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19

Abstract

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

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

Introduction

Estuaries are subjected to multiple anthropogenic or naturally occurring stress factors, and prone to be affected to different degrees by an array of pollutants including hydrophobic organic contaminants (HOCs). Polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) are two typical classes of HOCs which continue to be released into the environment mainly via natural (PAHs) and anthropogenic processes (PAHs and PDBEs) (Yunker et al., 2002; Hites, 2004; Lima et al., 2005; Takada, 2010; Parinos et al., 2013). In aquatic ecosystems, the dissolved PAHs and PBDEs are subjected to evaporation, adsorption to suspended particulates, uptake by aquatic organisms and bioaccumulation, bio-degradation and photo-degradation (Rayne and Ikonomou, 2005; Tsapakis et al., 2006; Guigue et al., 2014). They can be further transferred into the aquatic environment by urban run-off, municipal sewage, industrial effluents, oil spillage or leakage, gas-water exchange, and atmospheric deposition (Lima et al., 2005; Song et al., 2006; Tsapakis et al., 2006; Parinos et al., 2013). Previous work has suggested that aquatic ecosystems with high PAH and PBDE concentrations might pose potential ecological risks, causing carcinogenic, mutagenic, and toxic effects on aquatic organisms (Hall et al., 2003; 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^2 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 ($^{13}C_{12}$-BDE28, $^{13}C_{12}$-BDE47, $^{13}C_{12}$-

130 BDE99, $^{13}C_{12}$-BDE153 and $^{13}C_{12}$-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

Calculations/Data analysis

- Determination of sampling rate and ambient concentration

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

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

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

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

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

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

- Land-use regression and PAHs source analysis

Land-use regressions models are GIS-based spatial models that relate locations 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^2), 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≤RQ<10), significant potential for adverse effects (10≤

204   RQ<100), and adverse effects should be expected (RQ≥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 $\sum_{22}$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 $\sum_{12}$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 $\sum_{12}$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 pg L^{-1}, while the northern

243   samples displayed ΣPBDEs from 4.4 up to 224 pg 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 ΣPAH 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 ΣPAH

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

analysis since there was weak correlation between the compound and land-use variables

(Table S8, Figure S11).

In recent work, Yang et al (2018), showed that traffic congestion index and the

number of industrial sources within 25-km buffer were the significant predictors of

PAH concentrations in urban lake sediments. Similarly, we find that: 1) transportation

and industry continue to be dominant sources of PAHs to the environment; 2)

monitoring sites should be situated in the relevant buffer zone where PAHs in the

environment are most related to human activities.

PAHs & PBDEs toxicity predictions and assessments

Maybe not surprisingly, no risk for potential effects to aquatic organisms

associated to PBDE was observed, considering short-term exposure of acute toxicity.

ΣRQ were all well below 1, ranging from 1.4 e^{-4} to 5.9 e^{-3}, 4.0 e^{-5} to 3.3e^{-4}, and 4.3 e^{-4}

to 3.4 e^{-2} for fish, algae, and *Daphnia magna*, respectively (Table S10). Even so, the

continuous intake of PBDEs by water organisms can be accumulated in the food chain.

Therefore, more studies are needed concerning bioaccumulation and biomagnification

of PBDEs in biota for a better risk evaluation of these chemicals in the water

environment.

For PAHs, none of our sites exceeded a TU of one, suggesting that no toxicity

occurred at all the sampling sites (Figure 3). We recognize that our samples represented

surface water, which is generally expected to be less contaminated than pore water. A

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 Woonasquatucket 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

