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Transects of polycyclic aromatic hydrocarbons and organochlorine pesticides in an urban estuary using passive samplers

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Abstract

Hydrophobic organic contaminants (HOCs) are tracers of anthropogenic impacts, which can negatively affect water quality. The relative importance of new emissions versus the remobilization of HOCs from legacy reservoirs is not well constrained. Polyethylene passive samplers were deployed in vertical profiles at four sites to determine the concentrations and gradients of atmospheric and freely dissolved Polycyclic Aromatic Hydrocarbons (PAHs) and freely dissolved Organochlorinated Pesticides (OCPs) in Narragansett Bay, an urban estuary. The concentrations of the sum of 20 PAHs ranged from 4.3 – 240 ng/m^3 in the air and 3.2 – 21 ng/L in the water column, dominated by phenanthrene and pyrene. OCP concentrations varied from below the detection limit to 150 ng/L in the water column. Common OCPs included α-hexachlorocyclohexane, hexachlorobenzene, and aldrin. Gradients displayed net deposition for PAHs, but equilibrium through the water column. Results from this study provided evidence that key OCPs displayed mostly similar concentrations (at or near equilibrium) in the water at both Conimicut Point and Block Island.

Keywords
Polycyclic aromatic hydrocarbon, PAH, organochlorine pesticide, OCP, air water gradient, water porewater gradient, water pollution, urban estuary, passive sampler, passive sampling, polyethylene

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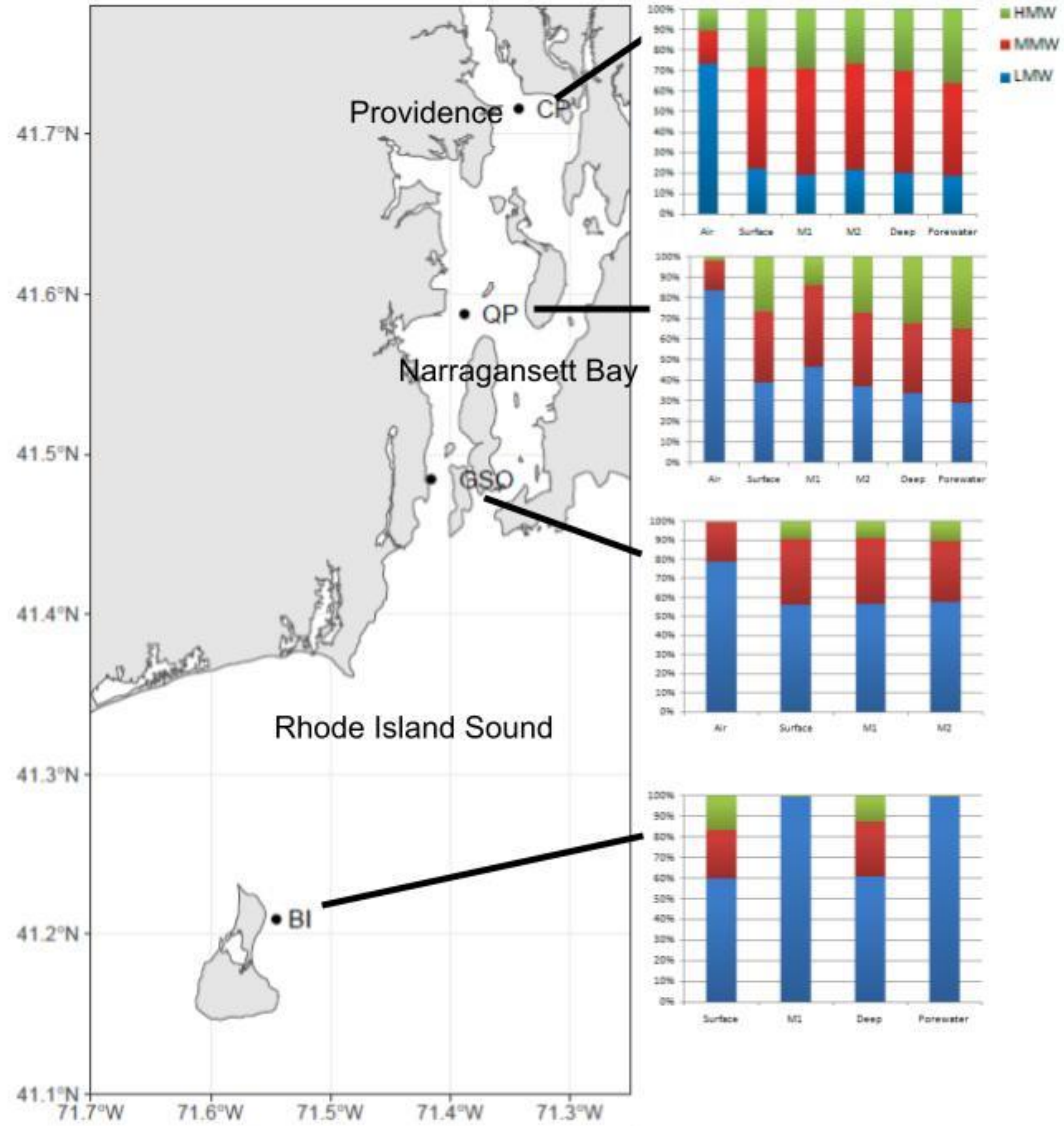
Graphical Abstract:



Molecular weight make up (HMW – high molecular weight, MMW – middle molecular weight, and LMW – low molecular weight) of PAHs through the water column with distance from the urban center at Providence, Rhode Island, USA

Introduction

Hydrophobic organic contaminants (HOCs) are nonpolar compounds that have a large octanol-water partition coefficient (log K_{ow}>2) and thus tend to sorb to lipids and other organic compounds. HOCs have been found to preferentially bind to suspended and bottom sediments in aquatic systems (Elzerman and Coates, 2009). HOCs are a large group of contaminants that include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) including dichlorodiphenyl-trichloroethane (DDT), and some emerging contaminants. HOCs have been and are currently in widespread use in modern society and as such are able to serve as markers of anthropogenic impacts. Pesticides, petroleum hydrocarbons, solvents, and industrial byproducts are some examples of HOCs, and broad use has contributed to their persistence in the environment, including marine ecosystems. HOCs overlap with persistent organic pollutants (POPs) with different levels of persistence based on individual compounds, and in this way are able to be both tracers of legacy contaminants (like PCBs and DDTs) and also current usage contamination to aquatic ecosystems that can impact and impair water quality.

