Environmental Chemistry

Field-Testing Polyethylene Passive Samplers for the Detection of Neutral Polyfluorinated Alkyl Substances in Air and Water

Erik Dixon-Anderson and Rainer Lohmann*
Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island, USA

Abstract: Fluorotelomer alcohols (FTOHs), perfluorooctane-sulfonamidoethanols (FOSEs), perfluorooctane-sulfonamides (FOSAs), and other poly- and perfluorinated alkyl substances (PFASs) are common and ubiquitous byproducts of industrial telomerization processes. They can degrade into various perfluorinated carboxylic acids, which are persistent organic contaminants of concern. We assessed the use of polyethylene (PE) passive samplers as a sampling tool for neutral PFAS precursors during field-deployments in air and water. A wide range of neutral PFASs was detected in polyethylene sheets exposed in wastewater treatment effluents in August 2017. Equilibration times for most neutral PFASs were on the order of 1 to 2 wk. Based on known sampling rates, the partitioning constants between polyethylene and water, $K_{PEw}$, were derived. Log $K_{PEw}$ values were mostly in the range of 3 to 4.5, with the greatest values for 8:2 FTOH, 10:2 FTOH, and $n$-ethyl-FOSE. To test the utility of polyethylene for gas-phase compounds, parallel active and passive sampling was performed in ambient air in Providence (RI, USA) in April 2016. Most PFASs equilibrated within 2 to 7 d. The greatest concentrations in polyethylene samplers were detected for MeFOSE and EtFOSE. Polyethylene/air partitioning constants, log $K_{PEa}$, were approximately 7 to 8 for the FTOHs, and approached 9 for $n$-methyl-FOSA and $n$-methyl-FOSE. Polyethylene sheets showed promise as a passive sampling approach for neutral PFASs in air and water. Environ Toxicol Chem 2018;37:3002–3010. © 2018 SETAC

Keywords: Poly- and perfluorinated alkyl substances; Fluorotelomer alcohols; Passive sampler; Dissolved concentration; Gas phase

INTRODUCTION

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, nonstick 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 the adverse effects that have been demonstrated on wildlife and humans. Elevated PFOS concentrations have been found in wildlife tissue at polar sites in both the Arctic and in the Antarctic (Giesy and Kannan 2001; Houde et al. 2006, 2011). At ambient pH, PFOS is ionic and has thus a low vapor pressure and high water solubility compared to other POPs (Giesy and Kannan 2002; Krusic et al. 2005); it would not be expected to be transported over long distances via the atmosphere. The PFASs have been detected in surface waters of the Arctic Ocean in the range of 100 pg/L, indicating that long-range transport is occurring (Yamashita et al. 2008; Yeung et al. 2017). However, 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). Hydroxyl radical attack on these precursors is very slow, and atmospheric lifetimes range from 10 to 20 d for FTOHs of varying carbon length and from 20 to 50 d for selected FOSAs (Stock

This article includes online-only Supplemental Data.
* Address correspondence to rlohmann@uri.edu
Published online 5 November 2018 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/etc.4264

© 2018 SETAC
The estimated atmospheric residence time for 8:2 FTOH is >50 d (Wania 2007). A 10- to 50-d lifetime is sufficient to allow for hemispheric transport to the Arctic from primary source regions (Ellis et al. 2004; Wallington et al. 2006).

Most of the studies on FTOHs and PFASs in the environment have used active sampling methods (Jahnke et al. 2007b; Ahrens et al. 2011a; Liu et al. 2013). These methods typically require a large amount of sample media to be collected (air, water, etc.) to quantify the low (pg range) environmental concentrations that are found. For these experimental setups, a large volume of media is pulled through a filter and adsorbent on which the POPs collect over time. Active sampling is expensive and time consuming, prohibiting the widespread monitoring of these compounds.

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

Passive sampling devices accumulate organic contaminants through diffusion. Due to their reliance on diffusion, polyethylene samplers inherently select only for gaseous compounds in the air and dissolved compounds in the water (Adams et al. 2007). In comparison with many active and passive methods, polyethylene sheets are best at accumulating hydrophobic organic contaminants, cost little, and are easy to handle and use (Lohmann et al. 2012). In addition, the ability to measure both aqueous and atmospheric concentrations at sampling sites provides insight into the transport processes that control a compound’s movement through the environment and the quantification of air–water fluxes (Morgan and Lohmann 2008; Khairy et al. 2014; McDonough et al. 2014).

