

2018

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

Wenlu Zhao

Minggang Cai

*See next page for additional authors*

Follow this and additional works at: <https://digitalcommons.uri.edu/gsofacpubs>

**The University of Rhode Island Faculty have made this article openly available.  
Please let us know how Open Access to this research benefits you.**

This is a pre-publication author manuscript of the final, published article.

Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

## Citation/Publisher Attribution

Zhao, W., Cai, M., Adelman, D., Khairy, M., August, P., & Lohmann, R. (2018). Land-use-based sources and trends of dissolved PBDEs and PAHs in an urbanized watershed using passive polyethylene samplers. *Environmental Pollution*, 238, 573-580. doi:10.1016/j.envpol.2018.02.057

This Article is brought to you for free and open access by the Graduate School of Oceanography at DigitalCommons@URI. It has been accepted for inclusion in Graduate School of Oceanography Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact [digitalcommons@etal.uri.edu](mailto:digitalcommons@etal.uri.edu).

---

**Authors**

Wenlu Zhao, Minggang Cai, Dave Adelman, Mohammed Khairy, Pete August, and Rainer Lohmann

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

3

4 **Wenlu Zhao<sup>a,b,c,d</sup>, Minggang Cai<sup>b,c,d</sup>, Dave Adelman<sup>c</sup>, Mohammed Khairy<sup>c</sup>, Pete**  
5 **August<sup>e</sup>, Rainer Lohmann<sup>c,\*</sup>**

6 <sup>a</sup>School of Environmental Science and Engineering, Zhejiang Gongshang University,  
7 Hangzhou 310018, PR China

8 <sup>b</sup>State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen  
9 361102, China

10 <sup>c</sup>Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode  
11 Island 02882-1197, USA

12 <sup>d</sup>College of Ocean and Earth Science, Xiamen University, Xiamen 361005, PR China

13 <sup>e</sup>Department of Natural Resources Science, University of Rhode Island, One  
14 Greenhouse Way, Kingston, RI 02881, USA

15

16 \* Corresponding Author:

17 Rainer Lohmann, Tel: (401) 874-6612; Email: rlohmann@uri.edu

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  $\Sigma_{22}$ PAH concentrations ranged from 3.6 - 340 ng L<sup>-1</sup>, and from 2.9 - 220 pg L<sup>-1</sup> for  
29  $\Sigma_{12}$ 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 km<sup>2</sup> 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 (<sup>13</sup>C<sub>12</sub>-BDE28, <sup>13</sup>C<sub>12</sub>-BDE47, <sup>13</sup>C<sub>12</sub>-



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  $\mu\text{L}$ , and spiked with 50 ng of  
132 p-terphenyl- $\text{d}_{14}$  (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  $21 \pm 14$  L/day and  $16 \pm 7$  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/km<sup>2</sup>), 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<sup>-1</sup> with the mean value of 44 ng L<sup>-1</sup> (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<sup>-1</sup>), and Mill Brook near Greenwich Bay (GB4) (75  
222 ng L<sup>-1</sup>). Sites around Bristol Harbor also had relatively high concentrations (BH8-10 ng  
223 L<sup>-1</sup>, BH1-57 ng L<sup>-1</sup>, BH12-18 ng L<sup>-1</sup>). 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<sup>-1</sup> with a mean value of 25 pg L<sup>-1</sup>  
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<sup>-1</sup>, followed by the Pawtuxet River, at 150  
232 pg L<sup>-1</sup>).

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<sup>-1</sup>, 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<sup>-1</sup>.

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  $\Sigma\text{PBDEs}$  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  $\Sigma$ 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  $\Sigma$ 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  $\Sigma$ RQ were all well below 1, ranging from  $1.4 \times 10^{-4}$  to  $5.9 \times 10^{-3}$ ,  $4.0 \times 10^{-5}$  to  $3.3 \times 10^{-4}$ , and  $4.3 \times 10^{-4}$   
319 to  $3.4 \times 10^{-2}$  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<sup>-1</sup>, while sum PBDEs were  
346 150-220 ng L<sup>-1</sup>. Previously measured PAH concentrations, unaffected by major storms,  
347 ranged from 0.5-2 ng L<sup>-1</sup> 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<sup>-1</sup>). For sum

350 PBDEs, previously measured concentrations ranged from 6.5  $\mu\text{g L}^{-1}$  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  $\sim 10$ -times lower  
353 than expected from the dilution of riverine inflows (12-20  $\mu\text{g L}^{-1}$ ). 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>.