PAHs are easily identifiable markers of anthropogenic pollution and the relative abundance of PAHs, compared to many other less abundant HOCs, can be used to fingerprint their emission sources (Khalili et al., 1995; Yunker et al., 2002). The carcinogenicity of PAHs has been investigated for several decades, and PAHs are widely believed to be contaminants of concern both for humans as well as aquatic life (Menzie et al., 2002; Pruell et al., 1986; Stegeman and Lech, 1991; World Health Organization, 2010). PAHs are introduced to the atmosphere through traffic emissions, gasoline evaporation, residential heating systems, wildfires, and various industrial processes (Khairy and Lohmann, 2012). The transport of PAHs in the environment is also limited by their photoreactivity, which implies that concentrations should decrease with distance from their source (Bertilsson and Widenfalk, 2002). In Narragansett Bay, Rhode Island, USA, based on ratios of individual compounds, PAHs have previously been found to originate from combustion processes rather than from petrogenic sources (Hartmann et al., 2005, 2004; Lake et al., 1979; Latimer et al., 1990; Latimer and Zheng, 2003; Lohmann et al., 2011; Zhao et al., 2018). OCPs are also indicators of anthropogenic pollution. The legacy OCPs analyzed in this work are no longer in use (having been banned in the 1970s), so they are able to provide historic and background data on anthropogenic contamination in Narragansett Bay.

PAHs and OCPs have the potential to enter Narragansett Bay and other coastal waters through urban runoff, and PAHs have been found in the sediments of Narragansett Bay (Hartmann et al., 2004; Latimer et al., 1990; Latimer and Quinn, 1996; Lima et al., 2002; Perron et al., 2013; Pruell et al., 1986). Dissolved PAHs were found in the surface waters of Narragansett Bay (Lohmann, 2011; Zhao et al., 2018) as well as in the deep waters (Perron et al., 2013) using passive sampling. This earlier research on the surface waters reported net deposition of PAHs from atmospheric sources, with the potential for sediment to act as a source but no supporting data for the latter (Booij et al., 2002; Lohmann, 2011). The research set forth here focused on a north to south transect, from the industrialized northern estuary near Providence (the capital city), and terminated near Block Island in Rhode Island Sound, outside of the mouth of Narragansett Bay with passive samplers deployed throughout the water column, from the atmosphere to the sediment porewater (Figure 1). Sample sites at Conimicut Point (CP) and Quonset Point (QP) are in the upper part of the estuary while the Graduate School of Oceanography (GSO) Dock site (GSO) is at the mouth of the estuary. The Block Island (BI) site is outside of the estuary and in mixed coastal waters.

This study relied on passive samplers as convenient sampling tools that can determine freely dissolved or gas-phase concentrations of HOCs simultaneously at different depths (atmosphere, water column, and porewater). In this case, polyethylene (PE) sheets were used, which are well characterized for their equilibrium partitioning constants for various PAHs and OCPs (Burgess et al., 2015). Performance reference compounds (PRCs) were included as in situ probes to assess the extent of equilibrium reached during the field deployments (Booij et al., 2002).

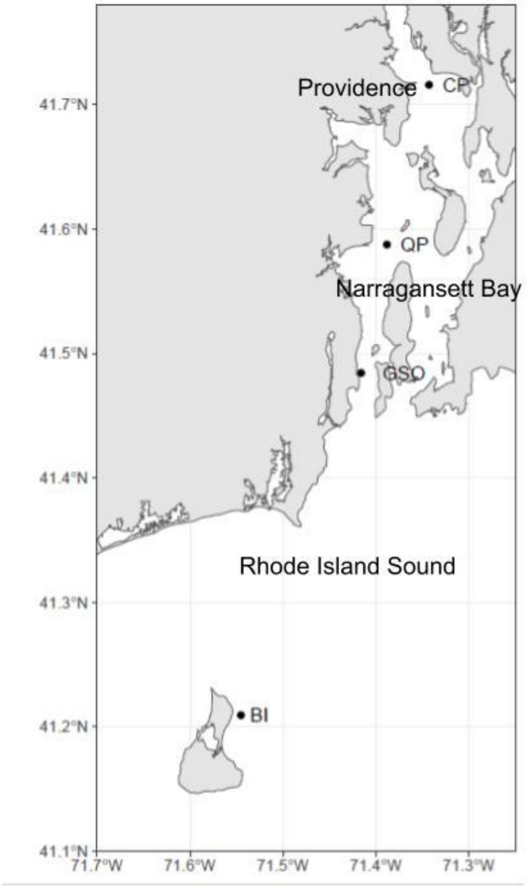


Figure 1: Sampling Sites in Narragansett Bay, RI. Samples for PAHs were collected at Conimicut Point (CP), Quonset Point (QP), GSO Dock (GSO), and Block Island (BI) and OCPs at CP and BI.

The goals of this study were to (i) determine the concentrations of PAHs and OCPs across vertical arrays at four sites in an urban estuary, (ii) derive air-water, within water and water-porewater gradients for PAHs and OCPs, and (iii) assess sources of these contaminants to the estuary.

Materials and Methods

Passive Sampler Preparation

Polyethylene sheets (PEs) of 25.4 μm in thickness were cut from commercial sheeting (Covalence Plastics, Inc., Minneapolis, MN, USA) into sizes of roughly 10 centimeters by 40 centimeters, weighing approximately 2 g each. PEs were prepared by cleaning and then spiking with PRCs to calculate sampling rate based on their loss following the method found in Booij et. al. (Booij et al., 2002), since the rate of uptake of similarly structured contaminants is directly related to the rate of dissipation of PRCs. This study used the following PRCs: d_8-naphthalene, d_{10}-pyrene, and d_{12}-benzo(a)pyrene for PAHs and dibromobiphenyl, tetrabromobiphenyl, and pentabromobiphenyl for OCPs. Additional PE samples not deployed in the field were used to determine initial PRC concentrations.

Passive Sampler Deployments

PEs were deployed at four stations in Narragansett Bay during September, October, and November 2009 from 12 to 22 days at fixed-site water quality monitoring buoys operated by the Office of Water Resources (RI Department of Environmental Management) and the Marine Ecosystems Research Laboratory at the University of Rhode Island, Graduate School of Oceanography, in addition to temporary buoys deployed by and for this study (Figure 1). Samplers were placed approximately 1m below the surface, 0.5 m above the bottom sediment, and at two depths in between. Due to the bathymetry of Narragansett Bay, depths vary due to tidal variations but overall increase from a minimum at CP of approximately 5 meters and a maximum at BI of approximately 80 meters. An additional PE was placed below a concrete masonry unit (anchor weight) attached to each buoy line in order to sample the sediment porewater, as well as inside inverted stainless-steel bowls attached to the portion of the buoy above the water to measure atmospheric concentrations.

Passive Sampler Analysis

Upon PE retrieval, samplers were cold extracted twice with dicholoromethane for 24 h, then combined, concentrated, and analyzed following the procedure in Khairy and Lohmann, 2012 for PAHs and Khairy et al., 2014 for OCPs and all 43 compounds were analyzed using an Agilent 6800 gas chromatogram operated in negative electron ionization mode coupled to an Agilent 5973N mass spectrometer operated in single ion monitoring mode.