The passive uptake of a water or air contaminant by a passive sampler is a well-characterized process (Vrana et al. 2001; Bartkow et al. 2005):

\[
N_s = C_tK_{PEw}m_s \left(1 - \exp\left(-\frac{R_s}{K_{PEw}m_s}\right)\right)
\]

where \(N_s\) is the amount or pollutant absorbed (pg); \(R_s\) is sampling rate (L/d); \(t\) is exposure time (d); \(m_s\) is the passive sampler mass (kg); \(K_{PEw}\) is the polyethylene/water partitioning constant (L/kg); and \(C_t\) is the ambient concentration (pg/L).

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

\[
N_s = C_wK_{PEw}m_s \text{ or } N_s = C_aK_{PEa}m_s
\]

where \(C_w\) and \(C_a\) are the ambient dissolved or gas-phase concentrations (pg/L). The uptake stage is dependent on the magnitude of \(K_{PEw}\) or \(K_{PEa}\), and environmental mass transfer coefficients.

The overarching goal for this research was the field-testing of polyethylene as a simple sampling technique for the monitoring of neutral PFASs. In particular, our goals were to 1) determine whether polyethylene passive samplers enrich PFASs in air and water sufficiently for detection; 2) estimate polyethylene/water and polyethylene/air partitioning coefficients, and compare them to predicted values; and 3) discuss whether and how polyethylene samplers can be used for the quantification of volatile, neutral PFASs.

**MATERIALS AND METHODS**

**Target compounds**

The present study targeted 9 individual neutral PFASs, specifically FTOHs, fluorotelomer acrylates (FTAc), FOSAs, and FOSAs, ranging in molecular weight from 364 to 619 g/mol (Table 1). Native and mass-labeled surrogate standards (\(^{13}\)C\(_{12}\)-6:2 FTOH, \(^{13}\)C\(_{12}\)-8:2 FTOH, \(^{13}\)C\(_{12}\)-10:2 FTOH, MeFOSA-d\(_3\), and MeFOSE-d\(_4\)) were purchased from Wellington Laboratories.

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

**Instrumental analysis**

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

**Polyethylene passive samplers**

The passive samplers used in this research consisted of low-density polyethylene, 25 μm (1 mil) in thickness, of approximately 0.9 g each for air (~10 × 40 cm), and approximately 1.6 g for wastewater treatment plant (WWTP) deployments (~15 × 45 cm). The polyethylene was manufactured by a commercial sheeting company (Covalence Plastics). Polyethylene samplers...
were cleaned by sequential extractions using acetone, DCM, and 2 x hexane for 24 h/solvent.

Sample processing and analysis took place in a clean laboratory at the University of Rhode Island (Narragansett, RI, USA). All glassware was rinsed with acetone, hexane, and DCM (~10 mL each) and then baked for at least 8 h at 450 °C. The XAD (Sigma-Aldrich) and XAD sandwiched between 2 polyurethane foam plugs (8-cm length x 9-cm diameter; Tisch Environmental) sandwiches were extracted in a Soxhlet apparatus using approximately 150 mL of hexane for 24 h. Polyethylenes were extracted in individual 60-mL amber vials using approximately 55 mL of hexane for 24 h. Extracts were concentrated first on a Rotovap to a few mL and then under a mild nitrogen stream to approximately 200 μL, after which 40 ng p-terphenyl-d14 was added as an injection standard.

### Field deployments

Aqueous deployments of polyethylene samplers were performed in September of 2016 at the South Kingston WWTP (Narragansett, RI, USA). Ambient temperatures ranged from 22 to 24 °C; water flow was approximately 2 million gal/d (~3800 m3/d; Supplemental Data, Table S2). Polyethylene passive samplers were submerged in the effluent outflow of the WWTP (Supplemental Data, Figure S1) for 1, 2, 4, 7, 14, and 21 d, at which time 3 sheets each were collected, plus a field blank. Prior to extraction, each polyethylene sheet was wiped with Kimwipes to remove the biofouling. Active sampling using a pump filtered approximately 20 L/d through a filter-polyurethane foam plug combination. The polyurethane foam plugs were Soxhlet extracted, followed by a silica gel column cleanup, but poor chromatography prevented the quantification of PFASs in these samples.