376 **Acknowledgments**

377 We thank Linda Green and Elizabeth Herron, URI Watershed Watch program  
378 leaders as well as the many URI Watershed Watch volunteer water quality monitors  
379 who deployed and retrieved passive samplers and collected water samples. For more  
380 information on the URI Watershed Watch program please see  
381 <http://web.uri.edu/watershedwatch/>. This research was financially supported by the  
382 China Scholarship Council (CSC) program, the National Natural Science Foundation  
383 of China (41576180 & 40776040), and the Zhejiang Provincial Natural Science  
384 Foundation of China (LQ18D060001). Professor John Hodgkiss is thanked for his  
385 assistance with English in this manuscript.

386

387 **References**

388 Adams, R. G., Lohmann, R., Fernandez, L. A., Macfarlane, J. K., Gschwend, P. M.,  
389 2007. Polyethylene devices: passive samplers for measuring dissolved  
390 hydrophobic organic compounds in aquatic environments. *Environmental Science*  
391 *& Technology*, 41 (4), 1317-23.

392 Alvarez, D. A., Maruya, K. A., Dodder, N. G., Lao, W., Furlong, E. T., Smalling, K. L.,  
393 2014. Occurrence of contaminants of emerging concern along the California coast  
394 (2009-10) using passive sampling devices. *Marine Pollution Bulletin*, 81 (2), 347-  
395 54.

396 Antweiler, R. C., Taylor, H. E., 2008. Evaluation of statistical treatments of left-  
397 censored environmental data using coincident uncensored data sets: I. Summary  
398 statistics. *Environmental Science & Technology*, 42 (10), 3732-3738.

399 Arp, H. P. H., Breedveld, G. D., Cornelissen, G., 2009. Estimating the in situ sediment-  
400 porewater distribution of PAHs and chlorinated aromatic hydrocarbons in  
401 anthropogenic impacted sediments. *Environmental Science & Technology*, 43  
402 (15), 5576-5585.

403 Arp, H. P., Azzolina, N. A., Cornelissen, G., Hawthorne, S. B., 2011. Predicting pore  
404 water EPA-34 PAH concentrations and toxicity in pyrogenic-impacted sediments  
405 using pyrene content. *Environmental Science & Technology*, 45 (12), 5139-5146.

406 Baldwin, A. K., Corsi, S. R., Lutz, M. A., Ingersoll, C. G., Dorman, R., Magruder, C.,  
407 Magruder, M., 2017. Primary sources and toxicity of PAHs in Milwaukee-area  
408 streambed sediment. *Environmental Toxicology and Chemistry*, 36 (6), 1622-1635.

409 Booij, K., Smedes, F., van Weerlee, E. M., 2002. Spiking of performance reference  
410 compounds in low density polyethylene and silicone passive water samplers.  
411 *Chemosphere*, 46 (8), 1157.

412 Booij, K., Smedes, F., 2010. An improved method for estimating in situ sampling rates  
413 of nonpolar passive samplers. *Environmental Science & Technology*, 2010,  
414 44(17): 6789-6794.

415 Boonyatumanond, R., Murakami, M., Wattayakorn, G., Togo, A., Takada, H., 2007.  
416 Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical  
417 Asian mega-city, Bangkok, Thailand. *Science of the Total Environment*, 384 (1),  
418 420-432.

419 Bragin, G. E., Parkerton, T. F., Redman, A. D., Letinksi, D. J., Butler, J. D., Paumen,  
420 M. L., Sutherland, C. A., Knarr, T. M., Comber, M., Haan, K. D., 2016. Chronic  
421 toxicity of selected polycyclic aromatic hydrocarbons to algae and crustaceans  
422 using passive dosing. *Environmental Toxicology & Chemistry*, 35 (12), 2948-2957.