Samplers for PAHs were deployed at different times than those for OCPs. Samplers for OCPs were lost during deployment at two sites, so while data for PAHs was available for four sites, OCP data was only available for two sites.

Quality Assurance and Quality Control

Surrogate standards, added prior to extraction of the recovered passive samplers, were used to correct for losses during sample processing. Average recoveries were 30±9% for d_{10}-acenaphthene, 110±25% for d_{10}-phenanthrene, 152±29%for d_{12}-chrysene, and 62±11% for d_{12}-perylene. The surrogate standard for OCPs was ^{13}C-hexachlorobenzene (HCB) and recoveries averaged 97±4.1%.

Detection limits were calculated as the average concentration from six PE blanks plus three times the standard deviation of the average (detection limits were on the order of 0.2 – 20 ng compound per L water). Mean blank concentrations varied from 0.1 – 4.8

nanograms per gram of sampler (ng/g) and detection limits ranged from 0.3 ng/g (benzo(g,h,i)perylene) to 18.8 ng/g (acenaphthene) (see SI Table 1 for complete blank values). OCP blank mean concentrations varied by compound from 0.08 ng/g (methoxychlor) to 3.10 ng/g (endrin) while detection limits ranged from 0.18 ng/L (methoxychlor) to 10.3 ng/L (endrin) (See SI Table 1 for complete blank values).

Sampling Rates and Equilibration of Target Compounds

Pre-loaded PRCs were used to derive the percentage of equilibrium reached for target analytes. For PAHs, d_8-naphthalene was depleted 96-99%; d_{10}-pyrene 83-99%, except in the air (23-68%); and d_{12}-benzo(a)pyrene 3-56%. For OCPs, three PRCs were used: 4,4'-dibromobiphenyl (97-99%), 3,3',5,5'-tetrabromobiphenyl (at least 72% at Conimicut Point, 42-77% at Block Island), and 2,2',4,5',6-pentabromobiphenyl (PBB 103) (~99% at Conimicut Point, but 22-51% at Block Island).

The sampling rate, Rs, is the volume of water or air sampled by the PE over the duration of the deployment (L/d) as measured by the loss of the d_{10}-pyrene PRC:

$$\%\ \text{equilibration} = 1 - e^{-\frac{Rs\,x\,t}{Kpe\,x\,Vpe}},$$

where

Rs = sampling rate (L/day),

t = deployment time (days),

Kpe = equilibrium partitioning constant between PE and water or air, and

Vpe = volume of the PE sampler (L).

Rs values varied from 11 – 43 L/d (see Table 1) with a median of 28 L/d, which fell among literature values of 2 to 200 L/d (Booij et al., 2003; Lohmann et al., 2011), but were higher than those found by (Huckins et al., 1999) of 1.0 – 8.0 L/d and those found by (Tomaszewski and Luthy, 2008) of 0.5 – 1.5 L/d in the porewater. In a study from (Shoeib and Harner, 2002), air sampling rates for semi-permeable membrane device (SPMD) passive samplers had values ranging from 3 – 5 m^3/d for pesticides, but the air sampling rates found in this study using PEs and PAHs had a much wider range, from 1.8 – 15 m^3/d (see Table 1). This discrepancy may be due to the difference in the way SPMD samplers partition compared to the way PE samplers partition, and the longer equilibration period for the SPMD study.

Table 1. Sampling Rates for PE Passive Samplers in Air, Water Column, and Sediment Porewater for PAHs Based on d_{10}-Pyrene PRC Loss.

	Conimicut Point	Quonset Point	GSO Dock	Block Island
Air (m^3/d)	6.5	15	1.75	-
Surface (L/d)	28	37	24	34
M1 (L/d)	40	33	24	43
M2 (L/d)	32	35	20	-
Deep (L/d)	25	21	-	19
Sediment Porewater (L/d)	22	11	-	17

Calculation of Dissolved Concentrations

To calculate the concentrations of PAHs and OCPs in the environment, previously determined partition coefficients were used (PAHs: Khairy and Lohmann, 2012; Lohmann, 2011; Lohmann et al., 2011) (OCPs: Hale et al., 2010; Lohmann, 2011). Partition coefficients (K_{pe}) were temperature-adjusted to the measured air and water temperatures during the deployments (See SI Table 2 for air and water temperatures, SI Table 3 for PAH Kpea values, SI Table 4 for PAH Kpew values, SI Table 5 for OCP Kpew values). Partition values were also corrected for lack of equilibrium as deduced from PRC-loss using the following equation:

$$C_{\text{water/air}} = \frac{C_{pe}}{K_{pe}\ (T, salinity) x\ (1 - \%\ equilibrium)}$$

A complete table of percent of PAH PRC loss at each depth and location is presented in SI Table 6.

For comparison purposes only, porewater concentrations were estimated from previously reported bulk sediment concentrations using a dual partitioning model, as described in the SI.

Results and Discussion

OVERVIEW– PAH Concentrations and Profiles

PAH concentrations, after non-equilibrium corrections using the PRCs, were highly variable throughout the locations and depths. PAH concentrations ranged from below the detection limit to 8.9 ng/L (phenanthrene) at the surface at the GSO Dock, and up to 130 ng/m^3 (phenanthrene) in the atmosphere at the GSO Dock (see SI Table 7 for a complete list of concentrations). The concentrations of Σ_{20} PAHs reported here ranged from 3.2 – 21 ng/L in the water column at the GSO Dock (Table 2). The dominant PAHs in the water were phenanthrene, fluoranthene, and pyrene, while the dominant PAHs in the atmosphere were phenanthrene, acenaphthene, and fluoranthene (see Table 2 for dominant PAH concentrations and see SI Figure 1 for percent makeup in the air, water, and sediment porewater across all locations).

ΣPAHs were divided into molecular weight groups, low molecular weight (LMW) compounds were those under 203 g/mol, high molecular weight compounds (HMW) above 250 g/mol, and middle molecular weight compounds (MMW) between 203 and 250 g/mol. LMW PAHs included naphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and methyl phenanthrenes; fluoranthene, pyrene, retene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo(h)fluoranthene were MMW compounds; and benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene made up the HMW PAHs. At Conimicut Point the ΣMMW PAHs made up the major fraction of the total (the ΣMMW compounds contributed approximately 50%) and that fraction decreased with distance from Conimicut Point (see Table 2). ΣLMW made up the largest percentage of Σ_{20} PAHs at Block Island.

ΣHMW PAHs made up increasingly larger fractions with depth at all estuarine sites but not at Block Island where molecular weight fractions were consistent throughout the water column.

Table 2. PAH Concentrations (ng/L in water, or ng/m^3 in air) in Air, Surface Water, Intermediate Water Depths (M1 for upper and M2 for deeper depths), Deep, and Sediment Porewater determined using passive sampling in Narragansett Bay and Rhode Island Sound. Sum molecular weight concentration values are in italicized bold while total concentrations are bolded.

