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POLYETHYLENE PASSIVE SAMPLER METHOD DEVELOPMENT FOR
FLUOROTELOMER ALCOHOLS AND OTHER NEUTRAL PERFLUORINATED
ALKYL SUBSTANCES

BY

ERIK R. DIXON-ANDERSON

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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MASTER OF SCIENCE THESIS

OF

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ABSTRACT

Fluorotelomer alcohols (FTOHs) and other poly- and per-fluorinated alkyl substances (PFASs) are common and ubiquitous by-products of various industrial telomerization processes. This class of volatile and semi-volatile compounds has been shown to degrade into a wide variety of perfluorinated carboxylic acids (PFCAs) including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), persistent organic pollutants. Recent atmospheric studies have shown fluorotelomer alcohols and their degradation products present in high concentrations spreading out from point sources in North America, Europe, and Asia. This study developed a method for measuring fluorotelomer alcohols through the use of polyethylene (PE) passive samplers coupled to their analysis via gas chromatography-mass spectrometry (GC/MS). Polyethylene-water partitioning coefficients, $\log K_{PEW}$, were determined in a laboratory study and ranged from $\log K_{PEW}$ 3.2 to 6.7. Field deployment of PE samplers in aqueous systems was conducted in the outflow of a local waste-water treatment plant. Target FTOH, perfluorosulfonamidoethanol (FOSE), and perfluorosulfonamide (FOSA) compounds were detected in all PE samplers above background concentrations. Maximum accumulated amounts from aqueous exposure ranged from 1860 ng per sheet for 6:2 FTOH down to 3.5 ng per sheet for EtFOSE. Polyethylene-air partitioning coefficients, $\log K_{PEA}$, were estimated using a field deployment of PEs directly compared to active sampling. Atmospheric concentrations of targeted PFASs in Providence (RI, USA) varied daily, with the FTOHs found to be most prevalent (average 10.1 – 14.5 pg/m^3). Measured concentrations fall within accepted range of literature values for urban

environments and indicate the effectiveness of PE passive samplers in detecting FTOHs, FOSAs, and FOSEs in atmospheric deployments. This thesis demonstrated PE samplers are effective in ambient aqueous environments for detecting and quantifying FTOHs, FOSAs, and FOSEs above their blank levels. Additional laboratory experiments are necessary to verify estimated PE-water partitioning constants.

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INTRODUCTION

Fluorinated compounds have become ubiquitous 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). These fluorinated compounds are usually composed of a saturated carbon chain with many or all of its hydrogens replaced with fluorine and the terminal carbon ending in various functional groups such as hydroxyls, sulfonates, carboxylic acids, etc. Fluorine is highly electronegative and correspondingly has a high ionization potential and low polarizability (Kissa 1994). When bound to carbon, the large difference in ionization potential results in a strong, highly polarizable bond. The resulting fluorine sheath causes a low-energy surface that is both hydrophilic and lipophilic and consequently repels both oil and water (Lewandowski et al. 2006). As these compounds repel oil and water they reduce the surface tension between the water and another phase surface 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).

Production:

There are two primary synthetic pathways that are used in the industrial production of these fluorochemicals: the Simons Electro-Chemical Fluorination (ECF) process developed by 3M and the telomerization process used by DuPont®. The ECF process involves the fluorination of long carbon chain feedstocks in a stepwise manner (Abe 1999). Theoretically this leads to the formation of every possible partially

fluorinated intermediate compound, and in practice there is a significant amount of byproducts and waste (Sartori & Ignat'ev 1998). These byproducts can be either fully fluorinated or only partially fluorinated with reactive functional groups. The later byproducts of interest include FOSEs, FOSAs, and several other POPs such as PFOS and PFOA (Kissa 1994). The other major industrial synthetic pathway for fluorochemicals involves a controlled polymerization reaction using tetrafluoroethylene (TFE) as the base-polymer unit and an alcohol functional group as the cap. The use of 2-carbon polymer units promotes the formation of linear homologues containing an even-number of carbons (6, 8, 10 etc.) as well as limiting waste byproducts (Schultz et al. 2003). FTOHs and PFOAs are two of the primary fluorinated intermediates created using this process (Lehmler 2005). PFOA, PFOS, FTOHs, FOSEs, and FOSAs are the compounds of interest in this study.

Chemical properties:

PFOS and PFOA have been targeted as persistent organic pollutants (POPs) due to their intrinsic physicochemical properties, their global distribution, and demonstrated adverse effects in wildlife and humans. The unusual strength of the carbon-fluorine bond that provides PFASs with their attractive surfactant properties also makes the molecules' resistant to degradation. The half-lives for PFOS and PFOA in human blood-serum are estimated at approximately 5 years and 3.5 years, respectively (Olsen et al. 2007). Such long half lives, if applicable to other organisms, prolong an organism's exposure times to these compounds and when considering their toxic effects exacerbate their potential to cause harm. Human chronic effects of PFOS and PFOA are poorly characterized,

although it is known that elevated levels of PFOA in infants and children have been associated with vaccine immunosuppression (Grandjean et al. 2012; Granum et al. 2013). In rodents both PFOS and PFOA have been shown to be associated with increased incidences of cancer, decreased body weight, and increased liver weight (Seacat et al. 2003; Kennedy et al. 2010).

Global Distribution:

Elevated PFOS concentrations have been found present in wildlife tissue at polar sites in both the Arctic and in the Antarctic (Giesy & Kannan 2001; Houde et al. 2006; Houde et al. 2011). PFOS has a relatively low vapor pressure and high water solubility compared to other POPs (Giesy & Kannan 2002; Krusic et al. 2005) and would not be expected to be transported long distances via the atmosphere. The high concentrations found at both poles indicate long-range transport is occurring and additional processes contribute to long-range transport. A secondary atmospheric source of PFOS and PFOA is possibly from the degradation of FTOHs and other semi-volatile PFASs such as FOSEs and FOSAs. These parent compounds have been identified as precursors for PFOS and PFOA as well as several other perfluorocarboxylic acids (Wallington et al. 2006; Hurley et al. 2004). Hydroxyl radical attack on these precursors is very slow and atmospheric lifetimes range from 10-20 days for FTOHs of varying carbon length and from 20-50 days for selected FOSAs (Stock et al. 2004; Piekarz et al. 2007). The estimated atmospheric residence time for 8:2 FTOH is greater than 50 days (Wania 2007). A 10-50 day lifetime is sufficient to allow for hemispheric transport to the Arctic from primary source regions.

Further evidence of the long-range transport of the precursor compounds exist. FTOHs and other neutral PFASs have been found all around the world, in both the atmosphere and the surface ocean (Gawor et al. 2014; González-Gaya et al. 2014). Several cruise transects along the Atlantic have reported elevated atmospheric concentrations in the Arctic, along the coast of Europe, off the coast of Brazil, and Antarctica (Dreyer, Langer, et al. 2009; Xie et al. 2013; Wang et al. 2015). These more remote oceanic areas are far downwind of the elevated concentrations found in populated areas near large-scale industrial production of fluorochemicals, such as Toronto or in Northern Europe, where high concentrations of FTOHs have been observed in the atmosphere as well as in indoor environments (Harner et al. 2006; Jahnke, Ahrens, et al. 2007; Barber et al. 2007; Björklund et al. 2009).

The global distribution of PFASs is rapidly changing as the global fluoropolymer industry continues to grow. For more than a half-century the demand for consumer products using fluoropolymer coatings has been continuously rising; global production has increased at ~5% per year. The global budget for FTOHs produced in 2002 was estimated at 5×10^6 kg/yr (Hurley et al. 2004). By 2020, industry experts have predicted that production will approach 4.78×10^7 kg/yr, an order of magnitude growth in less than 20 years (Hexa Research 2015). Much of this growth is centered in developing countries such as China, India, and Brazil where there are abundant raw materials, less-rigorous regulations, and low operating costs (Anon 2015). These increases in localized production, particularly in countries such as China and Brazil have already begun altering global distributions. Recent atmospheric and marine studies that reach poleward of 70° S have shown elevated concentrations of fluorinated compounds off the Antarctic coast

(Dreyer, Weinberg, et al. 2009; Wei et al. 2007; Del Vento et al. 2012). Measured concentrations are lower than those measured in the Arctic, but nonetheless indicate long-range atmospheric transport is taking place in the Southern Hemisphere. Clearly, the long-range transport of the PFOS and PFOA precursors makes volatile PFASs a global concern and their concentrations are worth monitoring

Sampling:

The majority of studies that observe FTOHs and PFASs in the environment utilize active sampling methods. These methods typically require a large amount of sample media to be collected (e.g. air, water, sediment, etc.) to quantify the low environmental concentrations that are found. For active sampling of air or water, a large volume of media is pulled through a filter and adsorbent on which the POPs collect over time. The instrumentation associated with 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 in order to measure many POPs in the environment (Jahnke et al. 2007; Harner et al. 2006; Lohmann et al. 2012). These techniques include sorbent-impregnated polyurethane discs, solid-phase extraction cartridges, activated carbon felts, and polyethylene sheets (PE). PEs have not yet been applied to monitoring FTOHs and other neutral PFASs, which so far are typically collected using high-volume air samplers (Ahrens et al. 2011; Jahnke, Huber, et al. 2007; Liu et al. 2013).

