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Land-Use-Based Sources and Trends of Dissolved pPBDEs and PAHs in an Urbanized Watershed Using Assive Polyethylene Samplers

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1 **Land-use-based sources and trends of dissolved PBDEs and PAHs in**
2 **an urbanized watershed using passive polyethylene samplers**

3

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18

19

20 **Abstract**

21 Narragansett Bay is a temperate estuary on the Atlantic coast of Rhode Island in North
22 United States, which receives organic pollutants from urban and industrial activities in
23 its watershed, though detailed knowledge on sources and fluxes is missing. Twenty-
24 four polyethylene passive samplers were deployed in the surface water of the watershed
25 around Narragansett Bay during June-July of 2014, to examine the spatial variability
26 and possible sources of priority pollutants, namely dissolved polycyclic aromatic
27 hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs). Dissolved
28 Σ_{22} PAH concentrations ranged from 3.6 - 340 ng L⁻¹, and from 2.9 - 220 pg L⁻¹ for
29 Σ_{12} PBDE. The spatial variability of the concentrations was correlated to land use
30 pattern and population distribution, in particular with human activities within 2 km of
31 sampling sites. River discharges derived from the concentrations of PAHs and PBDEs
32 measured here were 10-20 times greater than their previously measured concentrations
33 in the open waters of Narragansett Bay. These results imply that river waters are the
34 main source of PAHs and PDBEs to the Bay and that major sink terms (e.g.,
35 sedimentation, degradation) affect their concentrations in the estuary. Predicted PAH
36 and PBDE toxicity based on dissolved concentrations did not exceed 1 toxic unit,
37 suggested that no toxicity occurred at the sampling sites.

38

39 **Capsule:** This work represents the first survey of dissolved PAHs and PBDEs using
40 passive samplers in an urbanized estuary's watershed, helping to constrain pollutant
41 flows from land-based sources.

42

43 **Keywords:** Polycyclic aromatic hydrocarbons (PAHs); Polybrominated diphenyl ethers
44 (PBDEs); polyethylene passive samplers; urbanized watershed; land-use-based source.

45

46 **Introduction**

47 Estuaries are subjected to multiple anthropogenic or naturally occurring stress
48 factors, and prone to be affected to different degrees by an array of pollutants including
49 hydrophobic organic contaminants (HOCs). Polycyclic aromatic hydrocarbons (PAHs)
50 and polybrominated diphenyl ethers (PBDEs) are two typical classes of HOCs which
51 continue to be released into the environment mainly via natural (PAHs) and
52 anthropogenic processes (PAHs and PDBEs) (Yunker et al., 2002; Hites, 2004; Lima et
53 al., 2005; Takada, 2010; Parinos et al., 2013). In aquatic ecosystems, the dissolved
54 PAHs and PBDEs are subjected to evaporation, adsorption to suspended particulates,
55 uptake by aquatic organisms and bioaccumulation, bio-degradation and photo-
56 degradation (Rayne and Ikonomou, 2005; Tsapakis et al., 2006; Guigue et al., 2014).
57 They can be further transferred into the aquatic environment by urban run-off,
58 municipal sewage, industrial effluents, oil spillage or leakage, gas-water exchange, and
59 atmospheric deposition (Lima et al., 2005; Song et al., 2006; Tsapakis et al., 2006;
60 Parinos et al., 2013). Previous work has suggested that aquatic ecosystems with high
61 PAH and PBDE concentrations might pose potential ecological risks, causing
62 carcinogenic, mutagenic, and toxic effects on aquatic organisms (Hall et al., 2003;
63 Oliveira et al., 2012; Ikenaka et al., 2013).

64 Narragansett Bay is a temperate estuary on the Atlantic coast of Rhode Island,
65 USA. In previous work, the concentration of PAHs in Narragansett Bay and other
66 coastal waters was shown to have strong correlations with urban runoff, river flows and
67 wastewater treatment plant discharges (Lohmann et al., 2011). Due to its long industrial
68 history, PAHs are present in the sediments of Narragansett Bay (Hoffman et al., 1984;
69 Pruell et al., 1986; Latimer and Quinn, 1996; Lima et al., 2003; Hartmann et al., 2004;
70 Lohmann et al., 2011). Concentrations and profiles of PAHs in the water column of
71 Narragansett Bay were reported (Lohmann et al., 2011; Yonis, 2012), but so far no study
72 has actually measured PAHs in the watershed and contributing rivers directly. Likewise,
73 the freely dissolved PBDEs in Narragansett Bay probably originate from a combination
74 of air-water exchange, freshwater runoff, rivers, and wastewater treatment plants (Sacks
75 and Lohmann, 2012), and are still present in currently products, suggesting on-going
76 releases to Narragansett Bay and the surrounding areas. This prompted us to investigate
77 the relationship between the land-based activities and PAHs and PBDEs concentrations
78 using passive samplers, and whether river inputs responsible for the contaminants in
79 Narragansett Bay.