Conimicut Point

Compound	Air (ng/m3)	Surface (ng/L)	M1 (ng/L)	M2 (ng/L)	Deep (ng/L)	Sediment Porewater (ng/L)
Phenanthrene	4.5	2.3	1.4	1.6	1.5	1.7
ΣLMW	***6.8***	***4.0***	***2.9***	***3.0***	***2.9***	***3.5***
Fluoranthene	0.9	3.6	2.9	2.7	2.7	2.8
Pyrene	0.6	4.5	4.1	3.9	4.0	4.9
Chyrsene	0	0.7	0.5	0.4	0.3	0.4
Benz(a)anthracene	0	0.3	0.2	0.2	0.2	0.2
ΣMMW	***1.5***	***9.0***	***7.6***	***7.1***	***7.2***	***8.3***
Benzo(b)fluoranthene	0.1	3.5	2.9	2.6	2.9	4.4
Benzo(h)fluoranthene	0.8	1.4	1.3	0.9	1.1	1.8
Benzo(a)pyrene	0	0.1	0.1	0.1	0.1	0.2
ΣHMW	***0.9***	***5.2***	***4.3***	***3.7***	***4.3***	***6.6***
Σ_{20}PAHs	**9.3**	**18**	**15**	**14**	**14**	**18**

Quonset Point

Compound	Air (ng/m3)	Surface (ng/L)	M1 (ng/L)	M2 (ng/L)	Deep (ng/L)	Sediment Porewater (ng/L)
Phenanthrene	3.2	1.9	2.0	1.8	2.0	2.3
ΣLMW	***3.6***	***2.9***	***3.3***	***2.9***	***3.3***	***3.9***
Fluoranthene	0.4	1.2	1.3	1.2	1.4	2.0
Pyrene	0.2	1.1	1.4	1.4	1.6	2.6
Chyrsene	0	0.1	0.1	0.1	0.2	0.3
Benz(a)anthracene	0	0.1	0	0	0	0.1
ΣMMW	***0.6***	***2.5***	***2.8***	***2.8***	***3.3***	***4.9***
Benzo(b)fluoranthene	0	0.3	0.1	0.8	1.2	0.9
Benzo(h)fluoranthene	0	0.4	0.1	0.4	0.7	0.3
Benzo(a)pyrene	0	0	0	0	0	0.1
ΣHMW	***0.1***	***2.0***	***1.0***	***2.1***	***3.2***	***4.7***

Σ_{20} PAHs	**4.3**	**7.4**	**7.0**	**7.7**	**9.8**	**14**

GSO Dock						
Compound	Air (ng/m3)	Surface (ng/L)	M1 (ng/L)	M2 (ng/L)	Deep (ng/L) *ns	Sediment Porewater (ng/L) *ns
Phenanthrene	134	8.5	8.9	6.5	ns	ns
ΣLMW	***190***	***11***	***12***	***11***	ns	ns
Fluoranthene	40	3.4	3.6	2.7	ns	ns
Pyrene	11	3.0	3.0	2.6	ns	ns
Chyrsene	0.3	0.3	0.3	0.3	ns	ns
Benz(a)anthracene	0	0.3	0.3	0.3	ns	ns
ΣMMW	***51***	***6.9***	***7.3***	***5.9***	ns	ns
Benzo(b)fluoranthene	0	0.9	0.9	1.0	ns	ns
Benzo(h)fluoranthene	0	0.8	0.8	0.8	ns	ns
Benzo(a)pyrene	0	0.1	0.1	0.1	ns	ns
ΣHMW	***0***	***1.9***	***1.8***	***1.9***	ns	ns
Σ_{20} PAHs	**243**	**20**	**21**	**19**	ns	ns

Block Island						
Compound	Air (ng/m3) *ns	Surface (ng/L)	M1 (ng/L)	M2 (ng/L) *ns	Deep (ng/L)	Sediment Porewater (ng/L)
Phenanthrene	ns	0.9	1.3	ns	1.0	1.1
ΣLMW	ns	***1.8***	***2.7***	ns	***1.9***	***2.1***
Fluoranthene	ns	0.4	0.4	ns	0.4	0.4
Pyrene	ns	0.3	0.5	ns	0.4	0.3
Chyrsene	ns	0	0	ns	0	0
Benz(a)anthracene	ns	0	0	ns	0	0
ΣMMW	ns	***0.7***	***1.0***	ns	***0.8***	***0.7***
Benzo(b)fluoranthene	ns	0.3	0.3	ns	0.3	0.3
Benzo(h)fluoranthene	ns	0.2	0.1	ns	0.1	0.1
Benzo(a)pyrene	ns	0	0	ns	0	0
ΣHMW	ns	***0.5***	***0.4***	ns	***0.4***	***0.5***
Σ_{20} PAHs	ns	**2.9**	**4.1**	ns	**3.2**	**3.3**

*ns – not sampled. 0 values indicate concentrations above detection limit but below 0.1

PAH ratios can provide insight into the source of contaminants(Yunker et al., 2002). For example, the ratio of fluoranthene: (fluoranthene + pyrene) indicates uncombusted petroleum (i.e., oil spill) below 0.4, petroleum combustion between 0.4 and 0.5, and grass, wood, and/or coal combustion above 0.5 (Yunker et al., 2002). At all locations, PAHs were dominantly from petroleum and combustion of liquid fossil fuel (i.e., vehicle emissions and diesel combustion), with one exception (details are provided in the SI text, SI Table 8, and SI Figure 4). Overall, likely PAH sources were derived from four different PAH ratios; all showed the same source for the PAHs to be primarily from liquid fossil fuel and its combustion (see SI text for details).

COMPARISON TO OTHER DATA – PAHs

Surface water concentrations of individual PAHs at Conimicut Point and Quonset Point were the same order of magnitude (0 – 10 ng/L) as those previously reported by Lohmann et. al. (Lohmann et al., 2011) for Narragansett Bay. Perron et al. found similar concentration ranges for several PAHs measured in the water column at six stations in Narragansett Bay using PE and polyoxymethylene (POM) passive sampling (Perron et al., 2013). In a similar study performed in Oslo Harbor, Norway, polyoxymethylene and polydimethylsiloxane passive samplers reported Σ_{12} PAHs ranging from 0.4 – 230 ng/L in the water column and 1.1 – 310 ng/L in the sediment porewater (Cornelissen et al., 2008). These values are within the same range as concentrations found in this study, if occasionally higher. Sediment porewater concentrations in the New York Harbor using PE passive samplers were similar to results found in this study for benzo(a)pyrene (≤0.71 ng/L, see SI Table 7 for values) while the results for phenanthrene and pyrene were higher than in this study (94 and 32 ng/L, respectively) (Lohmann et al., 2004). The same study found sediment porewater concentrations in the Boston Harbor using PE passive samplers at 1,100 ng/L (phenanthrene), 560 ng/L (pyrene), and 10 ng/L (benzo(a)pyrene), which are orders of magnitude higher than those reported here (Lohmann et al., 2004). Overall, this confirms Narragansett Bay as not being as heavily polluted as bigger urban/industrial estuaries (Boston Harbor, Oslo Harbour).