Sampling rates (R) for aqueous polyethylene samplers were derived based on loss of performance reference compounds (PRCs; Booij et al. 2002). Three deuterated polycyclic aromatic hydrocarbons (PAHs; fluorene-d10, pyrene-d10, and benzo[a]pyrene-d12) were used as PRCs; average PRC losses were 97% for fluorene-d10, 61% for pyrene-d10, and 2% for benzo[a]pyrene-d12. Sampling rates (R) were calculated as detailed in previous studies (McDonough et al. 2016a, 2016b). In the WWTP deployments performed here, R averaged 28.1 ± 4.4 L/d.

Air sampling was performed at an active monitoring site for the Rhode Island Department of Environmental Management in eastern Providence (RI, USA) in April 2016. A pump-operated high-volume air sampler (TE-PNY-1123; Tisch Environmental) was deployed on the roof of a 4-story building using 2 polyurethane foam plugs with XAD sandwiched in between to collect target PFASs (Supplemental Data, Figure S3). Passive air samplers were colocated and deployed on top of the roof at a height of 1 m. Each passive sampler consisted of a polyethylene sheet placed inside an inverted, precleaned stainless steel bowl (Supplemental Data, Figure S4). The polyethylene sheet was woven onto a stainless steel wire, which was used to fasten the sheet to the rope holding the stainless steel in place. Passive polyethylene sheets were deployed for 2, 4, 8, 16, and 32 d. Active air samples were sampled continuously for 48 h each during the 32-d experiment. Temperatures averaged 13 to 19 °C; wind speed varied from 7 to 12 m/s (Supplemental Data, Table S3). The average high-volume sampling rate was 24 m3/h (based on flow measurements at the beginning and end of each sample). Passively and actively collected sample media, plus field blanks, were wrapped in baked aluminum foil, placed in an air-tight bag, and stored in a cooler surround with ice packs during transport. Samples were transported to the University of Rhode Island Bay Campus and placed in a 0 °C refrigerator until analysis.

### Quality control

A 5-point standard calibration curve for the native compounds and surrogate compounds was created and used to derive relative response factors (linear, nonweighed regression, \( r^2 \), was 0.94–0.99). Results were recovery-corrected to the nearest surrogate standard (6:2 FTOH-d4 for 6:2 FTOH, 8:2 FTOH-d4 for 8:2 FTOH, 10:2 FTOH-d4 for 10:2 FTOH, MeFOSA-d3 for MeFOSA and EtFOSA, and MeFOSA-d3 for EtFOSA and EtFOSA). Recoveries of the surrogate standards were 80 ± 48% for \[^{13}\text{C}_{12}-6:2\text{ FTOH}, 72 ± 23\% for \[^{13}\text{C}_{12}-8:2\text{ FTOH}, 75 ± 32\% for \[^{13}\text{C}_{12}-10:2\text{ FTOH}, 88 ± 29\% for MeFOSA-d3, and 87 ± 32\% for MeFOSA-d3. Recoveries tended to be greater for active sampling media (polyurethane foams: 70–123%; polyethylenes: 27–121%).