80 Low density polyethylene (LDPE) passive samplers are cost-effective, technically
81 simple tools with lower detection limits than traditional active sampling techniques
82 (McDonough et al., 2014). Instead of pumping air or water through a filter, passive
83 sampling relies on diffusion to accumulate analytes of interests and only accumulates
84 molecules which are freely dissolved in the water or the atmosphere (Adams et al.,
85 2007). This avoids the analytical interference of, e.g., dissolved organic carbon (DOC)

86 which can affect active sampling results (Lohmann et al., 2011). Moreover,
87 concentrations of freely dissolved PAHs and PBDEs are of interest because this fraction
88 is available for direct diffusive exchange between water and other reservoirs such as air,
89 biota, or sediment (Kane Driscoll et al., 2010; Mhadhbi et al., 2012; Bragin et al., 2017).
90 Different passive samplers have been used in seawaters, harbors, rivers and urban
91 waterways to determine freely dissolved concentrations of PAHs and PBDEs
92 (Cornelissen et al., 2008a; Sower and Anderson, 2008; Lohmann et al., 2011; Lohmann
93 et al., 2012; Sacks and Lohmann, 2012; Alvarez et al., 2014).

94 The objectives of this study were to enhance our understanding of the distribution
95 and behavior of PAHs and PBDEs across the Narragansett Bay watershed. We deployed
96 LDPE samplers in the surface water at 24 sites across the watershed in June-July 2014
97 with the aim of (1) establishing baseline concentrations and spatial trends of dissolved
98 PAHs and PBDEs in the Narragansett Bay watershed, (2) diagnosing the main sources
99 of dissolved PAHs and PBDEs to Narragansett Bay, (3) evaluating the importance of
100 land-based sources of dissolved PAHs and PBDEs by investigating the relationship
101 between land-use characteristics and concentrations, (4) elucidating the main factors
102 controlling the fate of PAHs and PBDEs in the watershed, and (5) lastly predicting and
103 assessing the PAH and PBDE toxicity.

104

105 **Materials and Methods**

106 *Study area*

107 The Narragansett watershed area in Rhode Island was 2077.6 km² including the

108 estuarine waters (43.6% total watershed). The land coverage pattern around the bay was
109 dominated by forest (58%), urban or built-up land (28%), agriculture (5.4%), water
110 (4%), wetland, barren land and rangeland (each < 2%, see TOC).

111

112 *Preparation and deployment of LDPE passive samplers*

113 Fifty-one micrometer thick LDPE samplers were cut and cleaned for yielding
114 passive samplers. Deuterated PAHs (pyrene-d10 and benzo(a)pyrene-d12) and
115 brominated biphenyls (2,5-Dibromobiphenyl, 2,2',5,5'-Tetrabromobiphenyl,
116 2,2',4,5',6-Pentabromobiphenyl, and octachloronaphthalene) were used as
117 performance reference compounds (PRCs) to infer the equilibrium concentration of
118 compounds in the passive samplers as in previous work (Booij et al., 2002; McDonough
119 et al., 2014). Both passive samplers and field blanks were picked up by trained
120 volunteers and deployed in surface waters throughout the Narragansett Bay watershed
121 in June-July 2014, as a part of the University of Rhode Island Watershed Watch program
122 (<http://www.uri.edu/ce/wq/ww/index.htm>). The detail methodology, map of
123 monitoring sites, and other related monitoring summary were provided in the
124 supporting information (Figure S1 & Table S1).

125

126 *Analysis*

127 LDPE samplers were wiped clean with Kimwipes and extracted once in hexane
128 for 24 h after addition of 20 ng of labeled PAHs (acenaphthalene-d10, phenanthrene-
129 d10, chrysene-d12 and perylene-d12) and PBDEs (¹³C₁₂-BDE28, ¹³C₁₂-BDE47, ¹³C₁₂-

130 BDE99, $^{13}\text{C}_{12}$ -BDE153 and $^{13}\text{C}_{12}$ -BDE183) surrogates. Extracted LDPE samplers were
131 air dried and weighed. Extracts were concentrated to 100 μL , and spiked with 50 ng of
132 p-terphenyl- d_{14} (injection standard) directly before instrumental analysis.

