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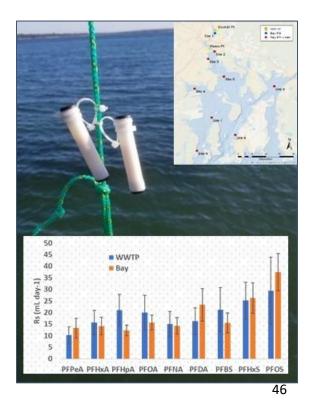
1 **Field validation of a novel passive sampler for dissolved PFAS in surface waters**

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11

12

13 **ABSTRACT**

14   Numerous per- and polyfluoroalkyl substances (PFAS) are of growing concern

15 worldwide, due to their ubiquitous presence, bioaccumulation and adverse effects. Surface

16 waters in the United States have displayed elevated concentrations of PFAS, but so far discrete

17 water sampling has been the commonly applied sampling approach. Here we field-tested a

18 novel integrative passive sampler, a microporous polyethylene (PE) tube, and derived sampling

19 rates (R_s) for 9 PFAS in surface waters. Three sampling campaigns were conducted, deploying

20 PE tube passive samplers in the effluent of two wastewater treatment plant (WWTP) effluent

21 sites plants (WWTPs) and across Narragansett Bay (RI, US) for one month each in 2017/2018.

22 Passive samplers exhibited linear uptake of PFAS in the WWTP effluents over 16-29 days, with

23   in-situ R_s for nine PFASs ranging from 10 mL day^{-1} (PFPeA) to 29 mL day^{-1} (PFOS). Similar

24   sampling rates of 19 ± 4.8 mL day^{-1} were observed in estuarine field deployments. Applying

25   these R_s values in a different WWTP effluent predicted dissolved PFAS concentrations mostly

26   within 50% of their observations in daily composite water samples, except for PFBA (where

27   predictions from passive samplers were 3x greater than measured values), PFNA (1.9), PFDA

28   (1.7) and PFPeS (0.1). These results highlight the potential use of passive samplers as

29   measurement and assessment tools of PFAS in dynamic aquatic environments.

30

31   **Keywords:** PFOS, PFOA, sampling rate, wastewater treatment plan effluent, surface water,

32   Narragansett Bay

33   **GRAPHICAL ABSTRACT**

34

35

46

47   **INTRODUCTION**

48   Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals that have been used

49   in commercial, industrial, and consumer products since the 1950s. Today the class includes over

50   9,000 chemicals with increasingly diverse chemistries (Lindstrom et al. 2011; Wang et al. 2017;

51   US EPA 2020). These chemicals have been found globally distributed in air, surface water,

52   sediment, biota, and drinking water due to their environmental mobility and remarkable

53   persistence in the environment (Wang et al. 2017).

54   A variety of sampling methods and extraction protocols have been developed to

55   measure the distribution of PFAS across complex and divergent environmental matrices,

56   including both discrete and limited use of passive sampling (Lai et al. 2019). Discrete sampling

57   provides a snapshot of contaminant levels at a discrete point in time. Passive samplers

58   accumulate organic pollutants via kinetic or equilibrium sampling; kinetic sampling generates a

59   time-weighted mean concentration of freely dissolved compounds in water or air (Vrana et al.

60   2005). Concentrations derived using passive sampling are therefore more representative of

61   mean contaminant levels compared to discrete sampling techniques. In general, passive

62   samplers also provide other benefits including low cost, small size, ease of use, and reduced

63   complexity of the chemical extraction process (Lohmann et al. 2012). They can be deployed

64   over large spatial and temporal scales, reducing or eliminating the need for frequent

65   environmental sampling campaigns (Ghosh et al. 2014).

66   Passive samplers like polyethylene (PE) sheets and semi-permeable membrane devices

67   have been widely used and shown to be suitable for sampling hydrophobic organic compounds

68   (Górecki and Namieśnik 2002; Vrana et al. 2005). Recent work incorporating passive sampling

69   materials and design has demonstrated the utility of passive sampling for amphiphilic and

70   hydrophilic compounds. The Polar Organic Chemical Integrative Sampler (POCIS) has been used

71   to sample dissolved polar compounds, including PFAS and pharmaceuticals. It incorporates a

72   metal ring sandwiching a charged powdered adsorbent which binds the polar compound,

73   between two thin (100-200 µm) polyethersulfone membranes (Alvarez et al. 2004). However,

74   the kinetic uptake and sampling rate of PFAS is dependent on the flow rate of the surrounding

75   medium, and the sorbent choice (Kaserzon et al. 2012; Kaserzon et al. 2014; Gobelius et al.

