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Wenlu Zhao
University of Rhode Island

Minggang Cai

David Adelman
University of Rhode Island

Mohammed Khairy
University of Rhode Island

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Legacy halogenated organic contaminants in urban-influenced waters using passive polyethylene samplers: Emerging evidence of anthropogenic land-use-based sources and ecological risks

Wenlu Zhao [a,b,c,d], Minggang Cai [d,e], David Adelman [c], Mohammed Khairy [c,g], Yan Lin [f], Zhiheng Li [a], Huijun Liu [a], Rainer Lohmann [c,*]

[a] School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310018, PR China
[b] Key Laboratory of Marine Ecosystem Dynamics, Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou, 310012, 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] State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, PR China
[f] School of Environmental Science and Engineering, Xiamen University of Technology, Xiamen 361000, China
[g] Department of Environmental Sciences, Faculty of Science, Alexandria University, 21511 Moharam Bek, Alexandria, Egypt

* Corresponding Author:

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

Abstract

Legacy halogenated organic pollutants, including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), remain ubiquitous in the environment and continue to pose potential (eco-)toxicological threats because of their ongoing releases from land-based sources. This study investigated the spatial trends of freely dissolved PCBs and OCPs by polyethylene passive samplers, and provided evidence of their land-use-based sources and ecological risk in an urbanized estuary area of Narragansett Bay. Dissolved Σ_{29}PCB concentrations ranged from 0.01 to 1.37 ng L^{-1}, and exhibited higher concentrations in the upper, more urban/built-up watershed, and in north coastal areas. Major inputs of urban stormwater or treated wastewater that might carry past releases of Aroclors, pigment manufacturing byproducts, and volatilization-associated PCBs from ageing buildings from the Narragansett watershed to the bay. The dioxins' toxicity equivalent values of Σ_5PCBs were 8.6E-03 pg L^{-1} in water. Dissolved OCP concentrations had similar spatial trends with PCBs and were dominated by DDTs (average 230 pg L^{-1}), followed by chlordanes (average 230 pg L^{-1}), and HCB (average 22 pg L^{-1}). Secondary sources of past usage and historic contamination were expected to re-enter the surface water via atmospheric transport and deposition. The risk quotients of DDE, DDD, DDT and α-Endosulfane showed medium to high ecological risks in north area, while chlordane, HCBz, oxychlordane, and heptachlor epoxide showed low to negligible risks in all zones. This study presented new insights into the presence, sources and transport of legacy halogenated organic contaminants in an urban estuary's watershed by combining passive samplers and

46 geographic information system (GIS) technology. The approach is promising and could
47 be extended to get better understand of terrestrial pollutant mobilization into estuaries
48 affected by anthropogenic activities.
49
50 **Capsule:** Passive sampler deployments revealed the continuous release of dissolved
51 PCBs and OCPs from land-based sources of legacy contaminants, related to the land
52 use pattern in the watershed, into Narragansett Bay.
53
54 **Keywords**: Organochlorine pesticides (OCPs); polychlorinated biphenyls (PCBs);
55 polyethylene passive sampler; urbanized watershed; land-use-based source.
56

Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are two classes of halogenated persistent organic pollutants (POPs) characterized by high lipophilicity, bioaccumulation, toxicity, and resistance to environmental degradation processes (Stringer & Johnston, 2001; Venier et al., 2016). They have been widely used in industrial, agricultural, commercial products from 1920s-1970s in the U.S. and been phased out under the Stockholm Convention (Choi et al., 2010). Despite the imposed ban, OCPs and PCBs are still residual and ubiquitous in the environment because of the ongoing land-based sources. PCBs might be released from improper disposal and leaks from hazardous waste (e.g. old PCB containing equipment, landfills) sites, as byproducts formed during waste incineration, in wastewater and from pigment manufacture in urban areas (Rodenburg et al., 2010). Since 2000s, non-Aroclor congeners, such as PCB-11 and PCB-209 were detected in a variety of environmental compartments, linked to azo pigments, (Hu et al., 2008; Basu et al., 2009; Anezaki et al., 2015; Jahnke & Hornbuckle, 2019). Sharing similar timeline as PCBs, OCPs have been widely used in agriculture worldwide for several decades (Barbiero et al., 2018). Their secondary sources resulting from large burdens stored in contaminated soils and lateral remobilization associated with non-point sources across the built urban environment have become increasingly influential. Therefore, PCBs and OCPs are continually posing potential (eco-)toxicological threats and drawing extensive attention from scientists and the public as legacy POPs (Holma-Suutari et al., 2016; Hu et al., 2020).