133 PAHs were analyzed using an Agilent 6890 GC System coupled with an Agilent
134 5973 Network Mass Selective Detector and quantified using Agilent Technologies
135 MSD Productivity ChemStation D.03.00552 software as presented elsewhere
136 (Lohmann et al., 2012). PBDEs were analyzed on a Waters Quattro micro GS
137 Micromass MS-MS and quantified using Waters QuanLynx V4.1 software as detailed
138 elsewhere (Sacks and Lohmann, 2012). Further details are given in the Supporting
139 Information. Samples were analyzed for 22 PAHs and 12 PBDEs (Table S2 and S3).

140

141 *Quality assurance/Quality control*

142 Method blanks were prepared with each batch of samples to monitor for laboratory
143 contamination. Samples were blank-corrected by subtracting the average of the method
144 and field blank concentrations. Target analytes were quantified by internal calibration
145 relative to surrogates. Average surrogate recoveries for PAHs and PBDEs ranged from
146 68%-86% and 39%-62%, respectively (Tables S2 to S4). Method detection limits
147 (MDLs) were calculated as 3 times the standard deviation of the average field blank
148 concentration. Concentrations $<$ MDL were reported as half of the MDL, as
149 recommended previously (Antweiler and Taylor, 2008). Compounds that were
150 measured above the MDL in less than 20% of samples were omitted from the discussion.

151

152 *Calculations/Data analysis*

153 ● Determination of sampling rate and ambient concentration

154 The fraction of equilibrium (f) achieved for each compound was determined by
155 fitting the equilibrium of the PRCs and their temperature-corrected log K_{PE} values to a
156 model curve derived as,

157
$$f = 1 - e^{-\frac{R_s t}{K_{PEW} M_{PE}}}$$

158 Where R_s (L/day) is the sampling rate defined as the amount of water that comes
159 into contact with the sampler per day; t is deployment time (days); M_{PE} is the PE weight
160 (kg); and K_{PEW} is the LDPE-water partitioning coefficient (L/kg). The values of R_s can
161 be estimated using nonlinear least squares methods, by considering f as a continuous
162 function of K_{PEW} , with R_s as an adjustable parameter using Excel Solver to obtain the
163 best fit (Smedes and Booij, 2010). The average aqueous sampling rate of PAHs and
164 PBDEs was 21 ± 14 L/day and 16 ± 7 L/day, respectively.

165 Freely dissolved concentrations, C_w (ng/L) of compounds were calculated from
166 the equation,

167
$$C_w = \frac{C_{PE}}{K_{PEW} \left(1 - e^{-\frac{R_s t}{K_{PEW} M_{PE}}} \right)}$$

168 Where C_{PE} is the PE-normalized concentrations (ng/L). For more details, see the
169 Supporting Information and Tables S1.

170

171 ● Land-use regression and PAHs source analysis

172 Land-use regressions models are GIS-based spatial models that relate locations
173 specific data on pollutant concentrations to location-specific source and environment

174 data using regression (Briggs et al., 1997). The following land-use classes were
175 considered: residential areas, commercial and industrial areas, facilities and institutes,
176 and recreational areas occupied by human activities (Figure S2). Other variables
177 included population density (Pop/km²), buildings, roads, sewer areas, and impervious
178 surface areas. All geospatial data were retrieved from the RIGIS web site
179 (<http://www.edc.uri.edu/rigis>). The analyses were conducted using ArcGIS version 10.2
180 software using coverage and grid data formats whenever possible. Statistical analyses
181 were performed using IBM SPSS Statistics 22. Linear regression was chosen as an
182 appropriate model based on the correlation between dissolved concentrations and major
183 descriptor variables. For more details, also for assessing PAHs sources, see the
184 Supporting Information.

185

186 *Toxicity assessment*

187 A toxic unit (TU) is defined as the ratio of the concentration in a medium to the
188 effect concentration in that medium (USEPA, 2003). The TUs for EPA-34 individual
189 PAHs, $C_{pw, EPA-34}$ (TUs), were considered one of the most accurate measures for
190 evaluating the toxicity of pyrogenic PAH-impacted sites (Arp et al., 2011). The
191 toxic/nontoxic threshold value for the protection of sensitive benthic organisms is 1.0
192 TU (USEPA, 2003). In this study, we chose pyrene, fluoranthene, benz(a)anthracene,
193 and chrysene, to estimate the $C_{pw, EPA-34}$ (TUs) and to predict the potential toxicity of
194 each sampling site by using the models in Arp et al. (2011), since these compounds were
195 the most commonly quantified compound in surface water (96-100% of samples, see in