OVERVIEW – OCP Concentrations

OCP concentrations varied from below the detection limit to 150 ng/L (γ-Hexachlorocyclohexane (HCH)) in the surface water at Conimicut Point (see Table 3 for a list of concentrations). γ-HCH is likely introduced to the waters of Narragansett Bay from anthropogenic activities due to the presence at the surface of Conimicut Point and its absence in deep water and sediment porewater. Aldrin, HCB, and α-HCH were detected throughout the water column and in the sediment porewater at both locations. B-HCH was detected at Block Island throughout the water column but not at all at Conimicut Point. Dieldrin was never above detection limit, while endrin ketone, p,p-DDT, endrin, and δ-HCH were rarely above detection limits (see SI Table 9 and Figure 5 for a complete list of concentrations and percent makeup in the water and sediment porewater across all locations).

Table 3. OCP Concentrations (ng/L) determined using passive sampling in Narragansett Bay and Rhode Island Sound. Values at or over 1 ng/L are bolded to bring attention to those compounds with higher concentrations

Conimicut Point					
Compound	Surface (ng/L)	M1 (ng/L)	M2 (ng/L)	Deep (ng/L)	Sediment (ng/L)
α-HCH	**2.1**	**1.7**	**1.8**	**3.0**	**3.9**
HCB	0.01	0.01	0.01	0.01	0.01
γ-HCH	**150**	**-**	**93**	**-**	**-**
Aldrin	0.08	0.03	0.06	0.04	0.03

Methoxychlor	0.01	-	0.01	0.02	-

Block Island

Compound	Surface (ng/L)	M1 (ng/L)	M2 – ns*	Deep (ng/L)	Sediment (ng/L)
α-HCH	**2.1**	**0.92**	ns	**1.1**	**3.0**
HCB	0.004	0.003	ns	0.01	0.01
γ-HCH	-	**97**	ns	-	-
Aldrin	0.01	0.02	ns	0.01	0.01
Methoxychlor	0.01	0.01	ns	0.04	-

*ns – not sampled; a value of – indicates a concentration below detection limit

COMPARISON TO OTHER DATA – OCPs

Direct comparisons of OCPs to sites in New England, were not possible because such data is unavailable. However, other studies conducted in the Great Lakes using passive samplers found concentrations of HCB at the same order of magnitude as those found throughout the water column at both locations in this study at concentrations of 3 – 10 pg/L (Khairy et al., 2014; Lohmann et al., 2012; Zhang et al., 2013). P,p'-DDT, p,p'-DDD, p,p'-DDE, and aldrin concentrations in this study were found at the same levels as those sampled using passive samplers in the Great Lakes (Khairy et al., 2014; Zhang et al., 2013). α-HCH was found at concentrations three orders of magnitude higher than those previously reported (Khairy et al., 2014; Lohmann et al., 2012; Zhang et al., 2013). Additionally, p,p'-DDT, p,p'-DDD, all four HCHs, and cyclodienes (aldrin, dieldrin, endosulfan I, endosulfan sulfate, endrin, heptachlor, and heptachlor epoxide) were found at similar concentrations as those in estuaries on Italy's west coast using grab sampling (Montuori et al., 2016). In contrast to PAH concentrations, then, OCP concentrations in Narragansett Bay were similar to other sites.

PAH and OCP TRENDS ACROSS THE ESTUARY

As expected, PAH concentrations throughout the water column were highest in the estuary (see Figure 1 for site locations and SI Figure 2 for gradients of individual compounds from Conimicut Point to Block Island), and porewater concentrations were typically greater than water column concentrations. Concentrations of OCPs throughout the water column were generally similar at both sites. Hence the typical gradient was from porewater to a well-mixed water column, and a gradient from the more contaminated urban/industrial north to the cleaner, southern mouth of the estuary.

Pyrene concentrations show the highest values near the urban center at Conimicut Point and a secondary concentration spike at the surface of the GSO Dock as visualized from Ocean Data View software (ODV) (Schlitzer, 2021) (see Figure 2). ODV was used to extrapolate and heat map based on data inputs using known current, bathymetry, temperature, and salinity data. It is designed to be used for visualizing purposes only, not to stand in for measured concentrations. In contrast, phenanthrene concentrations show the highest values at the GSO Dock surface with concentrations decreasing outward to the north, south, and deeper in the water column (see SI Figure 6).

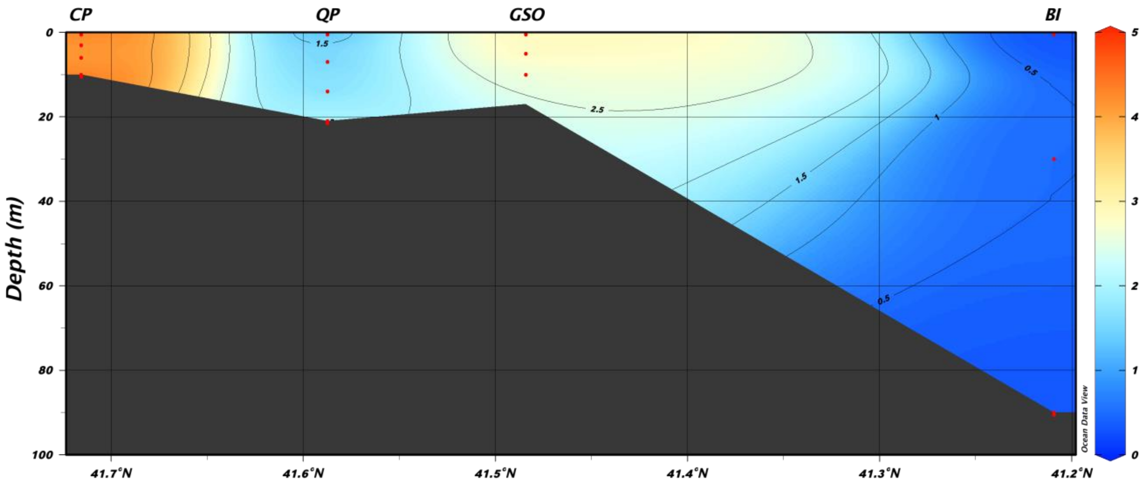


Figure 2. Cross section of pyrene water column concentrations (ng/L) (Ocean Data View Software Imaging (Schlitzer, 2021)**).**

The volatile, low molecular weight PAHs made up a larger portion of ΣPAHs with increasing distance from the Conimicut Point source (See SI Figure 3).