PE sampling devices are polymer matrices that rely on the accumulation of hydrophobic contaminants through passive diffusive processes. Due to its reliance on

diffusion, PE samplers inherently select only for gaseous compounds in the air and freely dissolved compounds in the water (Adams et al. 2007). In comparison to many active and passive methods, PE sheets have advantages in minimal intermolecular and environmental interactions, low cost, and the ease of handling and usage (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 & Lohmann 2008; McDonough et al. 2014; Khairy et al. 2014).

Statement of Problem:

The overarching goal for this research was the validation and field-testing PE as a novel sampling techniques for the monitoring of neutral PFASs. Several of the guiding questions included:

1. Can PE passive samplers collect and more importantly quantitatively collect PFASs in the water and air?
2. How do the predicted physicochemical partitioning properties between PE-water and PE-air of PFASs contrast with observed values?
3. Are PEs an effective method for measuring PFASs in the natural environment?

A comprehensive method for monitoring PFASs was developed for utilizing PE passive samplers.

MATERIALS AND METHODS

Overview:

This research was composed of laboratory experiments, as well as, field experiments in which air and water samples were analyzed. Laboratory uptake experiments consisted of immersing polyethylene (PE) passive samplers in aqueous solutions spiked with known concentrations of neutral PFASs. After equilibration, concentrations were determined and used to calculate water-polyethylene partitioning coefficients (K_{PEW}). These experimental K_{PEW} values were then compared to theoretical values calculated using polyparametric linear free-energy relationships (pp-LFERs). Field validation studies for the use of PE samplers to detect PFASs were conducted at two locations in two different media, air and water.

Target Compounds:

The broad categorization of compounds investigated in this study are neutral PFASs, with several subclasses of compounds including fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAcres), sulfonamidoethanols (FOSEs) and sulfonamides (FOSAs). A total of 9 compounds were analyzed, ranging in molecular weight from 364 g/mol to 619 g/mol (Table 1). Mass-labeled surrogates for the FTOHs and several of the FOSEs and FOSAs were utilized in this experiment as surrogate standards as well as d14 p-terphenyl for the injection reference recovery standard (Table 2). Standards for the compounds and their mass-labeled counterparts were purchased from Wellington Labs and were used as purchased. (Guelph, Ontario, Canada)

Quality Control:

For quality assurance and control, mass-labeled performance reference standards were added to each sample prior to extraction to allow for recovery calculations. A master solution containing solely the surrogates was mixed at 1000 ng/ml in 8:2:1 Hexane:DCM:Methanol, of which 25 μ l were added prior to each sample extraction. Furthermore, d14 p-terphenyl (40 ng) was added to the extracts after processing as an injection standard. A 5-point standard calibration curve for the native compounds and surrogate compounds was created and analyzed prior to the analysis of the samples (Appendices 1 - 4). The response factors for analytes and their mass-labeled surrogates were derived from said curve.

6:2 FTOH M4 was the mass-labeled surrogate standard used for 6:2 FTOH, 8:2 FTOH M4 was used to determine the concentrations for 8:2 FTOH, and 10:2 FTOH M4 was the compound used for 10:2 FTOH. All of the FTOH mass-labeled surrogates have 4 deuterated hydrogen atoms relative to their analyte compounds and behave in a similar manner. The mass-labeled surrogate used for MeFOSA and EtFOSA determination was MeFOSA d3 while the surrogate used for MeFOSE and EtFOSE was MeFOSE d7. These two mass-labeled surrogates have 3 and 7 deuterated hydrogens respectively in relation to their analyte compounds. In all cases, a known amount of each surrogate compound (25 ng) was added to each sample prior to the concentration step. The recovered concentrations of the surrogate compounds were used for the calculation of the recoveries listed in Appendices 6, 8, 10, 12, 14, 16, 18, 20. All calculated concentrations are corrected for recoveries when a relative response method is used. Recoveries of the surrogate standards were calculated relative to the injection standard. The recoveries for

6:2 FTOH M4, 8:2 FTOH M4, and 10:2 FTOH M4 were 65.1 +/- 19.3, 81.5 +/- 25.4, and 98.7 +/- 27.4 percent respectively. While the recoveries for MeFOSA d3 and MeFOSE d7 were 91.5 +/- 32.4 and 126.9 +/- 30.1 percent respectively.

Detection Limits:

Each experimental portion had blanks associated with it along with instrumental blanks. Blank values for the PE samplers were of the same order of magnitude across the laboratory experiment, the Providence air campaign and the Wastewater Treatment Plant (WWTP) campaign. 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH laboratory blank concentrations averaged 0.052 +/- 0.041 ng/g PE, 0.21 +/- 0.10 ng/g PE, and 0.44 +/- 0.14 ng/g PE respectively. The PE blank concentrations for MeFOSA, EtFOSA, MeFOSE and EtFOSE were slightly higher and averaged 1.59 +/- 0.35 ng/g PE, 1.23 +/- 0.17 ng/g PE, 4.75 +/- 0.95 ng/g PE, and 4.35 +/- 1.29 ng/g PE respectively (Appendices 5, 7, 11). The PUF/XAD blanks used in the Providence air campaign had average concentrations of 8.0 +/- 1.3 pg/g PE for 6:2 FTOH, 8.3 +/- 0.71 pg/g PE for 8:2 FTOH, and 12.6 +/- 2.4 pg/g PE for 10:2 FTOH. MeFOSA, EtFOSA, MeFOSE, and EtFOSE PUF/XAD concentrations averaged 21.5 +/- 0.8 pg/g PE, 14.4 +/- 0.7 pg/g PE, 12.8 +/- 2.7 pg/g PE, and 14.9 +/- 0.7 pg/g PE respectively (Appendix 9). The results reported are blank corrected and the concentrations of the target analytes exceeded their respective blank value by at least 2 orders of magnitude. Detection limits were calculated using the instrumental and laboratory blanks and are 3 standard deviations of the mean blank values. Detection limits for 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH for PE samplers are as

follows: 0.13 ng/g PE, 0.29 ng/g PE, and 0.43 ng/g PE. Calculated detection limits for MeFOSA, EtFOSA, MeFOSE, and EtFOSE are slightly higher and are 1.04 ng/g PE, 0.52 ng/g PE, 2.84 ng/g PE, and 3.89 ng/g PE respectively.

Instrument Analysis:

All samples were analyzed using gas chromatography/mass spectrometry (GC/MS) on an Agilent 7890B chromatograph coupled with an Agilent 5977A MSD operating in positive chemical ionization (PCI) mode using selected-ion-monitoring (SIM). The ion source was held at 300 °C while 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 from the method outlined by Xie et al. 2013 and optimized for decreased 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 minutes, -10 °C/min to 270 °C hold for 10 minutes, -120 °C/min to 50 °C.

Polyethylene Passive Samplers:

The passive samplers used in this research consisted of low-density polyethylene (PE), 25 µm (1 mil) in thickness (Figure 1). The PE was manufactured by a commercial sheeting company (Covalence Plastics, IN., Minneapolis, MN, USA). PE samplers underwent a cleaning process which was comprised of 4 sequential extractions using acetone, dichloromethane, and hexane for a period of 24 hours per solvent.

Sample processing and analysis took place in a clean lab at the University of Rhode Island. All glassware used was rinsed with acetone, hexane, and DCM (~10 mL each) and baked for at least 8 hours at 450 °C. All samples were spiked with 25 µL of a 50 ng/mL mass-labeled surrogate reference standard solution containing 6:2 FTOH (M+4), 8:2 FTOH (M+4), 10:2 FTOH (M+4), MeFOSE D7, and MeFOSA D3 prior to processing. This solution mix was created using individual reference standards. PEs were extracted in individual 60 mL amber vials using ~55 mL of Hexane for 24 hours (Figure 3). Extracts were concentrated using a Rotovap under a mild nitrogen stream to ~200 µL. After which, 10 µL of a 100 ng/mL d14 p-terphenyl was added as an injection standard.