196 Table S2) and also exhibited good correlations with the other PAHs.

197 For PBDEs, the risk assessment for water organisms was performed on the basis
198 of the risk quotients (RQs) for non target organisms (Santos et al., 2007; Sánchez-Avila
199 et al., 2012). RQs were calculated as a quotient of the measured environmental
200 concentration (MEC) and the predicted no effect concentration (PNEC), and were
201 characterized using the maximum probable risks for ecological effect guideline
202 established by Marcus et al. (2010) as: no significant risk ($RQ < 1.0$), a small potential
203 for adverse effects ($1.0 \leq RQ < 10$), significant potential for adverse effects ($10 \leq$
204 $RQ < 100$), and adverse effects should be expected ($RQ \geq 100$). The risk assessment was
205 performed considering three trophic levels of fish, Daphnia and algae, following the
206 recommendation of the Technical Guidance Document on Risk Assessment (European
207 Commission, 2003). For more details, see the Supporting Information.

208

209 **Results and Discussion**

210 *Dissolved PAHs & PBDEs in surface water*

211 ● Concentrations and spatial trends

212 The concentrations of dissolved \sum_{22} PAH in the surface water ranged from 3.6 to
213 340 ng L⁻¹ with the mean value of 44 ng L⁻¹ (Figure 1, Table S5). The dominant PAHs
214 were phenanthrene (5-53%), pyrene (5-43%) and fluoranthene (<MDL-38%).
215 Phenanthrene contributed more to the dissolved \sum_{22} PAH in the lower watershed, while
216 pyrene and fluoranthene were the main contributors in the upper areas. Retene
217 accounted for 2.9-19.4% of the total freely dissolved concentrations.

218 PAH concentrations were greater in the upper, more urban/industrialized
219 watershed, and in coastal areas. The greatest dissolved $\sum_{22}\text{PAH}$ concentration was
220 recorded at Knowles Brook (BB_KB), followed by Woonasquatucket River near
221 Donigian Park (WR_DP) (184 ng L⁻¹), and Mill Brook near Greenwich Bay (GB4) (75
222 ng L⁻¹). Sites around Bristol Harbor also had relatively high concentrations (BH8-10 ng
223 L⁻¹, BH1-57 ng L⁻¹, BH12-18 ng L⁻¹). These sites were, by and large, also surrounded
224 by largest population densities.

225 Freely dissolved concentrations of $\sum_{12}\text{PBDE}$ in the surface water were more than
226 three orders of magnitude lower than PAHs across the Narragansett Bay watershed.
227 PBDE concentrations ranged from 2.9 to 220 pg L⁻¹ with a mean value of 25 pg L⁻¹
228 (Figure 2, Table S6). Dissolved PBDEs were dominated by BDE-47 (29-66%), BDE-
229 99 (16-40%) and BDE-100 (2-14%). PBDE concentrations were also greater in the
230 upper watershed and coastal areas. Dissolved $\sum_{12}\text{PBDE}$ concentrations were greatest in
231 rivers (Woonasquatucket River, at 224 pg L⁻¹, followed by the Pawtuxet River, at 150
232 pg L⁻¹).

233 The presence of PAHs in the surface water, away from major urban/industrialized
234 sources, most likely stemmed from atmospheric deposition, and represented
235 background contamination of PAHs across the northeastern United States. These were
236 typically characterized by low concentrations of PAHs, typically below 10 ng L⁻¹, as
237 can be seen for all samplers deployed in the southern half of the state. All northern sites,
238 with the exception of an upstream river sample displayed much greater PAH
239 concentrations, ranging from 10 to greater than 300 ng L⁻¹.

240 For PBDEs, although the gradient from north to south was not as strong as for
241 PAHs, a similar separation of sites could be seen. The lowest concentrations of PBDEs
242 occurred in the southern samples, which ranged from 3-19 $\mu\text{g L}^{-1}$, while the northern
243 samples displayed ΣPBDEs from 4.4 up to 224 $\mu\text{g L}^{-1}$.

244

245 ● Comparison to other studies

246 PAH concentrations derived here were about 3-9 times higher than those obtained
247 by passive sampling in the Great Lakes (USA/Canada) (Ruge, 2013; McDonough et al.,
248 2014), and about 5 times higher than those reported in the seawater of Narragansett Bay
249 (Table S7) (Yonis, 2012). Clearly, surface waters continued to act as sources of PAHs
250 to the Narragansett Bay estuary and the ocean. PAH concentrations were comparable
251 to those of southern Chesapeake Bay in the USA, the River Seine and its estuary in
252 France, and on the Dalian coast in China (Gustafson and Dickhut, 1997; Fernandes et
253 al., 1997; Liu et al., 2013).