76   2019; Hale et al. 2021). Additional complications of the standard POCIS sampler include the

77   potential of sorption to the polyethersulfone membrane (Endo et al. 2019). Alternatives to

78   POCIS include diffusive gradients in thin film (DGT) samplers for PFAS (Challis et al. 2016; Guan

79   et al. 2018), though their performance under ambient conditions in the field has only recently

80   been assessed (Fang et al. 2021). Additionally, the use of isotopic performance reference

81   compounds (PRCs) in passive samplers of ionic compounds is difficult due to anisotropy and

82   competition for sorption sites (Vrana et al. 2005).

83   A novel passive sampler design, consisting of a hollow microporous PE tube filled with

84   charged powdered adsorbent, has been proposed and initial tests in groundwater

85   contaminated with aqueous film forming foam (AFFF) have been performed (Kaserzon et al.

86   2019). The PE tubes have thick (2 mm) microporous walls that provide a diffusion layer

87   sufficiently thick to dominate the overall mass transfer from the bulk water to the sorbent

88   hence flow/turbulence does not affect sampling kinetics much. Pollutant uptake is presumably

89   limited by passive diffusion through the tube's porous PE walls. These passive samplers have

90   been previously used for the assessment of polar herbicides (Fauvelle, Montero, et al. 2017;

91 Cárdenas-Soracá et al. 2020), and licit and illicit drugs in surface waters with some success

92 (McKay et al. 2020; Verhagen et al. 2021), but require further validation to evaluate sampling

93 performance under a wider range of environmentally relevant conditions, including dynamic

94 water bodies, such as estuaries.

95 Estuaries act as an interface between freshwater systems and ocean environments and

96 as such encompass a wide range of physical and chemical conditions based on ever-changing

97 tidal flow, freshwater inputs, and anthropogenic inputs (Nixon and Buckley 2002). PFAS have

98 previously been identified in estuarine surface water, introduced via wastewater treatment

99 plant (WWTP) effluent, riverine flow, septic system leakage, atmospheric deposition, and (near)

100 coastal AFFF use (Moody and Field 2000; Möller et al. 2010; Schaider et al. 2016; Ruyle et al.

101 2021). Elucidating the distribution and behavior of PFAS in multiple compartments of estuarine

102 environments remains a research priority given the proximity of estuaries to anthropogenic

103 PFAS sources, the highly variable environmental conditions found in estuaries, and the

104 importance of estuarine habitats for key ecosystem services (Sharp et al. 1984; Vasconcelos et

105 al. 2011; Munoz et al. 2017).

106 This study was hence performed to field-test a novel passive sampler for PFAS in two

107 different dynamic surface water environments—first in the effluent of two WWTPs in

108 Providence, Rhode Island (RI), USA, while daily 24 hour composite samples for PFAS were

109 collected; followed by a field campaign in Narragansett Bay (NB), a well-mixed, tidally

110 influenced estuary in RI, USA (Pilson 1985). In summary, the aims were to elucidate i) the

111 integrative uptake of PFAS by PE tube passive samplers in a wastewater treatment plant

112 effluent; ii) the sampling rates of different PFAS relative to daily composite PFAS samples; iii)

113   the validity of the thus derived sampling rates in a parallel wastewater treatment plant effluent;

114   and iv) performance of the PE tube samplers across an estuary.