PUF/XAD Sandwiches:

PUF/XAD sandwiches were prepared using precleaned XAD and PUF materials, a modified Soxhlet extraction thimble, and precleaned aluminum foil. XAD polymeric beads, purchased from Sigma Aldrich, were precleaned using subsequent 24 hours extractions using acetone, dichloromethane, hexane, and methanol respectively. The PUFs used to create the sandwiches were cleaned in a high-temperature pressurized automated solvent extraction system using multiple rinses of hexane and dichloromethane. Soxhlet extraction thimble were modified by removing the bottom portion. Each sandwich was prepared by: 1) A single PUF was wedged in the bottom, 2) 25 grams of XAD was poured in over the first PUF, and 3) a second PUF was placed in the top of the extraction thimble sealing in the XAD (Figure 2). Assembled PUF/XAD sandwiches were then wrapped in muffled aluminum foil and stored in a refrigerator until deployment.

PUF/XAD sandwiches were extracted in precleaned and muffled Soxhlet extraction apparatuses assembled in series using ~150 mL of hexane. Prior to extraction, each sample was spiked with 25 μ L of a 50 ng/mL mass-labeled surrogate reference standard solution. After 24 hours, hexane extracts were concentrated down to ~200 μ L in a Rotovap under a mild nitrogen stream. Concentrated extracts were then spiked with 10 μ L of a 100 ng/mL d14 p-terphenyl solution as an injection standard and placed in -10 °C freezer until instrument analysis.

K_{PEW} Determination:

The PE sheets were cut into 50x50 mm sections, each weighing ~ 0.05 g. A standard aqueous solution containing the compounds of interest at a known concentration of 100 ng/ml was prepared for laboratory experiments. PE samplers were placed in 40 mL amber glass vials that had been precleaned, baked, and then immersed in the aqueous solution containing the target PFASs. The vials were wrapped in aluminum foil to prevent chemical alteration of the spiked analyte mixture by UV radiation and then placed on a shaker table rotating at 120 RPM (Figure 4). PE sheets were immersed for increasing amounts of time; effectively doubling from 1 to 64 days: the first sampler was deployed for 1 day, the second sampler for 2 days, the third for four, the fourth for eight, the fifth for sixteen, the sixth for the 32, and the seventh for 64. PE's were deployed in triplicate for each time point, e.g. there were 3 PE's deployed for 1 day, 3 PE's deployed for 2 days etc. Every PE was isolated in a separate vial. In addition, each time point had a blank PE deployed in pure water for the duration. Extraction and cleanup procedures for

the method blanks followed the same manner as the sample PE's. Recoveries for instrument and method blanks are listed in Appendices 5 & 6.

Aqueous concentrations for each vial were analyzed at the end of the laboratory experiment. PFASs were extracted from the water onto Oasis WAX solid-phase microextraction cartridges (SPME) on a vacuum manifold (Figure 5). Prior to use, each cartridge was conditioned using 5 mL 0.3% NH_4OH in MeOH followed by 5 mL of 0.1M formic acid in water and equilibrated with 5 mL of plasma-grade reagent water. After the sample was passed through the cartridge, the SPME fibers were washed with 5 mL of 20% MeOH in 80% 0.1M formic acid in reagent water followed by 2 mL of 0.3% (v/v) NH_4OH in water. Cartridges were dried for 15 minutes and then eluted in clean centrifuge tubes using 3, 15 mL hexane rinses. The 3 hexane rinse extracts were combined and then blown down to ~100 μL under a gentle nitrogen stream. The concentrated hexane extracts were then transferred into GC/MS autosampler vials and the injection standard was added.

Field Validation-Aqueous Deployment:

A field validation test for the aqueous deployment of PE was completed in September of 2016 at the South Kingston Waste Water Treatment Plant (WWTP), Narragansett, RI, USA (Figure 6). PE passive samplers were submerged in the effluent outflow of the WWTP (Figure 7). The deployments began after the beginning of the University of Rhode Island fall term, to avoid a changing population between summer vacationers and returning students. No sudden change of population was expected during the course of the field experiments. The deployment period for these PE sheets was in

increasing time increments (1, 2, 4, 7, 14, and 21 days) and at the end of each time increment 3 sheets were collected. Additionally, each deployment period had a blank PE associated with it that was brought to the sampling site and was handled in a similar manner. Concentrations and recoveries for these field blanks are given in Appendices 7 & 8. Effluent outflow water was also sampled using an actively pumped PUF system. This was operated throughout the entirety of the experiment and the PUF collection samplers were changed daily. Significant bio-fouling was observed on all PE sheets deployed longer than 4 days (Figure 8). Prior to extraction, each PE sheet was wiped down with Kimwipes to remove the bio-foul layer.

Airside Deployment:

A field test comparing the relative efficiency of active versus passive air sampling using PE samplers was run in East Providence, RI USA in the spring of 2016. The sampling site is an active monitoring site for the RI Department of Environmental Management in East Providence (Figure 9). A high-volume air sampler was deployed on the roof of a 7-story building (Figure 10). This active air sampling used PUF/XAD sandwiches to collect targets PFASs. Continuous PUF/XAD samples were collected every 48 hours over the course of the 32-day experiment. In addition to the active samples, several PUF/XAD sandwiches were designated field blanks and were handled in a similar manner to the active samples. Concentrations and recoveries for these field blanks are listed in Appendices 9 & 10. Passive PE air samplers were co-located and deployed on top of the roof at a height of 3 meters. Each passive sampler consisted of a PE sheet mounted between precleaned stainless steel protective bowls (Figure 11).

Passive PE sheets were deployed for 2, 4, 8, 16 and 32 days. Each deployment period also had a field blank; concentrations and recoveries for these blanks are given in Appendices 11 & 12. Passively and actively collected sample media were wrapped individually in muffled aluminum foil 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.

Calculations:

Accurate predictions for the fate and transport of PFASs in the environment across multiple media rely on experimentally derived physiochemical constants including vapor pressure, aqueous solubility, as well as partitioning constants between air/water, water/octanol, and air/octanol. When experimental partitioning coefficients are not available, semi-empirical estimates can be used to approximate these constants, such as polyparametric linear free energy relationships (PP-LFERs). PP-LFERs provide a robust and accurate method for predicting equilibrium partitioning coefficients for organic contaminants (Goss and Schwarzenbach 2000; Abraham et al. 2004; Schwarzenbach et al. 2005). PP-LFERs are a series of multiple linear regression models that utilize solute and system descriptors to describe partition and sorption properties that takes into account solute-system interactions. The PP-LFER used in the prediction of hexadecane-water and hexadecane-air is as follows

$$\log K = c + aA + bB + vV + eE + sS \quad (1)$$

Where $\log k$ is the logarithmic partition coefficient. Capital letters are solute descriptors: A, solute H-bond acidity; B, solute H-bond basicity; V, McGowan's molar volume with units of (cm³/mol); E, excess molar refraction; S, polarizability/dipolarity parameter. The lower letters are fitting coefficients, or system parameters, and were determined through multiple linear regression analysis against experimental partition coefficients (Endo & Goss 2014).

The passive uptake of a water or air contaminant by the PE sheets is a well characterized phenomenon, e.g. Lohmann et al., 2012 (Figure 12). The general form of the equation is valid for linear, curvilinear, and equilibrium stages. PE sampler operation is best when operated in either the linear or equilibrium stages described below. During an initial linear uptake stage, the amount of pollutant absorbed (N_s) is directly proportional to the sampling rate (R_s), exposure time (t), and the concentration (C_t).

$$N_s = \int_{t_{start}}^{t_{stop}} R_t C_t dt \quad (2)$$

If C_t is a constant concentration over time, then equation 2 reduces to equation 3

$$N_s = C_t R_s t \quad (3)$$

(Vrana et al. 2001; Bartkow et al. 2005) As the exposure time increases with constant concentration, the sampler approaches an equilibrium uptake stage and the amount absorbed can be represented by the product of PE-water or PE-air partitioning coefficient (K_{pew} or K_{pea}) -times- the air or aqueous concentration -times- the mass of the sampler (m_s) (4)

$$N_s = C_w K_{pew} m_s \text{ or } = C_a K_{pea} m_s \quad (4)$$

Equations 2 and 3 are the two specialized forms of the general uptake equation and specifically describe the end-member conditions for passive sampler deployment times, $t=0$ and $t=\infty$. The uptake stage is dependent on the K_{pew} or K_{pea} and environmental mass transfer coefficients. An objective during the field deployment was to determine the uptake stage of FTOHs, FOSAs, and FOSEs. In order to calculate non-endmember conditions, equation 2 expands into equation 5.

$$N_s = C_t K_{pew} m_s \left[1 - \exp\left(-\frac{R_s t}{K_{pew} m_s}\right) \right] \quad (5)$$

Equation 5 applies to PE-water partitioning while replacing K_{pew} with K_{pea} allows the equation to apply to PE-air partitioning. Combining and rearranging equations 4 and 5 in order to isolate the sampling volume (V_c) allows for the calculation of said value in equation 6.

$$C_t K_{pew} m_s \left[1 - \exp\left(-\frac{R_s t}{K_{pew} m_s}\right) \right] = C_w V_c \quad (6)$$

