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EVALUATION OF A NOVEL PASSIVE SAMPLER FOR POLY- AND PERFLUOROALKYL SUBSTANCES IN AQUATIC ENVIRONMENTS

Christine Gardiner
University of Rhode Island, clgardiner@uri.edu

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EVALUATION OF A NOVEL PASSIVE SAMPLER FOR
POLY- AND PERFLUOROALKYL SUBSTANCES IN
AQUATIC ENVIRONMENTS

BY

CHRISTINE GARDINER

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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OF
CHRISTINE GARDINER

APPROVED:

Thesis Committee:

Major Professor Rainer Lohmann

Rebecca Robinson

Geoffrey Bothun

Mark Cantwell

Nasser H. Zawia
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
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ABSTRACT

Poly- and perfluoroalkyl substances (PFASs) are of growing concern worldwide, due to their ubiquitous presence and adverse health effects in humans and the environment. Surface waters in the northeastern United States in particular have displayed elevated concentrations of PFASs. Passive sampling devices are excellent monitoring tools, that accumulate contaminant loadings through passive diffusion and adsorption to the sampler, and provide a long-term, time-weighted average of the contaminant over large temporal and spatial scales. Here we utilize a novel integrative passive sampler—a microporous polyethylene (PE) tube filled with Hydrophilic-Lipophilic-Balanced sorbent—to gain a better understanding of its function, utility, and uptake rates in field environments. Three sampling campaigns were conducted in the fall of 2017 and summer 2018, deploying a total of seventy-two PE tube passive samplers across nine sites in a well-mixed estuary and in two wastewater treatment plant effluents for one month's duration. Twenty-four PFASs (including carboxylic acids, sulfonates, and precursors) were measured across all sites in the passive samplers, as well as complementary water samples, using Ultra Performance Liquid Chromatography/Mass Spectrometry. In the estuary, the PE tube samplers accumulated a sum PFASs of 2 to 15 ng sampler⁻¹, and in the waste water treatment plant effluent 60 to 70 ng sampler⁻¹. *In situ* sampling rates, which are essential when needed to calculate the contaminant concentrations in water, were characterized using a first order kinetic model, yielding sampling rates of 10-50 mL day⁻¹. Results from this study imply that these passive samplers can be successfully used to determine dissolved concentrations

of PFASs in surface waters, though the sampling rate seems to vary with external water flow velocity.

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PREFACE

This thesis is presented in manuscript format, and is currently in preparation for submission to the journal *Environmental Science and Technology*.

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INTRODUCTION

This thesis is presented in manuscript format, and is currently in preparation for submission to the journal *Environmental Science and Technology*.

BACKGROUND

Poly- and perfluoroalkyl substances (PFASs) are a class of man-made chemicals, composed of over 4,000 individual compounds, which are of growing global concern (Wang et al. 2017). Production of PFASs began in the 1940s and 50s; they are used for various industrial purposes in non-stick and water-resistant coatings used in consumer products, as well as a major component of aqueous film forming foams (AFFF) (Lindstrom et al. 2011). In the last couple of decades, these contaminants have been found globally distributed in the air, environment and drinking water sources, and due to their fluorinated chemical structure—polar, hydrophilic, high thermal, chemical, and biological inertness—PFASs are highly persistent in the environment (Wang et al. 2017). They are known to bioaccumulate in wildlife (Kannan et al. 2005), are found prevalently in human blood samples (Karrman et al. 2006), and are considered immunosuppressants by decreasing the antibody count from vaccines in children (Grandjean et al. 2012). PFASs are also linked to several negative health effects (immune, developmental, neurobehavioral, endocrine, and metabolic) in laboratory rodent experiments (Benskin et al. 2009). Due to their negative health impacts, production of a few compounds (namely perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and other legacy compounds) has been voluntarily phased out in the United States, with the support of the U.S. Environmental Protection Agency (U.S. EPA 2016), and they are being evaluated for listing, under the Stockholm Convention on Persistent Organic Chemicals (UN Environment Programme).

PFASs enter the environment primarily through waste water treatment plant (WWTP) effluent, septic system leaking and discharge, and aqueous film forming foams (AFFF) used by airports, military bases and fire training areas (Möller et al. 2010, Moody & Field 2000, Schaider et al. 2016). One of the biggest environmental sources of these compounds are through manufacturing discharge. An estimated 2,610-21,400 tons of perfluoroalkyl carboxylic acids were produced globally from 1951-2015, and 65%-98% of this was discharged into surface waters (Wang et al. 2014). These compounds then leach into the ground water, aquifers and enter drinking water supplies. The northeastern United States, in particular, has shown to have elevated levels of PFAS in its surface and groundwaters (Zhang et al. 2016; Weber et al. 2017).

Passive sampling tools have been successfully used for decades to easily and time-effectively monitor different groups of contaminants in the environment. These sampling tools work through the passive diffusion of analyte molecules from the sampled medium to a collecting medium due to a difference in chemical potentials (Górecki & Namieśnik 2002). Passive samplers are inexpensive, small, easy to use, and can be deployed over large spatial and temporal scales, without the need of daily environmental sampling. Passive samplers accumulate compounds over the deployment period and generate a reliable time weighted average of those compounds in water/air (Vrana et al. 2005), which is more representative of the environmental variation of contaminant concentration over time, as compared to an active grab sample which only represents a single moment in time. Due to the accumulation and concentration of the compounds onto the sampler overtime, contaminant concentrations can often be detected in the sampler that would otherwise be undetectable in a grab sample at lower concentrations.

Another benefit of passive samplers is that they can mimic the portion of contaminants bioavailable to organisms and help predict biomonitoring results (Vrana et al. 2005). These sampling devices are especially useful when studying remote areas, large spatial scales or long-term monitoring projects, because they vastly decrease the amount of field and lab work needed to determine environmental contaminant concentrations. Traditional passive samplers, such as polyethylene sheets or polyurethane foam, are excellent monitoring tools for nonpolar contaminants, such as dioxins, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) (Lohmann et al. 2012).

For these traditional samplers, Performance Reference Compounds (PRCs) are added prior to sampler deployment, to determine uptake rates (the rate at which the target analytes are taken up by the sampler), which are greatly dependent on environmental conditions, such as flow rate, temperature and biofouling. PRCs are non-interfering, mass-labeled compounds which slowly diffuse out of the sampler, while the compounds of interest sorb to the sampler. The known PRC loss is related to the uptake of the target compound, and thus an uptake rate can be derived (Huckins et al. 2002).

Due to their polar nature, and high affinity for water, PFASs do not sorb strongly to traditional passive samplers, which typically target non-polar analytes. A Polar Organic Chemical Integrative Sampler (POCIS) has been developed for polar compounds, including PFASs. This device incorporates a metal ring sandwiching a charged powered adsorbent which binds the polar compound, between a thin polyethersulfone membrane (Alvarez et al. 2004). The main drawback of the POCIS sampler is that the thin membrane is very permeable to water, thus causing the sampling uptake rate to be strongly dependent on the flow rate of the medium the sampler is

deployed in (Gobelius et al. 2019; Kaserzon et al. 2012; Kaserson et al. 2013).

Additionally, PRCs cannot be used for these polar samplers, because the PRC affinity to the adsorbent powder is much too great, and the compounds would not diffuse out of the sampler.

Another, much newer and less widely used passive sampler has been developed for polar compounds (see Figure 1). This sampler consists of a hollow microporous polyethylene (PE) tube filled with charged powdered adsorbent and sealed at both ends (Kaserzon et al. 2019). The PE tubes have thick porous walls (2 mm) to reduce the effects of the flow rate of the medium. Instead, uptake is presumably limited by the passive diffusion of the compounds (i.e. their chemical properties) through the polyethene walls. These passive samplers have been previously used for the detection of polar herbicides (Fauvelle et al. 2017a) and PFASs in ground water (Kaserzon et al. 2019), but more work still needs to be performed to better characterize these samplers.

The research performed for this MS thesis consists of initial field studies to determine if these samplers are a promising tool for detection of dissolved PFASs in surface water. If these tube samplers prove useful, further studies should be conducted assessing these specific variables to better understand the applicability of these samplers for PFASs uptake. For example, to be able to predict the uptake rate of individual PFASs, we would need to understand the permeability of the tube and mass transfer of the compounds by studying the porosity of the tube, the particle size of the analyte, the membrane resistance and therefore resistance to flow rate of the medium as discussed by Fauvelle et al. (2017b).

This study will evaluate and field validate the PE tube passive sampler as a sampling tool for PFASs in aquatic environments. While drinking water is a main human exposure source, studying PFASs concentrations in surface waters is critical. Surface water can often be predictive of contaminant levels in ground water (Heberer et al. 1998; Thurman et al. 1991) as the aquifers recharge with human use and rainfall. Additionally, marine and fresh water organisms bioaccumulate PFASs from the environment, which humans are later exposed to through consumption of seafood and shellfish (Berger et al. 2009). A regular monitoring tool, such as this passive sampler, could be used to provide baseline concentrations of PFASs, and predict levels of contaminant bioaccumulation and set advisory limits for human consumption.

A suite of twenty-five PFASs compounds were analyzed in all samples and are comprised of legacy compounds (including PFOA and PFOS) produced in high volumes and emerging compounds (short and long chain compounds, fluorotelomer sulfonates and Gen-X) which replaced the legacy compounds after they were phased out. Specifically, this suite of compounds was selected due to their known prevalence in the environment, and occurrence in waste water treatment plants, airports and military bases. This study was conducted in two parts, with initial deployments in two waste water treatment plants in Providence followed by a field deployment in Narragansett Bay. WWTPs are ideal study sites, due to their high concentrations of PFASs, controlled and consistent conditions (flow rate, temperature, salinity, dissolved oxygen) and availability of daily composite water samples from the regular maintenance and monitoring by the WWTP staff. PE tube samplers were initially deployed in the final effluent of the two WWTPs, to observe preliminary uptake rates, PFASs concentrations, and method validation. A follow

up time series study was also conducted at each WWTP to determine the linear uptake phase, optimal deployment time and any preferential compound uptake over time. A secondary study was performed in Narragansett Bay (NB), to test the application of the PE tube sampler in the field, and determine how the samplers work in a natural environment.

Main questions of the project:

1. Do these novel PE tube samplers take up PFASs? Which ones? What is the reproducibility of the sampler?
2. How long is the linear uptake phase? What is the optimal deployment time?
3. What is the sampling rate of the sampler? A sampling range for the different compounds?

METHODS

Polyethylene tube integrative passive samplers

Passive samplers were made from microporous polyethylene Filtroplast tubing, model FL10, 2.5 μm filtration grade (manufactured by Pall Corp., Germany), 7 cm in length and membrane thickness of 2 mm. These tubes were filled with 0.6 g of Oasis Hydrophilic-Lipophilic-Balanced (HLB) sorbent (Waters Corp., Milford, MA, USA), allowing room for 1 cm of head space. The tubes were then capped with push-in polyethylene plugs (McMaster-Carr Supply Company, Elmhurst, IL), creating an exposed surface area of 18.8 cm^2 and a surface area to mass sorbent ratio of 31 cm^2g^{-1} . To condition the sorbent for compound uptake in the field, the samplers were placed on a shaker table in methanol for 24 hours, followed by basic methanol (1.0% ammonium hydroxide in methanol) for 24 hours, followed by LC/MS Optima grade water for 24 hours.

