which is in-line with
343 previous studies in WWTPs using active sampling techniques (Ahrens, Shoeib, Harner, Lee, et
344 al. 2011). This confirms that PE samplers can be used to derive air-water exchange gradients for
345 neutral PFASs, too.

346

CONCLUSIONS

347
348 This study assessed the use of PE passive samplers as a sampling tool for neutral PFAS
349 precursors in air and water. Results show the potential utility of PE samplers for a wide range of
350 neutral PFASs, including 6:2, 8:2 and 10:2 FTOHs, Me/EtFOSE, Me/EtFOSA and 8:2 FTAc,
351 which were regularly detected both in a WWTP effluent and in the ambient air of Providence
352 (RI). While $\log K_{PEw}$ ranged only from 3.5 – 5.0, this was sufficient for a routine detection of
353 neutral PFASs in WWTP effluent. Equilibration times varied between a few days to a couple of
354 weeks for a 25 μm PE sampler placed in the effluent. For gas-phase compounds, all targeted
355 neutral PFASs accumulated in the PE samplers; $\log K_{PEA}$, were ~ 7 -8 for the FTOHs, and
356 approached 9 for MeFOSA and MeFOSE. Neutral PFASs equilibrated within days to 1 week
357 with the 25 μm PE sampler. A comparison of PE-based concentrations between WWTP effluent
358 and ambient air implies net volatilization for all compounds. Future work should explore the use
359 of different thicknesses as a tool to verify equilibrium, in addition to classical time-series uptake
360 curves. Now that we have shown that PE can be used as a passive sampler for neutral PFASs,
361 controlled uptake studies, ideally with PFAs used as PRCs, would help confirm the K_{PE} values
362 derived here. The results presented here imply that PE samplers can be used to detect precursor
363 PFASs in sites with elevated concentrations, but it is unclear whether PE samplers can be used
364 for their detection at background and remote sites. Thicker PEs could also be used for gas-phase
365 sampling to accumulate a greater mass of neutral PFASs. As industrial production of PFASs
366 diversifies, it is unclear whether the neutral PFASs targeted here (still) constitute the dominant
367 PFASs in the gas-phase. It would thus be interesting to assess what fraction the targeted PFASs
368 represent of total neutral PFASs in the PE samplers.

369

370 *Supplemental Data*

371 Additional information on deployments, concentrations and comparison to neutral gas-phase
372 PFAS concentrations from other sites are provided. The Supplemental Data are available on the
373 Wiley Online Library at DOI: 10.1002/etc.xxxx

374

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381

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Table 1. Compounds investigated in this study with corresponding molecular weights and blank concentrations

| Name | Abbreviation | Molecular Weight (g/mol) | Average PE blank (pg/gPE)^a | Average PUF blank amount (pg)^a |
|---|---------------------|---------------------------------|--|--|
| 6:2 Fluorotelomer alcohol | 6:2 FTOH | 364.10 | 23 ± 16 | 420 ± 240 |
| 8:2 Fluorotelomer alcohol | 8:2 FTOH | 464.12 | 26 ± 17 | 760 ± 640 |
| 10:2 Fluorotelomer alcohol | 10:2 FTOH | 564.13 | 71 ± 28 | 1,800 ± 1,500 |
| <i>N</i> -methyl perfluorooctane sulfonamide | MeFOSA | 513.17 | 210 ± 200 | 190 ± 110 |
| <i>N</i> -ethyl perfluorooctane sulfonamide | EtFOSA | 527.20 | 870 ± 780 | 130 ± 100 |
| <i>N</i> -methyl perfluorooctane sulfonamidoethanol | MeFOSE | 557.22 | 34 ± 21 | 560 ± 380 |
| <i>N</i> -ethyl perfluorooctane sulfonamidoethanol | EtFOSE | 571.25 | 49 ± 15 | 360 ± 300 |
| 8:2 Fluorotelomer acrylate | 8:2 FTAc | 518.17 | 24 ± 25 | 160 ± 50 |
| 10:2 Fluorotelomer acrylate | 10:2 FTAc | 618.19 | 14 ± 11 | 90 ± 40 |