Sample Concentrations

A series of calibration curves were generated for the response of each compound, surrogate compound, and injection standard (Appendices 1, 2, 3, and 4). The response factor for each compound and surrogate compound at each standard concentration was calculated by the division of the response area (A) by the concentration of the compound (C), equation 7. The response factors for each compound and surrogate compound at the various concentration levels were averaged to calculate the average response factor, which is referred to henceforth as the response factor (RF).

$$RF = \frac{A}{C} \quad (7)$$

The relative response factor (RRF) was calculated for each surrogate compound using the response area of the surrogate compounds (A_{sc}), the response area of the injection standard (A_{IS}), the concentration of the surrogate compound (C_s), and the concentration of the injection standard (C_{IS}) at 4 different concentration levels, equation 8; which were then averaged to generate the relative response factor (RRF) used for calculation.

$$RRF = \frac{(A_{IS} * C_s)}{(A_s * C_{IS})} \quad (8)$$

For samples, the compound concentrations (C_x) were calculated using the response area of the surrogate compounds (A_s), the response area of the surrogate standard (A_S), the concentration of the surrogate standard (C_S), and the relative response factor (RRF), equation 9.

$$C_x = \frac{(C_S * A_x)}{(RRF * A_S)} \quad (9)$$

RESULTS AND DISCUSSION

Providence Air Campaign:

Fluorotelomer alcohols were detected at low concentrations, 0.10 – 0.54 ng/g PE, on the PE passive samplers over the course of the Providence air sampling experiment. The PE observations are reported as mass of analyte per unit mass of PE sheet (a mass mixing ratio), as this is a fundamental measurement provided by this method. For all three compounds the concentration remained relatively constant during the respective deployment times (Figure 13). Initial PE exposure began at 12:00 on April 7th, 2016 and the end of the PE exposure on day 32 was at 12:00 on May 9th, 2016. 10:2 FTOH was found in higher concentrations, 0.36 – 0.88 ng/g PE, than 6:2 or 8:2 FTOH, but all compounds were below 1 ng/g PE. Several of the compounds, EtFOSA and MeFOSE, were also found at trace levels, 0.06 – 0.28 ng/g PE and 0.71 – 2.02 ng/g PE respectively (Figure 14). In comparison, the fluorotelomer acrylates were found in concentrations an order of magnitude larger, ranging from n.d. – 52.9 ng/g PE for 8:2 FTAcr and 1.83 – 29.8 ng/g PE for 10:2 FTAcr (Figure 15). There appears to be a gradual decrease in concentration over time for both FTAcrs, with a distinct minimum concentration at the end of the experiment. EtFOSE concentrations were found to range from 0.92 – 22.7 ng/g PE and follow a similar trend to the FTAcrs; there is a distinct drop in concentration between the beginning and the ending samples (Figure 16). The compound found in the highest concentration in every sample was MeFOSA and ranged from 6.8 – 451 ng/g PE. There does not appear to be any significant changes in the concentration, as the averaged concentrations range between 50 and 200 ng/g PE (Figure 17). On each of the days 16

and 32, a single aberrant no detect for MeFOSA led to increased standard deviations on those days.

Atmospheric air sampling using the PUF/XAD sandwiches at the Providence site exhibited different trends across the sampling period than what was found in the PE passive samplers. The first PUF/XAD samples started at 12:00 on April 7th, 2016, and the final PUF/XAD sample ended at 12:00 on April 29th, 2018. One factor that added to this discrepancy is the difference between sampling and resolution times; the resolution time for the PUF/XAD samplers was discrete 96 hour intervals while the PE samplers were deployed and concentrations were moving towards equilibrium across the entire 30 day sampling period. The range of FTOH concentrations detected was 5.9 – 27.7 pg/m³ for 6:2 FTOH, 1.60 – 31.2 pg/m³ for 8:2 FTOH, and 0.36 – 20.7 pg/m³ for 10:2 FTOH. The PUF/XAD measurements are reported as mass of analyte per unit volume of air sampled, or mass concentration, as this is the fundamental measurement provided by this method. The variation of FTOH concentrations lie within an order of magnitude across the experiment, but they all present minimum values during the middle of the April 2018 on day 16, and increased values at the beginning and end (Figure 18). The ratio of 6:2 – 8:2 – 10:2 remains relatively constant with the exception during sampling period 4/20 – 4/22, indicating no significant changes in atmospheric concentrations or source inputs within twice a single sample's collection time. The aberrant low concentrations found during this sampling period reflect the low recoveries of the mass-labeled 8:2 and 10:2 FTOH compounds used as the surrogate standards while a normal recovery of the 6:2 FTOH surrogate standard led to its relatively high value. Daily concentrations for 8:2 FTAc and 10:2 FTAc were barely above detection limit and were 2 orders of magnitude

lower than those concentrations found for the FTOHs (Figure 19). The 8:2 and 10:2 FTAc_r atmospheric concentrations remain relatively constant and exhibit similar trends over the course of the sampling period. Atmospheric concentrations of MeFO_SA, EtFO_SE, and MeFO_SE were well above detection limits and remained consistent across the sampling period (Figure 20). EtFO_SA was found barely above detection limits at concentrations of a similar magnitude to the FTAc_rs.

These concentrations provide accurate depictions of the atmospheric concentrations across the sampling period in discrete time intervals. The resolution time for PE equilibration is unknown, but is longer than the 48 or 96 hour resolution provided by the PUF/XAD samples. Therefore, in order to compare the PE samples to the PUF/XAD samples a weighted time-averaging of the PUF/XAD sample concentrations were used in order to flatten out small daily fluctuations. PUF/XAD measurements were then smoothed using a moving average over the course of the sampling period. The time-averaged atmospheric concentrations for FTOHs are very consistent and approach 11.7 pg/m³ for 6:2 FTOH, 14.5 pg/m³ for 8:2 FTOH and 10.0 pg/m³ for 10:2 FTOH (Figure 21). The FTAc_r concentrations appear to be increasing slightly over the course of the month, approaching 0.11 pg/m³ and 0.15 pg/m³ for 8:2 and 10:2 FTAc_r respectively (Figure 22). Of the FO_SEs and FO_SAs, MeFO_SE was found at the greatest concentration and decreases over the course of the month (Figure 23). In both cases of FO_SAs and FO_SEs, the methylated compound was found in higher concentrations than the ethylated congener, i.e. MeFO_SA concentrations were greater than EtFO_SA and the same is true for the FO_SEs.

The experimental K_{PEA} partitioning constants for the compounds of interest were calculated using the measured PUF/XAD concentrations and the measured PE concentrations. It was assumed that the PUF/XAD concentrations accurately reflected atmospheric concentrations with no significant losses of degradation. PE concentrations for each sampling period were extrapolated from the linear fitting of the measured concentrations. There were two sets of calculations performed to generate the K_{PEA} constants; the first of which utilized the daily averages of the PUF/XAD concentrations, while the second utilized the time-weighted averages of the PUF/XAD concentrations. The first set of K_{PEA} values increase over the course of the sampling period, as the PE samplers approached equilibrium, but the internal variability is larger. In comparison, the time-weighted calculations dampen out daily variability in atmospheric concentrations and provide more consistent experimental values across the entire experiment.

The atmospheric concentrations found in East Providence for FTOHs using active sampling methods are of the same order of magnitude or within one order of magnitude as found in several other urban studies (Table 4). The relationship between the various FTOHs, 6:2 : 8:2 : 10:2, differs in this study compared to others. In Providence the concentrations of all three FTOHs targeted are very similar, while in Shoieb et al. 2004, Jahnke et al. 2007, Barber et al. 2007, and the Oono et al. 2008 the 8:2 FTOH is significantly more prevalent. 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 8:2 FTOH was the primary precursor used in the production of and a major degradation product of PFOS and PFOA, environmental concentrations of 8:2 FTOH are expected to have dropped and to continue dropping as

the input of C-8 fluorocarbons into the environment dropped and continues to decrease. The production method of fluoropolymers has changed since 2009 with increased use of other non-regulated 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 this study and those of Wang et al. 2014 and Ahrens et al. 2011.

FOSE and FOSA atmospheric concentrations are low when compared to several of the earlier studies, but are of a similar order of magnitude to the more recent study of Wang et al. 2014. These other studies utilized active-sampling methods and the relative concentrations indicate the efficacy of the PE samplers as a monitoring tool in urban, more polluted sites. In more pristine environments the higher detection limit of PE samplers in comparison to active-sampling methods makes them less effective as a tool. Atmospheric concentrations of PFASs in Providence were detectable by both active and passive sampling methods. As these compounds are completely anthropogenic in nature, any measured atmospheric concentrations are above pristine levels. It is unclear how important this exposure is for residents, compared to other exposure pathways to (volatile) PFASs.