### Table 1: Compounds investigated with corresponding molecular weights and blank concentrations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Molecular weight (g/mol)</th>
<th>Average PE blank (pg/gPE)*</th>
<th>Average PUF blank amount (pg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:2 Fluorotelomer alcohol</td>
<td>6:2 FTOH</td>
<td>364.10</td>
<td>23 ± 16</td>
<td>420 ± 240</td>
</tr>
<tr>
<td>8:2 Fluorotelomer alcohol</td>
<td>8:2 FTOH</td>
<td>464.12</td>
<td>26 ± 17</td>
<td>760 ± 640</td>
</tr>
<tr>
<td>10:2 Fluorotelomer alcohol</td>
<td>10:2 FTOH</td>
<td>564.13</td>
<td>71 ± 28</td>
<td>1800 ± 1500</td>
</tr>
<tr>
<td>N-methyl perfluorooctane sulfonamide</td>
<td>MeFOSA</td>
<td>513.17</td>
<td>210 ± 200</td>
<td>190 ± 110</td>
</tr>
<tr>
<td>N-ethyl perfluorooctane sulfonamide</td>
<td>EtFOSA</td>
<td>527.20</td>
<td>870 ± 780</td>
<td>130 ± 100</td>
</tr>
<tr>
<td>N-methyl perfluorooctane sulfonamidoethanol</td>
<td>MeFOSE</td>
<td>557.22</td>
<td>34 ± 21</td>
<td>560 ± 380</td>
</tr>
<tr>
<td>N-ethyl perfluorooctane sulfonamidoethanol</td>
<td>EtFOSE</td>
<td>571.25</td>
<td>49 ± 15</td>
<td>360 ± 300</td>
</tr>
<tr>
<td>8:2 Fluorotelomer acrylate</td>
<td>8:2 FTACr</td>
<td>518.17</td>
<td>24 ± 25</td>
<td>160 ± 50</td>
</tr>
<tr>
<td>10:2 Fluorotelomer acrylate</td>
<td>10:2 FTACr</td>
<td>618.19</td>
<td>14 ± 11</td>
<td>90 ± 40</td>
</tr>
</tbody>
</table>

*Average ± 1 standard deviation.

PE = polyethylene; PUF = polyurethane foam.
**Detection limits**

Instrumental detection limits (IDLs) based on the least detectable amount on the gas chromatograph were ≤30 pg on the column (except for 6:2 and 8:2 FTOHs with 100 and 400 pg; Supplemental Data, Table S1). Average blank values were <0.1 ng/g polyethylene, except for MeFOSA (0.4 ng/g polyethylene) and EtFOSA (0.1 ng/g polyethylene) in the WWTP field blanks. The PFAS amounts in samples exceeded blanks typically by at least 10-fold, so results were not blank-corrected. Method detection limits (MDLs) for polyethylene samplers based on mean field blank concentrations + 3 standard deviations (n = 10) were approximately 0.1 ng/g polyethylene, except for MeFOSA (0.8 ng/g polyethylene) and EtFOSA (0.3 ng/g polyethylene; Table 1). Five polyurethane foam/XAD blanks were run to determine blank concentrations (Table 1) and derive MDLs, ranging from 0.1 to 4.6 ng/sample.

**Uncertainty of K_{PEw} values**

The uncertainty of the $K_{PEw}$ values represents the analytical uncertainty from the replicates at each time point and the reliance of $R_s$ values derived from d-PAHs. There is a systemic deviation of a $R_s$ values for specific compounds, with decreasing $R_s$ for increasing molecular weight or molar volume (e.g., Lohmann et al. 2012). All neutral PFASs considered in the present study possess larger molecular weight and molar volume than the d-PAHs used as PRCs. Relative to d-pyrene, $R_s$ values of neutral PFASs are lower by an average of 39% (Supplemental Data, Table S4).

**RESULTS AND DISCUSSION**

**Passive sampling of PFASs in WWTP effluent**

All the target compounds were detected in the polyethylene passive samplers, at concentrations well above those in blank samplers, except for 10:2 FTAc. The compound detected at the highest concentration throughout the field study was MeFOSA, with the polyethylene accumulating an average of 140 ng/g polyethylene (Figure 1 and Supplemental Data, Table S5), followed by 8:2 FTAc and 10:2 FTOH at approximately 30 ng/g polyethylene. Other PFASs were ≤10 ng/g polyethylene.