Standards and materials

For all extractions, conditioning, and standard preparation LC/MS grade methanol (Honeywell Burdick & Jackson, Muskegon, MI, USA), LC/MS Optima grade water and ammonium hydroxide (28-30 w/w%) (Thermo Fisher Scientific, Waltham, MA, USA) were used. All laboratory equipment (test tubes, pipettes, graduated cylinders, sampling bottles) were high density polyethylene and rinsed three times each with basic methanol

(3% ammonium hydroxide in water), regular methanol, and Optima-grade water before handling the samples. All analytical standards were purchased from Wellington Laboratories (Guelph, Canada). A native standard mix of PFAC-24PAR (a mixture of 24 native PFASs compounds) along with hexafluoropropylene oxide dimer acid (Gen-X) were used to prepare calibration standards in 25:75 methanol:water with 4mM ammonium acetate, ranging from 0.25 to 50.0 ng mL⁻¹. A 10.0 ng mL⁻¹ native standard was also prepared in the same way for matrix effect determination and recovery standards. A mass-labeled surrogate standard was prepared from MPFAC-24ES (a mixture of 19 mass-labeled (13C or 2H) PFASs compounds) and M-Gen-X (M3HFPO-DA) at 50 ng mL⁻¹. See Table A and B in the Appendix for further standard information.

Waste water treatment plant deployment

Two waste water treatment plants (Field's Point and Bucklin Point, see Figure 3) servicing Providence, RI, were used as the study site for an *in situ* calibration deployment for these novel passive samplers. A pilot study was conducted for a one-month duration in the fall of 2017, Field's Point and Bucklin Point, Providence, RI. . At each WWTP, 3 samplers were deployed sequentially for consecutive 10-day periods (for a total of 6 passive samplers between the two sites). Water samples were also collected in pre-cleaned polyethylene bottles, during deployment and recovery of the passive samplers (for a total of 8 water samples between the two sites). Field blanks were collected for quality assurance—optima-grade water was brought along and transferred at the site of water collection into another pre-cleaned polyethylene bottle, to mimic the water collection process and account for any potential environmental contamination.

In the late spring of 2018, a second deployment was conducted in the final WWTP effluents. At each WWTP, passive samplers were deployed in triplicate for 2, 4, 8, 16, and 29 day periods, to gain an understanding of the kinetic PFASs uptake by the passive samplers (5 time periods x 3 samplers = 15 samplers per site) daily composite water sample (sub samples collected every hour for the twenty-four-hour period and combined) was collected every day. Field blanks were also collected for quality assurance as described above.

Estuary field trial deployment

Narragansett Bay (NB) is a well-mixed, tidally influenced estuary in Rhode Island, USA (Pilson 1985). Many of the Bay's sources of PFASs are freshwater inputs, including WWTP effluents, industrial point sources, septic leaching and AFFF run off from airports and military bases in the northern part of NB (i.e. higher impacted sites). The less impacted sites, e.g., areas with little or no known sources of PFASs, are located towards the (southern) mouth of the Bay. PFASs sources are linked with human activity, and this relationship can be observed in Figure 2. Nine deployment sites (see Figure 3) were chosen in NB to cover this North-South gradient of high to low PFASs concentrations, and five sites were chosen next to long-term monitoring buoy locations (run by the Rhode Island Department of Environmental Management), to compare PFASs concentration to water quality parameters from buoy data (temperature, salinity, dissolved oxygen, and pH).

Duplicate passive samplers were anchored to sediment traps to sample the mid water column, roughly 3 meters from the bottom. The samplers were deployed for a one-month

duration, from September to October of 2017, and grab water samples were collected during deployment and recovery. A follow up study was conducted in July of 2019 to test the reproducibility of the passive samplers. Six ‘caged’ and six ‘naked’ passive samplers were deployed at the Pawtuxet River site for three weeks duration, and water samples were collected upon deployment and recovery. The naked samplers consist of the bare PE tube being zip-tied to the anchored line (the style of samplers deployed at both waste water treatment plants), and the caged samplers had a polyethylene mesh cage wrapped around them, to minimize biofouling (the style of samplers deployed throughout Narragansett Bay).

Extraction of water grab samples

Samples were stored in 1 L pre-rinsed polyethylene bottles at -20°C and thawed to room temperature for extraction. 300 to 500 mL of the sample were spiked with 10 ng (100 μL at 0.05 ng mL^{-1}) 25 mix mass-labeled PFAS mixture, as surrogate standards for quantification. The water samples were then filtered using glass fiber filters, and extracted using Oasis Weak Anion EXchange (WAX) solid phase extraction cartridges (6 mL, 150 mg of sorbent), collecting the final methanol elution as the sample extract. The water extraction procedure follows EPA method LOP-AED/PEB/DK17-01-00.

Extraction of polyethylene tube samplers

Passive samplers were cleaned with deionized water to remove algal growth. Whole passive samplers were centrifuged three times for three minutes at 4,000 rpms, to remove remaining water trapped inside the tube. Passive samplers were then transferred to

precleaned 15 mL Falcon centrifuge tubes, filled with 6mL methanol, spiked with 10 ng internal PFAS standard and let sit for 24 hours. The methanol was then transferred to another precleaned Falcon tube, and the PE Tube were fill with another 6 mL methanol and the process repeated three more times, for a total of four extraction steps per passive sampler. All individual sampler extracts were combined as the sample extract.

Instrument analysis and QA/QC

All final sample extracts (water and passive samplers) were volume reduced using a nitrogen evaporator (Microvap) to 250 μ L, and reconstituted with 750 μ L 4 mM ammonium acetate water, yielding a final sample of 1000 μ L 25:75 methanol:water. Extracts were centrifuged to remove any remaining particulates, and the supernatant were transferred to auto sampler vials for analysis. Samples were analyzed at the Environmental Protection Agency's ORD Narragansett Bay location through liquid chromatography mass spectrometry on a Waters Acquity H-Class Ultra Performance Liquid Chromatography System (UPLC) paired with a Waters Xevo Triple Quadrupole MS/MS System (Waters, Milford, MA) run in negative electrospray ionization (-ESI) mode. A 40 μ L sample injection is run in duplicate, followed by an injection blank to insure no carry-over between samples. Analytes of interest are separated using a BEH C18 column and a mobile phase gradient of 75% aqueous to 10% aqueous. Compound identification is carried out through ion fragmentation and referenced to calibration standards and quantified through isotope dilution mass spectrometry.

All equipment used to handle samples (collection bottles, spatulas, aluminum foil, test tubes, extraction manifold, etc.) were washed three times with basic methanol (3%

ammonium hydroxide), follow by three washes with LC/MS grade methanol, to insure no previous PFASs contamination on the equipment. Gloves and protective equipment were used when handling samples (to protect the samples and myself). No PFASs containing products (i.e. Teflon) or glass (to prevent compound sorption to the container) were used to handle/store the samples, only high-density polyethylene and polypropylene were used (as they have much less reactive surfaces to prevent compound sorption). Mass-labeled internal standard were always added to the sample prior to any manipulation, to account for any losses in the method.

Field blanks, process blanks and instrument blanks were performed at every step of collection, extraction and analysis to account for any outside contamination or sample loss. Matrix samples were also performed to determine how the water matrix effects the PFASs behavior and recovery.

Data analysis

A five-point calibration curve was made and analyzed on the instrument to determine linearity of the MS detector and derive sample concentrations. All integrations and chromatogram analysis were done using Mass/Target Lynx software. Sample concentrations were then volume/mass, blank and recovery corrected.

Histograms of water and passive sampler concentrations were computed, and a heat map of Narragansett Bay PFASs concentrations was created by extrapolating the known concentrations from the 9 sampling sites on Ocean Data View computing software. Sampler concentrations of PFASs were compared to water parameters

(temperature, salinity, dissolved oxygen, etc.) through a generalized linear model on R to determine if environmental conditions effect uptake rate of the samplers.

The sampler concentration of the WWTP time series experiment were plotted against the samplers' deployment time, to observe the PFASs uptake kinetics, and to determine whether the uptake remains linear. Regressions were ran to calculate the linearity of the uptake rate, and determine an optimal deployment time, by calculating the time needed to reach equilibrium The optimal deployment time was based on how long the uptake is linear (before it reaches equilibrium with the environment), and if the samplers have accumulated a high enough concentration of PFASs to pass the detection limits of the instrument.

Compound specific uptake rates were analyzed to discern if there is differential uptake between chain lengths and functional groups (carboxylic acids vs sulfonates). Shorter chain compounds are expected to have higher uptake rates, due to their higher diffusivity when compared to long chain compounds.

RESULTS AND DISCUSSION

Waste water treatment plant

The initial pilot study demonstrated that the passive samplers, the extraction and analytical method could be successfully used for the detection for 24 target analytes in both WWTPs (with the exception of HFPODA-Gen- due to instrument interference). The detection of these compounds in both the effluent (Figure 4) and in the passive samplers (Figure 5) validates the extraction and instrument procedure, thus providing a good protocol for the other sampling campaigns. In the time series study, both effluents were dominated by carboxylic acids, primarily PFBA, PFPeA, PFHxA, PFHpA, and PFOA. Those five compounds combined were present at 86 ng L^{-1} (67%) of the PFASs load in Fields Point and 86 ng L^{-1} (64%) in Bucklin Point (Figures 6 and 7, Table 1 and 2). Sulfonates (PFBS, PFHxS, PFHpS, and PFOS) combined reached 24 ng L^{-1} (25%) at Fields Point and 28 ng L^{-1} (21%) at Bucklin's WWTP. Precursors and longer chain PFASs (greater than nine carbons) were observed at much lower concentrations, ranging from 3.0 to 0.01 ng L^{-1} . Across the month-long sampling period, both locations maintained fairly steady PFASs concentrations, with sum 24 PFASs of $110 \pm 20 \text{ ng L}^{-1}$ at Fields Point and $130 \pm 20 \text{ ng L}^{-1}$ at Bucklin Point. These stable conditions will allow for an accurate analysis and calibration the passive sampler uptake in this environment.

The accumulation of PFASs in the PE-tube samplers deployed in the Fields Point WWTP exhibited a linear uptake for the compounds observed (Figure 8, Table 3),

accumulating a sum 24 PFASs of 74 ng sampler⁻¹ after 29 days. PFHxA had the highest concentration of 17 ng sampler⁻¹, and 4:2-FTS the lowest with 0.01 ng sampler⁻¹. The carboxylic acids made up a predominant portion of the sum PFASs, similar to the concurrently collected effluent grab samples.

Bucklin Point WWTP displayed a different uptake pattern (Figure 9, Table 3), with the greatest PFASs concentration accumulating on day 16 (69 ng sampler⁻¹), and tapering off slightly on day 29 (60 ng sampler⁻¹). At both time periods, PFHxA had the highest concentration and 4:2-FTS the least, with carboxylic acids making up the bulk of the PFASs loading, which is also consistent with the concurrently taken effluent grab samples. There are several factors that could be contributing to this leveling off the sampler's PFAS uptake—flow rate, biofouling, saturation of the sorbent, other conflicts with in the WWTP—and these will be discussed in greater depth later.

Estuary field deployment

The Narragansett Bay PFASs surface water concentrations (mean of the two grab samples collected on deployment and recovery of the passive samplers) were mapped and extrapolated to cover the Bay as a whole (Figure 10). The PFASs distribution is in line with what was predicted, with the highest concentrations being north near a large human population and industry, and lower concentrations towards the mouth of the Bay. Throughout the Bay, total PFASs were also dominated by carboxylic acids, with sulfonates comprising the next biggest fraction (Figure 11, Table 4). Some of the spatial distribution can be explained: Site 1 (Phillipsdale Landing) is located just south of the Bucklin Point WWTP outfall, and while it is lower than the WWTP effluent itself (42

ng L⁻¹ compared to 130 ng L⁻¹) it is the second highest concentration we observed in the Bay. Site 2 (Field's Point Bay) is located near the Fields Point WWTP outfall, and also displayed elevated PFASs levels of 22 ng L⁻¹. Site 3 (Pawtuxet River) is located at the mouth of a tributary meeting Narragansett Bay, and displays the highest PFASs levels (62 ng L⁻¹) we observed in the Bay. There is a big industry presence up stream of the Pawtuxet River, most notably electrical and metal plating, which use some PFASs containing surfactants in their production, and it is likely that industry discharge is leading to these elevated concentrations (Clara et al. (2008); Lin et al. (2009)). Site 7 (Quonsett Point) is located off an air force base, and it displays a very unique PFASs signature, where 6:2-FTS and EtFOSAA are the dominant compounds (34% and 20% respectively, compared to the average of the other sites 1.3% and 2.6% respectively). These two precursors are known additives to aqueous film forming foams (AFFF), which are pervasively used across the military for fire training, and a recent fire training activity could lead to this unique PFAS signature observed at site 7 (Barzen-Hanson et al. (2017); Houtz et al. (2013)). The remaining five sites are located in the wider part of the Bay with more mixing with the Atlantic Ocean water and lower human population density leading to lower PFASs levels than observed at the previous four sites. This broad range of PFASs concentrations and field conditions creates a good opportunity to test how well samplers work across a range of environmental settings.