115

116   **MATERIALS & METHODS**

117   *Chemicals, reagents and materials.*

118   A total of 24 PFAS were evaluated in this study, including C4–C14 perfluorocarboxylates

119   (PFCAs), C4-C10 perfluorosulfonates (PFSAs), three fluorotelomer sulfonates (FTS), and three

120   sulfonamide precursors (Tables S1 and S2). Analytical standards, including mass-labeled

121   surrogates, were purchased from Wellington Laboratories (Guelph, ON, Canada) (see SI). HPLC

122   grade methanol, ammonium hydroxide, and ammonium acetate were purchased from Fisher

123   Scientific (Waltham, MA, USA). Ultrapure water was obtained from a Milli-Q system fit with an

124   HPLC water polisher or via HPLC grade water purchased from Fisher Scientific (Waltham, MA,

125   USA). Weak-anion exchange solid phase extraction cartridges (150 mg/6 cc, Oasis WAX) and

126   bulk hydrophilic-lipophilic-balanced (HLB) sorbent were from Waters Inc. (Milford, MA, USA).

127   Microporous high-density polyethylene Filtroplast tubing (FL10, 2.5 µm filtration grade, 12 mm

128   outer diameter, 2 mm membrane thickness) were purchased from Pall Corp. (Germany) and

129   push-in polyethylene plugs to seal tube samplers were from McMaster-Carr Supply Company

130   (Elmhurst, IL, USA).

131

132   *Preparation of PE tube samplers.*

133   Microporous PE tubing was cut to a length of 7 cm, filled with 0.6 g of HLB sorbent and

134   capped with push-in polyethylene plugs, creating an exposed surface area of 18.8 cm^2 and a

135   surface area to mass sorbent ratio of 31 $cm^2 g^{-1}$. The sorbent-packed sampler was conditioned

136   prior to field deployment via agitation in methanol, 0.1% ammonium hydroxide in methanol,

137   and ultrapure water for 24 hours each, respectively.

138

139   *Wastewater treatment plant deployments.*

140   The PFAS passive samplers were field-tested in two WWTP final, disinfected, effluents

141   due to their elevated concentrations of PFAS, controlled and consistent conditions (such as flow

142   rate and temperature) and availability of daily composite water samples for PFAS analysis. At

143   Field's Point, a WWTP servicing 225,000 customers (discharge 160 million L day^{-1}) from

144   Providence, RI, passive samplers were deployed in triplicate for 2, 4, 8, 16, and 29 day periods

145   each. In parallel, triplicate passive samplers were also deployed at a second WWTP, Bucklin

146   Point, serving 160,000 customers (discharge 70 million L day^{-1}, see Figure S1) to test the derived

147   Rs values in a controlled study (as water concentrations were known). Composite water

148   samples (1 L) were collected daily, made up of effluent sub-samples collected every hour for a

149   given 24-hour period and combined. Field blanks were included for both discrete samples and

150   passive samplers.

151

152   *Estuary field trial deployments.*

153   Previous work suggests a gradient of organic pollutant concentrations across

154   Narragansett Bay (NB), with higher concentrations in the north, near larger population centers

155   (Sacks and Lohmann 2011). At each of the chosen nine NB sites (Figure 1), PE-tube passive

156   samplers were deployed in duplicate anchored to sediment traps, roughly 3 m above the

157 seafloor, from September to October 2017. Surface grab water samples (top 10 cm) were

158 collected at each site during sampler deployment and recovery. Narragansett Bay is partially

159 well mixed, so we typically do not expect major gradients between surface and deeper waters,

160 particularly in the fall.

161   The reproducibility of the passive samplers under different deployment designs was

162 tested in July 2019. Six 'caged' and six 'naked' passive samplers were deployed near the surface

163 of the Pawtuxet River site at 0.5 m depth for three weeks, and water samples were collected

164 upon deployment and recovery. The naked samplers consisted of bare PE tube zip-tied to the

165 anchored line (the style of samplers deployed at both WWTPs), and the caged samplers were

166 housed in a PE mesh cage to minimize biofouling on the samplers (the style of samplers

167 deployed throughout NB) (See sampler design and photos in Figure S1).

168

169 *Sample Extraction.*

170   Water samples were stored in 1 L HDPE bottles at −15°C and thawed to room

171 temperature for extraction. Aliquots of 300 to 500 mL were each spiked with 10 ng of mass-

172 labeled surrogates. The water samples were extracted using Oasis WAX solid phase extraction

173 cartridges conditioned and eluted according to previously published methods (Taniyasu et al.

174 2005; Yamashita et al. 2005).