Narragansett Bay (NB) is located on the Atlantic coast of Rhode Island, USA, which is an example of urbanized estuary area. PCBs and OCPs represent legacy contamination in NB, with PCBs remaining an important contaminant class in the aquatic environment (Häder et al., 2020). Previous studies showed that a history of industrial activities, such as textiles, local jewelry and metal working in the urban upper reaches of the bay, had contributed large quantities of PCBs to the bay's sediments (Desbonnet & Lee, 1991; Latimer & Quinn, 1996). PCBs in migratory fishes from NB had been found to consistently exceed the safe-eating guidelines by the U.S. EPA in this century, which indicated the elevated local inputs of PCBs (Morgan & Lohmann, 2010). DDT and Chlordane were likewise extensively used in homes and agriculture, possibly reaching the bay through run-off (Hartmann et al., 2005). Furthermore, anthropogenic activities with land use change were able to affect the river input, wastewater discharge, and air-water exchange of contaminants, creating a dynamic situation in which changes the concentrations in the watershed-estuary-bay area could alter the direction of the resulting flux (Zhao et al., 2018). Populations moving toward the more south rural areas along the shoreline of the bay had potential negative impacts on the mid and lower bay areas (Hartmann et al., 2005). Thus, understanding how freely dissolved PCBs and OCPs are distributed and affected by population pressures and land use changes spatially are important for assessing the risk to organisms and human that depend on Narragansett Bay.

The data discussed here were acquired by low density polyethylene sheets (LDPE), which had been successfully used as passive samplers and considered as an effective,

simplest, and cheapest tool for monitoring gaseous and truly dissolved POPs. LDPEs were deployed in the surface water during June-July in 2014 to (i) investigate the spatial trends of the freely dissolved PCBs and OCPs in Narragansett watershed-coast area, (ii) identify their possible sources, (iii) examine the influence of the population and land use patterns on their spatial variations, and (iv) lastly deriving and assessing the PCB and OCP toxicity.

Materials and Methods

Detailed materials and methods pertaining to the passive sampling and analytical methods employed in this study were described in Zhao et al. (2018). Information specific to the PCB and OCP analytes are specified below and in the Supporting Information (SI).

Preparation and deployment of LDPE passive samplers

The 50-μm thick LDPE samplers were cut and cleaned for yielding passive samplers. 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, 2010; 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,

123 map of monitoring sites, and other related monitoring summary were provided in the
124 supporting information (Figure S1 & Table S1).
125
126 *Analytical Methodology*
127 LDPE samplers were wiped clean with Kimwipes and extracted once in hexane
128 for 24 h after addition of 20 ng of labeled PCBs ($^{13}C_{12}$-PCB8, $^{13}C_{12}$-PCB28, $^{13}C_{12}$-
129 PCB52, $^{13}C_{12}$-PCB118, $^{13}C_{12}$-PCB138, $^{13}C_{12}$-PCB180, $^{13}C_{12}$-PCB129) and OCPs ($^{13}C_{6}$-
130 HCBz, $^{13}C_{12}$-DDT) surrogates. Extracted LDPE samplers were air dried and weighed.
131 Extracts were concentrated to 100 μL, and spiked with 35 ng of 2,4,6-tribromobiphenyl
132 (injection standard) directly before instrumental analysis.
133 PCBs and OCPs were analyzed on a Waters Quattro micro GS Micromass MS-MS
134 and quantified using Waters QuanLynx V4.1 software as detailed elsewhere (Sacks and
135 Lohmann, 2012). Further details are given in the Supporting Information. Samples were
136 analyzed for 29 PCBs and 22 OCPs (Table S2).
137
138 *Quality assurance/Quality control*
139 Method blanks were prepared with each batch of samples to monitor for laboratory
140 contamination. Samples were blank-corrected by subtracting the average of the method
141 and field blank concentrations. Target analytes were quantified by internal calibration
142 relative to surrogates. Average surrogate recoveries for PCBs and OCPs ranged from
143 57%-107% and 57%-104%, respectively (Tables S3). Method detection limits (MDLs)
144 were calculated as 3 times the standard deviation of the average field blank