In the Narragansett Bay field deployments, the passive samplers accumulated a sum 24 PFASs of 2.5 to 15 ng sampler⁻¹ (Figure 12, Table 5). In general, the trend is that higher PFASs water concentration lead to a higher passive sampler concentration. The accumulation of PFASs by the passive samplers seemed to conserve their general

contribution in the water, with carboxylic acids being the dominant fraction. A notable exception, is that the passive samplers at site 7 were not dominated by 6:2-FTS and EtFOSAA like the water grab, which will be further explored in a later section.

Reproducibility and sampler type

The twelve passive samplers deployed to test the reproducibility of the PE tubes, accumulated an average of 7.1 ± 0.3 ng sampler⁻¹, and had consistent concentrations across all replicates (Figure 13, Table 6). For fourteen out of the twenty-four compounds observed, the relative percent difference between replicates was between 20% and 30%, and as low as 5% for PFDS and 4:2-FTS, indicating very good reproducibility for the more abundant compounds. For the longer chain compounds (chain length greater than ten) and precursors, greater variability is observed. This variability is likely due to the compounds being present at such low concentrations (two or three orders of magnitude lower than the dominate compounds), that any fluctuation has a much greater relative impact. This variability is likely exacerbated by instrumental detection limits and poor optimization for these larger compounds with much longer retention times. Generally, the PE tube samplers appear to be reproducible, with reproducibility being mainly limited by instrumental detection limits and acquisition.

The uptake of the two different sampler types was also compared. For the Bay study, ‘caged’ samplers (PE tubes wrapped in polyethylene mesh) were deployed throughout the Bay, in hopes of preventing biofouling. While ‘naked’ samplers (bare PE tubes) were used in both WWTPs, in anticipation of less biofouling due to the sterilization of the treatment process. For all twenty-four compounds, there was found to

be no significant difference ($p > 0.05$) in mean uptake between the two sampler types (Table 6). By visual observation, the cage did not reduce biofouling, so the simpler naked design should be used in future studies for ease of use. Additionally, in most cases the reproducibility of the naked samplers was better (lower standard error) than of the caged passive samplers (Table 6). Lastly, this lack of difference between the two samplers, enables the comparison of the Bay and WWTP sampler uptake without needing to correct for the different sampler design.

Sampling rate

The sampling rate is needed to back-calculate the water concentration of the environment the passive sampler was deployed in. The sampling rates (R_s) for individual compounds were calculated using a first-order kinetic model:

$$(equ. 1) \quad R_s = \frac{-\ln\left(1 - \frac{C_s}{K_{sw}C_w}\right)m_s K_{sw}}{t} = \frac{L}{day} \quad (Kaserzon et al. 2019)$$

Where C_s is the passive sampler concentration, C_w is the water concentration, m_s is the mass of the sorbent used, K_{sw} is the sorbent-water sorption coefficient, t is time in days. K_{sw} values were taken from Urik & Vrana (2019) (see values in Table C), where they only calculated values for eleven PFASs compounds, so of those, I focused on the nine dominate compounds.

Across all three study locations, sampling rates displayed similar values, ranging from 10 to 50 mL day⁻¹ (Figure 15) for the nine compounds examined (PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA). However, Bucklin Point

displays significantly greater sampling rates ($40 \pm 5.1 \text{ mL day}^{-1}$) than both Fields Point ($29 \pm 2.9 \text{ mL day}^{-1}$) and Narragansett Bay ($23 \pm 4.2 \text{ mL day}^{-1}$), and Fields point displayed significantly greater R_s than the Bay as well (Table 7). Sampling rates at all study locations also seem to be linked to the chain length of the compound (Figure 16), where compounds with longer chain lengths, exhibit higher sampling rates. Similar results were also noted by Kaserzon et al. (2019). An increase of R_s with increasing chain length is contrary to expectations, as molecular diffusivity decreases with increasing chain length. It might indicate the importance of PFASs adsorbing to the sampler surface, as partitioning constants will increase with increasing chain length (Urik and Vrana (2019)).

The sampling rate was further explored using a more simplified linear uptake model:

$$\text{(equ. 2)} \quad R_s = \frac{C_s}{C_{wt}} = \frac{L}{\text{day}}$$

The sampling rates calculated from both equations were compared (Figure 17, Table 8), and at all three study sites, were not found to be significantly different (p-value > 0.32), with Fields Pt WWTP linear calculation being $29 \pm 2.2 \text{ mL day}^{-1}$ and $29 \pm 2.9 \text{ mL day}^{-1}$ for the kinetic model, $40 \pm 4.1 \text{ mL day}^{-1}$ for Bucklin's linear and $40 \pm 5.1 \text{ mL day}^{-1}$ for the kinetic, and $22 \pm 3.0 \text{ mL day}^{-1}$ for the Bay's linear and $23 \pm 4.2 \text{ mL day}^{-1}$ for the kinetic. This is useful when wanting to calculate the sampling rate for compounds whose partitioning constants (K_{sw}) are not known, we can estimate the sampling rates by using this more simplified linear calculation.

Linear uptake

The duration of linear uptake is an important consideration for integrative passive samplers, such as this PE tube, and helps determine the optimal deployment period. The Fields Point time series study displayed linear uptake ($R^2 > 0.96$) for the nine compounds examined (PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA) (Figure 18, Table 9). Calculating the time the sampler takes to reach equilibrium (t_{eq}) is a useful metric to determine the maximum deployment period:

$$(equ. 3) \quad t_{eq} = \frac{K_{sw}m_s}{R_s} \quad (\text{Lohmann et al. 2012})$$

Using the mean K_{sw} , 201368 L kg^{-1} , of the nine compounds analyzed, sorbent mass (m_s) of $6 \times 10^{-4} \text{ kg}$, and mean R_s of $0.02921 \text{ L day}^{-1}$, we get a t_{eq} value of 4166 days. Indicating that our thirty-day deployment was well within the linear uptake phase. The optimal deployment period is typically constrained by temporal resolution, over-coming instrumental detection limits, and biofouling, so finding a compromise between these factors (likely one to several months) would be a useful deployment period for the future.

Environmental factors

Five of the Narragansett Bay fields deployment sites were located next to long term monitoring buoys that record temperature, salinity, density, dissolved oxygen, pH and chlorophyll a. When these environmental factors were plotted against the mean sampling rates at each site (Figure 19), regressions suggest there are probable links between sampling rate and environmental factors, most notable pH ($R^2 = 0.62$) and density

($R^2=0.52$). To explore these relationships further, a generalized linear model and Akaike Information Criterion (AIC) likelihood of fit indices were analyzed (Table D).

Chlorophyll (which can be used as a proxy for organic carbon) and pH generated the strongest relationship with the sampling rate. However, this data interpretation is likely skewed by one low outlier, so this sample set is too small to derive useful conclusions on these variables.

Potential effect of water flow velocity

Kaserzon et al. (2019) presented a similar study conducted with these polyethylene tube samplers in ground water, and the R_s values derived in their study were compared to the sampling rates calculated for Narragansett Bay and the two waste water treatment plants. Water flow velocities were estimated based on average expected conditions for the three environments and compared to the calculated R_s values (Figure 20). Their sampling rate for ground water (3.2 mL day^{-1}) was an order of magnitude lower than the sampling rates for the Bay (23 mL day^{-1}) and WWTP (37 mL day^{-1}). These results indicate that environmental flow rate is likely more impactful on the sampling rate than initially expected. Where higher flow environments facilitate a higher sampling rate, by reducing the water boundary layer between the sampler and medium (Fauvelle et al. 2017b).

Back-calculating surface water concentrations using the sampling rate

Knowing that the one month's deployment is well within the linear uptake phase, and that the sampler design (caged vs naked) does not affect the uptake, we can use the

sampling rates derived from Field's Point validation study to back calculate the surface water concentrations of Narragansett Bay. In order to do so, the linear model to determine the sampling rate was used, due to the fact that not all K_{sw} values are known for all twenty-four compounds needed for the kinetic model. The passive sampler concentration and time deployed is also needed to make the calculation such that: $C_w = \frac{C_s}{tR_s} = \frac{ng}{L}$ (Table 10).

Water grab concentrations of PFASs at deployment and recovery of the passive sampler in the Bay were plotted independently, along with the calculated surface water values (Figure 21). Quite a bit of variability is observed between the two water grabs, particularly for site 7 (Quonsett Point), which displayed extremely high levels of 6:2-FTS and EtFOSAA only during the first grab sampling event. This was possibly due to release from AFFF application event, due to the proximity of the air force base, and that these concentrations dissipated quickly, thus not being represented in the passive samplers or in second grab sample. Sites 1 and 3 also display some variability in the two different water grab concentrations, while sites 6, 8, and 9 have more consistent PFASs levels, perhaps due to being located further from direct point sources and therefore are only exposed to consistent background levels. These observations further the notion that estuaries fluctuate quite a bit, and that a long-term passive sampler could be incredibly beneficial for more representative data.

The calculated surface water concentrations appear to underestimate the observed PFASs concentrations, particularly for the sites in the north of the Bay (1, 2, and 3) (Figure 21 and 22). Suspecting that the flow rate of the system does indeed factor in to the sampling rate of the PE tube, the R_s values from Field's Point are likely not

representative of what is observed in the specific nine sites throughout Narragansett Bay, especially with tidal and freshwater influence. Moving forward, measuring the flow rate of a deployment site is recommended in order to derive a flow rate specific sampling rate and derive more accurate PFAS concentrations.

POCIS versus Polyethylene Tube Sampler

Two previous studies have been conducted using POCIS to monitor PFASs in aquatic environments. A Swedish study used a traditional POCIS in a drinking water treatment plant, and found an average sampling rate of 45 mL day^{-1} (Gobelius et al. 2019), and correcting for the surface area (46 cm^2), its uptake rate is $0.98 \text{ mLday}^{-1}\text{cm}^{-2}$. Another Australian study used a modified POCIS (smaller surface area and greater sorbent amount than a traditional POCIS) and found an uptake rate of $16.8 \text{ mLday}^{-1}\text{cm}^{-2}$ (270 mLday^{-1} over 16 cm^2) (Kaserzon et al. 2012). Comparatively, the uptake rate produced by the PE tube sampler in Narragansett Bay was $1.28 \text{ mLday}^{-1}\text{cm}^{-2}$ (23 mLday^{-1} over 19 cm^2). While each study has its own limitations for comparison—the Gobelius study taking place in a drinking water treatment plant, thus without the environmental and tidal fluctuations of an estuary, and the Kaserzon study, while in an estuary, however did use a modified POCIS—the PE tube sampler seems comparable to the POCIS, and has a much lower sampling rate than the modified POCIS, stipulating that the PE tubes have a reduced effect of flow rate in comparison. These PE tube samplers with a lower R_s and reduced flow rate dependence are more desirable in field deployments in order to control for environmental impacts as much as possible. However, to gain a better

understanding of how these two passive samplers compare, a side by side deployment would be helpful to determine how the sampling rates correlate.