175   Passive samplers were scrubbed and rinsed with deionized water to remove algal

176 growth. Intact passive samplers, composed of the PE tube packed with sorbent, were

177 centrifuged three times for three minutes at a relative centrifugal force of 1,300 to remove

178 water. Passive samplers were then transferred to 15 mL polypropylene tubes and 6 mL of

179   methanol was added. The solvent was spiked with mass-labelled surrogates and allowed to

180   equilibrate for 24 hours. The methanol was then decanted to a fresh polypropylene tube; this

181   extraction process was repeated for a total of four solvent extractions per passive sampler, and

182   extracts combined.

183

184   *Instrumental analysis.*

185   Extracts were evaporated to 250 µL and reconstituted with 750 µL 2 mM ammonium

186   acetate in ultrapure water, yielding a final sample makeup of 3:1 aqueous to organic phases.

187   Reconstituted extracts were centrifuged at 21,3000 x g to remove any remaining particles, and

188   the supernatant transferred to autosampler vials. Samples were analyzed via liquid

189   chromatography- tandem mass spectrometry in negative electrospray ionization (-ESI) mode, as

190   detailed elsewhere (Robuck et al. 2020). Compound identification and quantification was

191   performed using the isotope dilution approach, based on a five-point calibration curve ranging

192   from 0.25-50 ng mL^{-1}.

193

194   *QA/QC.*

195   Field blanks, process blanks and instrument blanks were included during collection,

196   extraction, and analysis for water and passive samplers. Blank concentrations were at 0-20% of

197   the measured samples; sample concentrations were hence not blank corrected. Method

198   detection limits (MDL) were derived for both water and passive samplers as follows: if no

199   analyte signal was detected in process or field blanks, instrumental detection limits (IDL),

200   representing the analyte concentration with a signal-to-noise ratio of 10, were used as MDL. If

201   an analyte was detected in process and/or field blanks, MDLs were calculated as average value

202   plus 3 times the standard deviation (SD) of the concentrations in all blanks. If the observed

203   levels in field blanks were significantly higher compared to process blanks, only values from

204   field blanks were used for the MDL determination (see SI Table S3).

205   Thresholds for recoveries were acceptable between 60-130%. Recoveries of mass-

206   labeled internal standard for nine of the most abundant compounds (PFBS, PFHxS, PFOS,

207   PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA) ranged from 60% to 90%. These 9 PFAS were

208   combined to Σ_9PFAS. Longer chain and precursor compounds had more variable recoveries (20-

209   300%), probably due to varying sorption artifacts during handling, and were not included in

210   further analysis. Only PFAS with detection frequencies > 50% were considered for the further

211   analysis (Antweiler and Taylor 2008), values < MDL were replaced with ½ MDL (Antweiler 2015;

212   George et al. 2021).

213

214   *Calculation of sampling rates, R_s.*

215   The general uptake equation for a passive sampler in which compound uptake is

216   kinetically controlled by either the water boundary layer, membrane transport, or a

217   combination of both is:

218
$$N_s = m_s K_{sw} C_w \left[1 - exp^{-\left(1 - \frac{R_s t}{K_{sw} C_w}\right)} \right] \qquad (1),$$

219   where N_s is the amount in the passive sampler (ng),

220   K_{sw} is the sorbent-water sorption coefficient (L kg^{-1}),

221   C_w is the average water concentration during sampler deployment (ng L^{-1}),

222   R_s is the sampling rate (L d^{-1}),

223   t is time (d), and

224   m_s is the mass of the sorbent used (kg).

225   Sampling rates (R_s, in L day^{-1}) were calculated using a first-order kinetic model (Kaserzon et al.

226   2019), assuming samplers were in the linear uptake regime:

227                                $$R_s = \frac{N_s}{C_w t}$$ (2).