K_{PEW} Estimation:

For many of the partitioning experiments, equilibrium was not reached. The shortest and lightest of compounds in the study, 6:2 FTOH, was found to reach equilibrium the fastest (Figure 24). While there is some variation present and a slight maximum at day 24, the variation lies within the standard deviation. We infer from our data that 6:2 FTOH reached equilibrium within the PE. The K_{PEW} of 6:2 FTOH was calculated using the average concentration of the final two deployments. The other fluorotelomer alcohols, 8:2 and 10:2, did not reach equilibrium over the course of the 32-day deployment (Figures 25 & 26). 8:2 FTAcA appeared to have an uptake rate comparable to 6:2 FTOH and reached equilibrium by the end of the experiment (Figure 27). The heavier 10:2 FTAcA had a much slower uptake rate, similar to 8:2 and 10:2 FTOH and equilibrium was not achieved (Figure 28).

The uptake rates and overall diffusion of the sulfonamides into the PE was very high. MeFOSA reached an equilibrium state by day 24, with consistent concentrations for the final two sampling deployments (Figure 29). The large variability present on the days 24 and 32 are both due to a single low point on each day where the surrogate recovery was high, but the low number of samples restricts the statistical power required to declare these outliers. EtFOSA experienced very linear uptake over 24 days, with a single anomalous surrogate recovery on day 16 (Figure 30). The inclusion of the final day's concentrations skew the linear fit and were excluded for the linear sampling rate calculation. It was then assumed that the final deployment was considered to have reached equilibrium. EtFOSE and MeFOSE both experienced high variability on days 16 and 24 (Figures 31 & 32). As both compounds use d7-MeFOSE as the surrogate for their

calculations, the large variation in its recovery on these deployment days led to this high variability.

All compounds except for 8:2 FTOH, 10:2 FTOH, and 10:2 FTAcr appeared to reach equilibrium over the course of the 32-day experiment. For these 3 compounds the linear fitting was best when including all data points, indicating that equilibrium was not reached for these compounds. In the absence of other data, we have used these concentrations as the equilibrium concentrations with the understanding that subsequent calculated values represent lower limit concentrations. Lower limit data has value when the alternative is no data.

The water used as the solvent system was then tested in several different manners in order to hopefully ascertain the ending aqueous concentrations. The first method that was employed was a liquid-liquid extraction in the manner of van Leeuwen using a 50:50 hexane:DCM mixture (van Leeuwen & de Boer 2007). The small amount of water used in each sample, ~40 mL, was not conducive to the extraction procedure, leading to low recoveries of the surrogate standards for the test samples. Another attempt was made to determine the ending aqueous concentrations using a solid-phase extraction (SPE) with Oasis WAX cartridges, as described elsewhere (Taniyasu et al. 2005). These extractions were also unsuccessful; higher recoveries were found than in the liquid-liquid extraction attempt, but were too low for accurate calculation of the aqueous concentrations. Due to the difficulties in establishing the ending concentrations, the aqueous concentrations used for the determination of the partitioning constants were simply subtracted from the initial added amount. A major flaw with this method of calculation is that it does not take into

account the degradation or loss of any of the compounds. Due to the volatile nature of these compounds it is likely that some losses would occur.

A comparison between the PP-LFER predicted $\log K_{\text{pew}}$ values and the laboratory experimental values indicate different trends for the FTOHs and the FOSAs/FOSEs (Figure 33). In this comparison, compounds lying along or near the 1:1 ratio exhibit environmental partitioning behavior that correlates with predicted behavior. In this experiment MeFOSA, EtFOSA, MeFOSE, EtFOSE, and 8:2 FTOH lie near the 1:1 ratio and thus for these compounds the predictive PP-LFER calculations appear accurate. The physico-chemical property values used for the PP-LFER calculation for these five compounds can be used in future estimations of partitioning coefficients between other media than hexadecane, water, and air. However, the 6:2 and 10:2 FTOHs predicted PP-LFER values and laboratory K_{PEWS} are only within a factor of 3 of each. It is unknown whether experimental problems such as low recoveries and degradation caused this disagreement, or that their K_{PEWS} are poorly represented using the PP-LFER model. Additional experimentation is needed to corroborate experimental PP-LFER physico-chemical property values with observed partitioning behavior.

WWTP Field Validation:

All of the compounds of interest except 10:2 FTAc were detected in the PE passive samplers regardless of their deployment length. The compound found in the highest concentration throughout the experiment was MeFOSA, with the PEs picking up an average of 140 ng/g PE (Figure 34). The fluorotelomer alcohols were found in increasing concentrations over the course of the experiment. 8:2 FTOH concentrations remained relatively constant and at similar concentrations as the 6:2 FTOH (Figure 35 & 36). The uptake for 10:2 FTOH follows the idealized uptake curve quite well and an apparent equilibrium is reached (Figure 37). Of the FTAc, only the 8:2 FTAc was found present in any concentration in the WWTP effluent. The uptake of 8:2 FTAc does not appear linear, however 1 exceedingly large concentration within deployments 7 and 14 is the cause for this large variation (Figure 38). When the two outliers are removed the uptake becomes linear and an equilibrium concentration can be extrapolated. Present in slightly higher concentrations, EtFOSA was found to range from 4.2 – 15.9 ng/g PE (Figure 39). MeFOSE concentrations were barely above the detection limit and were consistently below 1.5 ng/g PE (Figure 40). Slightly higher in concentration, EtFOSE was found to reach an equilibrium over the course of the sampling period at 3 ng/g PE (Figure 41).

The corresponding active water sampling of the WWTP filtered between 16 and 20 L of effluent each day through 2 PUFs. The laboratory extraction of the PUFs encountered difficulties when the PUFs retained some water. This led to water still being present in conjunction with the extraction solvent. Samples were run through a silica gel column in an attempt to remove the water present. The samples were then blown down in

the manner of (McDonough et al. 2014) and analyzed. Low surrogate recoveries were present in all samples as well as high background noise, leading to no detects for all of the compounds in every sample. An inspection of the injection port seals after the runs had been completed revealed a large amount of residue indicative of large amounts of particulates and other contaminants. This is further shown in the high background noise which, despite running in SIM mode using the target and primary ion for identification, picks up any compound which splits into these ions; there are no discernable or discrete peaks. Due to the concentration step of the extraction process, the low sample volume present is not able to undergo further cleaning procedures. Additional sample cleaning and preparation to remove other contaminants present in the water are necessary to establish accurate environmental concentrations in the future.

Despite the fact that the concentrations found in the active water sampling were flawed due to contaminant overload, the PE samplers picked up a majority of the target compounds in concentrations well exceeding blank values in the WWTP effluent. The estimate of the aqueous concentrations was calculated using both the estimated PP-LFER value and the experimental laboratory value in order to convey the range of possible concentrations (Table 6). Aqueous concentrations for the FOSAs and FOSEs for both estimates were within an order of magnitude of each other due to the similarity of K_{PEW} values. As such, these aqueous concentrations are believed to accurately reflect environmental concentrations. The PP-LFER and experimental values have differing relationships for the fluorotelomer alcohols; the estimated K_{PEW} for 10:2 FTOH is several orders of magnitude lower than the experimental value while the reverse is true for the 6:2 FTOH. The observed concentrations in the PE samplers from the WWTP for 10:2

FTOH indicate elevated concentrations on the order of magnitude similar to EtFOSA and MeFOSA.

There are only a few studies that have reported values for FTOH concentrations in WWTP water effluent (Table 7). 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 what would be expected in a sewage and WWTP. In an order of magnitude lower, Mahmoud et al. 2009 reported aqueous concentrations similar to what was found in this study. Several studies attempted to measure the concentrations of MeFOSA and EtFOSA in WWTP effluent, but in all cases the compounds registered below the detection limit (Arvaniti et al. 2012; Stasinakis et al. 2013; Ma & Shih 2010). This study is the first to report detectable aqueous concentrations of MeFOSA, EtFOSA, MeFOSE, and EtFOSE in WWTP outflow.

CONCLUSIONS

As an aqueous sampling tool, PE samplers can detect 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, EtFOSA, MeFOSA, EtFOSE, and MeFOSE in both a laboratory and field setting. The laboratory experiments to determine the PE-water partitioning constants were completed under high concentrations using small amounts of PE sampler and provided a high end estimate of the K_{PEW} . In order to attain a better estimate for the K_{PEW} additional experiment should be completed. These experiments should lower the concentrations of each compound present in the solution medium, increase the individual solution volume, and use larger PE samplers. Proposed changes would reflect the lower environmental concentrations likely to be encountered. The field validation of the PE at the WWTP was successful in detecting all of the target compounds except for the FTAcres. This study is the first to report the detection of FTOHs, FOSAs, and FOSEs in WWTP effluent using passive sampling methods. The elevated concentrations of FTOHs indicate that the WWTP effluent is a potential point source for the volatilization of these compounds. Future experiments at WWTPs should include atmospheric samplers deployed in conjunction with the aqueous samplers. Aqueous active-sampling should also be completed, with stricter and more rigorous cleaning procedures put into place prior to GC/MS analysis. As a sampling tool for PFASs, PE samplers can be used for monitoring and detection purposes in most areas. In urban and more polluted areas, PE samplers can be deployed to take air measurements with greater efficiency and accuracy.