423 Briggs, D. J., Collins S., Elliott, P., Fischer, P., Kingham, S., Lebet, E., Pryl, K.,  
424 Reeuwijk, H. V., Smallbone, K., Veen, A. V. D., 1997. Mapping urban air pollution

425 using gis: a regression-based approach. *International Journal of Geographical*  
426 *Information Systems*, 11 (7), 699-718.

427 Cornelissen, G., Pettersen, A., Broman, D., Mayer, P., Breedveld, G. D., 2008a. Field  
428 testing of equilibrium passive samplers to determine freely dissolved native  
429 polycyclic aromatic hydrocarbon concentrations. *Environmental Toxicology and*  
430 *Chemistry*, 27 (3), 499-508.

431 Cornelissen, G., Arp, H. P. H., Pettersen, A., Hauge, A., Breedveld, G. D., 2008b.  
432 Assessing PAH and PCB emissions from the relocation of harbour sediments using  
433 equilibrium passive samplers. *Chemosphere*, 72 (10): 1581-1587.

434 Covino, S., Fabianová, T., K\_resinová, Z., Čvančarová, M., Burianová, E., Filipová,  
435 A., Voříšková, J., Baldrian, P., Cajthaml, T., 2015. Polycyclic aromatic  
436 hydrocarbons degradation and microbial community shifts during co-composting  
437 of creosote-treated wood. *Journal of Hazardous Materials*, 301 (8), 17-26.

438 Crane, J. L., 2014. Source apportionment and distribution of polycyclic aromatic  
439 hydrocarbons, risk considerations, and management implications for urban  
440 stormwater pond sediments in Minnesota, USA. *Archives of Environmental*  
441 *Contamination and Toxicology*, 66 (2), 176-200.

442 Fernandes, M. B., Sicre, M. A., Boireau, A., Tronczynski, J., 1997. Polyaromatic  
443 hydrocarbon (PAH) distributions in the Seine River and its estuary. *Marine*  
444 *Pollution Bulletin*, 34 (11), 857-867.

445 Guigue, C., Tedetti, M., Ferretto, N., Garcia, N., Méjanelle, L., Goutx, M., 2014. Spatial  
446 and seasonal variabilities of dissolved hydrocarbons in surface waters from the  
447 Northwestern Mediterranean Sea: results from one year intensive sampling.  
448 *Science of the Total Environment*, 466-467 (1), 650-662.

449 Gustafson, K. E., Dickhut, R. M., 1997. Distribution of polycyclic aromatic  
450 hydrocarbons in southern Chesapeake Bay surface water: Evaluation of three  
451 methods for determining freely dissolved water concentrations. *Environmental*  
452 *Toxicology and Chemistry*, 16 (3), 452-461.

453 Hale, R. C., La Guardia, M. J., Harvey, E., Gaylor, M. O., Mainor, T. M., 2006.  
454 Brominated flame retardant concentrations and trends in abiotic media.  
455 Chemosphere, 64 (2), 181-6.

456 Hall, A. J., Kalantzi, O. I., Thomas, G. O., 2003. Polybrominated diphenyl ethers  
457 (PBDEs) in grey seals during their first year of life--are they thyroid hormone  
458 endocrine disrupters? Environmental Pollution, 126(1):29-37.

459 Hartmann, P. C., Quinn, J. G., Cairns, R. W., King, J. W., 2004. The distribution and  
460 sources of polycyclic aromatic hydrocarbons in Narragansett Bay surface  
461 sediments. Marine Pollution Bulletin, 48 (3-4), 351-358.

462 Hites, R. A., 2004. Polybrominated diphenyl ethers in the environment and in people:  
463 a meta-analysis of concentrations. Environmental Science & Technology, 38 (4),  
464 945-56.

465 Hoffman, E. J., Mills, G. L., Latimer, J. S., Quinn, J. G., 1984. Urban runoff as a source  
466 of polycyclic aromatic hydrocarbons to coastal waters. Environmental Science &  
467 Technology, 18 (8), 580.

468 Huang, Y., Min, L., Wang, R., Khan, S. K., Gao, D., Zhang, Y., 2017. Characterization  
469 and source apportionment of pahs from a highly urbanized river sediments based  
470 on land use analysis. Chemosphere, 184, 1334-1345.