228   Weighted linear regressions were performed in GraphPadPrism® Version 9.3.1.

229

230   **RESULTS AND DISCUSSION**

231   *Reproducibility of PFAS uptake by passive samplers.*

232   Twelve passive samplers were co-deployed at site 9 in NB simultaneously to test the

233   reproducibility of the PE tube samplers during a three week deployment. Passive samplers

234   accumulated Σ_9PFAS at an average of 9.1 ± 0.8 ng, consistent across all replicates (Figure S5,

235   Table S16). For seven of the target compounds detected in all passive samplers (PFHxS, PFOS,

236   PFPeA, PFHxA, PFHpA, PFOA, and PFNA), the relative standard deviation between replicates

237   was between 15% and 28% (Figure S6) indicating good reproducibility. A somewhat higher

238   variability was observed for PFBS (48%) and PFDA (36%). For PFDA, this might reflect a

239   combination of lower concentrations and a stronger sorption to surfaces; we are unsure why

240   PFBS varied between replicates. Overall, these passive samplers can be used to reproducibly

241   accumulate dissolved PFAS under ambient conditions.

242   A comparison was made whether the uptake of PFAS differed between two different

243   sampler deployment configurations–either 'caged' or 'naked', bare PE tube samplers (Figure

244   S1). The 'caged' approach had been used for deployments in NB for additional protection

245   against physical damage and enhanced chance of biofouling. By visual observation, the cage did

246   not reduce biofouling, and there was no significant difference for the accumulated mass by the

247   2 sampler deployment types for nine dominant PFAS (PFBS, PFHxS, PFOS, PFPeA, PFHxA,

248   PFHpA, PFOA, PFNA, and PFDA, Table S23). The effect of the cage on water-side resistance to

249   uptake was hence negligible, so protective cages can be used in the field if warranted.

250

251   *PFAS uptake by passive samplers in WWTP effluent.*

252   *Concentrations of PFAS.* The Field's Point WWTP effluent was dominated by PFCAs, primarily

253   PFBA, PFPeA, PFHxA, PFHpA, and PFOA, with those five PFCAs combined at 82 ± 7 ng L^{-1}

254   (standard error, SE), contributing 68 % to Σ_{24}PFAS in composite water samples. Sulfonates

255   (PFBS, PFPeS, PFHxS, PFHpS, and PFOS) combined to 29 ± 2 ng L^{-1}, 24% of total PFAS (Figure S2,

256   Table S5). Individual neutral precursors were typically < 1 ng L^{-1}; longer chain PFAS (> C9) and

257   6:2 FTS were each ≤ 3.0 ng L^{-1}. Across the month-long sampling period, effluent PFAS

258   concentrations remained fairly constant, with Σ_{24}PFAS of 120 ± 4 ng L^{-1} (Table S4).

259   At the other WWTP, Bucklin Point, PFCAs also contributed most to total PFAS, with the

260   same 5 PFCAs combined at 85 ± 2.0 ng L^{-1} (Table S8). The 5 PFSA combined to an additional 42 ±

261   4.9 ng L^{-1}, while the other PFASs contributed little, except for 6:2 FTS at an average of 8.3 ± 1.0

262   ng L^{-1}.

263   The effluent concentrations observed here were similar to those reported for other

264   WWTPs in the United States (Schultz et al. 2006; Loganathan et al. 2007) and in Australia

265   (Coggan et al. 2019), with the exception of PFOA. These stable PFAS concentrations (relative

266   standard errors were < 10% for most – ionic- compounds across the 29 days, see Tables S4 and

267   S8) allowed for an ideal calibration of the PFAS uptake by the passive samplers.

268   The accumulation of PFAS in the PE-tube samplers deployed in the Field's Point effluent

269   exhibited a linear uptake for the compounds observed (Figure 2, Table S6, Table S19), with

270   passive sampler Σ_9PFAS amounts of 7.7, 13, 16, 35, and 66 ng after 2, 4, 8, 16, and 29 day

271   deployments, respectively. Samplers accumulated the largest amount of PFHxA, at 17 ng, with

272   several longer chain compounds and precursors below detection limits (PFUdA, PFDoA, PFTrDa,

273   PFTeDA, PFNS, PFDS, 4:2 FTS, 8:2 FTS). PFCAs comprised the predominant portion of the

274    $\sum_{24}$PFAS, similar to the concurrently collected effluent grab samples, making up 55 % of the

275   passive sampler load, with sulfonates making up 32 %.

276   At Bucklin Point, the accumulation of PFAS in the effluent increased up to 16 days, with

277   little additional accumulation observed beyond 16 days. Accumulation profiles were dominated

278   by PFPeA, PFHxA, PFOA, and PFBS (Table S10).