TABLES

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

Name	Abbreviation	Molecular Weight (g/mol)
6:2 Fluorotelomer alcohol	6:2 FTOH	364.1
8:2 Fluorotelomer alcohol	8:2 FTOH	464.12
10:2 Fluorotelomer alcohol	10:2 FTOH	564.13
<i>N</i> -methyl perfluorooctane sulfonamide	MeFOSA	513.17
<i>N</i> -ethyl perfluorooctane sulfonamide	EtFOSA	527.2
<i>N</i> -methyl perfluorooctane sulfonamidoethanol	MeFOSE	557.22
<i>N</i> -ethyl perfluorooctane sulfonamidoethanol	EtFOSE	571.25
8:2 Fluorotelomer acrylate	8:2 FTAc	518.17
10:2 Fluorotelomer acrylate	10:2 FTAc	618.19

Table 2. Mass-labeled surrogates and injection standard used in this study with corresponding molecular weights

Mass-labeled Surrogate	Molecular Weight (g/mol)
6:2 FTOH (M+4)	368.1
8:2 FTOH (M+4)	468.1
10:2 FTOH (M+4)	568.1
d3 MeFOSA	516.1
d7 MeFOSE	560.2
Injection Standard	Molecular Weight (g/mol)
d14 p-terphenyl	244

Table 3. Atmospheric concentrations measured at Providence sampling site using PUF/XAD and active sampling techniques

Compound	Atmospheric Concentration (pg/m ³)									
	4/11/2016	4/13/2016	4/15/2016	4/18/2016	4/20/2016	4/25/2016	4/27/2016	4/29/2016		
6:2 FTOH	10.2	27.7	11.9	9.8	12.4	5.9	9.9	6.2		
8:2 FTOH	15.4	20.0	12.7	31.2	1.6	5.0	13.2	16.9		
10:2 FTOH	8.7	12.0	8.6	20.7	0.4	4.2	13.1	13.0		
8:2 FTAc	0.07	0.09	0.08	0.12	0.18	0.091	0.078	0.19		
10:2 FTAc	0.07	0.08	0.16	0.18	0.14	0.15	0.20	0.23		
EtFOSA	0.18	0.13	0.30	0.06	0.19	0.06	0.17	0.12		
MeFOSA	0.59	0.35	0.68	0.71	0.57	0.42	2.05	1.36		
EtFOSE	2.2	1.03	1.07	1.62	1.42	0.66	1.30	0.88		
MeFOSE	3.27	4.34	2.87	1.75	2.27	1.27	0.91	2.00		

Table 4. Average atmospheric concentrations (pg/m³) of PFASs at various urban sites, range given in parentheses

Sampling Location	Toronto, Canada	Toronto, Canada	Hamburg, Germany	Manchester, UK	Japan	Toronto Canada	Büsum, Germany	Providence RI, USA
Reference	Martin et al. 2002	Shoeib et al. 2006	Jahnke et al. 2007	Barber et al. 2007	Oono et al. 2008	Ahrens et al. 2012	Wang et al. 2014	(this study)
6:2 FTOH	87	18 (13-28)	66 (33-149)	61	18.3	293	85	11.8
8:2 FTOH	55	41 (25-61)	119 (62-275)	237	90.2	284	17	14.5
10:2 FTOH	29	22 (12-38)	35 (16-93)	62	18.5	106	5.4	10.1
EtFOSA	14	N/A	3.1 (1.3-5.9)	10	N/A	7.3 (6.1-9.1)	1.2	0.15
MeFOSA	101	N/A	9.0 (3.4-20)	7.6	N/A	8.0 (6.1-11)	1.9	0.85
EtFOSE	205	3.3 (1.4-4.7)	26 (4.5-56)	17	N/A	3.4 (n.d.-11)	0.9	1.27
MeFOSE	N/A	12 (8.1-18)	41 (5.1-107)	48	N/A	4.8 (1.1-9.9)	1.5	2.34

Table 5. Estimated WWTP aqueous concentrations using the experimentally-derived K_{PEW} and the PP-LFER generated K_{PEW}

Compound	Experimental K_{pew}	PP-LFER K_{pew}	Ratio Experimental/Predicted
6:2 FTOH	1857.8	12.6	147
8:2 FTOH	243.0	696.6	0.349
10:2 FTOH	58.4	153479.1	0.000381
EtFOSA	40.9	49.0	0.835
MeFOSA	1071.0	281.6	3.80
EtFOSE	3.5	13.6	0.257
MeFOSE	5.2	6.6	0.788

Table 6. Aqueous concentrations of WWTP outflow studies. The study site in Dauchy et al. is the WWTP attached to a local industrial fluoropolymer plant

Sampling Location	France	Yamato, Japan	South Kingston, RI
Reference	Dauchy et al. 2017	Mahmoud et al. 2009	this study
Sampling Medium	WWTP flotation tank	Urban river runoff	WWTP effluent
Units	ng/L	ng/L	ng
6:2 FTOH	N/A	N/A	12.6
8:2 FTOH	110	2.59	696.6
10:2 FTOH	110	4.06	153479.1
EtFOSA	b.d.	b.d.	49.0
MeFOSA	b.d.	b.d.	281.6
EtFOSE	N/A	N/A	13.6
MeFOSE	N/A	N/A	6.6

FIGURES

Figure 1. 0.5 mil PE sheeting used in this experiment (A) and the chemical makeup of low-density polyethylene (B)

Figure 2. Cutaway for the XAD/PUF sandwiches created for this experiment. The layer of XAD sits between two PUFs. Each PUF is compressed to fit inside of the soxhlet extraction tube.

Figure 3. Extraction vials for the WWTP blanks and samples

Figure 4. Shaker table set up used to assist the PE samplers to reach equilibrium

Figure 5. SPME vacuum manifold.

Figure 6. Zoning plans for the South Kingstown waste water treatment plant. The area outlined is the current service zone for the WWTP

Figure 7. PE rosette for each deployment time point (A) and the WWTP outflow area with PEs deployed in the effluent (B)

Figure 8. Bio-fouled PEs on day 21 prior to cleaning and extraction

Figure 9. Location of the Providence sampling site.

Figure 10. High-volume air sampler positioned exposed on a 5-story rooftop in downtown Providence.

Figure 11. PE half-bowl air sampler (A) and the full deployment close to the high-volume air sampler (B).

Figure 12. Idealized PE uptake curve

Providence Air Samples

Figure 13. 6:2, 8:2, and 10:2 FTOHs found at Providence site in PEs

Figure 14. 8:2 and 10:2 FTAcrs found at Providence site in PEs

Figure 15. EtFOSEA and MeFOSE found at Providence site in PEs

Figure 16. EtFOSE found at Providence site in PEs

Figure 17. MeFOSA found at Providence site in PEs

Figure 18. Daily PUF/XAD concentrations (pg/m³) for 6:2, 8:2 and 10:2 FTOH

Figure 19. Daily PUF/XAD concentrations (pg/m³) for 8:2 and 10:2 FTAc

Figure 20. Daily PUF/XAD concentrations (pg/m³) for MeFOSA, EtFOSA, MeFOSE, and EtFOSE

Figure 21. Time-averaged PUF/XAD concentrations (pg/m³) for 6:2, 8:2 and 10:2 FTOH

Figure 22. Time-averaged PUF/XAD concentrations (pg/m³) for 8:2 and 10:2 FTAc

Figure 23. Time-averaged PUF/XAD concentrations (pg/m³) for MeFOSA, EtFOSA, MeFOSE, and EtFOS

Water equilibration

Figure 24. Water equilibration experiment uptake curve of 6:2 FTOH in PEs

Figure 25. Water equilibration experiment uptake curve of 8:2 FTOH in PEs

Figure 26. Water equilibration experiment uptake curve of 10:2 FTOH in PEs

Figure 27. Water equilibration experiment uptake curve of 8:2 FTAc in PEs

Figure 28. Water equilibration experiment uptake curve of 10:2 FTAc in PEs

Figure 29. Water equilibration experiment uptake curve of EtFOSA in PEs

Figure 30. Water equilibration experiment uptake curve of MeFOSA in PEs

Figure 31. Water equilibration experiment uptake curve of EtFOSE in PEs

Figure 32. Water equilibration experiment uptake curve of MeFOSE in PEs

Figure 33. Experimentally-derived and PP-LFER predicted log K_{pew} comparison

Waste Water Treatment Plant

Figure 34. MeFOSA found in PEs at the South Kingston WWTP

Figure 35. 6:2 FTOH found in PEs at the South Kingston WWTP

Figure 36. 8:2 FTOH found in PEs at the South Kingston WWTP

Figure 37. 10:2 FTOH found in PEs at the South Kingston WWTP

Figure 38. 8:2 FTAc found in PEs at the South Kingston WWTP

Figure 39. EtFOSA found in PEs at the South Kingston WWTP

Figure 40. MeFOSE found in PEs at the South Kingston WWTP

Figure 41. EtFOSE found in PEs at the South Kingston WWTP

Appendix

Appendix 1: FTOH calibration curve

Appendix 2: FOSA & FOSE calibration curve

Appendix 3: Surrogate FTOH calibration curve

Appendix 4: Surrogate FOSA & FOSE calibration curve

Appendix 5: Laboratory instrument and method blank concentrations (ng/g PE)