concentration. For compounds that measured above the MDL in ⩾ 80% of samples, concentrations < MDL were reported as half of the MDL as recommended by Antweiler & Taylor (2008), to minimize bias in the statistical analysis. Compounds that were measured above the MDL in < 20% of samples were omitted from the discussion.

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 encounters 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). The average aqueous sampling rate of PCBs and OCPs was 16 ± 7 L/day.

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.

- Source identification

The diagnostic ratios of TC/CC, TN/TC, DDT/(DDD + DDE), DDD/DDE, and Principle components analysis (PCA) were performed using the dissolved OCP concentrations in the surface water. PCA computation was done using the software SPSS 22.0. As a receptor model, positive matrix factorization (PMF) was able to weight each data point individually and provide better quantification of impact of its improved resolved sources (Paatero and Tapper, 1994; Du et al., 2008; Rodenburg et al., 2020). Combing with PCA, PMF model was applied to estimate composition of possible sources of PCBs and the United States Environmental Protection Agency (USEPA) PMF 2.0 software was used. For more details, see the Supporting Information.

- Land-use regression

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 Figure S1). Land-use regressions (LUR) models are GIS-based spatial models that relate locations specific data on pollutant concentrations to location-specific source and environment data using regression (Briggs et al., 1997).

The following land-use classes were considered: residential areas, commercial and industrial areas, facilities and institutes, and recreational areas occupied by human

189 activities (Figure S2). Other variables included population density (Pop/km^2), buildings,
190 roads, sewer areas, and impervious surface areas. All geospatial data were retrieved
191 from the RIGIS web site (http://www.edc.uri.edu/rigis). The analyses were conducted
192 using ArcGIS version 10.2 software using coverage and grid data formats whenever
193 possible. Statistical analyses were performed using IBM SPSS Statistics 22. Linear
194 regression was chosen as an appropriate model based on the correlation between
195 dissolved concentrations and major descriptor variables.

196 - Toxicity assessment

197 For PCBs, the toxicity equivalent (TEQ), established by the World Health
198 Organization (WHO 2005), was calculated by summing the multiplication of dioxin-
199 like PCB congener concentrations with the corresponding Toxic Equivalency Factors
200 (TEFs) (Montuori et al., 2020). For OCPs, an ecological risk assessment for water
201 organisms was conducted using the risk quotient (RQ) model. RQ is established based
202 on the equation,

203 $$RQ = \frac{MEC}{PNEC}$$

204

205 $$PNEC = \frac{NOEC\ or\ LC50\ or\ EC50}{Assessment\ Factor}$$

206

207 Where, MEC is the measured environmental concentration and PNEC is the
208 predicted no effect concentration. PNEC is derived from the lowest toxicity value (i.e.,
209 no-observed effect concentration (NOEC) value) observed for the most sensitive
210 species. When NOEC values were not available, we used the median lethal
211 concentration (LC_{50}) or the median effective concentration (EC_{50}) after correction by

an assessment factor intended to extrapolate from acute to chronic toxicity and for removing the uncertainty arising from the extrapolation from intra- and inter-species variability in sensitivity (Table S13). The levels of risk were divided into four categories according to the value of RQ: insignificant risk (RQ < 0.01), low risk (0.01 < RQ < 0.1), medium risk (0.1 < RQ < 1), and high risk (RQ > 1) (Sah et al., 2020). For more details, see the Supporting Information.