Limitations

An uncertainty of this study is the uptake pattern of the Bucklin Point time series, which could be affected by a number of factors. With a t_{eq} of 4000 days, the sampler is unlikely to be at sorptive capacity for PFASs after 28 days. After the month's deployment and an approximate R_s of 40 mL day^{-1} , the sampler would have sampled 1.2 liters of water, and with 6 grams of sorbent in the sampler, it can sample 40 liters of water. A more likely reason for the leveling off of the uptake is the biofouling of the sampler and the pores getting clogged. Water samples from Fields Point and Bucklin Point were filtered with glass fiber filters. The particulates accumulated from Fields Point weighed twice as much as Bucklin Point, but Bucklin Point took twice as long to filter, indicating that the particles in Bucklin Point WWTP are smaller than in Fields Point WWTP, and more likely to clog the pores in the samplers. The two waste water treatment plants are set up differently—Fields Point uses chlorine whereas Bucklin Point uses UV to sterilize the effluent—and these differences in treatment could lead to differences in particle size and effluent composition which could lead to differences in the sampler uptake. Visually, the effluent flow at Bucklin Point appeared to be faster than at Fields Point, which could explain why Bucklin exhibited higher sampling rates than Fields, but without measuring the effluent with a flow meter, no definite conclusions can be drawn. Within the effluent, there are likely hundreds of other compounds, beyond PFASs, that could interfere with the sampler uptake. In order to rule out the potential effect of interference, whole effluent

samples should be analyzed and screened for other compounds, in particularly pharmaceuticals, which are polar and would accumulate in the PE tubes samplers as well.

Another limitation of this study is the lack of flow rate measurements, especially in light of the data presented here that the flow of the water is a driver of the sampling rate. The WWTP flow is likely fairly stable, but the Bay is tidally influenced, and knowing the flow rate at the specific sites would be helpful to calibrate the sampling rate. Additionally, PFASs concentration is inherently correlated with other environmental factors in the Bay (salinity, temperature, etc.) due to the physical set up of the estuary. The generalized linear model accounted for some of the variability of the PFAS water concentration, but a study with the same PFASs concentration and a wider range of environmental factors would be better to discern specific environmental effects.

Conclusions

Twenty-four PFASs were detected *in situ* in the polyethylene tube sampler, across both waste water treatment plants and Bay deployments, with the samplers being optimized for carboxylic acid and sulfonate groups. Sampling rates vary from 10 to 50 mL day⁻¹ across all sites, with mean rates of 40 ± 5.1 mL day⁻¹ for Bucklin Point WWTP, 29 ± 2.9 mL day⁻¹ for Fields Point WWTP, and 23 ± 4.2 mL day⁻¹ for Narragansett Bay. Unexpectedly, sampling rates tended to increase with increasing chain length of the compounds, possibly due to adsorption of the longer-chain compounds. The samplers show good agreement with the PFASs water concentrations, with the most abundant compounds (PFBA, PFPeA, PFHxA, PFHpA, and PFOA) in the active grab samples, also being the most abundant in the passive samplers. The one-month deployment was well

within the linear uptake phase (which could last for years). The optimal deployment will hence be a compromise between the desired temporal resolution, limitations from biofouling and amassing sufficient PFAS to overcome detection limits easily. The samplers appear to be reproducible across all sites, with PFASs uptake being 2 to 15 ng per sampler in the Bay and 60 to 70 ng per sampler in the waste water treatment plants. For the most prominent compounds, the samplers display 5% to 30% variability between replicates, suggesting that reproducibility is mainly limited by instrumental detection limits and analytical uncertainty. The water flow velocity is likely an important driver for the sampling rate, which leads to the difference in PFASs uptake between the samplers in the Bay and WWTP. Overall, these polyethylene tube samplers exhibit the successful accumulation of PFASs in surface waters, and provide a suitable solution for long-term monitoring of these compounds. Moving forward, more detailed experimentation needs to be conducted in order to understand how the flow rate and other water properties, including particles, effect the uptake rate of the passive samplers. A controlled laboratory experiment, with consistent PFASs concentrations and varying environmental conditions, would be beneficial to calibrate the sampling rates of the samplers across a wide range of environmental conditions.

Figure 1. Polyethylene tube sampler. 1a) In clockwise order: HLB sorbent in weighing tin, empty polyethylene tubes, caps used to close sampler, assembled PE tube sampler (Image taken by Christine Gardiner). 1b) Cross section of PE tube sampler demonstrating how the compounds diffuse from the water through the tube membrane and accumulate in the sorbent receiving phase (Image taken from Górecki & Namieśnik 2002).

Figure 2. Population density map of Rhode Island. Image taken from Irwin 2011, with data based on the 2010 U.S. Census and modeled on GIS software.

Figure 3. Map of Narragansett Bay deployment sites and WWTP locations, modeled on Ocean Data View computing software.

Figure 4. PFASs concentration in WWTP effluent from the pilot study. Average of four water grabs collected on deployment and recovery of passive sampler.

Figure 5. Passive sampler concentration from the pilot WWTP study. Note: The data representing Bucklin point has been divided by a factor of ten, in order to view it on the same scale as Fields Pt (total Bucklin Pt accumulations were ten-fold higher than that of Fields Pt).

Figure 6. PFASs concentration from daily composite samples from Fields Point WWTP from time series study.

Table 1. Fields Point composite effluent PFASs concentrations (ng L ⁻¹). Effluent samples from June 4, 2018 to July 3, 2018. FC=Fields Pt composite. Total=sum 24 PFASs. Averages computed from 6/4 to 6/23. ND=no data. SD=standard deviation of average. *=samples effected by a contamination event when processing samples 6/25 to 7/3 and blank. **=totals computed using average value for PFPeA, PFHxA, PFHpA, PFNA, PFDA, and PFUdA, and these values are also used to plot Figure 4. % total computed from average.													
Date	PFBA	PFPeA	HFPODA	PFBS	PFHxA	4:2- FTS	PFPeS	PFHpA	PFHxS	PFOA	6:2- FTS	PFHpS	PFNA
FC 6/4	15.13	21.71	ND	22.26	29.29	0.11	2.64	6.64	5.38	18.14	3.92	0.34	2.40
FC 6/5	15.64	15.18	ND	14.57	23.36	0.12	1.86	5.12	5.55	15.04	4.68	0.44	2.69
FC 6/6	10.75	13.54	ND	13.03	21.87	0.10	1.65	5.53	4.00	13.20	3.79	0.31	2.20
FC 6/7	11.84	10.99	ND	9.15	19.00	0.10	1.02	5.26	3.61	12.18	3.30	0.21	2.11
FC 6/8	15.42	20.99	ND	18.25	30.51	0.11	1.67	6.80	5.65	17.17	4.81	0.43	2.56
FC 6/9	17.27	23.20	ND	21.32	32.54	0.19	1.79	7.16	5.19	17.81	3.83	0.34	2.65
FC 6/10	13.47	23.73	ND	21.47	31.40	0.12	1.85	7.15	6.73	18.44	3.35	0.41	2.48
FC 6/11	14.02	19.94	ND	18.03	28.65	0.11	2.09	6.89	6.26	17.45	3.15	0.31	2.92
FC 6/13	15.26	22.49	ND	30.60	27.38	0.02	2.60	8.45	8.75	22.72	3.72	0.62	3.81
FC 6/15	22.85	21.83	ND	19.69	27.61	0.03	2.14	6.49	5.24	15.21	2.77	0.15	2.32
FC 6/17	16.20	24.46	ND	23.16	32.47	0.04	1.75	6.79	5.91	14.69	2.60	0.22	2.15
FC 6/19	18.23	22.12	ND	21.79	30.33	0.06	1.65	7.27	6.12	17.10	1.84	0.36	2.30
FC 6/21	17.32	22.30	ND	22.17	28.53	0.01	2.40	6.68	5.77	15.95	1.60	0.24	2.45
FC 6/23	16.92	19.68	ND	18.82	27.40	0.03	1.99	5.85	4.65	13.55	3.75	0.41	1.97
FC 6/25	17.14	591.94*	ND	18.33	129.55*	0.01	2.11	7.66*	9.99*	15.40	2.36	0.27	6.26*
FC 6/27	19.40	607.82*	ND	20.59	141.87*	0.02	1.71	8.94*	11.21*	14.96	3.75	0.15	6.60*
FC 6/29	11.41	629.16*	ND	12.85	135.24*	0.05	1.76	6.02*	4.26*	11.82	2.93	0.53	6.41*
FC 7/1	9.27	639.10*	ND	9.58	125.59*	0.00	1.24	6.27*	8.24*	11.54	2.40	0.18	6.08*
FC 7/3	16.24	629.60*	ND	18.95	127.74*	0.00	1.62	6.73*	5.72*	12.45	1.42	0.38	5.79*
Blank	0.66	914.48*	ND	0.29	119.01*	0.01	0.04	2.31*	4.27*	0.98	0.35	0.01	4.10*
Avg. 6/4-6/23	15.74	20.15	ND	19.59	27.88	0.08	1.93	6.58	5.63	16.33	3.36	0.34	2.50
SD	2.94	4.05	ND	5.12	3.99	0.05	0.43	0.89	1.23	2.69	0.93	0.12	0.45
% total	12.192	15.613	ND	15.180	21.600	0.064	1.498	5.095	4.360	12.652	2.606	0.264	1.937

Table 1. (continued) Fields Point composite effluent PFASs concentrations (ng L ⁻¹).													
Date	FOSA	PFOS	PFDA	8:2- FTS	PFNS	PFUdA	N-Me FOSAA	Et FOSAA	PFDS	PFDoA	PFtrDA	PFTeDA	Total
FC 6/4	0.34	6.23	2.49	0.09	0.06	0.12	0.28	0.40	0.03	0.07	0.12	0.00	138.17
FC 6/5	0.25	6.62	3.06	0.31	0.13	0.11	0.21	0.35	0.03	0.01	0.00	0.37	115.71
FC 6/6	0.28	7.26	2.86	0.13	0.09	0.13	0.17	0.33	0.03	0.01	0.00	0.26	101.52
FC 6/7	0.32	6.01	2.33	0.29	0.02	0.07	0.37	0.60	0.05	0.01	0.00	0.20	89.04
FC 6/8	0.55	5.41	2.12	0.23	0.01	0.08	0.18	0.45	0.03	0.04	0.00	0.21	133.67
FC 6/9	0.26	6.26	2.23	0.20	0.08	0.07	0.15	0.32	0.05	0.02	0.00	0.23	143.16
FC 6/10	0.38	6.16	2.40	0.25	0.03	0.14	0.12	0.34	0.02	0.03	0.00	0.21	140.67
FC 6/11	0.33	6.53	2.94	0.21	0.02	0.13	0.28	0.32	0.04	0.01	0.00	0.21	130.84
FC 6/13	0.17	5.74	3.05	0.46	0.04	0.09	0.21	0.27	0.06	0.02	0.00	0.00	156.51
FC 6/15	0.00	3.33	1.66	0.07	0.03	0.02	0.65	0.25	0.03	0.04	0.00	0.00	132.39
FC 6/17	0.09	3.27	1.97	0.23	0.04	0.05	0.50	0.15	0.03	0.03	0.00	0.00	136.76
FC 6/19	0.22	3.46	1.93	0.16	0.09	0.06	1.08	0.30	0.03	0.03	0.00	0.00	136.53
FC 6/21	0.32	3.57	1.47	0.24	0.02	0.06	0.71	0.14	0.06	0.05	0.00	0.00	132.06
FC 6/23	0.28	2.94	1.24	0.08	0.04	0.04	0.22	0.16	0.03	0.04	0.00	0.00	120.08
FC 6/25	0.16	3.37	5.52*	0.23	0.07	0.86*	0.17	0.62	0.05	0.81	0.00	0.00	120.08**
FC 6/27	0.26	3.24	4.15*	0.39	0.12	0.66*	0.15	0.22	0.04	0.91	0.00	0.39	125.67**
FC 6/29	0.17	3.53	4.80*	0.17	0.03	0.50*	0.34	0.21	0.04	0.32	0.00	0.00	130.76**
FC 7/1	0.20	3.02	4.96*	0.15	0.12	0.87*	0.23	0.23	0.04	0.56	0.00	0.00	111.25**
FC 7/3	0.31	2.47	3.74*	0.29	0.05	0.75*	0.11	0.30	0.05	0.46	0.00	0.00	103.58**
Blank	0.13	0.09	2.27*	0.11	0.05	0.54*	0.06	0.17	0.03	0.39	0.00	0.00	1050.35*
Avg. 6/4-6/23	0.27	5.20	2.27	0.21	0.05	0.08	0.37	0.31	0.04	0.03	0.01	0.13	129.11
SD	0.11	1.52	0.58	0.10	0.03	0.04	0.28	0.12	0.01	0.02	0.03	0.13	17.43
% total	0.226	4.028	1.756	0.164	0.038	0.064	0.284	0.243	0.028	0.023	0.007	0.101

Figure 7. PFASs concentration from daily composite samples from Bucklin Point WWTP from time series study.