Compound	Instr. 1	Instr. 2	Instr. 3	Day 8	Day 16	Day 24	Day 32
6:2 FTOH	0.01	0.00	0.02	0.12	0.08	0.09	0.05
8:2 FTOH	0.00	0.31	0.21	0.31	0.19	0.25	0.18
10:2 FTOH	0.69	0.19	0.47	0.51	0.46	0.32	0.44
8:2 FTAc	0.00	0.05	0.09	0.01	0.05	0.04	0.03
10:2 FTAc	0.00	0.00	0.00	0.00	0.00	0.00	0.00
EtFOSA	1.51	1.32	1.02	1.03	1.11	1.23	1.4
MeFOSA	2.21	1.68	1.34	1.32	1.09	1.85	1.65
EtFOSE	5.21	2.98	3.12	4.11	3.25	4.95	6.81
MeFOSE	4.22	3.65	4.61	3.54	5.28	5.81	6.13

Appendix 6: Laboratory instrument and method blank surrogate recoveries (%)

Surrogate	Instr. 1	Instr. 2	Instr. 3	Day 8	Day 16	Day 24	Day 32
6:2 FTOH M4	78.3	68.3	82.2	106	59.9	84.2	74.8
8:2 FTOH M4	85.5	101	83.5	98.3	78.9	79.5	89.4
10:2 FTOH M4	74.8	86.4	95.8	78.5	83.2	63.5	59.9
MeFOSA d3	99.7	108	121	122	85.6	78.4	74.5
MeFOSE d7	115	87.5	115	134	87.9	75.2	78.3

Appendix 7: WWTP PE blank concentrations (ng/g PE)

Compound	Day 2	Day 4	Day 7	Day 14	Day 21
6:2 FTOH	0.01	0.01	0.03	0.02	0.02
8:2 FTOH	0.04	0.03	0.03	0.05	0.05
10:2 FTOH	0.11	0.1	0.08	0.1	0.09
8:2 FTAc	0.01	0.06	0.06	0.05	0.04
10:2 FTAc	-	-	-	-	-
EtFOSA	0.12	0.18	0.15	0.2	0.14
MeFOSA	0.46	0.35	0.38	0.41	0.39
EtFOSE	0.05	0.06	0.04	0.05	0.03
MeFOSE	0.02	0.01	0.01	0.03	0.01

Appendix 8: WWTP PE blank surrogate recoveries (%)

Surrogate	Day 2	Day 4	Day 7	Day 14	Day 21
6:2 FTOH M4	69.8	78.6	64.7	89.5	74.6
8:2 FTOH M4	89.5	93.1	78.3	74.2	79.5
10:2 FTOH M4	79.6	69.4	65.2	85.6	93.2
MeFOSA d3	89.9	108	74.1	87.4	92.1
MeFOSE d7	83.3	99.4	69.8	78.6	107

Appendix 9: PUF/XAD blank concentrations (ng)

	Blank 1	Blank 2	Blank 3
6:2 FTOH	6.20	9.30	8.54
8:2 FTOH	8.11	7.52	9.23
10:2 FTOH	10.0	12.1	15.8
8:2 FTAc	0.00	0.02	0.05
10:2 FTAc	-	-	-
EtFOSA	15.2	13.5	14.6
MeFOSA	21.2	22.6	20.9
EtFOSE	18.7	12.9	13.2
MeFOSE	9.12	15.3	14.0

Appendix 10: PUF/XAD blank surrogate recoveries (%)

Surrogate	Blank 1	Blank 2	Blank 3
6:2 FTOH M4	124	87.4	68.3
8:2 FTOH M4	98.3	104	64.8
10:2 FTOH M4	102	79.4	75.1
MeFOSA d3	117	72.5	83.2
MeFOSE d7	128	74.8	87.8

Appendix 11: Providence PE blank concentrations (ng/g PE)

Compound	Day 2	Day 4	Day 8	Day 16	Day 32
6:2 FTOH	0.01	0.02	0.01	0.04	0.06
8:2 FTOH	0.01	0.01	0.00	0.02	0.02
10:2 FTOH	0.05	0.04	0.04	0.04	0.06
8:2 FTAcr	0.00	0.01	0.00	0.01	0.00
10:2 FTAcr	0.02	0.01	0.01	0.00	0.03
EtFOSA	0.02	0.02	0.01	0.01	0.02
MeFOSA	0.05	0.04	0.05	0.01	0.00
EtFOSE	0.06	0.06	0.05	0.02	0.07
MeFOSE	0.07	0.04	0.04	0.05	0.06

Appendix 12: Providence PE blank surrogate recoveries (%)

Surrogate	Day 2	Day 4	Day 8	Day 16	Day 32
6:2 FTOH M4	84.6	108	123	75.2	87.5
8:2 FTOH M4	74.3	98.8	89.7	83.4	114
10:2 FTOH M4	65.9	110	78.5	69.4	84.9
MeFOSA d3	87.3	126	102	73.2	63.4
MeFOSE d7	86.5	115	108	71.1	61.8

Appendix 13: Laboratory concentrations (ng/g PE)

Day	8-1	8-2	8-3	16-1	16-2	16-3	24-1	24-2	24-3	32-1	32-2	32-3
6:2 FTOH	9.59	7.88	8.69	12.10	6.29	8.02	15.04	11.81	14.94	2.81	13.5	2.63
8:2 FTOH	32.05	38.37	56.55	40.8	37.39	12.48	68.13	52.96	42.18	103.83	81.4	108.1
10:2 FTOH	98.78	221.01	162.84	227.1	285.32	610.79	1141.9	1116.3	394.51	4830.0	1960.	3688.1
8:2 FTAcr	10.84	12.18	14.31	55.0	33.35	14.62	36.02	42.92	34.74	23.2	39.8	44.6
10:2 FTAcr	4.17	13.34	11.09	13.7	5.77	1.23	7.70	16.17	7.51	17.27	35.5	30.6
EtFOSA	160.9	537.2	141.9	627.6	196.7	103.5	323.7	639.6	225.0	845.2	1034.9	391.8
MeFOSA	267.9	456.6	170.2	764.1	384.7	219.9	569.0	1112.7	1325.5	1155.5	1392.1	615.8
EtFOSE	1056.1	2110.5	1716.2	5817.4	2983.9	3682.1	5730.3	9003.0	1531.8	5222.7	3761.5	2625.9
MeFOSE	774.5	2555.5	1394.9	5745.6	3099.4	1720.7	5113.5	8008.8	1653.1	4325.9	3158.8	2130.3

Appendix 14: Laboratory surrogate recoveries (%)

Day	8-1	8-2	8-3	16-1	16-2	16-3	24-1	24-2	24-3	32-1	32-2	32-3
6:2 FTOH M4	22.7	29.2	33.8	52.6	26.8	56.2	73.5	67.8	26.3	17.5	28.4	17.8
8:2 FTOH M4	47.3	63.7	62.1	89.8	47.1	144.1	105.0	156.9	30.3	38.1	54.7	33.4
10:2 FTOH M4	76.2	107.3	97.1	190.5	129.5	180.3	193.6	185.9	145.7	127.4	97.8	78.5
MeFOSA d3	64.3	93.4	90.9	168.6	81.2	179.1	205.1	226.1	94.9	60.2	81.3	45.6
MeFOSE d7	175.5	190.8	206.1	229.5	208.6	275.6	182.4	250.8	163.8	179.5	200.4	167.3

Appendix 15: WWTP PE concentrations (ng/g PE)