254 The concentrations of PBDEs in the present study were more than 20 times higher
255 than those also measured with PE samplers in the seawater of Narragansett Bay, off
256 Dutch Island, and those in the North American Great Lakes (Table S7) (Booij et al.,
257 2002; Sacks and Lohmann, 2012; Ruge, 2013). Also for PDBEs, surface waters
258 continue to act as sources to the estuary and the ocean. The dissolved PBDEs in our
259 study area were similar to those of San Francisco Bay, USA (Latimer and Quinn, 1996)
260 and the NW Mediterranean Sea off Spain (Sánchez-Avila et al., 2012). However, our
261 freely dissolved PBDE values were much lower than those found in the New York/New

262 Jersey Harbor, Raritan Bay, USA (Zarnadze and Rodenburg, 2008), and Gwangyang
263 Bay, Korea (Kim et al., 2012) (Table S7), though different sampling approaches were
264 used. Active sampling methods used in the compared studies would overestimate and
265 report much higher “dissolved” concentrations of PBDEs than what we found using
266 LDPE samplers in Narragansett Bay (Oros et al., 2005; Sacks and Lohmann, 2012).

267

268 *Sources of dissolved PAHs*

269 We used established source diagnostics, including diagnostic ratios, PAH profile,
270 principal component analysis to identify where the PAHs originated from. In brief,
271 dissolved PAHs were primarily from pyrogenic sources including fossil fuel
272 combustion combustion at most sites. Some coastal sites were affected by petrogenic
273 sources, and some remote sites by wood combustion. Principal component analysis of
274 dissolved PAHs (Figure S4a) and gaseous PAHs from a previous study (Figure S4b)
275 demonstrated the importance of atmospheric deposition for PAHs. The results of PAH
276 profiles further indicated the deposition and transportation of gasoline vehicle
277 particulate emissions and tire particles as indicators of potential anthropogenic sources
278 (Figure S6 & S7). For more details, see the Supporting Information.

279

280 *Sources of dissolved PBDEs*

281 Tetra- and penta-BDEs were most commonly detected at the Narragansett Bay
282 watershed sites, likely stemming from the penta-BDE commercial mixture. The
283 contributions of the lower brominated BDEs to the Narragansett Bay watershed

284 suggested that residences and municipal sewage treatment plant effluents may be
285 significant sources of PBDEs (Hale et al., 2006; Song et al., 2006).

286 In contrast to PAHs, the results for PDBEs showed that neighboring sites were
287 similar to each other and clustered together (Figure S5). This implies that environmental
288 sources of PBDEs are regional in nature rather than location-specific, and related to the
289 usage of flame retardants in anthropogenic activities, and the proximity to sources.

290

291 *Land-Use Regression Analysis*

292 Recently, land-use regression methods have been developed and applied in
293 exploring the relations between ambient PAHs and anthropogenic factors (Noth et al.,
294 2011; Melymuk et al., 2013; Machado et al., 2014; Huang et al., 2017; Yao et al., 2017;
295 Zhang et al., 2017). Most researches focus on the PAHs in atmosphere and sediments
296 while only few focus on the dissolved PAHs.

297 The results for the Σ PAH and each individual compound are given in Table 1,
298 which was able to explain 39-80% of PAH variability. Roads and commercial and
299 industrial areas within 2 km radius explained 73% of the variability in Σ PAH
300 concentrations (Table 1, FigureS8-S10). Road vehicle emissions are credited as a major
301 source of dissolved MMW PAHs in the watershed areas (Figure S8), which were
302 consistent with the results of PAH profiles from gasoline vehicle particulate emissions
303 and tire particles in roads. Population density and sewer areas within 2 km radius were
304 the other variables accounting for ~40% of the variability in LMW PAH concentrations
305 (Acy, Ace, and Flr) (Table 1). For PBDEs, we did not conduct any further regression

306 analysis since there was weak correlation between the compound and land-use variables
307 (Table S8, Figure S11).

308 In recent work, Yang et al (2018), showed that traffic congestion index and the
309 number of industrial sources within 25-km buffer were the significant predictors of
310 PAH concentrations in urban lake sediments. Similarly, we find that: 1) transportation
311 and industry continue to be dominant sources of PAHs to the environment; 2)
312 monitoring sites should be situated in the relevant buffer zone where PAHs in the
313 environment are most related to human activities.