471 Ikenaka, Y., Sakamoto, M., Nagata, T., Takahashi, H., Miyabara, Y., Hanazato, T.,  
472 Ishizuka, M., Isobe, T., Kim, J.W., Chang, K.H., 2013. Effects of polycyclic  
473 aromatic hydrocarbons (PAHs) on an aquatic ecosystem: acute toxicity and  
474 community-level toxic impact tests of benzo[a]pyrene using lake zooplankton  
475 community. Journal of Toxicological Sciences, 38(1): 131-136.

476 Itoh, N., Tamamura, S., Kumagai, M. 2010. Distributions of polycyclic aromatic  
477 hydrocarbons in a sediment core from the north basin of Lake Biwa, Japan.  
478 Organic Geochemistry, 41 (8), 845-852.

479 Kane Driscoll, S. B., Mcardle, M. E., Menzie, C. A., Reiss, M., Steevens, J. A., 2010.  
480 A framework for using dose as a metric to assess toxicity of fish to PAHs.  
481 Ecotoxicology and Environmental Safety, 73 (4), 486-490.

482 Kim, Y. H., Kim, H. S., Choi, H. G., 2012. Contamination and bioaccumulation of  
483 polybrominated diphenyl ethers (PBDEs) in Gwangyang Bay, Korea. *Toxicology  
484 and Environmental Health Sciences*, 4 (1), 42-49.

485 Lai, Y. J., Xia, X. H., Dong, J. W., Lin, W. T., Mou, X. L., Zhao, P. J., Jiang, X., M., Li,  
486 Z. H. Tong, Y. L., Zhao, Y. L., 2015. Equilibrium State of PAHs in Bottom  
487 Sediment-Water-Suspended Sediment System of a Large River Considering Freely  
488 Dissolved Concentrations. *Journal of Environmental Quality*, 44 (3):823-832.

489 Latimer, J. S., Quinn, J. G., 1996. Historical Trends and Current Inputs of Hydrophobic  
490 Organic Compounds in an Urban Estuary: The Sedimentary Record.  
491 *Environmental Science & Technology*, 30 (2), 623-633.

492 Li, C. T., Mi, H. H., Lee, W. J., You, W. C., Wang, Y. F., 1999. PAH emission from  
493 the industrial boilers. *Journal of Hazardous Materials*, 69 (1), 1-11.

494 Li, A., Jang, J.-K., Scheff, P. A., 2003. Application of EPA CMB8.2 model for source  
495 apportionment of sediment PAHs in Lake Calumet, Chicago. *Environmental  
496 Science & Technology*, 37 (13), 2958-2965.

497 Lima, A. L. C., And, T. I. E., Reddy, C. M., 2003. High-Resolution Record of Pyrogenic  
498 Polycyclic Aromatic Hydrocarbon Deposition during the 20th Century.  
499 *Environmental Science & Technology*, 37 (1), 53.

500 Lima, A. L. C., Farrington, J. W., Reddy, C. M., 2005. Combustion-derived polycyclic  
501 aromatic hydrocarbons in the environment—a review. *Environmental Forensics*, 6  
502 (2), 109-131.

503 Liu, X., Jia, H., Wang, L., Qi, H., Ma, W., Hong, W., Guo, J., Yang, M., Sun, Y., Li, Y.  
504 F., 2013. Characterization of polycyclic aromatic hydrocarbons in concurrently  
505 monitored surface seawater and sediment along Dalian coast after oil spill.  
506 *Ecotoxicology and Environmental Safety*, 90 (3), 151-156.

507 Lohmann, R., Dapsis, M., Morgan, E. J., Dekany, V., Luey, P. J., 2011. Determining air-  
508 water exchange, spatial and temporal trends of freely dissolved PAHs in an urban  
509 estuary using passive polyethylene samplers. *Environmental Science &  
510 Technology*, 45 (45), 2655-2662.



511 Lohmann, R., Booij, K., Smedes, F., Vrana, B., 2012. Use of passive sampling devices  
512 for monitoring and compliance checking of POP concentrations in water.  
513 Environmental Science and Pollution Research, 19 (6), 1885-1895.

514 Ma, J., Qiu, X., Zhang, J., Duan, X., Zhu, T., 2012. State of polybrominated diphenyl  
515 ethers in China: an overview. Chemosphere, 88 (7), 769.