PAH GRADIENTS ACROSS THE ESTUARY AND SOURCES OF PAHS

Gradients between the air and surface water were determined by calculating the ratio of the PE normalized concentration from passive samplers in air to those in surface water, and between samplers at different depths in the water column and porewater. Values larger than 1.3 for LMW PAHs indicated the compound has a larger concentration in the air, and therefore had a net gradient favoring deposition; values of 1± 0.3 indicate the compound's concentrations in both air and water were not substantially different, and were at or near equilibrium (meaning similar chemical activities). Uncertainties in gradient calculations were 30% for all LMW PAHs across locations and depths but increased with higher molecular weight compounds to 650% for MMW PAHs. Due to the high uncertainties, gradients for compounds heavier than LMW cannot be determined (see the SI for uncertainty calculations and SI Table 1 for blank values).

Focusing on the air – surface water gradient, most LMW PAHs showed net deposition at Conimicut Point (CP) and GSO Dock (GSO), except for acenaphthylene at both locations (see Figure 3 for LMW air-surface gradients). Quonset Point (QP) LMW PAHs were mostly in equilibrium between the air and surface water, with gradient values very close to 1 except for acenaphthylene, which was strongly volatilizing.

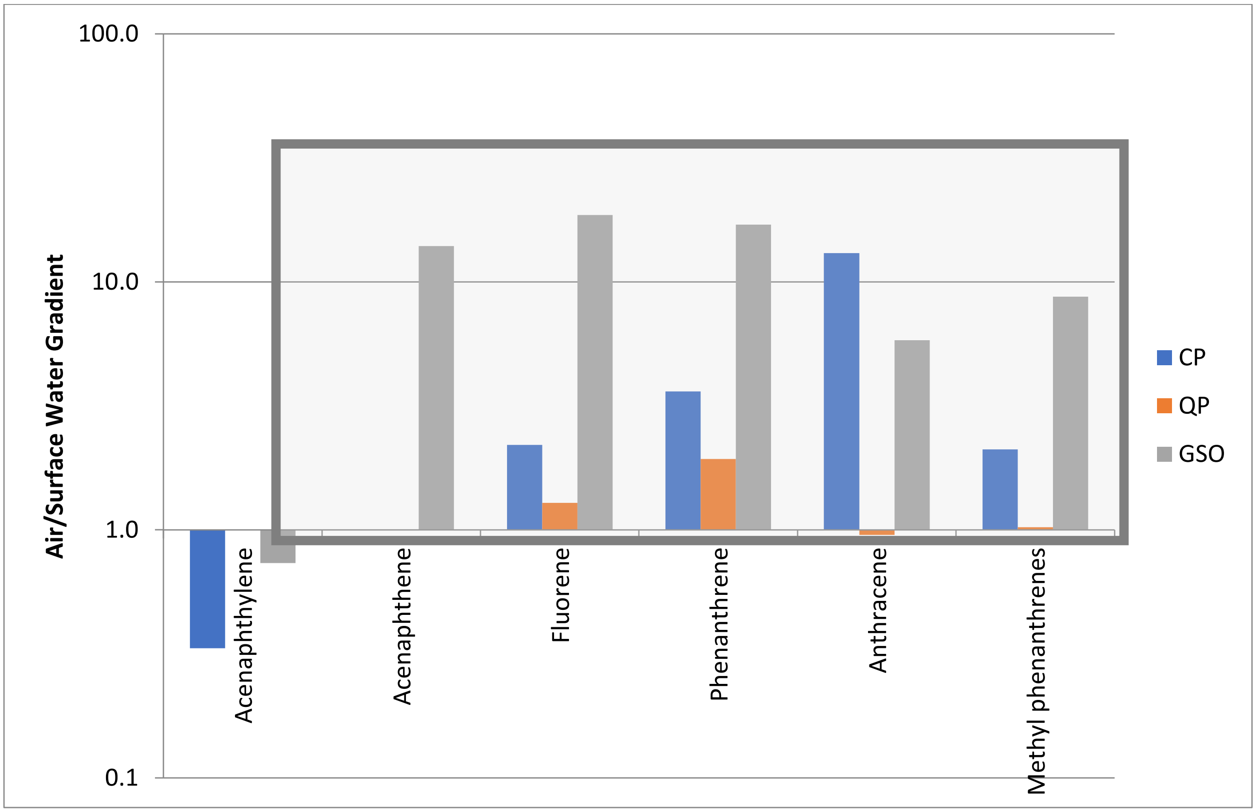


Figure 3. Low Molecular Weight PAH Gradients from Air to Surface Water. The box highlights all compounds showing deposition.

Lastly, PAH concentrations were compared to aquatic life adverse effects thresholds. In all cases, PAH concentrations were below levels of concern (see SI text).

OCP PROFILES

Concentrations of α-HCH were mostly constant throughout the water column at both Block Island and Conimicut Point, ranging from 0.92 – 3.9 ng/L. β-HCH was similarly found throughout the water column at Block Island while endrin aldehyde (79 ng/L), γ-HCH (97 ng/L), and δ-HCH (16 ng/L) were found in one depth at high concentration. However, at Conimicut Point γ-HCH (150 and 94 ng/L) and δ-HCH (17 ng/L) were the dominant OCPs (see SI Table 9 for a complete list of concentrations).

OCP GRADIENTS ACROSS THE ESTUARY AND SOURCES OF OCPs

OCPs were mostly near or at equilibrium in the water at both Conimicut Point and Block Island. Please see the SI Figure 7 for the full gradients at both locations. Figure 4 shows the gradient through the water column between the northern part of the Narragansett Bay estuary near Providence and the open mouth of the Bay by dividing the concentration of a compound at Conimicut Point by the concentration at Block Island. α-HCH, heptachlor epoxide, p,p'-DDE, and methoychlor were at or near equilibrium both throughout the water column and throughout Narragansett Bay (Figures 4 and 5). No significant gradients exist within the water column, or even from porewater to overlying water column for OCPs. However, Narragansett Bay was a fresh source of HCB, heptachlor, aldrin, p,p'-DDD, o,p'-DDT, p,p'-DDT, and endrin ketone to Rhode Island Sound (Figure 5). β-HCH, endosulfan 1, and endrin aldehyde were no longer present in the urban estuary of Narragansett Bay, but remained detectable in Rhode Island Sound.