^a average ± 1 standard deviation

Table 2. Estimated log K_{PEW} values from this study with single standard deviations, and predicted values based on pp-LFER approaches. (These values were derived using a 39% reduced sampling rate)

| | log K_{PEW}^1 | log K_{PEW}^2 | pp-LFER³ |
|------------------|-----------------------------------|-----------------------------------|----------------------------|
| 6:2 FTOH | 3.5 ± 0.1 | 2.7 ± 0.1 | 3.3 |
| 8:2 FTOH | 4.4 ± 0.1 | 4.3 ± 0.1 | 5.0 |
| 10:2 FTOH | 4.6 ± 0.1 | 4.5 ± 0.1 | 6.7 |
| 8:2 FTAc | 4.8 ± 0.2 | 4.3 ± 0.2 | - |
| 10:2 FTAc | 5.3 [§] | 4.7 [§] | - |
| MeFOSA | 3.9 ± 0.1 | 3.5 ± 0.1 | - |
| EtFOSA | 4.4 ± 0.1 | 4.1 ± 0.1 | - |
| MeFOSE | 3.7 ± 0.1 | 3.0 ± 0.1 | - |
| EtFOSE | 4.2 ± 0.1 | 3.1 ± 0.1 | - |

¹ from unweighed LSR; uncertainty reflects analytical variability

² from weighed LSR; uncertainty reflects analytical variability

³ (Endo and Goss 2014a)

§ K_{PEW} for 10:2 FTAc was estimated relative to 8:2 FTAc with an increase of 0.5 log units

Table 3. Comparison of aqueous concentrations of neutral PFASs (ng/L) in WWTP effluents from selected studies (based on active sampling) to results from this study using passive samplers.

| Sampling Location | France | South Korea | China | Yamato, Japan | South Kingston, RI |
|-------------------|--|-------------------------------|--------------------------------|--------------------------------|--|
| Reference | (Dauchy et al. 2017) | (Kwon et al. 2017) | (Chen et al. 2017) | (Mahmoud et al. 2009) | this study using passive samplers ¹ |
| Water type | Raw effluent from WWTP flotation tank with fluorochemical industry influents | Effluent from 81 Korean WWTPs | Effluent from 12 Chinese WWTPs | River water and WWTP effluents | WWTP effluent |
| 6:2 FTOH | 11-110 | N/A | 0.64 (0.49-0.98) | N/A | 1.0 – 3.2 |
| 8:2 FTOH | 13-4300 | N/A | 5.3 (3.1-12) | 1.4±1.1 | 0.35 – 0.40 |
| 10:2 FTOH | 14-1800 | N/A | 1.1 (<0.03-4.6) | 1.2±2.0 | 0.71 – 0.94 |
| 8:2 FTAc | N/A | N/A | N/A | 0.1±0.1 | 0.63 – 1.0 |
| EtFOSA | < 20 | ~ 0.7 | N/A | N/A | 0.39 – 0.58 |
| MeFOSA | < 20 | N/A | N/A | N/A | 14 – 30 |
| EtFOSE | N/A | N/A | N/A | N/A | 0.11 – 0.52 |
| MeFOSE | N/A | N/A | N/A | N/A | 0.35 – 1.2 |

N/A – not analyzed

¹ best-fitted results from unweighed or weighed LSR.

Table 4. Atmospheric concentrations measured at Providence sampling site using PUF/XAD active sampling

| Compound | Atmospheric Concentration (pg/m ³) | | | | | | | |
|-----------|--|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | 2016/4/11 | 2016/4/13 | 2016/4/15 | 2016/4/18 | 2016/4/20 | 2016/4/25 | 2016/4/27 | 2016/4/29 |
| 6:2 FTOH | 9.8 | 27 | 12 | 9.4 | 12 | 5.7 | 9.5 | 5.8 |
| 8:2 FTOH | 15 | 19 | 12 | 31 | < IDL | 4.6 | 12 | 16 |
| 10:2 FTOH | 7.1 | 11 | 7.0 | 19 | < IDL | 3.1 | 11 | 11 |
| 8:2 FTAc | < IDL | < IDL | < IDL | < IDL | < IDL | < IDL | < IDL | < IDL |
| 10:2 FTAc | < IDL | < IDL | < IDL | 0.1 | < IDL | 0.1 | < IDL | 0.1 |
| EtFOSA | < IDL | < IDL | < IDL | < IDL | < IDL | < IDL | < IDL | < IDL |
| MeFOSA | 0.4 | < IDL | 0.5 | 0.5 | 0.4 | 0.3 | 1.9 | 1.2 |
| EtFOSE | 1.9 | < IDL | < IDL | 1.3 | 1.1 | < IDL | 0.9 | < IDL |
| MeFOSE | 2.8 | 3.9 | 2.4 | 1.2 | 1.7 | 0.9 | < IDL | 1.4 |