314

315 *PAHs & PBDEs toxicity predictions and assessments*

316 Maybe not surprisingly, no risk for potential effects to aquatic organisms
317 associated to PBDE was observed, considering short-term exposure of acute toxicity.
318 Σ RQ were all well below 1, ranging from 1.4×10^{-4} to 5.9×10^{-3} , 4.0×10^{-5} to 3.3×10^{-4} , and 4.3×10^{-4}
319 to 3.4×10^{-2} for fish, algae, and *Daphnia magna*, respectively (Table S10). Even so, the
320 continuous intake of PBDEs by water organisms can be accumulated in the food chain.
321 Therefore, more studies are needed concerning bioaccumulation and biomagnification
322 of PBDEs in biota for a better risk evaluation of these chemicals in the water
323 environment.

324 For PAHs, none of our sites exceeded a TU of one, suggesting that no toxicity
325 occurred at all the sampling sites (Figure 3). We recognize that our samples represented
326 surface water, which is generally expected to be less contaminated than pore water. A
327 few of the highest contaminated sites (Woonasquatucket River, Buckeye Brook and

328 Greenwich Bay), however, displayed TU values between 0.3-0.7, indicating cause for
329 concern. A consistent trend appeared for $C_{pw, EPA-34}$ (TU) values predicted by different
330 PAHs, which might indicate the potential feasibility of the models using the freely
331 dissolved concentrations from surface water in Narragansett watershed area (Figure 3).
332 This trend further implied the similar pattern or content of PAHs could be found
333 between sediment pore water and surface water due to the river transportation, thus
334 aqueous distribution of PAHs at surface water layer might be sufficient to reflect the
335 overall contamination level for the bulk overlying water column in the watershed
336 (Cornelissen et al., 2008b; Lai et al., 2015). Although, more research should be
337 conducted to prove the above assumption.

338

339 *Riverine runoff as a vector for transporting PAHs and PDBEs to Narragansett Bay*

340 This study enable us to perform a first estimation of the potential importance of riverine
341 discharges to pollutant concentrations in the Narragansett Bay estuary itself (Figure
342 S12). At steady-state, river water inflow concentrations would be diluted by ca 12 times
343 in the estuary (ratio of freshwater flow times flushing time divided by the total volume)
344 (Pilson, 1985). The Pawtuxet and Woonasquacket Rivers were measured near their
345 discharge into the Bay; sum PAHs ranged from 70-180 ng L⁻¹, while sum PBDEs were
346 150-220 ng L⁻¹. Previously measured PAH concentrations, unaffected by major storms,
347 ranged from 0.5-2 ng L⁻¹ for open water stations (Lohmann et al., 2011). Dissolved
348 PAH concentrations in the estuary are lower, by almost an order of magnitude, to what
349 can be expected based on the dilution of riverine discharges (6-15 ng L⁻¹). For sum

350 PBDEs, previously measured concentrations ranged from 6.5 pg L⁻¹ in the northern part
351 of the Bay to below detection limit in the southern part (Sacks and Lohmann, 2012).
352 Overall, the open water concentrations for Narragansett Bay are again ~ 10-times lower
353 than expected from the dilution of riverine inflows (12-20 pg L⁻¹). Common processes
354 that could reduce dissolved concentrations of both PAHs and PDBEs in the estuary
355 include sorption to solids, sedimentation, and degradation.

356

357 **Implications**

358 This work represents the first survey of dissolved PAHs and PBDEs using passive
359 samplers, deployed by a long-running volunteer network around the Narragansett Bay
360 watershed. Results suggest that this sampling approach is viable and could be extended
361 to get a better grasp on pollutant flows from the terrestrial sources into the Narragansett
362 Bay estuary. In particular, it could be extended to cover temporal trends of
363 concentrations in the watershed, and target all major point sources into the estuary
364 repeatedly. Surprisingly, several sites appear close to toxic effects based on the presence
365 of key PAHs. The results presented here suggest that rivers are the main conduits of
366 PAHs and PDBEs into the estuary, and imply that neither air-water exchange nor
367 particle-bound deposition of pollutants affects dissolved concentrations to a significant
368 degree. Instead, the evidence indicates that major sinks exists for both PAHs and
369 PBDEs upon their discharge into the estuary, probably including uptake by sediment
370 and degradation. These results should be tested in future work.

371

372 **Supporting Information**

373 Additional details relating to sampling locations, chemical analysis, and dissolved
374 concentrations of PAHs and PBDEs are available free of charge via the Internet at
375 <http://pubs.acs.org>.