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

We experienced problems with determining concentrations from concurrent active sampling of WWTP effluents using polyurethane foam plugs (collecting 20 L), with residual water and residues resulting in poor chromatography. The $K_{PEw}$ values were thus determined using a different approach. Knowing the sampling rate of the polyethylene sheets from the loss of PRCs, we thus estimated the 2 remaining unknowns, $K_{PEw}$ and $C_w$, in Microsoft Excel with the Solver using the least square difference between model curve and measurements. This approach

![Figure 1](https://wileyonlineibrary.com/ETC)
estimated $K_{F EW}$, because it is solely responsible for the shape of the uptake curve (the $C_w$ term only affects the maximum concentration accumulated in the sampler, but not the curvature of the modeled uptake curve). Two approaches were used—an unweighted least square regression (LSR) for each sampling time between measured and modeled polyethylene concentrations, and a weighed LSR approach by which the difference between measured and modeled was normalized to the average polyethylene concentrations to give more weight to the initial data points. To account for the discrepancy between the use of d-PAHs as PRCs, and the higher molecular weights of the neutral PFASs, deduced $R_e$ values were reduced by 39% (Supplemental Data, Table S8).

Derived log $K_{F EW}$ values for FTOHs increased from 2.7 to 3.5 (for 6:2) and from 4.3 to 4.4 (for 8:2) to 4.5 to 4.7 (10:2 FTOH; Table 2). These results imply an average increase of approximately 0.7 in log $K_{F EW}/C_2F_4$ unit. Log $K_{F EW}$ increased from 3.5 to 3.9 for MeFOSA to 4.1 to 4.4 for EtFOSA, and from 3.0 to 3.7 for MeFOSE to 3.1 to 4.2 for EtFOSE (Table 2). Addition of a CH$_2$-unit (Me to EtFOSA or –FOSE) increased log $K_{F EW}$ by 0.44 units on average, similar to reported increases of log $K_{F EW}$ by 0.4 to 0.5 for each additional alkyl carbon (Choi et al. 2013; Reitsma et al. 2013). Derived values of $K_{F EW}$ were 4.3 to 4.8 for 8:2 FtAcr (Table 2). The uncertainties of the $K_{F EW}$ values derived (mostly 0.1 log units) in the present study stem from the analytical uncertainty (average 36%).

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

The present study is the first to report detectable aqueous concentrations of MeFOSA, EtFOSA, 8:2 FtAcr, MeFOSE, and EtFOSE in a passive sampler deployed in a WWTP outflow. We derived dissolved concentrations for our study site based on the $K_{F EW}$ values just given. Dissolved concentrations were $\leq$ 1 ng/L for most compounds. Greater concentrations were derived for 6:2 FTOH (1–3 ng/L) and MeFOSA (14–30 ng/L).

Only a few studies have reported values for FTOH concentrations in WWTP water effluent (Table 3). The concentrations reported in Duachy et al. (2017) were measured in the WWTP of a fluoropolymer production plant and as such reflect significantly higher concentrations than would be expected for a residential WWTP. Mahmoud et al. (2009) reported aqueous concentrations similar to what was found in the present study. Several studies attempted to measure the concentrations of MeFOSA and EtFOSA in WWTP effluent, but in all cases the levels were below detection limits (Ma and Shih 2010; Arvaniti et al. 2012; Stasinakis et al. 2013). For FTOHs, 8:2 FTAc, and MeFOSA, dissolved concentrations that we derived were in the range previously reported from other locations around the world, whereas we found no data to use for comparison with our MeFOSA and EtFOSE findings (Table 3).

### Neutral PFASs from active air sampling

Gas-phase concentrations of volatile PFASs in Providence were dominated by the FTOHs, each approximately 10 pg/m$^3$, followed by MeFOSA and EtFOSA at approximately 1 to 2 pg/m$^3$. Levels of MeFOSA were mostly $< 1$ pg/m$^3$, whereas EtFOSA was $< IDL$ throughout. Traces of the 10:2 FtAcr were detected, close to the IDL at approximately 0.1 pg/m$^3$, with 8:2 FtAc always $< IDL$ (Table 3). Within the FTOHs, 8:2 FTOH displayed the greatest average concentrations (16 pg/m$^3$), followed by 6:2 FTOH (11 pg/m$^3$) and 10:2 FTOH (9.9 pg/m$^3$). The FTOHs varied in their concentrations by an order of magnitude across the study, but they all exhibited minimum values during the middle of the sampling period. The relative abundances of the FTOHs varied throughout the sampling campaign, although 8:2 FTOH was always more abundant than 10:2 FTOH; the ratio of 6:2 to 8:2 FTOH, however, varied from 2.1 to 1.3.