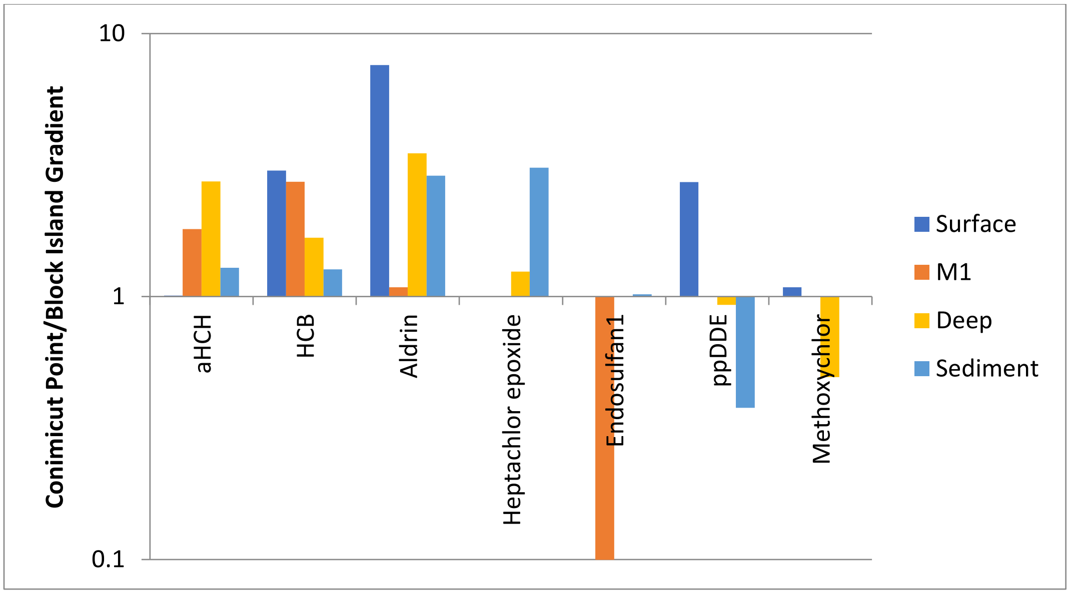


Figure 4. OCP Gradients between Conimicut Point and Block Island.

Average concentrations throughout the water column were the same order of magnitude for all OCPs in this study except endrin aldehyde, which was only found at Block Island (See SI Table 9). Figure 5 shows a cross section of α-HCH concentrations throughout the water column in Narragansett Bay, showing slightly higher concentrations in Conimicut Point than Block Island and in the sediment than the middle of the water column (Schlitzer, 2021). As with the PAHs, ODV was used to visualize concentrations throughout Narragansett Bay, not replace sampling methods to determine concentrations in situ.

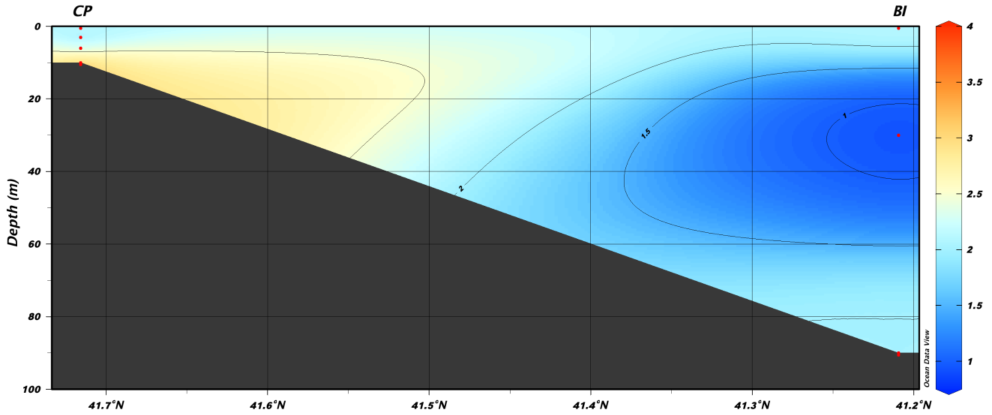


Figure 5. Cross Section of α-HCH Water Column Concentrations (ng/L) (Ocean Data View Software Imaging (Schlitzer, 2021)**).**

Endrin ketone and γ-HCH were introduced to the waters of Narragansett Bay from anthropogenic activities as evidenced by their higher concentrations in the surface water at Conimicut Point. Endrin aldehyde was present in the surface and sediment porewater at Block Island and not at all at Conimicut Point, indicating that the compound has been removed (flushed out) from the estuary waters. α-HCH, heptachlor, and endrin ketone were present at higher concentrations in the surface water of Conimicut Point than the surface water of Block Island. These compounds were still introduced to the estuary in the upper Narragansett Bay near the city center of Providence. Low concentrations of p,p'-DDT, o,p'-DDD, and p,p'-DDE were present throughout the water column at Conimicut Point and in the deep and sediment porewater at Block Island, which is expected since DDT is no longer used in the United States.

Conclusions

This study suggests that the atmosphere remained a source of PAHs to the water column across Narragansett Bay. Based on PAH ratios, the PAHs were primarily derived from liquid fossil fuel and its combustion (i.e., vehicle emissions), while the GSO Dock atmosphere sample indicates a separate source than the other locations. The porewater was acting as a (secondary) source of PAHs to the overlying water column at Conimicut Point, Block Island, and Quonset Point. The water column was well mixed at most locations based on the fact that individual PAH compounds and ΣPAH molecular weight groups were roughly equivalent from the surface to the deep water.

OCP data supported a well-mixed water column as well. Overall the data indicate that the lower Narragansett Bay water column PAHs originated from sources in the atmosphere of the upper bay but were diluted away from the population center. OCP data supported the population center as the source of anthropogenic compounds to the open ocean. Legacy OCPs were equally distributed through the water column and from the pollution source out to the open ocean. Compounds such as DDT were still found in the water column near Providence and sediment porewater as far away from Providence as Block Island. Newer OCPs such as endrin ketone and γ-HCH continue being introduced to Narragansett Bay and the Atlantic Ocean from the urban/industrial center of Providence.

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References

Bertilsson, S., Widenfalk, A., 2002. Photochemical degradation of PAHs in freshwaters and their impact on bacterial growth – influence of water chemistry. Hydrobiologia 469, 23–32. https://doi.org/10.1023/A:1015579628189

Booij, K., R. Hoedemaker, J., F. Bakker, J., 2003. Dissolved PCBs, PAHs, and HCB in Pore Waters and Overlying Waters of Contaminated Harbor Sediments. Environmental Science & Technology 37, 4213–4220. https://doi.org/10.1021/es034147c

Booij, K., Smedes, F., Van Weerlee, E.M., 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. Chemosphere 46, 1157–1161. https://doi.org/10.1016/S0045-6535(01)00200-4

Burgess, R.M., Lohmann, R., Schubauer-Berigan, J.P., Reitsma, P., Perron, M.M., Lefkovitz, L., Cantwell, M.G., 2015. Application of passive sampling for measuring dissolved concentrations of organic contaminants in the water column at three marine superfund sites. Environ Toxicol Chem 34, 1720–1733. https://doi.org/10.1002/etc.2995

Cornelissen, G., Pettersen, A., Broman, D., Mayer, P., Breedveld, G.D., 2008. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. Environ Toxicol Chem 27, 499–508. https://doi.org/https://doi.org/10.1897/07-253.1

Elzerman, A.W., Coates, J.T., 2009. Hydrophobic Organic Compounds on Sediments: Equilibria and Kinetics of Sorption, Advances in Chemistry. https://doi.org/10.1021/ba-1987-0216.ch010