Table 2. Bucklin Point composite effluent PFASs concentrations (ng L ⁻¹). Effluent samples from June 4, 2018 to July 3, 2018. BC=Bucklin Pt composite. Total=sum 24 PFASs. Averages computed from 6/4 to 7/3. ND=no data. SD=standard deviation of average. % total computed from average.													
Date	PFBA	PFPeA	HFPODA	PFBS	PFHxA	4:2- FTS	PFPeS	PFHpA	PFHxS	PFOA	6:2- FTS	PFHpS	PFNA
BC 6/4	18.50	35.20	ND	14.60	27.30	0.10	ND	6.70	4.80	11.30	20.60	0.50	2.10
BC 6/5	28.60	24.60	ND	8.20	19.60	0.10	ND	4.90	3.50	10.60	15.10	0.60	1.90
BC 6/6	25.10	19.60	ND	11.90	18.00	0.10	ND	5.20	2.70	10.30	12.60	0.40	2.30
BC 6/7	29.40	19.90	ND	13.70	18.20	0.20	2.00	5.90	3.80	13.10	10.80	0.40	2.30
BC 6/8	17.60	21.70	ND	15.50	19.20	0.00	2.10	6.00	4.80	13.30	10.80	0.40	2.40
BC 6/9	23.10	24.20	ND	13.10	19.80	0.10	2.00	6.50	4.80	13.70	8.80	0.40	2.40
BC 6/10	22.00	23.80	ND	19.40	19.10	0.10	2.20	6.20	4.10	13.50	6.90	0.50	2.60
BC 6/11	34.50	26.60	ND	20.80	19.10	0.20	2.00	5.70	4.40	13.40	6.00	0.40	2.00
BC 6/13	16.60	20.32	ND	21.32	20.90	0.00	0.66	6.65	5.68	13.17	8.12	0.05	2.43
BC 6/15	19.43	23.22	ND	16.27	18.61	0.00	0.63	6.45	4.87	12.22	7.70	0.23	2.13
BC 6/17	0.00	21.29	ND	22.69	19.04	0.00	0.54	5.85	3.88	15.51	5.59	0.09	2.34
BC 6/19	16.02	22.98	ND	14.22	19.34	0.00	0.72	6.06	4.32	14.77	8.63	0.03	2.36
BC 6/21	9.65	27.72	ND	15.14	25.08	0.00	ND	9.14	9.19	14.92	6.42	0.61	2.12
BC 6/23	9.16	27.31	ND	16.40	27.98	66.95	ND	7.92	19.41	13.78	5.96	0.32	2.25
BC 6/25	13.40	30.36	ND	23.11	28.40	0.00	ND	8.55	10.91	13.72	5.09	0.60	2.19
BC 6/27	16.90	23.59	ND	14.03	24.36	0.00	ND	9.38	18.99	13.20	5.52	0.29	1.52
BC 6/29	18.18	26.67	ND	7.69	22.40	0.00	1.95	6.89	6.66	12.88	5.36	0.06	2.32
BC 7/1	16.52	22.34	ND	11.69	28.89	0.00	0.70	8.92	12.46	14.40	4.17	0.18	2.14
BC 7/3	16.90	26.01	ND	11.36	22.61	0.00	0.48	10.48	11.79	16.47	3.59	0.02	1.97
Blank	0.09	0.02	ND	0.14	0.02	0.02	0.03	0.04	0.04	0.29	0.03	0.00	0.04
Avg. 6/4-7/3	18.50	24.60	ND	15.32	22.00	3.57	1.33	7.02	7.42	13.38	8.30	0.32	2.20
SD	7.85	3.87	ND	4.47	3.82	15.35	0.75	1.57	5.06	1.55	4.21	0.20	0.24
% total	13.77	18.31	ND	11.40	16.37	2.66	0.99	5.22	5.52	9.96	6.18	0.24	1.64

Table 2. (continued) Bucklin Point composite effluent PFASs concentration (ng L ⁻¹).													
Date	FOSA	PFOS	PFDA	8:2- FTS	PFNS	PFUdA	N-Me FOSAA	Et FOSAA	PFDS	PFDoA	PFTrDA	PFTeDA	Total
BC 6/4	0.20	4.60	1.40	2.10	0.00	0.00	0.20	0.40	0.00	0.00	0.00	0.20	150.80
BC 6/5	0.30	5.10	1.70	2.80	0.00	0.00	0.20	0.40	0.00	0.00	0.00	0.20	128.40
BC 6/6	0.40	6.80	1.70	2.60	0.00	0.20	0.40	0.40	0.00	0.00	0.00	0.30	121.00
BC 6/7	0.50	4.00	1.30	2.90	0.10	0.00	0.20	0.40	0.00	0.00	0.00	0.20	129.30
BC 6/8	0.50	4.90	1.40	2.40	0.00	0.10	0.50	0.40	0.10	0.00	0.00	0.20	124.30
BC 6/9	0.20	6.00	1.40	2.10	0.00	0.10	0.60	0.40	0.00	0.00	0.00	0.20	129.90
BC 6/10	0.40	5.50	1.30	2.20	0.00	0.00	0.20	0.40	0.00	0.00	0.00	0.30	130.70
BC 6/11	0.20	5.20	1.30	2.30	0.00	0.00	0.50	0.50	0.00	0.00	0.00	0.20	145.30
BC 6/13	0.09	5.82	1.06	1.95	0.00	0.00	0.50	0.06	0.00	0.05	0.30	9.88	135.60
BC 6/15	0.43	4.93	1.41	1.36	0.00	0.00	0.74	0.00	0.00	0.00	0.00	1.82	122.44
BC 6/17	2.52	5.34	1.07	1.71	0.00	0.23	0.48	0.22	0.00	0.00	0.00	2.43	110.84
BC 6/19	0.78	4.80	1.29	1.18	0.00	0.00	0.45	0.27	0.00	0.00	0.00	0.45	118.67
BC 6/21	0.41	5.52	1.97	1.32	0.00	0.03	0.64	0.00	0.00	0.03	0.12	0.68	130.72
BC 6/23	0.48	4.96	1.46	0.55	0.00	0.07	0.76	0.00	0.00	0.29	0.17	1.17	207.37
BC 6/25	0.18	4.97	1.55	0.24	0.00	0.12	0.47	0.00	0.00	0.34	0.18	1.42	145.79
BC 6/27	0.08	5.17	1.29	0.46	0.00	0.26	0.52	0.23	0.00	0.75	0.51	1.04	138.09
BC 6/29	0.08	5.75	1.66	0.53	0.00	0.02	0.58	0.00	0.00	0.27	0.00	0.21	120.17
BC 7/1	0.25	5.74	1.68	0.21	0.00	0.22	0.48	0.05	0.00	0.00	0.00	1.02	132.07
BC 7/3	0.10	6.56	1.47	0.49	0.00	0.09	0.55	0.00	0.00	0.11	0.31	0.61	131.97
Blank	0.07	0.04	0.01	0.00	0.00	0.04	0.05	0.14	0.02	0.02	0.09	0.19	1.37
Avg. 6/4-7/3	0.43	5.35	1.44	1.55	0.01	0.08	0.47	0.22	0.01	0.10	0.08	1.19	134.39
SD	0.54	0.67	0.23	0.92	0.02	0.09	0.17	0.19	0.02	0.19	0.15	2.20	20.29
% total	0.32	3.98	1.07	1.15	0.00	0.06	0.35	0.16	0.00	0.07	0.06	0.88

Figure 8. Passive sampler concentration from Fields Point times series study. Average of samplers deployed in triplicate per time period (2, 4, 8, 16, and 29 days).

Figure 9. Passive sampler concentration from Bucklin Point times series study. Average of samplers deployed in triplicate per time period (2, 4, 8, 16, and 29 days).

Table 3. Waste water treatment plant passive sampler (PS) concentrations (ng sampler ⁻¹). Average of samplers deployed in triplicate per time period, all samplers deployed on June 4, 2018 and collected after 2, 4, 8, 16, 29 days. ND=no data. Total=sum 24 PFASs. Fields % 16=percent PFASs in passive sampler collected on day 16. Buck % 16=percent PFASs in passive sampler collected on day 16.													
Days deployed	PFBA	PFPeA	HFPODA	PFBS	PFHxA	4:2- FTS	PFPeS	PFHpA	PFHxS	PFOA	6:2- FTS	PFHpS	PFNA
Fields PS 2	0.539	0.995	ND	1.486	1.820	0.001	0.188	0.497	0.553	1.235	0.336	0.036	0.189
Fields PS 4	0.576	1.393	ND	2.500	3.049	0.001	0.388	0.922	1.084	2.178	0.561	0.048	0.383
Fields PS 8	0.792	1.980	ND	3.896	3.733	0.007	0.719	0.924	1.518	2.343	0.498	0.054	0.379
Fields PS 16	0.912	3.973	ND	8.637	7.932	0.009	1.596	2.061	3.172	5.236	1.276	0.142	0.993
Fields PS 29	1.744	8.170	ND	13.848	17.074	0.028	2.095	4.732	4.976	10.421	3.397	0.204	1.679
Bucklin PS 2	0.458	1.964	ND	0.949	2.693	0.011	0.845	0.880	0.726	2.068	3.174	0.074	0.487
Bucklin PS 4	0.675	2.587	ND	1.702	3.923	0.002	1.527	1.150	0.860	2.574	3.290	0.080	0.617
Bucklin PS 8	2.564	3.668	ND	2.170	4.647	0.015	1.447	1.511	1.231	3.537	3.450	0.076	0.773
Bucklin PS 16	2.212	7.966	ND	7.872	11.389	0.011	6.966	3.929	3.892	8.748	6.400	0.278	2.123
Bucklin PS 29	5.327	7.837	ND	7.367	9.267	0.022	1.201	3.661	3.536	7.941	5.767	0.201	1.779
Blanks	0.110	0.100	ND	0.098	0.130	0.002	0.015	0.378	1.658	0.091	0.229	0.004	0.017
Fields % 16	2.269	9.886	ND	21.490	19.737	0.022	3.970	5.129	7.892	13.028	3.175	0.354	2.471
Buck % 16	3.187	11.479	ND	11.344	16.412	0.016	10.038	5.662	5.608	12.605	9.223	0.400	3.059

Table 3. (continued) Waste water treatment plant passive sampler concentrations (ng sampler ⁻¹).												
Days deployed	FOSA	PFOS	PFDA	8:2- FTS	PFNS	PFUdA	N-Me FOSAA	Et FOSAA	PFDS	PFDoA	PFTeDA	Total
Fields PS 2	0.450	0.722	0.214	0.048	0.010	0.016	0.078	0.066	0.010	0.016	0.000	9.506
Fields PS 4	0.038	0.752	0.403	0.061	0.011	0.027	0.038	0.089	0.013	0.020	0.205	14.737
Fields PS 8	0.030	0.992	0.394	0.084	0.025	0.017	0.089	0.079	0.009	0.012	0.000	18.573
Fields PS 16	0.048	2.027	0.883	0.100	0.023	0.020	0.088	0.086	0.016	0.015	0.947	40.189
Fields PS 29	0.026	3.236	1.482	0.163	0.047	0.104	0.100	0.131	0.013	0.128	0.019	73.815
Bucklin PS 2	0.039	0.998	0.407	0.595	0.119	0.029	0.045	0.087	0.012	0.015	0.000	16.672
Bucklin PS 4	0.043	1.102	0.472	0.781	0.015	0.039	0.060	0.074	0.031	0.019	0.000	21.624
Bucklin PS 8	0.125	1.497	0.531	0.875	0.019	0.038	0.063	0.075	0.019	0.014	0.247	28.592
Bucklin PS 16	0.197	3.285	1.428	2.140	0.064	0.076	0.271	0.077	0.050	0.024	0.000	69.395
Bucklin PS 29	0.119	2.720	1.170	1.314	0.023	0.389	0.089	0.097	0.032	0.231	0.120	60.209
Blanks	0.026	0.023	0.029	0.034	0.009	0.033	0.078	0.082	0.010	0.208	1.844	5.208
Fields % 16	0.118	5.042	2.196	0.248	0.058	0.050	0.219	0.215	0.040	0.036	2.356	
Buck % 16	0.284	4.734	2.057	3.083	0.092	0.110	0.390	0.111	0.072	0.034	0.000

Figure 10. PFASs heat map of Narragansett Bay surface water (average of two water grabs collected on deployment and recovery of the passive samplers), extrapolated from surface water samples collected at nine sites, and modeled on Ocean Data View computing software.

