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Land-use-based sources and trends of dissolved PBDEs and PAHs in an urbanized watershed using passive polyethylene samplers[☆]

Wenlu Zhao [a, b, c, d], Minggang Cai [b, c, d], David Adelman [c], Mohammed Khairy [c, e], Peter August [f], Rainer Lohmann [c, *]

[a] School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310018, PR China
[b] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, PR China
[c] Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882-1197, USA
[d] College of Ocean and Earth Science, Xiamen University, Xiamen 361005, PR China
[e] Department of Environmental Sciences, Faculty of Science, Alexandria University, 21511 Moharam Bek, Alexandria, Egypt
[f] Department of Natural Resources Science, University of Rhode Island, One Greenhouse Way, Kingston, RI 02881, USA

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ABSTRACT

Narragansett Bay is a temperate estuary on the Atlantic coast of Rhode Island in the north-eastern 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 to 340 ng L^{-1}, and from 2.9 to 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.

1. 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, 2012; 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 bio-accumulation, 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).

Narragansett Bay is a temperate estuary on the Atlantic coast of Rhode Island, USA. In previous work, the concentration of PAHs in Narragansett Bay and other coastal waters was shown to have strong correlations with urban runoff, river flows and wastewater

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[*] Corresponding author. Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA.

E-mail address: rlohmann@uri.edu (R. Lohmann).

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treatment plant discharges (Lohmann et al., 2011). Due to its long industrial history, PAHs are present in the sediments of Narragansett Bay (Hoffman et al., 1984; Pruell et al., 1986; Latimer and Quinn, 1996; Lima et al., 2003; Hartmann et al., 2004; Lohmann et al., 2011). Concentrations and profiles of PAHs in the water column of Narragansett Bay were reported (Lohmann et al., 2011; Yonis, 2012), but so far no study has actually measured PAHs in the watershed and contributing rivers directly. Likewise, the freely dissolved PBDEs in Narragansett Bay probably originate from a combination of air-water exchange, freshwater runoff, rivers, and wastewater treatment plants (Sacks and Lohmann, 2012), and are still present in currently-used products, suggesting on-going releases to Narragansett Bay and the surrounding areas. This prompted us to investigate the relationship between the land-based activities and PAHs and PBDEs concentrations using passive samplers, and whether river inputs responsible for the contaminants present in Narragansett Bay.

Low density polyethylene (LDPE) passive samplers are cost-effective, technically simple tools with lower detection limits than traditional active sampling techniques (Mcdonough et al., 2014). Instead of pumping air or water through a filter, passive sampling relies on diffusion to accumulate analytes of interests and only accumulates molecules which are freely dissolved in the water or the atmosphere (Adams et al., 2007). This avoids the analytical interference of, e.g., dissolved organic carbon (DOC) which can affect active sampling results (Lohmann et al., 2011). Moreover, concentrations of freely dissolved PAHs and PBDEs are of interest because this fraction is available for direct diffusive exchange between water and other reservoirs such as air, biota, or sediment (Kane Driscoll et al., 2010; Mhadhbi et al., 2012; Bragin et al., 2016). Different passive sampler types have been used in seawaters, harbors, rivers and urban waterways to determine freely dissolved concentrations of PAHs and PBDEs (Cornelissen et al., 2008a; Sower and Anderson, 2008; Lohmann et al., 2011, 2012; Sacks and Lohmann, 2012; Alvarez et al., 2014).

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

2. Materials and methods

2.1. Study area

The Narragansett watershed area in Rhode Island was 2077.6 km^2 including the estuarine waters (43.6% total watershed). The land coverage pattern around the bay was dominated by forest (58%), urban or built-up land (28%), agriculture (5.4%), water (4%), wetland, barren land and rangeland (each < 2%, see TOC).

2.2. Preparation and deployment of LDPE passive samplers

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

2.3. Analysis

LDPE samplers were wiped clean with Kimwipes and extracted once in hexane for 24 h after addition of 20 ng of labeled PAHs (acenaphthalene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) and PBDEs ($^{13}C_{12}$-BDE28, $^{13}C_{12}$-BDE47, $^{13}C_{12}$-BDE99, $^{13}C_{12}$-BDE153 and $^{13}C_{12}$-BDE183) surrogates. Extracted LDPE samplers were air dried and weighed. Extracts were concentrated to 100 μL, and spiked with 50 ng of *p*-terphenyl-d$_{14}$ (injection standard) directly before instrumental analysis.

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

2.4. Quality assurance/Quality control

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

2.5. 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 (Booij and Smedes, 2010).