516 Machado, K. S., Figueira, R. C., Côcco, L. C., Froehner, S., Fernandes, C. V., Ferreira,  
517 P. A., 2014. Sedimentary record of PAHs in the Barigui River and its relation to  
518 the socioeconomic development of Curitiba, Brazil. Science of the Total  
519 Environment, 482-483 (1), 42-52.

520 Mcdonough, C. A., Khairy, M. A., Muir, D. C., Lohmann, R., 2014. Significance of  
521 population centers as sources of gaseous and dissolved PAHs in the lower Great  
522 Lakes. Environmental Science & Technology, 48 (14), 7789-97.

523 Melymuk, L., Robson, M., Helm, P. A., Diamond, M. L., 2013. Application of land use  
524 regression to identify sources and assess spatial variation in urban SVOC  
525 concentrations. Environmental Science & Technology, 47 (4), 1887-1895.

526 Metre, P. C. V., Mahler, B. J., Wilson, J. T., Burbank, A. T. L., 2008. Collection and  
527 Analysis of Samples for Polycyclic Aromatic Hydrocarbons in, Dust and Other  
528 Solids Related to Sealed and Unsealed Pavement From 10 Cities Across the United  
529 States, 2005-07. Director.

530 Metre, P. C. V., Mahler, B. J., 2014. PAH Concentrations in lake sediment decline  
531 following ban on coal-tar-based pavement sealants in Austin, Texas.  
532 Environmental Science & Technology, 48 (23), 7222-7228.

533 Mhadhbi, L., Fumega, J., Boumaiza, M., Beiras, R., 2012. Acute toxicity of  
534 polybrominated diphenyl ethers (PBDEs) for turbot (*Psetta maxima*) early life  
535 stages (ELS). Environmental Science & Pollution Research, 19 (3), 708-717.

536 Neff, J. M., 2002. Bioaccumulation in Marine Organisms: Effect of Contaminants from  
537 Oil Well Produced Water. Elsevier, Amsterdam, The Netherlands.

538 Noth, E. M., Hammond, S. K., Biging, G. S., Tager, I. B., 2011. A spatial-temporal  
539 regression model to predict daily outdoor residential PAH concentrations in an

540 epidemiologic study in Fresno, CA. *Atmospheric Environment*, 45 (14), 2394-  
541 2403.

542 Okafor, E. C., Opuene, K., 2007. Preliminary assessment of trace metals and polycyclic  
543 aromatic hydrocarbons in the sediments. *International Journal of Environmental*  
544 *Science and Technology*, 4 (2), 233-240.

545 Oliveira, M., Gravato, C., Guilhermino, L., 2012. Acute toxic effects of pyrene on  
546 *Pomatoschistus microps* (Teleostei, Gobiidae): Mortality, biomarkers and  
547 swimming performance. *Ecological Indicators*, 19 (8): 206-214.

548 Oros, D. R., Hoover D., Rodigari F., Crane D., Sericano, J., 2005. Levels and  
549 Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and  
550 Bivalves from the San Francisco Estuary. *Environmental Science & Technology*,  
551 39 (1), 33-41.

552 OSPAR Commission EDs., 2001 Quality Status Report 2000 (Chemistry), OSPAR  
553 Commission, London.

554 Parinos, C., Gogou, A., Bouloubassi, I., Stavrakakis, S., Plakidi, E., Hatzianestis, I.,  
555 2013. Sources and downward fluxes of polycyclic aromatic hydrocarbons in the  
556 open southwestern Black Sea. *Organic Geochemistry*, 57 (4), 65-75.

557 Pilson, M. E. Q., 1985. On the Residence Time of Water in Narragansett Bay. *Estuaries*  
558 *Coasts*, 8 (1), 2-14.

559 Pruell, R. J., Lake, J. L., Davis, W. R., Quinn, J. G., 1986. Uptake and depuration of  
560 organic contaminants by blue mussels (*Mytilus edulis*) exposed to  
561 environmentally contaminated sediment. *Marine Biology*, 91 (4), 497-507.