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386

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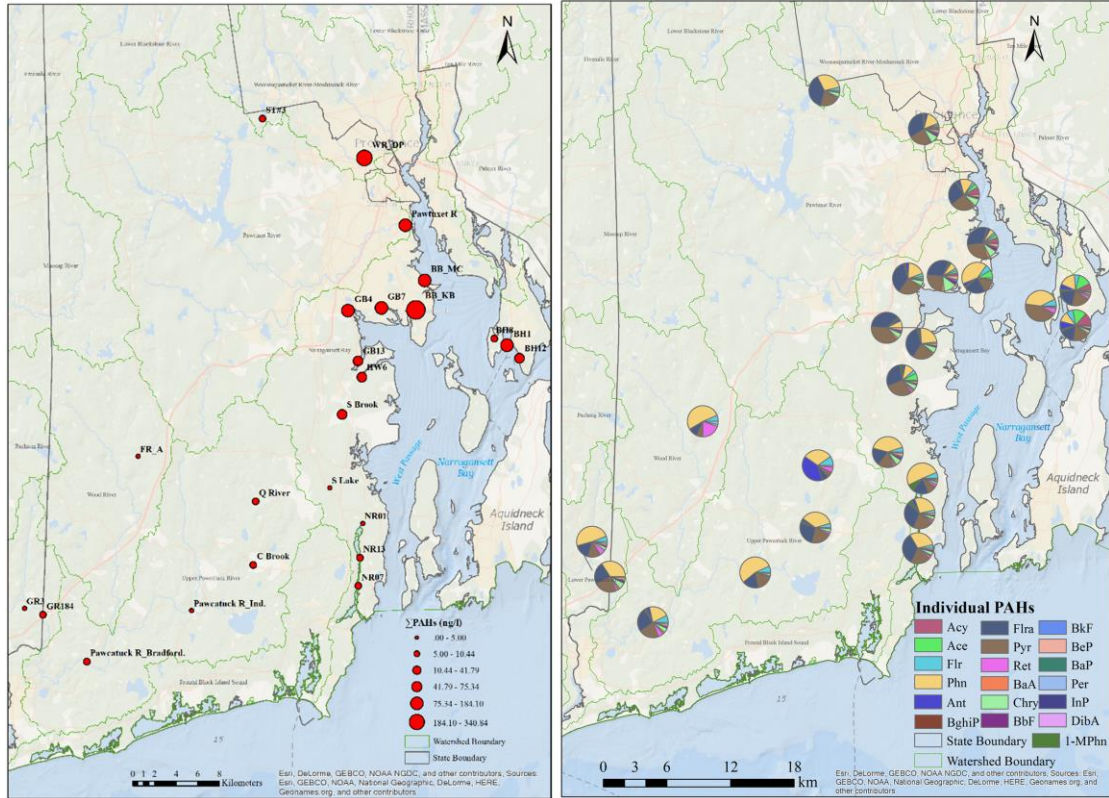
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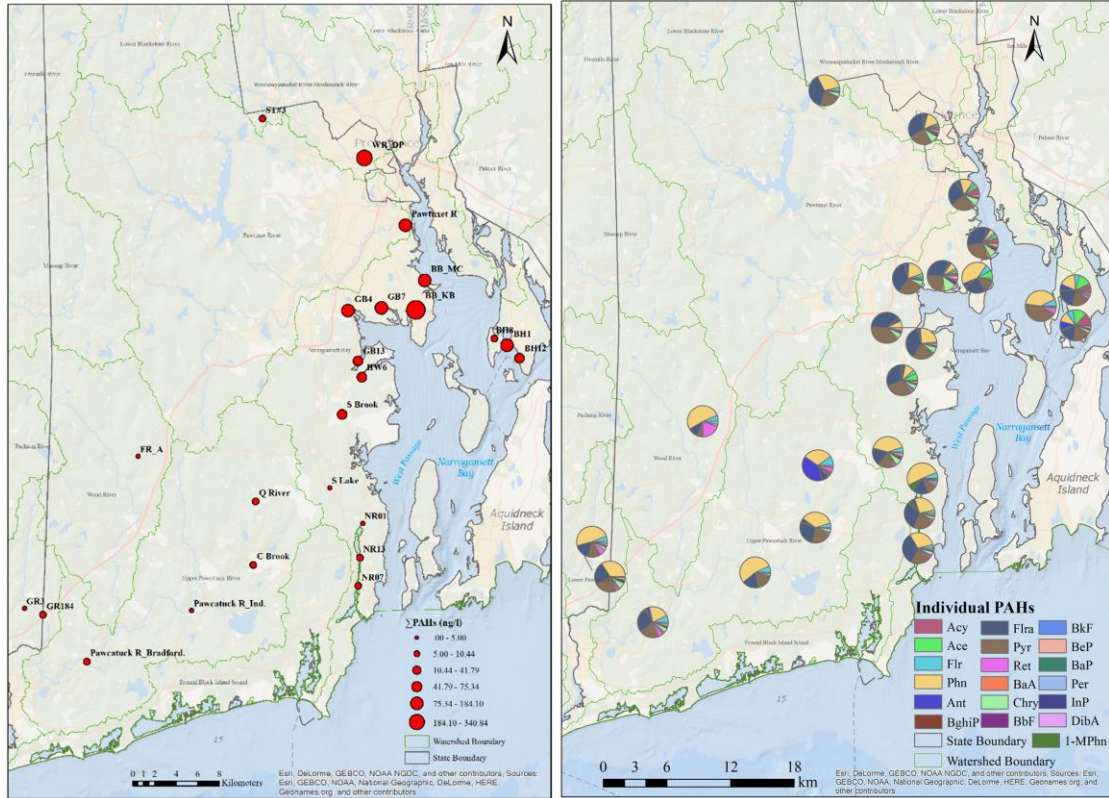
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Figure 1. Dissolved Σ_{22} PAH and individual PAHs in the Narragansett Bay