Results and Discussion

Freely-dissolved PCBs in surface water

- Overview of concentration and distribution

PCBs were detected at every site in the summer (Figure 1). Concentrations of freely-dissolved $\sum_{29}$PCB in the surface water ranged from 0.01 to 1.37 ng L^{-1} with a mean value of 0.20 ng L^{-1} (Figure 1, Table S5). Samples were dominated by hexa-, penta-, di- and tetra-chlorinated biphenyls comprising 81.0-99.6% of the total PCB concentrations, whereas nona- and deca- chlorinated congeners were only detected in a few of the samples (Figure S3). The dominant PCBs were PCB11 (0.5-55%), PCB101 (5.5-24%), PCB153 (4.4-22%), and PCB138 (3.8-21%).

PCB concentrations were greater in the upper, more urban/built-up watershed, and in north coastal areas. The greatest freely-dissolved $\sum_{29}$PCB concentration was recorded at Sand Hill Brook (S brook), followed by Pawtuxet River (Pawtuxet R) (0.87 ng L^{-1}), Woonasquatucket River near Donigian Park (WR_DP) (0.86 ng L^{-1}), and GB13 (0.42 ng L^{-1}). Sites around Bristol Harbor also had relatively high concentrations (BH8-

234 0.26 ng L^{-1}, BH1-0.20 ng L^{-1}, BH12-0.25 ng L^{-1}). The south rural sites exhibited the
235 lowest dissolved concentrations (0.03 ng L^{-1} on average).

236 PCB concentrations derived here were more than 100-1000 times higher than
237 those obtained by passive sampling in the Great Lakes (USA/Canada) (Liu et al., 2015;
238 Ruge et al., 2018). The concentrations in surface water in the northern basin of this
239 study area were about 10 times higher than those reported in the seawater of
240 Narragansett Bay (Morgan, 2008), indicating that runoff acted as sources of PCBs from
241 watershed to the Narragansett Bay (Table S7). However, our freely dissolved PCB
242 values were much lower than those found in River Ravi, Pakistan (Baqar et al., 2017),
243 and nine rivers in South China (Yang et al., 2015), though different sampling
244 approaches were used.