279

280   *Sampling Rates.* Sampling rates were derived for passive samplers relative to averaged water

281   concentrations at Field's Point after 2, 4, 8, 16 and 29 days. For the 29-day results, sampling

282   rates ranged from 10 mL day^{-1} (PFPeA) to 34 mL day^{-1} (6:2 FTS), with a mean of 19 ± 7.4 mL day^{-}

283   ^{1} (standard error), see Table 1.

284   There was potentially an increase of Rs with the molar mass of the compound (Figure

285   S9), but this was inconclusive. Sampling rates were overall within a factor of 3.5 from smallest

286   to greatest, and, given the measurement uncertainties, no major differences in Rs emerged

287   from these field trials. A general increase of Rs with molecular weight or size was reported

288   earlier (Kaserzon et al. 2019).

289

290   *Linear uptake.* The duration of linear uptake is an important consideration for integrative

291   passive samplers, such as this PE tube, and helps determine the optimal deployment period.

292   Sampling rates decreased with increasing length of deployments, (see Figure 3) with faster

293   initial uptake. This might be due to some contribution from adsorption and residual PFAS in the

294   passive samplers early on, but stabilized for the 8, 16 and 29-day sampling rates, in particular

295   for the PFCAs, at about 15 mL day^{-1} (range 3.4-21 mL day^{-1}). It could also indicate some degree

296   of sorbent-controlled kinetics (Booij 2021). Overall, though, the Field's Point WWTP time series

297   displayed linear uptake for the nine compounds examined by the PE tube samplers over 29

298   days (Figure 2, Table S19).

299   The time for PFAS to reach 10% of time to equilibrium (t_{10}) in the passive sampler can be

300   derived to determine the maximum deployment period while staying in the linear uptake

301   regime (Lohmann et al. 2012) (equation 3):

302
$$t_{10} = \frac{-\ln\left(1-\frac{C_s}{K_{sw}C_w m_s}\right)m_s K_{sw}}{R_s}$$
(3),

303   where the term $\left(1 - \frac{C_s}{K_{sw}C_w m_s}\right)$ equals (1- 0.1) for 10% equilibrium and K_{sw} were taken from

304   (Urík and Vrana 2019) (Table 2).

305   The time to reach equilibrium were derived using equation (3), and ranged from several

306   weeks for PFPeA and PFBS to 4.4 years for PFDA (Table 2). Somewhat similar time scales were

307   estimated for this PE tube sampler in groundwater, with half-times to equilibrium between 120

308   and 490 days, albeit for a different sorbent (WAX) (Kaserzon et al. 2019).

309   These calculations indicate that our thirty-day deployment was well within the linear

310   uptake phase for most compounds, with the possible exception of PFBA. However, this is based

311   on the assumption of a well-characterized and well-mixed sorbent without concentration

312   gradients, which might not happen during field deployments. The optimal deployment period is

313   typically constrained by the desired temporal resolution, the need to over-come instrumental

314   detection limits, and an incentive to minimize biofouling. Finding a compromise between these

315   factors would suggest that deployment periods for up to several months could be explored in

316   future sampling campaigns if typical surface water concentrations on seasonal scales were the

317   desired outcome.

318

319   *Field-validation of R_s.* The Rs values derived for 2, 4, 8, 16 and 29 day deployments at Field's

320   Point were field-validated in the concurrent Bucklin Point WWTP deployment, where passive PE

321   samplers were also retrieved after 2, 4, 8, 16 and 29 days, while 24 hour composite water

322   samples were collected daily during sampler deployment (Figure 4). The use of the Rs values

323   derived from Field's Point resulted in an overestimation of the actual dissolved PFAS

324   concentrations at Bucklin Point for the shorter deployment periods, typically by a factor of 2.