Figure 11. PFASs concentration from surface water in field deployment (Narragansett Bay). Average concentrations from two grabs collected on deployment and recovery of sampler.

Table 4. Narragansett Bay surface water PFASs concentration (ng L ⁻¹). Average of water grabs collected on sampler deployment and recovery. Total=sum 24 PFASs. ND=no data. SD=standard deviation. % total computed from average concentration.													
	PFBA	PFPeA	HFPODA	PFBS	PFHxA	4:2- FTS	PFPeS	PFHpA	PFHxS	PFOA	6:2- FTS	PFHpS	PFNA
PDL W (Site 1)	2.420	5.750	ND	2.155	6.050	0.030	0.205	2.560	1.705	6.015	0.640	0.300	1.280
FPB W (Site 2)	1.905	3.248	ND	3.005	3.378	0.023	0.123	1.243	0.708	3.273	0.365	0.463	0.528
PR W (Site 3)	5.023	9.335	ND	5.090	9.063	0.020	0.385	6.453	2.540	9.255	0.983	2.740	2.643
GWB W (Site 4)	0.870	1.210	ND	0.920	0.870	0.020	0.090	0.570	0.280	1.500	0.050	0.040	0.320
NP W (Site 5)	0.850	1.770	ND	1.590	1.580	0.020	0.100	0.870	0.250	1.680	0.040	0.150	0.470
MHB W (Site 6)	0.805	1.775	ND	0.760	1.460	0.035	0.115	0.730	0.405	1.935	0.190	0.140	0.265
QP W (Site 7)	2.588	0.763	ND	0.305	1.018	0.030	0.055	0.783	0.145	3.145	11.965	0.125	0.153
New W (Site 8)	0.500	0.510	ND	0.340	0.685	0.035	0.075	0.235	0.140	1.285	0.105	0.325	0.180
BC W (Site 9)	0.735	0.540	ND	0.510	0.455	0.025	0.040	0.295	0.105	1.105	0.085	0.000	0.315
Blank	0.145	0.065	ND	0.130	0.040	0.015	0.025	0.035	0.045	0.325	0.030	0.020	0.080
Average	1.744	2.767	ND	1.631	2.729	0.026	0.132	1.526	0.698	3.244	1.603	0.476	0.684
SD	1.456	2.974	ND	1.584	2.963	0.006	0.106	1.973	0.854	2.726	3.899	0.862	0.809
% total avg	7.584	12.032	ND	7.091	11.866	0.115	0.574	6.638	3.033	14.106	6.969	2.069	2.973

Table 4. (continued) Narragansett Bay surface water PFASs concentration (ng L⁻¹).

	FOSA	PFOS	PFDA	8:2- FTS	PFNS	PFUdA	N-Me FOSAA	Et FOSAA	PFDS	PFDoA	PFTrDA	PFTeDA	Total
PDL W (Site 1)	0.330	7.365	1.270	0.000	0.205	0.410	2.115	0.805	0.145	0.120	0.040	0.180	42.095
FPB W (Site 2)	1.228	1.335	0.293	0.000	0.103	0.105	0.180	0.450	0.043	0.090	0.055	0.178	22.315
PR W (Site 3)	0.800	3.820	0.835	0.070	0.595	0.208	0.303	0.703	0.200	0.093	0.110	0.905	62.168
GWB W (Site 4)	0.280	0.870	0.030	0.000	0.080	0.060	0.110	0.230	0.020	0.030	0.060	0.170	8.680
NP W (Site 5)	0.160	0.820	0.200	0.000	0.210	0.100	0.150	0.240	0.020	0.030	0.040	0.160	11.500
MHB W (Site 6)	0.210	1.080	0.245	0.000	0.225	0.055	0.135	0.275	1.570	0.055	0.055	0.450	12.970
QP W (Site 7)	0.483	1.538	0.458	0.000	0.113	0.070	3.963	6.945	0.028	0.198	0.053	0.290	35.208
New W (Site 8)	0.210	0.245	0.050	0.000	0.130	0.075	0.140	0.300	0.035	0.045	0.050	0.425	6.120
BC W (Site 9)	0.145	0.755	0.115	0.000	0.000	0.065	0.090	0.220	0.035	0.035	0.050	0.180	5.900
Blank	0.060	0.030	0.010	0.000	0.010	0.030	0.085	0.140	0.015	0.020	0.020	0.085	1.460
Average	0.427	1.981	0.388	0.008	0.184	0.128	0.798	1.130	0.233	0.077	0.057	0.326	22.995
SD	0.364	2.261	0.413	0.023	0.170	0.116	1.353	2.191	0.505	0.055	0.021	0.245	27.929
% total avg	1.858	8.614	1.689	0.034	0.802	0.554	3.472	4.913	1.012	0.336	0.248	1.419

Figure 12. Passive sampler concentrations from field deployments. Average of samplers deployed in duplicate at each site.

Table 5. Narragansett Bay passive sampler concentrations (ng sampler ⁻¹). Average of samplers deployed in duplicates. Total=sum 24 PFASs. ND=no data. SD=standard deviation. % total computed from average Bay PFASs concentration.													
	PFBA	PFPeA	HFPODA	PFBS	PFHxA	4:2- FTS	PFPeS	PFHpA	PFHxS	PFOA	6:2- FTS	PFHpS	PFNA
PDL PS (Site 1)	0.205	0.325	ND	0.315	0.350	0.020	0.020	0.215	0.080	0.495	0.020	0.000	0.210
FPB PS (Site 2)	0.190	0.780	ND	0.300	0.790	0.010	0.075	0.390	0.190	0.540	0.075	0.000	0.185
PR PS (Site 3)	0.705	1.850	ND	0.780	2.150	0.020	0.070	1.645	0.600	2.630	0.145	0.055	1.130
GWB PS (Site 4)	0.600	0.415	ND	0.260	0.420	0.020	0.070	0.260	0.145	0.790	0.030	0.040	0.200
NP PS (Site 5)	0.330	1.520	ND	0.480	1.220	0.020	0.200	0.835	0.475	1.615	0.090	0.065	0.340
MHB PS (Site 6)	0.180	0.690	ND	0.415	0.825	0.015	0.120	0.645	0.390	1.785	0.025	0.020	0.490
QP PS (Site 7)	0.335	0.470	ND	0.260	0.325	0.020	0.135	0.225	0.180	0.790	0.070	0.355	0.210
New PS (Site 8)	0.155	0.265	ND	0.220	0.180	0.020	0.120	0.140	0.085	0.320	0.025	0.195	0.100
BC PS (Site 9)	0.175	0.718	ND	0.385	0.110	0.020	0.065	0.130	0.110	0.310	0.030	0.005	0.090
Blanks	0.740	0.063	ND	0.068	0.047	0.000	0.000	0.024	0.056	0.306	0.000	0.000	0.020
Average	0.319	0.781	ND	0.379	0.708	0.018	0.097	0.498	0.251	1.031	0.057	0.082	0.328
SD	0.202	0.548	ND	0.172	0.648	0.004	0.052	0.492	0.190	0.801	0.042	0.119	0.325
% total avg.	4.599	11.251	ND	5.463	10.191	0.264	1.400	7.175	3.608	14.838	0.816	1.176	4.727

Table 5. (continued) Narragansett Bay passive sampler concentrations (ng sampler ⁻¹).													
	FOSA	PFOS	PFDA	8:2- FTS	PFNS	PFUdA	N-Me FOSAA	Et FOSAA	PFDS	PFDoA	PFRrDA	PFTeDA	Total
PDL PS (Site 1)	0.055	1.355	0.160	0.000	0.000	0.050	0.145	0.165	0.020	0.035	0.020	0.085	4.34
FPB PS (Site 2)	0.055	1.355	0.275	0.000	0.000	0.070	0.380	0.170	0.015	0.030	0.025	0.085	5.98
PR PS (Site 3)	0.050	1.690	0.500	0.000	0.010	0.140	0.390	0.600	0.015	0.055	0.025	0.080	15.33
GWB PS (Site 4)	0.050	0.800	0.235	0.810	0.055	0.095	0.225	0.155	0.025	0.055	0.020	0.085	5.86
NP PS (Site 5)	0.060	2.150	0.280	0.030	0.010	0.080	0.380	0.870	0.030	0.015	0.020	0.085	11.20
MHB PS (Site 6)	0.140	2.065	0.390	0.000	0.010	0.110	0.100	0.420	0.025	0.010	0.030	0.090	8.99
QP PS (Site 7)	0.060	0.565	0.175	0.000	0.000	0.040	0.160	0.205	0.015	0.010	0.035	0.085	4.72
New PS (Site 8)	0.055	0.195	0.085	0.000	0.000	0.060	0.080	0.145	0.010	0.015	0.020	0.080	2.57
BC PS (Site 9)	0.060	0.460	0.090	0.000	0.000	0.075	0.290	0.230	0.010	0.035	0.020	0.080	3.49
Blanks	0.048	0.032	0.000	0.094	0.000	0.000	0.192	0.099	0.000	0.000	0.158	1.882	3.82
Average	0.065	1.182	0.243	0.093	0.009	0.080	0.239	0.329	0.018	0.029	0.024	0.084	6.94
SD	0.028	0.712	0.137	0.269	0.018	0.031	0.125	0.254	0.007	0.018	0.005	0.003	4.14
% total avg.	0.936	17.014	3.504	1.344	0.136	1.152	3.440	4.735	0.264	0.416	0.344	1.208

Figure 13. Passive sampler reproducibility, six naked (N) and six caged (C) samplers were deployed at the same location.

Figure 14. Passive sampler reproducibility relative percent difference. Calculated for all twelve replicates by taking the standard deviation and dividing by the mean of each compound, then multiplying by one hundred.