The atmospheric concentrations found in eastern Providence for FTOHs using active sampling tended to be lower than in several other urban studies (Supplemental Data, Table 57) by a wide range. Concentrations from Providence were lower by a factor of 2 compared with 2006 results for Toronto (Canada), but were 5 to 20 times lower than 2005 results from Manchester (United Kingdom). The relationship between the various FTOHs (6:2, 8:2, 10:2) differed in the present study compared with others. In Providence, the concentrations of all 3 FTOHs targeted were very similar, whereas 8:2 FTOH was significantly more prevalent in other studies (Shoeib et al. 2006; Barber et al. 2007; Jahneke et al. 2007a; Oono et al. 2008b). One possible explanation for the difference in ratios is the addition of PFOS and PFOA to Annex B of the Stockholm Convention on Persistent Organic Pollutants in 2009. As part of the US Environmental Protection Agency’s stewardship initiative (US Environmental Protection Agency 2010–2015), production of C-8 fluorochemicals has already been phased out, likely causing a decrease in environmental concentrations of 8:2 FTOH. The production method of fluoropolymers has changed since 2009.

### Table 2: Estimated log partitioning constant between polyethylene and water ($K_{F EW}$) values from the present study with single standard deviations and predicted values based on polyparameter-linear free energy relationship (pp-LFER) approaches

<table>
<thead>
<tr>
<th>FTOH</th>
<th>$\log K_{F EW}^{b}$</th>
<th>$\log K_{F EW}^{c}$</th>
<th>pp-LFER$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:2 FTOH</td>
<td>3.5 ± 0.1</td>
<td>2.7 ± 0.1</td>
<td>3.3</td>
</tr>
<tr>
<td>8:2 FTOH</td>
<td>4.4 ± 0.1</td>
<td>4.3 ± 0.1</td>
<td>5.0</td>
</tr>
<tr>
<td>10:2 FTOH</td>
<td>4.6 ± 0.1</td>
<td>4.5 ± 0.1</td>
<td>6.7</td>
</tr>
<tr>
<td>8:2 FTAc</td>
<td>4.8 ± 0.2</td>
<td>4.3 ± 0.2</td>
<td>—</td>
</tr>
<tr>
<td>10:2 FTAc</td>
<td>5.3$^*$</td>
<td>4.7$^*$</td>
<td>—</td>
</tr>
<tr>
<td>MeFOSA</td>
<td>3.9 ± 0.1</td>
<td>3.5 ± 0.1</td>
<td>—</td>
</tr>
<tr>
<td>EtFOSA</td>
<td>4.4 ± 0.1</td>
<td>4.1 ± 0.1</td>
<td>—</td>
</tr>
<tr>
<td>MeFOSE</td>
<td>3.7 ± 0.1</td>
<td>3.0 ± 0.1</td>
<td>—</td>
</tr>
<tr>
<td>EtFOSE</td>
<td>4.2 ± 0.1</td>
<td>3.1 ± 0.1</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$Derived using a 39% reduced sampling rate.

$^b$From unweighed least square regression; uncertainty reflects analytical variability.

$^c$From weighed least square regression; uncertainty reflects analytical variability.

$^d$Data from Endo and Goss 2014a.
with increased use of other non-C-8 length compounds, predominantly C-6, C-10, and C-12 fluorocarbons. This change is reflected in the elevated 6:2 and 10:2 FTOH concentrations in relation to the 8:2 FTOH in the present study and others (Ahrens et al. 2012; Wang et al. 2014).

Concentrations of MeFOSE and EtFOSE in Providence were similar to those previously reported for Toronto, whereas we detected much smaller concentrations for MeFOSA and EtFOSA (Table 4). There were no data with which to compare the ambient concentration of 10:2 FtAcr (8:2 FTAcr was <IDL).