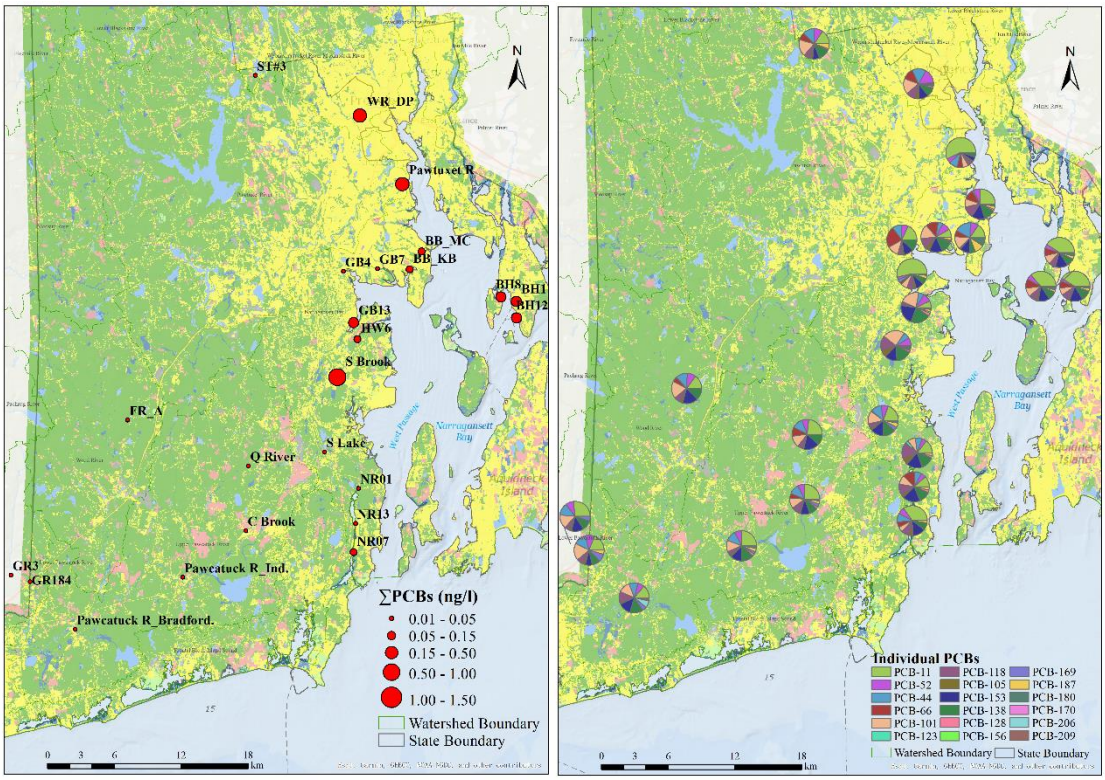


Figure 1 Dissolved $\sum_{29}$PCB and individual PCB profiles in the Narragansett watershed-coastal area. PCBs in the surface water presented higher concentrations in the north urban watershed-coastal areas and were dominated by PCB11, PCB101, PCB153, and PCB138. For land use pattern, please refer to Figure S1.

- Source identification of dissolved PCBs

Principal component analysis (PCA) extracted two components that captured 60% (PC-1) and 31% (PC-2) of total variability (Figure S4). The dominant homologs in PC-1 were tetra-, penta-, hexa-, and hepta-PCBs, which indicated that commercial PCB mixtures with low-chlorinated congeners, byproducts formed during thermal processes, and possibly also long-range atmospheric transport might be the major sources of PCBs to the surface waters. The PC-2 was strongly influenced by the di-PCB (PCB11), nona-

PCB (PCB206), and deca-PCB (PCB-209)，indicating potential sources of pigments. PCB-11, which serves as an indicator of azo pigments, was detected at every site and accounted for 1-55% of the total amount of PCBs. The contribution of PCB-206 and PCB-209, which serves as an indicator of phthalocyanine pigments derived by perchlorination in chlorobenzene (Hu & Hornbuckle, 2010; Jahnke & Hornbuckle, 2019), were mainly detected at the sites near Pawtuxet River, Pawcatuck River and Bristol Harbor, accounting for 0.4% and 0.2% of the total amount of PCBs, respectively. Previous studies indicated that PCB206 and PCB 209 might have been locally produced by the past release of Aroclor 1268, while residues in the contaminated soils moved down river to the surface water over time (Cantwell et al., 2006; Morgan & Lohmann, 2010).

The contribution levels of different pollution sources were further studied by applying a PMF model. The three factors resolved are shown in Figure 2 along with their percent contribution to the total PCBs. Each profile of the three factors was compared with several PCB profiles of specific sources reported in previous work (Table S14). The cosine theta similarity metric (cos θ) was used for the congener pattern matching. Factor 1 explained 44% of the total PCBs and showed high loadings on PCB 11, 44, 153, and 138. PCB 11 was known to be a non-Aroclor congener and was the dominant congener in this factor, constituting 23% of ΣPCBs. It was produced as a byproduct from the manufacture of the yellow pigment widely used in ink, paint, and textile printing (Rodenburg et al. 2010; Khairy et al. 2015), and was also used as a tracer to identify factors associated with stormwater and wastewater (Litten et al., 2002; Du

et al., 2008). Moreover, this factor contains the highest proportion of PCB 44 at 15 % of ΣPCBs. PCB 44 has been noted as an intermediate product of PCB dechlorination occurring in sewers (Magar et al., 2005; Rodenburg et al., 2010). Accordingly, we speculated this factor might be associated with wastewater/stormwater inputs.