Table 6. Comparison of naked versus caged passive sampler types (N=naked, C=caged). The mean is the average of the six replicates of each type of sampler ± the standard error (ng sampler ⁻¹). P-value was computed using a two-way t-test assuming equal variance.							
	Sampler Type	Mean ± SE	p-value		Sampler Type	Mean ± SE	p-value
PFBA	N	0.365 ± 0.046	0.3975	PFHxS	N	0.309 ± 0.031	0.0878
	C	0.348 ± 0.048			C	0.376 ± 0.034	
PFPeA	N	1.013 ± 0.144	0.1701	PFHpS	N	0.068 ± 0.002	0.1226
	C	0.859 ± 0.057			C	0.080 ± 0.010	
PFHxA	N	0.948 ± 0.039	0.2200	PFOS	N	0.588 ± 0.040	0.2694
	C	1.030 ± 0.095			C	0.639 ± 0.070	
PFHpA	N	0.566 ± 0.049	0.2046	PFNS	N	0.003 ± 0.001	0.5000
	C	0.630 ± 0.056			C	0.003 ± 0.001	
PFOA	N	0.960 ± 0.054	0.3662	PFDS	N	0.115 ± 0.000	0.1356
	C	0.993 ± 0.075			C	0.120 ± 0.004	
PFNA	N	0.361 ± 0.018	0.3452	4:2-FTS	N	0.045 ± 0.001	0.3810
	C	0.376 ± 0.033			C	0.045 ± 0.001	
PFDA	N	0.185 ± 0.025	0.4888	6:2-FTS	N	0.095 ± 0.041	0.4542
	C	0.184 ± 0.032			C	0.090 ± 0.012	
PFUdA	N	0.122 ± 0.027	0.0515	8:2-FTS	N	0.239 ± 0.014	0.2814
	C	0.068 ± 0.013			C	0.230 ± 0.004	
PFDoA	N	0.016 ± 0.002	0.2275	FOSA	N	0.073 ± 0.007	0.2383
	C	0.021 ± 0.006			C	0.067 ± 0.003	
PFtrDA	N	0.038 ± 0.003	0.1626	N-Me FOSAA	N	0.197 ± 0.029	0.2606
	C	0.035 ± 0.000			C	0.177 ± 0.011	
PFTeDA	N	0.000 ± 0.000	0.000	EtFOSAA	N	0.271 ± 0.107	0.1498
	C	0.000 ± 0.000			C	0.154 ± 0.005	
PFBS	N	0.409 ± 0.044	0.4422	Total	N	7.104 ± 0.284	0.4108
	C	0.419 ± 0.058			C	7.203 ± 0.323	
PFPeS	N	0.116 ± 0.015	0.2721				
	C	0.136 ± 0.027

Figure 15. Sampling rates calculated for field deployments and WWTP. Shown are box and whisker plots for Narragansett Bay (n=18), Bucklin Pt WWTP (n=15), and Fields Pt WWTP (n=15), displaying sampling rates calculated using equation 1 (kinetic model).

Figure 16. Plot of sampling rate (R_s) versus carbon chain length of the PFAS compound for Bay, Bucklin Point and Fields Point. Carboxylic acid plot consists of PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA. Sulfonate plot consists of PFBS, PFHxS, and PFOS.

Table 7. Sampling rates of WWTP and Narragansett Bay. Sampling rates computed from equation 1. Bucklin Point (n=15), Fields Point (n=15), Bay (n=18). SE=standard error. $\bar{T}$ <0.1. *<0.05. **<0.01. ***<0.001.									
	Bucklin Point		Fields Point		Bay		Buck vs Fields	Bay vs Buck	Bay vs Fields
	R_s (mL d ⁻¹)	± SE	R_s (mL d ⁻¹)	± SE	R_s (mL d ⁻¹)	± SE	p-value	p-value	p-value
PFBS	26.33	2.92	33.62	2.66	18.18	4.38	0.1159	0.0664 [†]	0.0029**
PFHxS	44.40	6.17	42.57	3.59	27.74	4.69	0.1859	0.0206*	0.0089**
PFOS	41.90	5.69	29.55	3.68	37.74	6.05	0.0240*	0.3104	0.1287
PFPeA	22.34	2.44	18.53	2.00	17.50	4.96	0.0741 [†]	0.1949	0.4247
PFHxA	34.30	4.29	24.81	2.51	13.84	1.77	0.0203*	0.0002***	0.0007***
PFHpA	38.37	4.54	29.04	3.19	15.17	2.33	0.0323*	<0.0001***	0.0008***
PFOA	42.24	5.23	27.19	2.77	15.16	2.27	0.0143*	<0.0001***	0.0011**
PFNA	53.45	6.26	29.12	3.11	27.80	5.18	0.0053**	0.0019**	0.4146
PFDA	60.21	8.61	28.42	2.66	33.70	6.15	0.0023**	0.0097**	0.2204
Avg	40.39	5.13	29.21	2.91	22.98	4.20

Figure 17. Sampling rate calculation comparison of linear model versus kinetic model.

Dashed line represents 1:1 ratio of the two parameters.

Table 8. Sampling rate calculation comparison of linear model versus kinetic model. C _s /C _w sampling rates computed from linear model (equation 2). K _{sw} sampling rates computed from kinetic model (equation 1). SE=standard error.															
	Fields Point WWTP					Bucklin Point WWTP					Narragansett Bay				
	C _s /C _w R _s ± SE (mL day ⁻¹)		K _{sw} R _s ± SE (mL day ⁻¹)		p-value	C _s /C _w R _s ± SE (mL day ⁻¹)		K _{sw} R _s ± SE (mL day ⁻¹)		p-value	C _s /C _w R _s ± SE (mL day ⁻¹)		K _{sw} R _s ± SE (mL day ⁻¹)		p-value
PFBS	33.10	2.68	33.62	2.66	0.4454	25.95	2.89	26.33	2.92	0.4635	17.61	3.75	18.18	4.38	0.4314
PFHxS	42.54	3.59	42.57	3.59	0.4978	44.37	6.17	44.40	6.17	0.4985	29.32	4.40	27.74	4.69	0.4950
PFOS	29.54	3.68	29.55	3.68	0.4990	41.87	5.69	41.90	5.69	0.4987	36.69	5.47	37.74	6.05	0.4933
PFPeA	18.08	2.00	18.53	2.00	0.4375	21.69	2.43	22.34	2.44	0.4265	14.65	3.37	17.50	4.96	0.3166
PFHxA	24.70	2.51	24.81	2.51	0.4876	34.10	4.28	34.30	4.29	0.4871	13.80	1.63	13.84	1.77	0.4730
PFHpA	28.98	3.19	29.04	3.19	0.4943	38.27	4.53	38.37	4.54	0.4934	15.00	2.07	15.17	2.33	0.4880
PFOA	27.14	2.77	27.19	2.77	0.4954	42.13	5.23	42.24	5.23	0.4943	14.70	2.04	15.16	2.27	0.4902
PFNA	29.09	3.11	29.12	3.11	0.4971	53.34	6.25	53.45	6.26	0.4952	26.45	4.70	27.80	5.18	0.4908
PFDA	28.41	2.66	28.42	2.66	0.4984	60.15	8.60	60.21	8.61	0.4978	33.65	5.42	33.70	6.15	0.4935
Avg	29.06	2.18	29.21	2.91		40.21	4.05	40.39	5.13		22.43	3.04	22.98	4.20

Figure 18. Linear uptake curve of passive samplers deployed in Fields Point WWTP. Average of samplers deployed in triplicate per time period (2, 4, 8, 16, 29 days). Similar linearity was observed in all compounds, see Table 9 for further information.

Table 9. Linear uptake curve of Fields Point time series study. Average of samplers deployed in triplicate per time period (2, 4, 8, 16, 29 days). SE=stand error, Slope, y-intercept, and R ² from Figure 11.										
	PFBS	PFHxS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	
Time (days)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	Avg ± SE (ng PS ⁻¹)	
2	1.49 ± 0.15	0.55 ± 0.05	0.72 ± 0.02	1.00 ± 0.11	1.8 ± 0.20	0.50 ± 0.06	1.23 ± 0.08	0.19 ± 0.03	0.21 ± 0.01	
4	2.50 ± 0.33	1.08 ± 0.16	0.75 ± 0.15	1.39 ± 0.21	3.05 ± 0.49	0.92 ± 0.13	2.18 ± 0.28	0.38 ± 0.05	0.40 ± 0.05	
8	3.90 ± 0.66	1.52 ± 0.29	0.99 ± 0.22	1.98 ± 0.32	3.73 ± 0.90	0.92 ± 0.20	2.34 ± 0.65	0.38 ± 0.14	0.39 ± 0.07	
16	8.64 ± 0.89	3.17 ± 0.19	2.03 ± 0.34	3.97 ± 0.25	7.93 ± 0.59	2.06 ± 0.20	5.24 ± 0.64	0.99 ± 0.19	0.88 ± 0.16	
29	13.85 ± 1.92	4.98 ± 0.52	3.24 ± 0.33	8.17 ± 1.36	17.07 ± 2.97	4.73 ± 0.62	10.42 ± 1.26	1.68 ± 0.26	1.48 ± 0.22	
slope	0.4653	0.1635	0.0979	0.2662	0.5594	0.1536	0.3367	0.0552	0.0463	
y-int	0.5824	0.3314	0.3906	0.1609	0.1212	0.0145	0.3092	0.0729	0.1286	
R²	0.9944	0.9927	0.9878	0.9857	0.9781	0.9616	0.9803	0.9816	0.9818

Figure 19. Plot of sampling rates (R_s) versus various environmental measurements for five sites in Narragansett Bay, with deployments located next to the DEM MERL monitoring buoys.

Figure 20. Plot of the log sampling rates (R_s) versus the log flow rates of aquatic environments. Bay is the average of the Narragansett Bay sampling rates, WWTP is the average of Bucking and Fields Point waste water treatment plants, and GW is ground water data taken from Kaserzon et al. (2019) where they deploy similar PE tube samplers in ground water. Note: all of these flow rates are estimated calculations based on average expected conditions at each of these sites, none of these are measured rates.

Figure 21. Calculated Narragansett Bay surface water. At each site, surface water concentrations are displayed for the water grabs collected on deployment (dep) and recovery (rec), as well as the calculated values using the sampling rate (calc). Deployment surface water concentrations are not available for stations 4 and 5.

Figure 22. Plot of the calculated versus measured Narragansett Bay surface water values.

The measured values displayed here are the mean from both water grabs upon passive sampler deployment and recovery. The dashed line represents the one to one ratio between the two parameters.

Table 10. Narragansett Bay surface water concentrations (ng L ⁻¹) back-calculated ($C_w = C_s/t \cdot R_s$) from Field's Point (FP) sampling rate (R _s) from the linear model (equation 2).														
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFtrDA	PFTeDA	PFBS	PFPeS	
FP R _s (L day ⁻¹)	0.009	0.018	0.025	0.029	0.027	0.029	0.028	0.042	0.140	0.000	0.117	0.033	0.048	
Site 1	0.796	0.620	0.489	0.256	0.629	0.249	0.194	0.041	0.009	0.000	0.025	0.328	0.014	
Site 2	0.690	1.392	1.032	0.434	0.642	0.205	0.312	0.054	0.007	0.000	0.024	0.292	0.050	
Site 3	2.561	3.301	2.808	1.831	3.126	1.253	0.568	0.107	0.013	0.000	0.022	0.760	0.047	
Site 4	2.180	0.741	0.548	0.289	0.939	0.222	0.267	0.073	0.013	0.000	0.024	0.253	0.047	
Site 5	1.199	2.712	1.593	0.930	1.919	0.377	0.318	0.061	0.003	0.000	0.024	0.468	0.134	
Site 6	0.654	1.231	1.077	0.718	2.121	0.543	0.443	0.084	0.002	0.000	0.025	0.404	0.081	
Site 7	1.217	0.839	0.424	0.250	0.939	0.233	0.199	0.031	0.002	0.000	0.024	0.253	0.091	
Site 8	0.563	0.473	0.235	0.156	0.380	0.111	0.097	0.046	0.003	0.000	0.022	0.214	0.081	
Site 9	0.657	1.323	0.148	0.150	0.381	0.103	0.106	0.059	0.008	0.000	0.023	0.388	0.045	
	PFHxS	PFHpS	PFOS	PFNS	PFDS	4:2- FTS	6:2- FTS	8:2- FTS	FOSA	N-Me FOSAA	Et FOSAA	Total		
FP R _s (L day ⁻¹)	0.043	0.030	0.030	0.043	0.067	0.006	0.030	0.062	0.166	0.059	0.040			
Site 1	0.065	0.000	1.582	0.000	0.010	0.111	0.023	0.000	0.011	0.085	0.142	5.680		
Site 2	0.144	0.000	1.480	0.000	0.007	0.052	0.081	0.000	0.011	0.209	0.137	7.255		
Site 3	0.455	0.059	1.846	0.008	0.007	0.103	0.157	0.000	0.010	0.215	0.484	19.741		
Site 4	0.110	0.043	0.874	0.042	0.012	0.103	0.033	0.419	0.010	0.124	0.125	7.490		
Site 5	0.360	0.070	2.348	0.008	0.014	0.103	0.098	0.016	0.012	0.209	0.702	13.678		
Site 6	0.296	0.022	2.255	0.008	0.012	0.078	0.027	0.000	0.027	0.055	0.339	10.503		
Site 7	0.137	0.383	0.617	0.000	0.007	0.103	0.076	0.000	0.012	0.088	0.165	6.090		
Site 8	0.064	0.210	0.213	0.000	0.005	0.103	0.027	0.000	0.011	0.044	0.117	3.176		
Site 9	0.086	0.006	0.519	0.000	0.005	0.107	0.034	0.000	0.012	0.165	0.192	4.516		