325   After 29 days, the overall agreement was very good, with almost all concentrations ratios of

326   passive divided by active sampling within 50% of unity, except for PFBA (ratio of 3), PFNA (1.9),

327   PFDA (1.7) and PFPeS (0.1).

328   A weighted linear regression between observation and prediction was derived (r^2=0.53,

329   slope = 1.0 with forced origin, n=48, root mean square error 0.82). Passive sampler-derived

330   concentrations somewhat underestimating observed grab sample results, by an average of 14

331   %. The two WWTPs serve a considerably different user base (residential vs. industrial) and differ

332   in size and in treatment and disinfection styles, likely resulting in different matrix effects for

333   PFAS in both effluents. Given these differences, we consider this agreement as satisfactory and

334   as validation that passive PE-tube style samplers can be used to derive time-weighted average

335   PFAS concentrations in surface waters.

336

337   *Narragansett Bay field deployment of PFAS passive samplers.*

338   *Surface water concentrations.* Narragansett Bay PFAS surface water concentrations from

339   individual grab water samples ranged from <DL to 102 ng L^{-1} for Σ_9PFAS Figure S3, Table S12).

340   Throughout the Bay, PFCAs dominated over PFSAs, similar to our results for the Field's Point

341   WWTP effluent (see above). The highest PFAS concentrations were observed in the northern

342   part of NB, near the largest cities (e.g., Providence) and industrial sites; lower concentrations

343   were observed towards the (southern) mouth of the Bay, with a lower human population

344   density and more tidal mixing with the Atlantic Ocean. Average Σ_9PFAS in the upper watershed

345   (sites 1-3) were 44 ± 12 ng L^{-1}, compared to 6.4 ± 2.0 ng L^{-1} for the lower estuary (sites 4-9). This

346   pattern is consistent with those in other urban estuaries, such as San Francisco Bay (Sedlak et

347   al. 2018). The broad range of PFAS concentrations and field conditions created a good

348   opportunity to test how well the PE samplers worked across a range of environmental settings.

349

350   *Field-derived sampling rates in Narragansett Bay.* The sampling rates for the nine compounds

351   were calculated using the linear uptake model (equation 1), and R$_s$ ranged from 12 to 37 mL

352   day^{-1}, with a mean of 23 ± 6.4 mL day^{-1} (Table 1). There was good agreement with the Rs values

353   derived after 29-day deployments at both waste water treatment plants, with values within a

354   factor of 2 for all compounds, except for PFBA, N-Me-FOSAA and Et-FOSAA, and no significant

355   differences observed.

356

357   *PFAS in an estuarine surface water.* Surface water concentrations of PFAS were calculated using

358   the average sampling rate derived from each of the WWTPs for the nine compounds and

359   compared to the grab sample concentration during sampler recovery (Figure S10). There was a

360   general good agreement between the two concentrations in either case (within ± a factor of 3),

361   however some variability remained, given that we observed large fluctuations between the two

362   grab samples at a couple of sites. In such a dynamic environment, with tidal flushing, storm run-

363   off, and variable point sources, these observations further the notion that PFAS concentrations

364   in estuaries fluctuate, and that a long-term passive sampling could be beneficial for obtaining

365   more representative data. Long-term time series PFAS data for NB surface waters show

366   significant fluctuations in concentration and distribution of PFAS (Katz et al. 2022).

367

368   *Comparison to other PFAS Passive Samplers.*

369   *Potential effect of water flow velocity.* The R_s values derived in our field studies (Field's Point

370   WWTP effluent and NB) were compared with those from Kaserzon et al. (2019) in ground water

371   (Figure S11). Water flow velocities were estimated based on average expected conditions for

372   the three environments and compared to the calculated R_s values. The sampling rate for ground

373   water (3.2 ± 0.6 mL day^{-1} for a 4 cm tube, or 5.6 ± 1.1 mL day^{-1} for a 7 cm tube) was lower than

374   the identical sampling rates for the WWTPs (20 ± 8.0 mL day^{-1} for Fields Point, and 18 ± 5.4 mL

375   day^{-1} for Bucklin Point) and the Bay (23 ± 6.4 mL day^{-1}). These results might indicate that water

376   flow velocity, and hence boundary layer diffusion, is different for the PE tube sampler in

377   stagnant (groundwater) versus flowing (surface) water. We interpret this that (higher flow)

378   surface waters facilitate a higher sampling rate of the PE tube samplers by reducing the effect

379   of the water boundary layer between the sampler and medium (Fauvelle, Kaserzon, et al.

380   2017). Once transfer of PFAS through the walls of the PE tubes becomes the rate-limiting step,

381   the uptake rates probably level off. This should be confirmed in future studies.