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watershed.



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632 **Figure 2. Dissolved Σ_{12} PBDE and individual PBDE in the Narragansett Bay**

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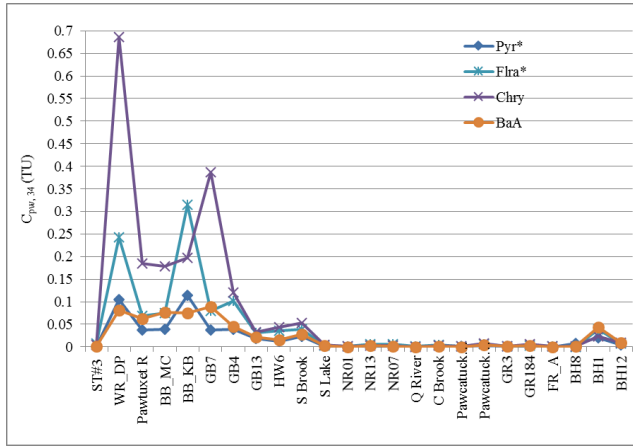
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Figure 3. Estimating the total EPA-34 freely dissolved pore water concentration,

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$C_{pw,EPA-34}$, expressed as toxic units (TUs) from the freely dissolved concentrations

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from surface water in Narragansett watershed.

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651 **Table 1. Multiple Linear Regression Results for PAHs**

Compound	Variable				Adjusted R ²	Standard Error
	ln(A+1)	ln(B+1)	ln(C+1)	ln(D+1)		
ln(Σ PAH+1)	0.573	0.353	/	/	0.73	0.67
ln(Acy+1)	/	/	0.646	/	0.39	0.55
ln(Ace+1)	/	/	/	0.661	0.41	0.70
ln(Flr+1)	/	/	/	0.651	0.40	0.54
ln(Phn+1)	0.688	/	/	/	0.45	0.72
ln(Ant+1)	/	0.674	/	/	0.43	0.52
ln(1-MPhn+1)	0.458	0.434	/	/	0.60	0.36
ln(Flra+1)	0.848	/	/	/	0.71	0.70
ln(Pyr+1)	0.587	0.373	/	/	0.80	0.53
ln(Ret+1)	N/A	N/A	N/A	N/A	N/A	N/A
ln(BaA+1)	0.823	/	/	/	0.66	0.24
ln(Chry+1)	0.846	/	/	/	0.70	0.46
ln(BbF+1)	0.536	0.385	/	/	0.72	0.26
ln(BkF+1)	0.504	0.408	/	/	0.70	0.18
ln(BeP+1)	0.523	0.405	/	/	0.73	0.25
ln(BaP+1)	/	0.850	/	/	0.71	0.16
ln(Per+1)	N/A	N/A	N/A	N/A	N/A	N/A
ln(InP+1)	0.412	0.533	/	/	0.76	0.85
ln(DibA+1)	/	0.775	/	/	0.55	0.03
ln(BghiP+1)	0.371	0.577	/	/	0.77	0.08

652 A = Roads within 2 km;

653 B = Commercial and industrial areas within 2 km;

654 C = Population density within 2 km;

655 D = Sewer area within 2 km;

656 The p values for these multiple regression equations were less or equal to 0.001.