Hale, S.E., Martin, T.J., Goss, K.U., Arp, H.P.H., Werner, D., 2010. Partitioning of organochlorine pesticides from water to polyethylene passive samplers. Environmental Pollution 158, 2511–2517. https://doi.org/10.1016/j.envpol.2010.03.010

Hartmann, P.C., Quinn, J.G., Cairns, R.W., King, J.W., 2005. Depositional history of organic contaminants in Narragansett Bay, Rhode Island, USA. Mar Pollut Bull 50, 388–395. https://doi.org/https://doi.org/10.1016/j.marpolbul.2004.11.020

Hartmann, P.C., Quinn, J.G., Cairns, R.W., King, J.W., 2004. The distribution and sources of polycyclic aromatic hydrocarbons in Narragansett Bay surface sediments. Mar Pollut Bull 48, 351–358. https://doi.org/https://doi.org/10.1016/j.marpolbul.2003.08.014

Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., Echols, K.R., 1999. Determination of Uptake Kinetics (Sampling Rates) by Lipid-Containing Semipermeable Membrane Devices (SPMDs) for Polycyclic Aromatic Hydrocarbons (PAHs) in Water. Environ Sci Technol 33, 3918–3923. https://doi.org/10.1021/es990440u

Khairy, M., Muir, D., Teixeira, C., Lohmann, R., 2014. Spatial Trends, Sources, and Air–Water Exchange of Organochlorine Pesticides in the Great Lakes Basin Using Low Density Polyethylene Passive Samplers. Environmental Science & Technology 48, 9315–9324. https://doi.org/10.1021/es501686a

Khairy, M.A., Lohmann, R., 2012. Field Validation of Polyethylene Passive Air Samplers for Parent and Alkylated PAHs in Alexandria, Egypt. Environ Sci Technol 46, 3990–3998. https://doi.org/10.1021/es300012u

Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. Atmos Environ 29, 533–542. https://doi.org/10.1016/1352-2310(94)00275-P

Lake, J.L., Norwood, C., Dimock, C., Robert, B., 1979. Origins of polycyclic aromatic hydrocarbons in estuarine sediments. Geochim Cosmochim Acta 43, 1847–1854. https://doi.org/10.1016/0016-7037(79)90033-4

Latimer, J.S., Hoffman, E.J., Hoffman, G., Fasching, J.L., Quinn, J.G., 1990. Sources of petroleum hydrocarbons in urban runoff. Water Air Soil Pollut 52, 1–21. https://doi.org/10.1007/BF00283111

Latimer, J.S., Quinn, J.G., 1996. Historical Trends and Current Inputs of Hydrophobic Organic Compounds in an Urban Estuary: The Sedimentary Record. Environ Sci Technol 30, 623–633. https://doi.org/10.1021/es950367h

Latimer, J.S., Zheng, J., 2003. The Sources, Transport, and Fate of PAHs in the Marine Environment. PAHs: An Ecotoxicological Perspective, Wiley Online Books. https://doi.org/https://doi.org/10.1002/0470867132.ch2

Lima, A.L.C., Eglinton, T.I., Reddy, C.M., 2002. High-Resolution Record of Pyrogenic Polycyclic Aromatic Hydrocarbon Deposition during the 20th Century. Environmental Science & Technology 37, 53–61. https://doi.org/10.1021/es025895p

Lohmann, R., 2011. Critical Review of Low-Density Polyethylene's Partitioning and Diffusion Coefficients for Trace Organic Contaminants and Implications for Its Use As a Passive Sampler. Environmental Science & Technology 46, 606–618. https://doi.org/10.1021/es202702y

Lohmann, R., Booij, K., Smedes, F., Vrana, B., 2012. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. Environmental Science and Pollution Research 19, 1885–1895. https://doi.org/10.1007/s11356-012-0748-9

Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, V., Luey, P.J., 2011. Determining Air–Water Exchange, Spatial and Temporal Trends of Freely Dissolved PAHs in an Urban Estuary Using Passive Polyethylene Samplers. Environmental Science & Technology 45, 2655–2662. https://doi.org/10.1021/es1025883

Lohmann, R., K. MacFarlane, J., M. Gschwend, P., 2004. Importance of Black Carbon to Sorption of Native PAHs, PCBs, and PCDDs in Boston and New York Harbor Sediments. Environmental Science & Technology 39, 141–148. https://doi.org/10.1021/es049424+

Menzie, C.A., Hoeppner, S.S., Cura, J.J., Freshman, J.S., LaFrey, E.N., 2002. Urban and suburban storm water runoff as a source of polycyclic aromatic hydrocarbons (PAHs) to Massachusetts estuarine and coastal environments. Estuaries 25, 165–176. https://doi.org/10.1007/BF02691305

Montuori, P., Aurino, S., Garzonio, F., Sarnacchiaro, P., Nardone, A., Triassi, M., 2016. Distribution, sources and ecological risk assessment of polycyclic aromatic hydrocarbons in water and sediments from Tiber River and estuary, Italy. Science of the Total Environment 566–567, 1254–1267. https://doi.org/10.1016/j.scitotenv.2016.05.183

Perron, M.M., Burgess, R.M., Suuberg, E.M., Cantwell, M.G., Pennell, K.G., 2013. Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. Environ Toxicol Chem 32. https://doi.org/10.1002/etc.2321

Pruell, R.J., Lake, J.L., Davis, W.R., Quinn, J.G., 1986. Uptake and depuration of organic contaminants by blue mussels (Mytilus edulis) exposed to environmentally contaminated sediment. Mar Biol 91, 497–507. https://doi.org/10.1007/BF00392601

Schlitzer, R., 2021. Ocean Data View.

Shoeib, M., Harner, T., 2002. Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. Environ Toxicol Chem 21, 984–990. https://doi.org/10.1897/1551-5028(2002)021<0984:UMOAPC>2.0.CO;2

Stegeman, J.J., Lech, J.J., 1991. Cytochrome P-450 monooxygenase systems in aquatic species: carcinogen metabolism and biomarkers for carcinogen and pollutant exposure. Environ Health Perspect 90, 101–109. https://doi.org/10.1289/ehp.90-1519513

Tomaszewski, J.E., Luthy, R.G., 2008. Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment. Environ Sci Technol 42, 6086–6091. https://doi.org/10.1021/es800582a

World Health Organization, 2010. IARC monographs on the evaluation of carcinogenic risks to humans. IARC Monogr Eval Carcinog Risks Hum 93, 9–38. https://doi.org/10.1136/jcp.48.7.691-a

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33, 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5

Zhang, L., Dickhut, R., DeMaster, D., Pohl, K., Lohmann, R., 2013. Organochlorine Pollutants in Western Antarctic Peninsula Sediments and Benthic Deposit Feeders. Environmental Science & Technology 47, 5643–5651. https://doi.org/10.1021/es303553h

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. https://doi.org/10.1016/j.envpol.2018.02.057