Day	2-1	2-2	2-3	4-1	4-2	4-3	7-1	7-2	7-3	14-1	14-2	14-3	21-1	21-2	21-3
6:2 FTOH	0.741	0.732	2.11	2.25	2.35	0.641	6.34	3.75	1.87	4.15	3.89	3.42	4.19	7.35	7.78
8:2 FTOH	9.19	5.53	4.70	2.74	3.74	10.8	11.8	7.77	4.70	5.60	8.49	10.6	4.53	9.19	9.39
10:2 FTOH	12.5	13.7	18.1	14.12	18.18	24.6	23.6	26.8	18.2	30.9	26.1	29.7	22.3	34.7	47.3
8:2 FTAcr	14.1	10.5	1.65	8.26	10.75	77.8	31.9	16.7	6.15	120	18.2	19.0	14.4	26.8	36.9
10:2 FTAcr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EtFOSA	12.5	4.26	5.08	4.93	5.83	6.34	5.73	8.08	5.97	9.29	9.33	9.55	6.04	9.80	15.9
MeFOSA	57.5	55.40	72.4	62.94	81.33	110	132	117	83.1	133	128	158	146	202	230
EtFOSE	0.73	0.49	0.379	0.449	0.59	0.67	0.96	1.23	2.08	3.84	3.08	2.31	1.39	2.85	2.77
MeFOSE	0.46	1.26	0.528	0.92	2.22	0.91	0.99	0.608	1.35	4.30	3.19	2.82	2.88	2.21	3.44

Appendix 16: WWTP PE surrogate recoveries (%)

Day	2-1	2-2	2-3	4-1	4-2	4-3	7-1	7-2	7-3	14-1	14-2	14-3	21-1	21-2	21-3
6:2 FTOH M4	88.4	165	106.2	81.0	94.1	93.6	186	163	162	109	151	152	81.7	97.6	90.0
8:2 FTOH M4	34.7	48.4	43.3	71.3	60.6	66.4	53.0	65.2	59.8	77.3	96.5	60.7	48.9	107	135
10:2 FTOH M4	72.5	50.0	42.3	40.1	33.5	56.6	77.8	39.9	40.0	36.0	44.3	37.8	31.5	51.2	57.1
MeFOSA d3	55.6	51.6	53.9	54.9	86.1	78.7	70.2	64.3	70.3	58.1	58.2	80.5	53.4	90.0	84.9
MeFOSE d7	44.6	50.7	52.5	62.3	60.2	53.6	63.3	52.8	59.4	71.3	66.0	66.5	72.7	76.9	108

Appendix 17: Providence PE concentrations (ng/g)

Day	2-1	2-2	2-3	4-1	4-2	4-3	8-1	8-2	8-3	16-1	16-2	16-3	32-1	32-2	32-3
6:2 FTOH	0.13	0.57	0.73	0.55	0.01	0.95	0.71	0.01	0.01	0.12	0	0.11	0.37	0.23	0.07
8:2 FTOH	0.19	0.07	0.19	0.17	0	0.20	0.23	0.13	0.20	0.22	0.15	0.26	0.51	0.10	0.07
10:2 FTOH	0.71	0.58	0.52	0.44	0.04	0.37	0.81	0.51	0.64	0.52	0.77	0.58	0.89	0.16	0.36
8:2 FTAc	0.24	0.22	0.21	0.18	0	0.35	0.43	0.22	0.34	0.34	0.33	0.62	0.33	0.19	0.07
10:2 FTAc	0.13	0.08	0.16	0.05	0.01	0.22	0.06	0.20	0.08	0.093	0.41	0.04	0.08	0.07	0.08
EtFOSA	0.16	0.17	0.15	0.17	0.01	0.14	0.18	0.38	0.16	0.26	0.38	0.22	0.055	0.06	0.08
MeFOSA	0.49	0.59	0.70	0.38	0.07	0.64	0.53	0.48	0.52	0.59	0.60	0.73	0.41	0.08	0.18
EtFOSE	0.67	1.12	0.56	0.28	0.34	2.47	0.71	0.99	1.56	2.41	1.77	2.81	1.47	0.10	0.11
MeFOSE	1.98	1.88	2.21	0.90	0.10	2.11	1.42	1.94	1.20	1.60	1.76	1.70	1.81	0.14	0.18

Appendix 18: Providence PE surrogate recoveries (%)

Day	2-1	2-2	2-3	4-1	4-2	4-3	8-1	8-2	8-3	16-1	16-2	16-3	32-1	32-2	32-3
6:2 FTOH M4	14.9	12.4	32.6	32.1	40.6	16.7	29.1	25.4	32.8	26.7	27.5	29.4	34.7	32.1	15.7
8:2 FTOH M4	52.1	50.4	95.3	91.2	84.5	58.3	84.9	61.4	49.8	74.7	34.2	83.0	28.9	10.9	36.4
10:2 FTOH M4	97.2	96.3	146	129	131	97.6	128	103	94.8	106	48.9	117	44.0	11.4	43.5
MeFOSA d3	116	107	152	131	126	108	145	102	106	107	49.1	128	41.4	8.19	40.0
MeFOSE d7	129	113	158	146	167	120	151	110	112	110	57.1	142	47.0	11.0	43.7

Appendix 19: PUF/XAD Extraction test spiked concentrations (ng)

	T1	T2	T3	T4	T5
6:2 FTOH	0.26	0.70	0.26	0.21	0.67
8:2 FTOH	0.31	0.79	1.86	0.57	0.29
10:2 FTOH	1.17	2.88	0.73	3.95	0.29
8:2 FTAc	0.096	0.23	0.13	0.20	0.15
10:2 FTAc	0.10	0.063	0.049	0.10	0.14
EtFOSA	0.068	0.20	0.25	0.087	0.031
MeFOSA	0.34	0.22	0.077	0.24	0.079
EtFOSE	0.040	0.44	0.36	0.81	0.16
MeFOSE	0.13	0.69	0.20	0.99	0.81

Appendix 20: PUF/XAD Extraction test surrogate recoveries (%)

	T1	T2	T3	T4	T5
6:2 FTOH M4	107	74.6	72.3	51.2	46.1
8:2 FTOH M4	146	132	159	98.4	117
10:2 FTOH M4	96.5	125	147	107	141
MeFOSA d3	66.6	79.9	132	106	138
MeFOSE d7	197	162	235	148	139

Appendix 21: Providence PUF/XAD concentrations (pg/m³)

	4/10/2016	4/13/2016	4/15/2016	4/18/2016	4/20/2016	4/25/2016	4/27/2016	4/29/2016
6:2 FTOH	12.01	32.6	13.46	10.95	12.64	9.85	10.10	6.10
8:2 FTOH	18.14	23.6	14.25	34.90	1.63	8.35	13.38	16.47
10:2 FTOH	10.19	14.2	9.72	23.11	0.37	6.93	13.31	12.70
8:2 FTAc	0.088	0.10	0.089	0.14	0.19	0.15	0.079	0.18
10:2 FTAc	0.082	0.097	0.17	0.20	0.15	0.26	0.20	0.22
EtFOSA	0.21	0.15	0.34	0.072	0.19	0.11	0.18	0.12
MeFOSA	0.70	0.41	0.76	0.80	0.58	0.70	2.08	1.33
EtFOSE	2.58	1.22	1.20	1.81	1.45	1.092	1.32	0.86
MeFOSE	3.85	5.13	3.23	1.96	2.32	2.12	0.93	1.95

Appendix 22: Providence PUF/XAD surrogate recoveries (%)

	4/10/2016	4/13/2016	4/15/2016	4/18/2016	4/20/2016	4/25/2016	4/27/2016	4/29/2016
6:2 FTOH M4	70.1	77.3	63.5	71.9	67.0	52.8	95.3	54.7
8:2 FTOH M4	71.2	99.9	60.0	64.4	54.8	87.7	78.7	89.9
10:2 FTOH M4	108	124	75.9	85.9	72.9	55.7	115	124
MeFOSA d3	75.8	113	54.1	72.0	56.3	46.9	90.0	64.5
MeFOSE d7	107	121	68.5	80.6	66.3	55.4	102	119

Appendix 23: Providence air volume sampled (L)

4/11/2016	4/13/2016	4/15/2016	4/18/2016	4/20/2016	4/25/2016	4/27/2016	4/29/2016	4/11/2016
1176558	1179625	1125097	1119082	1022217	1665738	1016573	976764	1176558

Appendix 24: Laboratory PE masses (g)

8-1	8-2	8-3	16-1	16-2	16-3	24-1	24-2	24-3	32-1	32-2	32-3
0.059	0.0549	0.0686	0.0422	0.0625	0.0554	0.0594	0.0581	0.0490	0.0547	0.0722	0.0619

Appendix 25: Providence PE masses (g)

2-1	2-2	2-3	4-1	4-2	4-3	8-1	8-2	8-3	16-1	16-2	16-3	32-1	32-2	32-3
0.864	0.936	0.847	0.895	0.932	0.895	0.948	0.937	0.939	0.977	0.999	0.790	0.792	0.953	0.947

Appendix 26: WWTP PE masses (g)

2-1	2-2	2-3	4-1	4-2	4-3	7-1	7-2	7-3	14-1	14-2	14-3	21-1	21-2	21-3
1.963	1.859	1.635	1.997	1.726	1.311	1.315	1.213	1.509	1.704	1.629	1.502	1.661	1.930	1.779

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