Factor 2 explained 32% of the total variability in the data and was heavily loaded on PCB 101, 11, 52, 138, and 187. This pattern was close to the profile of PCBs in volatilized Aroclor 1260 (Cos θ = 0.90) and other emission sources from sealant (Cos θ = 0.79), municipal solid waste incineration facility (Cos θ = 0.76), and cement plant (Cos θ = 0.72) with exclusion of PCB11. This factor was most prevalent near Bristol Harbor (BH1-81% and BH12-99%) and GB13 (83%), and dominant at sites of ST#3, Pawtuxet R, GB13, S Lake, and NR07, where it constitutes 23–41% of ΣPCBs. This likely represents sources of volatilized PCBs from the Harbor area and deposited throughout the watershed-estuary-bay area.

Factor 3 resembled Aroclor 1260 (cos θ = 0.86). It was present in the urban areas including sites of S Brook (79% of ΣPCBs), WR_DP (58%), Pawtuxet R (35%), and BB_MC (45%), which might represent a few localized contaminated sites where Aroclor 1260 was used. Aroclor 1260 represented about 11% of US production of PCBs and was distinct from the other Aroclors. Its use was limited to transformers, hydraulic fluids, as a plasticizer in synthetic resins, and dedusting agents (Rodenburg et al. 2010). Consequently, this factor was helpful to pinpoint the locations of sites with Aroclor 1260 contamination.

All three factors contained dechlorination (PCB 44) and wastewater input (PCB

311 11) signals. Thus, there are major inputs of urban stormwater or treated wastewater that
312 might carry pigment and volatilization-associated PCBs from Narragansett watershed
313 to the bay. Additionally, it seems to be shifting from the legacy Aroclor-like signature
314 to the current use (non-Aroclor) sources. There might also be some uncertainties
315 associated with source attribution being affected by physio-chemical processes such as
316 partitioning or degradation. The high similarity of factor 2 and 3 with Aroclor 1260
317 could possibly indicate the lack of weathering. However, the lack of gaseous and
318 particle-bound PCB datasets and measuring a limited number of PCB congeners might
319 overestimate contributions of the wastewater/stormwater source and the non-Aroclor
320 congeners and underestimate contributions from Aroclor congeners.