< IDL – below instrumental detection limit

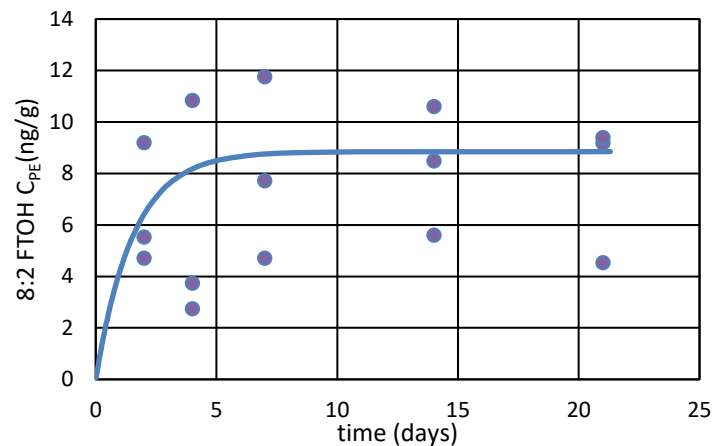
Table 5. Estimated log K_{PEa} values from this study, and predicted values based on pp-LFER approaches.

| | mean log K_{PEa} | pp-LFER ^a |
|-----------|--------------------|----------------------|
| 6:2 FTOH | 7.6 ± 0.2 | 2.8 |
| 8:2 FTOH | 7.1 ± 0.2 | 5.4 |
| 10:2 FTOH | 7.7 ± 0.4 | 8.0 |
| 8:2 FTAc | n/a | - |
| 10:2 FTAc | 9.1 | - |
| EtFOSA | n/a | - |
| MeFOSA | 8.8 ± 0.2 | - |
| EtFOSE | 9.0 ± 0.1 | - |
| MeFOSE | 8.9 ± 0.3 | - |

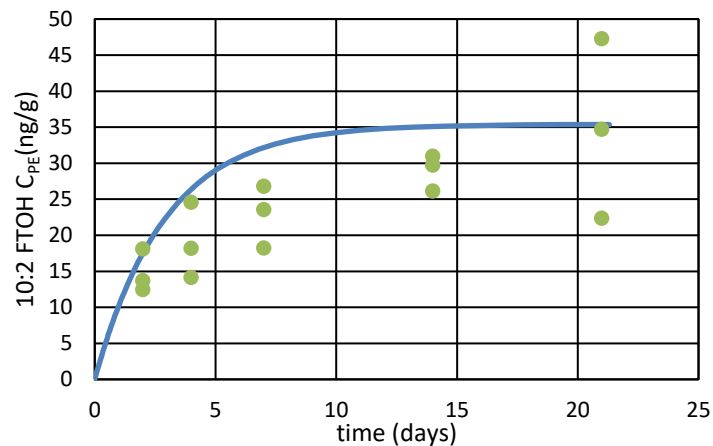
^a (Endo and Goss 2014a)

Figure 1: Measured (triplicates) versus modeled (solid line) PE-concentrations (ng/g) of (a) 10:2 FTOH, (b) 8:2 FTOH; (c) EtFOSE and (d) MeFOSE placed in effluents of a wastewater treatment plant over time.

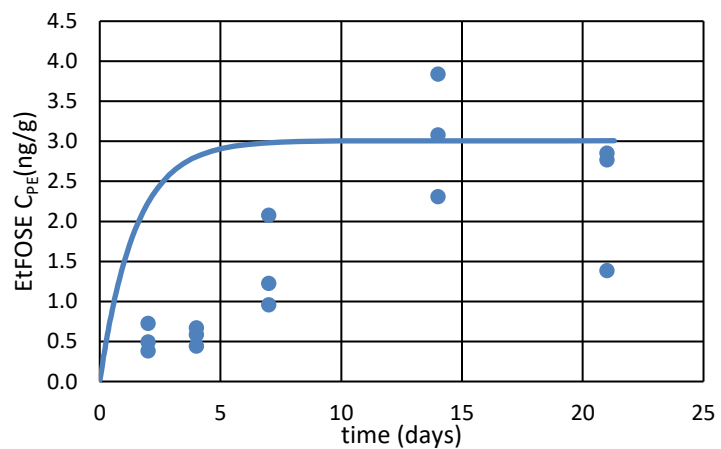
(a)



(b)



(c)



(d)