APPENDICES

Table A. List of native standards used to make calibration curve and native standard (24 compounds from PFAC-24PAR and HFPODA).			
Compound	Abbreviation	Compound	Abbreviation
Perfluoro-n-butanoic acid	PFBA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA
Perfluoro-n-pentanoic acid	PFPeA	Perfluoro-1-butanesulfonate	PFBS
Perfluoro-n-hexanoic acid	PFHxA	Perfluoro-1-pentanesulfonate	PFPeS
Perfluoro-n-heptanoic acid	PFHpA	Perfluorohexanesulfonate (linear & branched)	PFHxS
Perfluoro-n-octanoic acid	PFOA	Perfluoro-1-heptanesulfonate	PFHpS
Perfluoro-n-nonanoic acid	PFNA	Perfluorooctanesulfonate (linear & branched)	PFOS
Perfluoro-n-decanoic acid	PFDA	Sodium Perfluoro-1-nonaanesulfonate	PFNS
Perfluoro-n-undecanoic acid	PFUdA	Sodium Perfluoro-1-decanesulfonate	PFDS
Perfluoro-n-dodecanoic acid	PFDoA	Sodium 1H, 1H, 2H, 2H-perfluoro-1-hexanesulfonate	4:2-FTS
Perfluoro-n-tridecanoic acid	PFTTrDA	Sodium 1H, 1H, 2H, 2H-perfluoro-1-octanesulfonate	6:2-FTS
Perfluoro-n-tetradecanoic acid	PFTeDA	Sodium 1H, 1H, 2H, 2H-perfluoro-1-decanesulfonate	8:2-FTS
Perfluoro-1-octanesulfonamide	FOSA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	HFPODA-GenX
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA		

Table B. List of mass-labeled compounds used to make the internal standard (19 compounds from MPFAC-24ES and M3HFPODA)			
Compound	Abbreviation	Compound	Abbreviation
Perfluoro-n-[¹³ C ₄]butanoic acid	MPFBA	Perfluoro-1-[¹³ C ₈]octanesulfonamide	M8FOSA
Perfluoro-n-[¹³ C ₅]pentanoic acid	M5PFPeA	N-methyl-d ₃ -perfluoro-1-octanesulfonamidoacetic acid	d3-N-MeFOSAA
Perfluoro-n-[1,2,3,4,6- ¹³ C ₅]hexanoic acid	M5PFHxA	N-ethyl-d ₅ -perfluoro-1-octanesulfonamidoacetic acid	d5-N-EtFOSAA
Perfluoro-n-[1,2,3,4,4- ¹³ C ₄]heptanoic acid	M4PFHpA	Sodium Perfluoro-1-[2,3,4- ¹³ C ₃]butanesulfonate	M3PFBS
Perfluoro-n-[¹³ C ₈]octanoic acid	M8PFOA	Sodium Perfluoro[1,2,3- ¹³ C ₃]hexanesulfonate	M3PFHxS
Perfluoro-n-[¹³ C ₉]nonanoic acid	M9PFNA	Sodium Perfluoro[¹³ C ₈]octanesulfonate	M8PFOS
Perfluoro-n-[1,2,3,4,5,6- ¹³ C ₆]decanoic acid	M6PFDA	Sodium 1H, 1H, 2H, 2H-perfluoro-1-[1,2- ¹³ C ₂]hexanesulfonate	M2-4:2-FTS
Perfluoro-n-[1,2,3,4,5,6,7- ¹³ C ₇]undecanoic acid	M7PFUdA	Sodium 1H, 1H, 2H, 2H-perfluoro-1-[1,2- ¹³ C ₂]octanesulfonate	M2-6:2-FTS
Perfluoro-n-[1,2- ¹³ C ₂]dodecanoic acid	MPFDoA	Sodium 1H, 1H, 2H, 2H-perfluoro-1-[1,2- ¹³ C ₂]decanesulfonate	M2-8:2-FTS
Perfluoro-n-[1,2- ¹³ C ₂]tetradecanoic acid	M2PFTeDA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-[¹³ C ₃]-propanoic acid	M3HFPODA-GenX

Table C. Sorbent partitioning coefficient (K_{sw}) from Urik & Vrana (2019).							
Compound	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	
K_{sw} (L kg ⁻¹)	5370.318	42657.95	97723.72	120226.4	208929.6	407380.3	
Compound	PFDoDA	PFTTrDA	PFBS	PFHxS	PFOS		
K_{sw} (L kg ⁻¹)	251188.6	138038.4	15848.93	457088.2	457088.2		

Table D. Generalized Linear models, df (degrees of freedom) and AIC (Akaike Information Criterion) values.		
Model	df	AIC
mod11 <- glm(Rs ~ offset(Cw) + temp + sal + den + DO + pH + chl , family = gaussian)	mod11 7	-275.03569
mod50 <- glm(Rs ~ offset(Cw) , family = gaussian)	mod50 2	55.92087
mod51 <- glm(Rs ~ offset(Cw) + sal + pH + chl , family = gaussian)	mod51 5	38.07168
mod52 <- glm(Rs ~ offset(Cw) + temp , family = gaussian)	mod52 3	54.60389
mod53 <- glm(Rs ~ offset(Cw) + sal , family = gaussian)	mod53 3	46.99158
mod54 <- glm(Rs ~ offset(Cw) + den , family = gaussian)	mod54 3	45.73785
mod55 <- glm(Rs ~ offset(Cw) + DO , family = gaussian)	mod55 3	52.75848
mod56 <- glm(Rs ~ offset(Cw) + pH , family = gaussian)	mod56 3	41.93145
mod57 <- glm(Rs ~ offset(Cw) + chl , family = gaussian)	mod57 3	56.51503
mod58 <- glm(Rs ~ offset(Cw) + chl + sal , family = gaussian)	mod58 4	41.87912
mod59 <- glm(Rs ~ offset(Cw) + chl + pH , family = gaussian)	mod59 4	39.53314
mod60 <- glm(Rs ~ offset(Cw) + chl + temp , family = gaussian)	mod60 4	48.43180
mod61 <- glm(Rs ~ offset(Cw) + chl + DO , family = gaussian)	mod61 4	51.56552
mod62 <- glm(Rs ~ offset(Cw) + chl + den , family = gaussian)	mod62 4	41.16360
mod63 <- glm(Rs ~ offset(Cw) + chl + sal + pH , family = gaussian)	mod63 5	38.07168
mod64 <- glm(Rs ~ offset(Cw) + chl + sal + temp , family = gaussian)	mod64 5	43.53843
mod65 <- glm(Rs ~ offset(Cw) + chl + sal + DO , family = gaussian)	mod65 5	42.15721
mod66 <- glm(Rs ~ offset(Cw) + chl + sal + den , family = gaussian)	mod66 5	42.52617
mod67 <- glm(Rs ~ offset(Cw) + chl + pH + temp , family = gaussian)	mod67 5	41.32467
mod68 <- glm(Rs ~ offset(Cw) + chl + DO + temp , family = gaussian)	mod68 5	49.37312
mod69 <- glm(Rs ~ offset(Cw) + sal + DO + temp , family = gaussian)	mod69 5	40.52639
mod70 <- glm(Rs ~ offset(Cw) + sal + DO + den , family = gaussian)	mod70 4	51.56552
mod71 <- glm(Rs ~ offset(Cw) + sal + chl + temp , family = gaussian)	mod71 5	43.53843
mod72 <- glm(Rs ~ offset(Cw) + sal + pH + temp , family = gaussian)	mod72 5	36.24269
mod73 <- glm(Rs ~ offset(Cw) + den + DO + temp , family = gaussian)	mod73 5	38.33362
mod74 <- glm(Rs ~ offset(Cw) + pH + DO + temp , family = gaussian)	mod74 5	38.07476

Table D. (continued) Generalized Linear models, df (degrees of freedom) and AIC (Akaike Information Criterion) values.		
Model	df	AIC
mod75 <- glm(Rs ~ offset(Cw) + chl + pH + temp + sal , family = gaussian)	mod75 6	36.56776
mod76 <- glm(Rs ~ offset(Cw) + DO + den , family = gaussian)	mod76 4	45.18439
mod77 <- glm(Rs ~ offset(Cw) + sal + DO , family = gaussian)	mod77 4	47.86185
mod78 <- glm(Rs ~ offset(Cw) + sal + den , family = gaussian)	mod78 4	43.22773
mod79 <- glm(Rs ~ offset(Cw) + temp + DO + den , family = gaussian)	mod79 5	38.33362
mod80 <- glm(Rs ~ offset(Cw) + temp + DO , family = gaussian)	mod80 4	54.56848
mod81 <- glm(Rs ~ offset(Cw) + temp + den , family = gaussian)	mod81 4	43.87101
mod82 <- glm(Rs ~ offset(Cw) + temp + pH , family = gaussian)	mod82 4	40.34033
mod83 <- glm(Rs ~ offset(Cw) + temp + sal , family = gaussian)	mod83 4	44.24340
mod84 <- glm(Rs ~ offset(Cw) + temp + chl , family = gaussian)	mod84 4	48.43180
mod85 <- glm(Rs ~ offset(Cw) + den + pH , family = gaussian)	mod85 4	37.30988
mod86 <- glm(Rs ~ offset(Cw) + den + chl , family = gaussian)	mod86 4	41.16360
mod87 <- glm(Rs ~ offset(Cw) + den + sal , family = gaussian)	mod87 4	43.22773
mod88 <- glm(Rs ~ offset(Cw) + DO + pH , family = gaussian)	mod88 4	40.35324
mod89 <- glm(Rs ~ offset(Cw) + DO + sal , family = gaussian)	mod89 4	47.86185
mod90 <- glm(Rs ~ offset(Cw) + DO + chl , family = gaussian)	mod90 4	51.56552
mod91 <- glm(Rs ~ offset(Cw) + den + pH + sal, family = gaussian)	mod91 5	38.55523
mod92 <- glm(Rs ~ offset(Cw) * den * pH * sal, family = gaussian)	mod92 7	-192.14154
mod93 <- glm(Rs ~ offset(Cw) * temp * pH * sal, family = gaussian)	mod93 7	-282.49185
mod94 <- glm(Rs ~ offset(Cw) * chl * temp * pH * sal, family = gaussian)	mod94 7	-304.16993
mod95 <- glm(Rs ~ offset(Cw) * chl , family = gaussian)	mod95 3	56.51503
mod96 <- glm(Rs ~ offset(Cw) * chl * sal , family = gaussian)	mod96 5	43.84821
mod97 <- glm(Rs ~ offset(Cw) * chl * pH, family = gaussian)	mod97 5	34.19134

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