### Passive sampling of gas-phase PFASs

In contrast to active sampling results, all targeted PFASs were present in the passive samplers (Supplemental Data, Table S2). The greatest concentrations in polyethylene samplers were detected for MeFOSE and EtFOSE, with mean concentrations >1 ng/g polyethylene, whereas all other PFASs were <1 ng/g polyethylene. The polyethylene-based FTOH concentrations were dominated by the 10:2 FTOH and 6:2 FTOH forms, which were approximately 0.5 ng/g polyethylene, the same as for MeFOSA. Other volatile PFASs were approximately 0.2 ng/g polyethylene, including FTAcr, EtFOSA, and 8:2 FTOH (Supplemental Data, Table S6).

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

### Polyethylene/air partitioning constants

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

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

Average concentrations of $C_{PE}$ and $C_a$ were used for each sampling period (Table 5). Log $K_{PEa}$ values were approximately

### Table 3: Comparison of aqueous concentrations of neutral poly- and perfluorinated alkyl substances (ng/L) in wastewater treatment plant effluents from selected studies* with results from the present study using passive samplers

<table>
<thead>
<tr>
<th>Sampling Location</th>
<th>Water Type</th>
<th>Reference</th>
<th>Water Type</th>
<th>Reference</th>
<th>Measured Concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>France</td>
<td>Raw effluent from WWTP flotation tank with fluorochemical industry influents</td>
<td>Dauchy et al. 2017</td>
<td>Effluent from 81 Korean WWTPs</td>
<td>Kwon et al. 2017</td>
<td>6:2 FTOH 11–110, 8:2 FTOH 13–4300, 10:2 FTOH 14–1800, 8:2 FTAcr &lt;0.7, MeFOSA &lt;20, EtFOSA N/A, MeFOSE N/A</td>
</tr>
<tr>
<td>South Korea</td>
<td>Effluent from 81 Korean WWTPs</td>
<td>Kwon et al. 2017</td>
<td>Effluent from 12 Chinese WWTPs</td>
<td>Chen et al. 2017</td>
<td>6:2 FTOH 1.1 (0.49–0.98), 8:2 FTOH 5.3 (3.1–12), 10:2 FTOH 1.1 (&lt;0.03–4.6), 8:2 FTAcr 0.1 ± 0.1, MeFOSA N/A, EtFOSA N/A, MeFOSE N/A</td>
</tr>
<tr>
<td>China</td>
<td>Effluent from river water and WWTP effluents</td>
<td>Mahmoud et al. 2009</td>
<td>Effluent from 10:2 FtAcr</td>
<td>Yamato, Japan, 2009</td>
<td>6:2 FTOH 1.0–3.2, 8:2 FTOH 0.35–0.40, 10:2 FTOH 0.39–0.58, 8:2 FTAcr 0.1–0.2, MeFOSA N/A, EtFOSA N/A, MeFOSE N/A</td>
</tr>
<tr>
<td>South Kingston, RI, USA</td>
<td>WWTP effluent</td>
<td>Present study using passive samplersb</td>
<td>Effluent from 10:2 FtAcr</td>
<td></td>
<td>10:2 FTAcr 0.11–0.12, EtFOSA N/A, MeFOSA 0.35–1.2</td>
</tr>
</tbody>
</table>

*Based on active sampling.

bBest-fitted results from unweighed or weighed least square regression.

WWTP = wastewater treatment plant; N/A = not analyzed.

For other abbreviations, see Table 1.
7 to 8 for the FTOHs, and closer to 9 for MeFOSA, Et/MeFOSE, and 10:2 FTACr. As opposed to $K_{\text{PEw}}$ values, no consistent trend appeared with increasing molecular weight for FTOHs.

The comparison with $K_{\text{PEa}}$ values predicted by pp-LFER showed good agreement only for 10:2 FTOH ($K_{\text{PEa}}$ from pp-LFER prediction 8.0; measured 7.7 ± 0.4); the field-derived values were greater than model-predicted values for the other FTOHs. The pp-LFER approach might be biased in predicting much greater differences in $K_{\text{PEa}}$ values. (Strictly speaking, the prediction is for $K_{\text{hda}}$, but hexadecane is arguably an ideal proxy for the interactions provided by polyethylene chains.) The field-derived values probably lack precision. As neutral PFASs are also surfactants, their detection in passives might include a contribution by surface adsorption, which is not considered by the pp-LFER predictions.