562 Rayne, S., Ikonou, M. G., 2005. Polybrominated diphenyl ethers in an advanced  
563 wastewater treatment plant. Part 1: Concentrations, patterns, and influence of  
564 treatment processes. *Journal of Environmental Engineering and Science*, 4 (5),  
565 369-383.

566 Ruge, Z., 2013. Air-water exchange and trends of persistent bioaccumulative toxics  
567 (PBTs) across Lake Superior. MS Dissertation, University of Rhode Island,  
568 Kingston, RI.

569 Sacks, V. P., Lohmann, R., 2012. Freely dissolved PBDEs in water and porewater of an  
570 urban estuary. *Environmental Pollution*, 162 (5), 287-293.

571 Sánchez-Avila, J., Tauler, R., Lacorte, S., 2012. Organic micropollutants in coastal  
572 waters from NW Mediterranean Sea: sources distribution and potential risk.  
573 *Environment International*, 46 (15), 50-62.

574 Santos, J. L., Aparicio, I., Alonso, E., 2007. Occurrence and risk assessment of  
575 pharmaceutically active compounds in wastewater treatment plants. A case study:  
576 Seville city (Spain). *Environment International* 33, 596-601.

577 Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T., 2001. Measurement of  
578 emissions from air pollution sources. 3. C1–C29 organic compounds from  
579 fireplace combustion of wood. *Environmental Science & Technology*, 35 (9),  
580 1716-1728.

581 Song, M., Chu, S., Letcher, R. J., Seth, R., 2006. Fate, partitioning, and mass loading  
582 of polybrominated diphenyl ethers (PBDEs) during the treatment processing of  
583 municipal sewage. *Environmental Science & Technology*, 40 (20), 6241-6246.

584 Sower, G. J., Anderson, K. A., 2008. Spatial and temporal variation of freely dissolved  
585 polycyclic aromatic hydrocarbons in an urban river undergoing Superfund  
586 remediation. *Environmental Science & Technology*, 42 (24), 9065-71.

587 Takada, H., 2012. Establishing criteria of relative abundance of alkyl polycyclic  
588 aromatic hydrocarbons (PAHs) for differentiation of pyrogenic and petrogenic  
589 PAHs: an application to Indian sediment. *Environmental Forensics*, 13 (4), 312-  
590 331.

591 Tsapakis, M., Apostolaki, M., Eisenreich, S., Stephanou, E. G., 2006. Atmospheric  
592 deposition and marine sedimentation fluxes of polycyclic aromatic hydrocarbons  
593 in the Eastern Mediterranean Basin. *Environmental Science & Technology*, 40  
594 (16), 4922-4927.

595 USEPA, 2003. Equilibrium Partitioning Sediment Guidelines (ESBs) for the Protection  
596 of Benthic Organisms: PAH Mixtures, Office of Science and Technology and  
597 Office of Research and Development, U.S. Environmental Protection Agency:  
598 Washington, DC.

599 USEPA, 2008. Toxicological Review of 2,2',4,4',5,5'-Hexabromodiphenyl Ether (BDE-  
600 153). CAS No.68631-49-2, EPA/63S/R-07/1007F. 3-4.

601 Wakeham, S. G., Schaffner, C., Giger, W., 1980. Polycyclic aromatic hydrocarbons in  
602 Recent lake sediments—I. Compounds having anthropogenic origins. *Geochimica  
603 et Cosmochimica Acta*, 44 (3), 403-413.

604 Wang, J., Jia, C. R., Wong, C. K., Wong, P. K., 2000. Characterization of polycyclic  
605 aromatic hydrocarbons created in lubricating oils. *Water, Air, & Soil Pollution*,  
606 120 (3-4), 381-396.

607 Yang, J., Yang, Y., Chen, R. S., Meng, X. Z., Xu, J., Qadeer, A., Liu, M., 2018. Modeling  
608 and evaluating spatial variation of polycyclic aromatic hydrocarbons in urban lake  
609 surface sediments in Shanghai. *Environmental Pollution*, 235, 1-10.

610 Yao, Y., Huang, C. L., Wang, J. Z., Ni, H. G., Yang, Z. Y., Huang, Z. Y., Bao, L. J., Zeng  
611 E. Y., 2017. Significance of Anthropogenic Factors to Freely Dissolved Polycyclic  
612 Aromatic Hydrocarbons in Freshwater of China, *Environmental Science &  
613 Technology*, 51, 8304-8312.