382

383   *Comparison to other passive samplers.* Several previous studies have used passive samplers to

384   monitor PFAS in aquatic environments using the POCIS-style sampler while at least one

385 deployed a DGT-style sampler. In a drinking water treatment plant, an average sampling rate of

386 45 mL day^{-1} was reported for the classic POCIS-style sampler (Gobelius et al. 2019); correcting

387 for the surface area (46 cm^2), the uptake rate was 0.98 mL day^{-1} cm^{-2}. Hale et al. (2021) relied

388 on a nylon mesh for the standard surface area (46 cm^2)), and combined WAX with fluoroflash

389 sorbent to obtain much greater uptake of 20-60 mL day^{-1} cm^{-2}. A modified POCIS sampler set-up

390 (smaller surface area, greater sorbent amount, and larger pore size in the polyethersulfone

391 membrane than a traditional POCIS in order to maximize sampling rate) was used in an

392 Australian study, and an uptake rate of 17 mL day^{-1} cm^{-2} was derived (270 mL day^{-1} over 16 cm^2)

393 (Kaserzon et al. 2012). For the DGT samplers (3.1 cm^2), sampling rates of 11-13 mL day^{-1} were

394 derived, or roughly 4 mL day^{-1} cm^{-2} (Wang et al. 2021). Comparatively, the uptake rate

395 produced by the PE tube sampler in NB was 1.0 mL day^{-1} cm^{-2} (19 mL day^{-1} over 19 cm^{-2}).

396 Different sorbents were used in prior studies (WAX vs HLB), and this might affect uptake

397 (Kaserzon et al. 2012). Results from the PE tube sampler were comparable to the classical POCIS

398 configuration, while the PE tube sampler has the benefits of being easily scalable. Side by side

399 deployments of these different passive samplers for PFAS are needed—as was previously

400 performed for herbicides (Hageman et al. 2019)—to determine how the sampling rates and

401 overall performances correlate between these different PFAS passive sampling approaches.

402

403 **CONCLUSIONS**

404 Overall, these results demonstrate that PE tube samplers can be used to derive PFAS

405 concentrations in WWTP effluents, and more dynamic surface waters such as estuaries, and

406   provide a suitable long-term monitoring tool of these compounds. The PE tube samplers were

407   shown to be reproducible within 20-30%. Typical sampling rates were on the order of 20 mL

408   day^{-1} for most PFCAs based on calibration within a WWTP effluent. Very similar sampling rates

409   were derived for a 29-day estuarine field deployment, implying that these Rs values are

410   reasonable approximations for field deployments. Applying these Rs values in a different WWTP

411   effluent resulted in very good predictions, mostly within 50% of their measured dissolved

412   concentrations in the effluent. The field deployments highlighted the dynamic nature of PFAS

413   concentrations in an estuary; adopting passive samplers, such as the PE tubes, would enable

414   ready assessment of typical ambient concentrations and identify the importance of various

415   known and unknown sources of PFAS in urban estuaries. Moving forward, controlled

416   laboratory experiments with consistent PFAS concentrations and varying environmental

417   conditions would be beneficial to calibrate the sampling rates of the samplers across a wide

418   range of environmental conditions.

419

427

428   **SUPPLEMENTARY INFORMATION**

429   The Supporting Information is available free of charge at

430   https://setac.onlinelibrary.wiley.com/ doi-XXX. The SI contains details on further standard and

431   QA/QC measures, tables of all measured concentrations and percent recoveries, and additional

432   figures.

433

434   **Conflict of interest**

435   The authors declare no competing financial interests.

436   **Acknowledgment**:

440   **Author contribution statement**

441   Rainer Lohmann, Christine Gardiner, Mark Cantwell conceptualized the research. Christine
442   Gardiner performed the field work; Christine Gardiner, Jitka Becanova, Anna Robuck and Dave
443   Katz performed the laboratory analysis; Christine Gardiner and Rainer Lohmann wrote the
444   original draft; Jochen Mueller and Sarit Kaserzon contributed to the revised draft; all authors
445   reviewed and edited the final draft.

446   **Data Availability Statement**

447   Data pertaining to this manuscript will be deposited in the Open Science Framework. All relevant
448   data will also be available in the supplemental data.

449

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