Supporting Information

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

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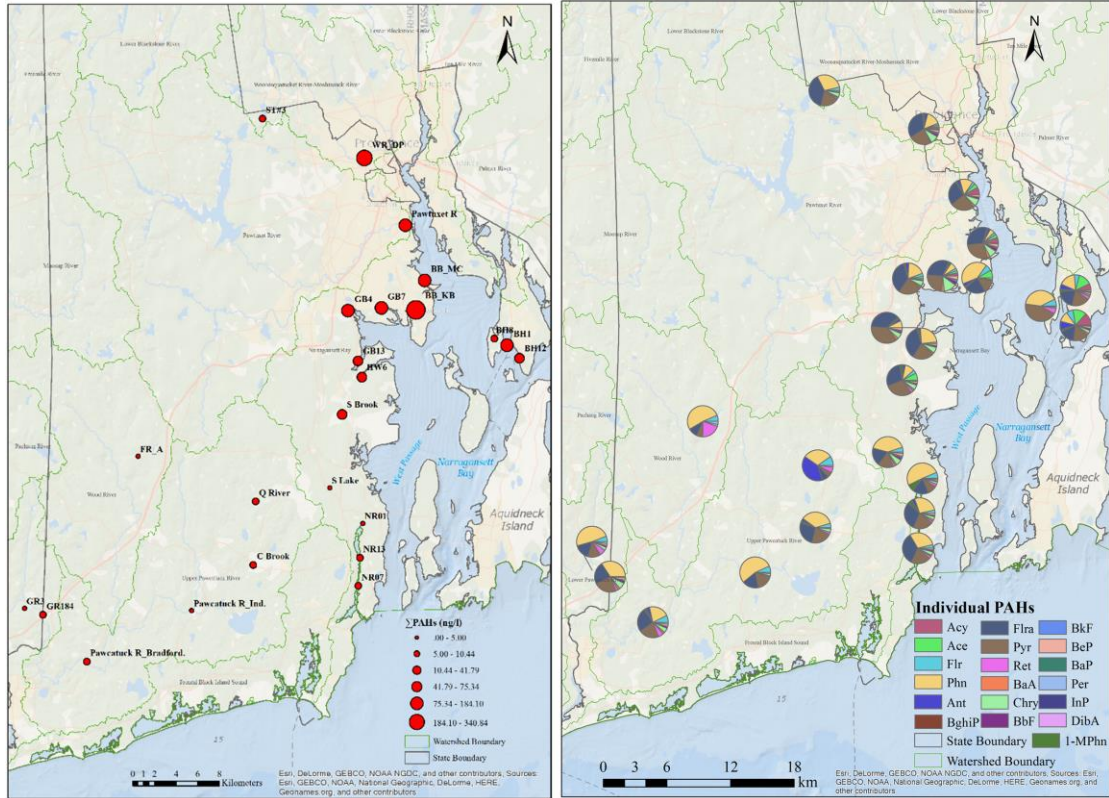
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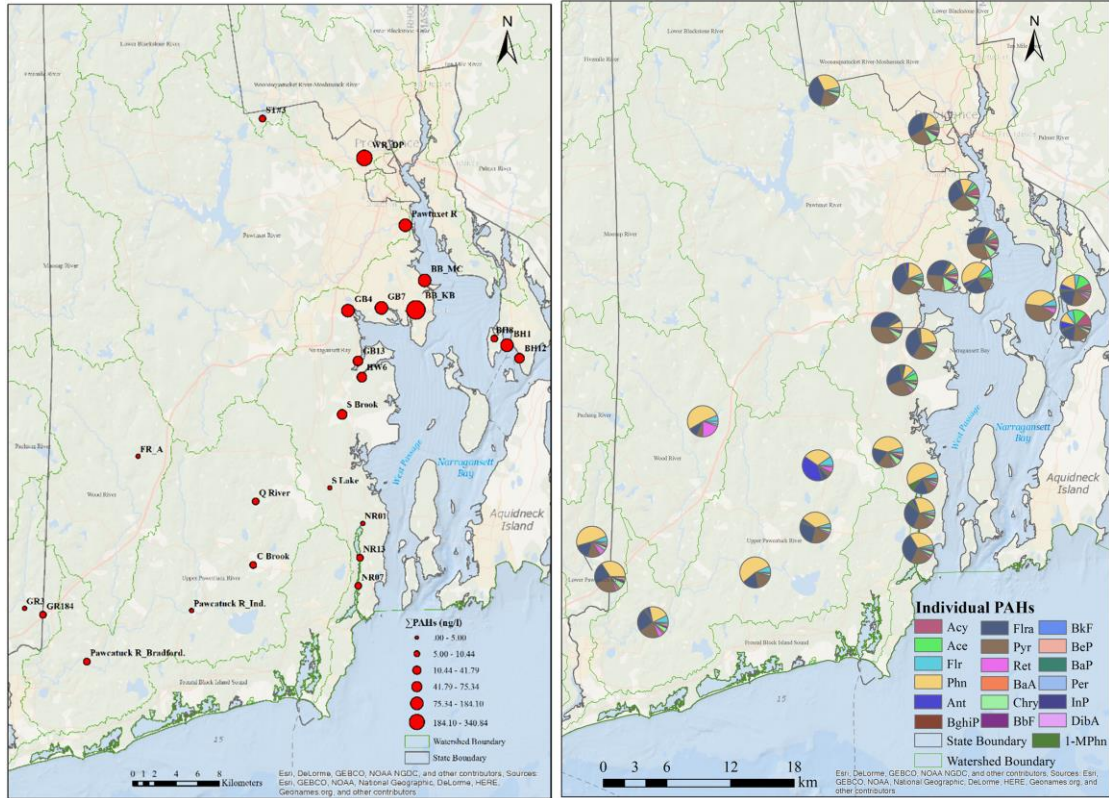
Figure 1. Dissolved $\sum_{22}$PAH and individual PAHs in the Narragansett Bay

629

watershed.

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Figure 2. Dissolved $\sum_{12}$PBDE and individual PBDE in the Narragansett Bay watershed
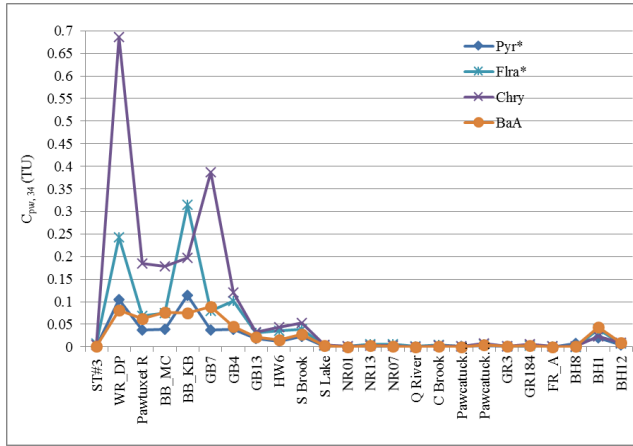
Figure 3. Estimating the total EPA-34 freely dissolved pore water concentration, $C_{pw, EPA-34}$, expressed as toxic units (TUs) from the freely dissolved concentrations from surface water in Narragansett watershed.

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($\sum$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

A = Roads within 2 km;

B = Commercial and industrial areas within 2 km;

C = Population density within 2 km;

D = Sewer area within 2 km;

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