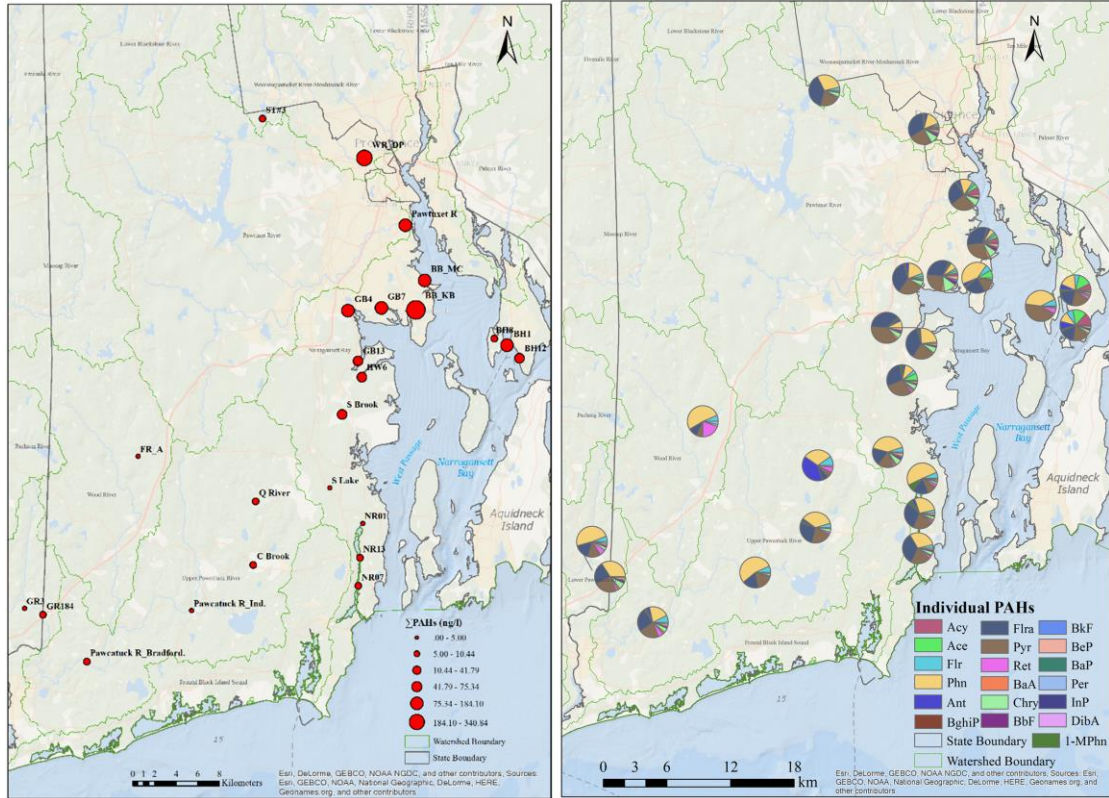
614 Yonis, S. R., 2012. Vertical profiles of PAH concentrations in Narragansett Bay using  
615 passive samplers. MS Dissertation, University of Rhode Island, Kingston, RI.

616 Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D.,  
617 Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH  
618 ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33 (4),  
619 489-515.

620 Zarnadze, A., Rodenburg, L. A., 2008. Water-column concentrations and partitioning  
621 of polybrominated diphenyl ethers in the New York/New Jersey Harbor, USA.  
622 *Environmental Toxicology and Chemistry*, 27 (8), 1636-1642.

623 Zhang, J., Wu, J. W., Hua, P., Zhao, Z. H., Wu, L., Fan, G. D., Bai, Y., Kaeseberg, T.,  
624 Krebs, P., 2017. The influence of land use on source apportionment and risk  
625 assessment of polycyclic aromatic hydrocarbons in road-deposited sediment.  
626 *Environmental Pollution*, 229, 705-714.