### Passive sampler-based water-air gradients

The ratio of target compound concentrations (at equilibrium) in the same passive sampler matrix between water and air was used to derive water-to-air gradients (chemical activity gradients), and corresponding gaseous air–water exchange fluxes (Liu et al. 2016; McDonough et al. 2016a, 2016b). Because ratios were based on PFASs that had equilibrated (day 28 for WWTP effluents, days 16 and 32 for air polyethylene), the ratios were not influenced by $R_s$ or $K_{\text{PE}}$ values. Instead, the polyethylene functioned as sensors of the relative chemical activities of the PFASs (Morgan and Lohmann 2008; Gobas et al. 2018). We should note that aqueous and atmospheric sampling were carried out approximately 50 km apart, and for different seasons. Atmospheric concentrations are arguably greater in a major town than around a small town’s WWTP, so the gradient derived there will be more conservative. Despite these uncertainties, water-based concentrations of neutral PFASs in polyethylene samplers exceeded those in the gas phase for most compounds (Supplemental Data, Table S9), indicating net volatilization. Exceptions were Me- and EtFOSE, for which gradients were not significantly different from equilibrium. In our case, there is strong evidence that most of the investigated PFASs are subject to strong volatilization from the WWTP effluent, which is in line with previous studies in WWTPs using active sampling techniques (Ahren et al. 2011b). This confirms that polyethylene samplers can also be used to derive air–water exchange gradients for neutral PFASs.

### CONCLUSIONS

The present study assessed the use of polyethylene passive samplers as a sampling tool for neutral PFAS precursors in air and water. The results show the potential utility of polyethylene samplers for a wide range of neutral PFASs, including 6:2, 8:2, and 10:2 FTOHs, Me/EtFOSE, Me/EtFOSA, and 8:2 FTACr, which were regularly detected both in a WWTP effluent and in the ambient air of Providence. Although $K_{\text{PEw}}$ ranged only from 3.5 to 5.0, this was sufficient for routine detection of neutral PFASs in WWTP effluent. Equilibration times varied between a few days to a few weeks for a 25-μm polyethylene sampler placed in the effluent. For gas-phase compounds, all targeted neutral PFASs accumulated in the polyethylene samplers; log $K_{\text{PEa}}$ values were approximately 7 to 8 for the FTOHs, and approached 9 for MeFOSA and MeFOSE. Neutral PFASs equilibrated within days to 1 wk with the 25-μm polyethylene sampler. A comparison of polyethylene-based concentrations between WWTP effluent and ambient air implies net volatilization for all compounds. Future work should explore the use of different thicknesses as a tool to verify equilibrium, in addition to classical time-series uptake curves. Now that we have shown that polyethylene can be used as a passive sampler for neutral PFASs, controlled uptake studies, ideally with isotope-labeled PFASs used as PRCs, would help confirm the $K_{\text{PE}}$ values derived in the present study. The results we present imply that polyethylene samplers can be used to detect precursor PFASs in sites with elevated concentrations, but it is unclear whether polyethylene samplers can be used for their detection at background and remote sites. Thicker polyethylene could also be used for gas-phase sampling to accumulate a greater mass of neutral PFASs. As industrial production of PFASs diversifies, it is unclear whether the neutral PFASs targeted in the present study (still) constitute the dominant PFASs in the gas phase. It would thus be interesting to assess what fraction the targeted PFASs represent of total neutral PFASs in the polyethylene samplers.

### Supplemental Data

Additional information on deployments, concentrations, and comparison with neutral gas-phase PFAS concentrations from other sites is provided. The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4264

### Acknowledgment

The present study was partially supported by the National Institute of Environmental Health Sciences (grant P42ES027706). We thank C. McDonough (Colorado School of Mines) for the sampling rate calculations and D. Adelman, R. Miller, and A. Robuck (all University of Rhode Island) for field sampling support. R.L. acknowledges a Fellowship at the Hanse-Wissenschaftskolleg Institute for Advanced Study, Delmenhorst, Germany, for work on the present study.
Data Accessibility—Contact the corresponding author to access the data (rlohrmann@uri.edu).

REFERENCES