627



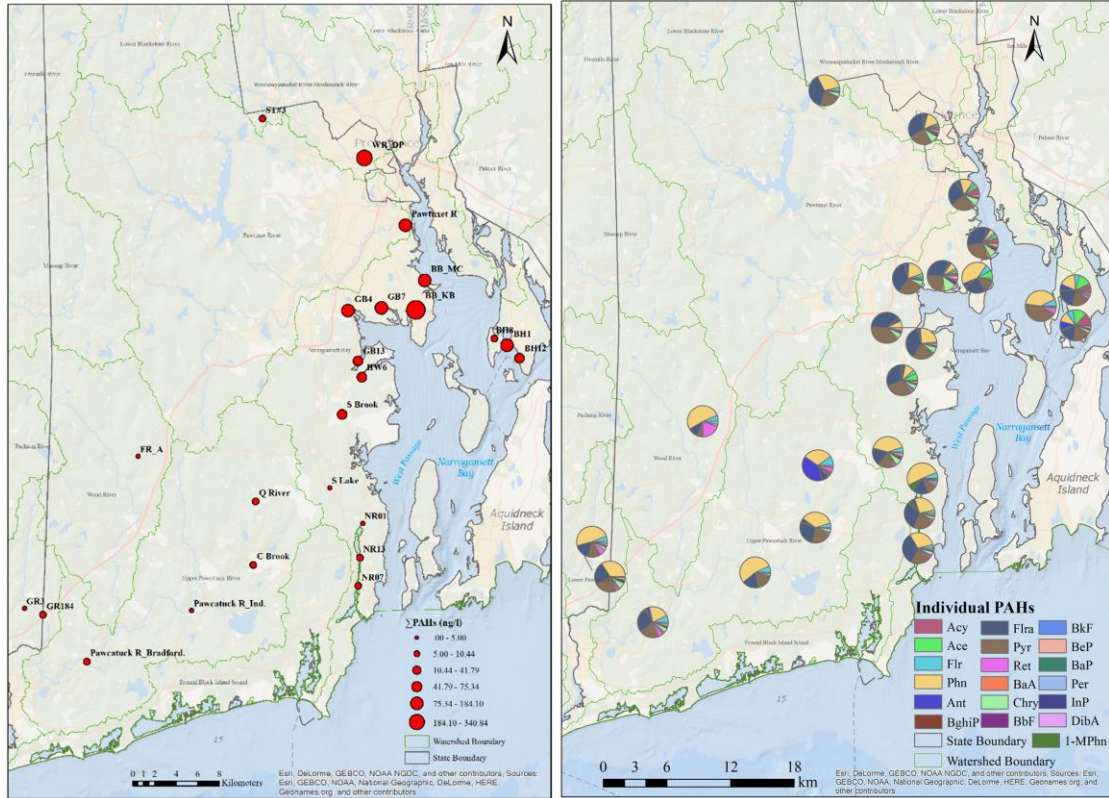
628

629

**Figure 1. Dissolved  $\Sigma_{22}$ PAH and individual PAHs in the Narragansett Bay**

630

**watershed.**



631

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

633

**watershed**

634

635

636

637

638

639

640

641

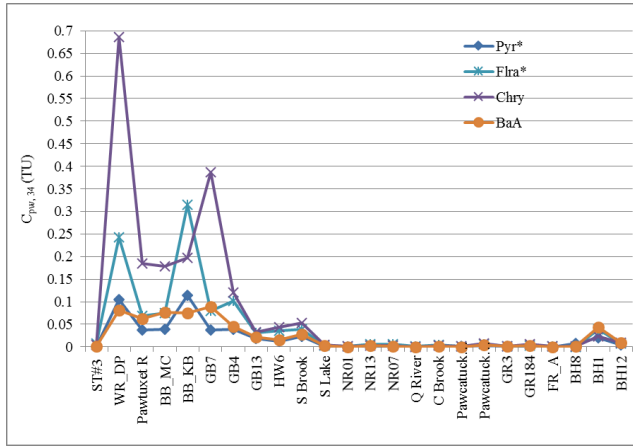
642

643

644

645

646



647

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

648

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

649

**from surface water in Narragansett watershed.**

650

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

Compound	Variable				Adjusted R <sup>2</sup>	Standard Error
	ln(A+1)	ln(B+1)	ln(C+1)	ln(D+1)		
ln( $\Sigma$ 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.