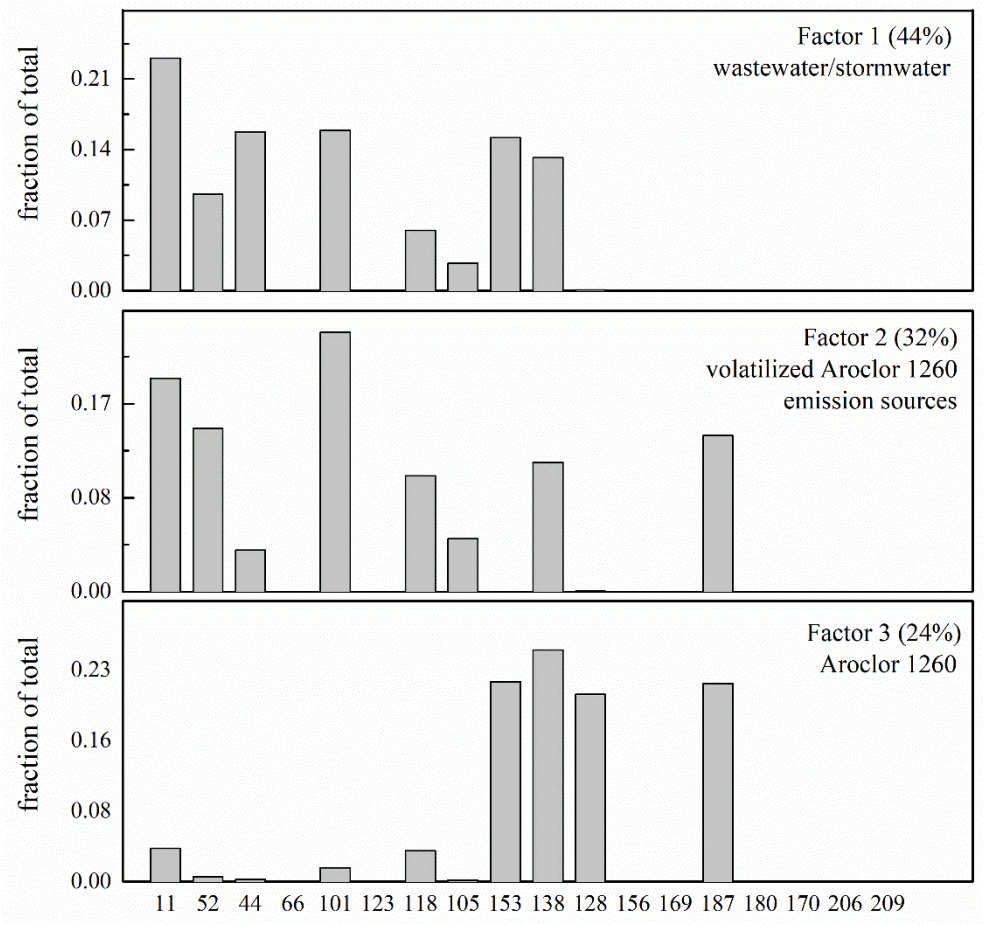


Figure 2 Three resolved factors by positive matrix factorization (PMF) model. Fraction of total PCBs for each factor is shown on the y axis, and PCB congener number is displayed on the x axis. Factor 1 represented wastewater/stormwater inputs of PCBs, Factor 2 represented the sources of volatilized Aroclor 1260 and other emission sources from sealant, municipal solid waste incineration facility, and cement plant after excluding PCB11, Factor 3 resembled Aroclor 1260.

Freely-dissolved OCPs in surface water

- Concentration and distribution

12 OCPs were regularly detected above the detection limit at all sites in the

summer: HCB，oxychlordane，heptachlor epoxide，*o,p'*-DDE，*p,p'*-DDE，trans-chlordane，cis-chlordane，endosulfane I，trans-Nonachlor，*o,p'*-DDD，*p,p'*-DDD+*o,p'*-DDT，*p,p'*-DDT (Figure 3, Table S6). Dissolved OCP concentrations were dominated by DDTs (average 230 pg L^{-1}), followed by chlordanes (average 230 pg L^{-1}), and HCB (average 22 pg L^{-1}) (Figure S5), which were detected at all sites and nearly 2-10 times higher than those obtained by passive sampling in the Great Lakes (Khairy et al., 2014; Ruge et al., 2018) (Table S8). OCP concentrations in north urban area were significantly greater than it in most south rural area. Elevated OCP concentrations were observed along the northern coast of Narragansett Bay, such as sites GB7 (chlordane, heptachlor epoxide, α-endosulfane, oxychlordane), Buckeye Brook near Knowles Brook (BB_KB) (DDTs), and Woonasquatucket River near Donigian Park (WR_DP) (HCB). Heptachlor epoxide and α-endosulfane were mainly found in the upper bay, like GB4 and GB7, where heptachlor epoxide was the main contaminant. α-Endosulfan showed an inconsistent trend and was concentrated in northern NB watershed, averaging 38.9 pg L^{-1}, which was comparable with the concentration reported by Venier et al. (2014).

- Potential sources of dissolved OCPs

Technical chlordane (sum of trans-chlordane (TC), cis-chlordane (CC), and trans-nonachlor (TN)) was used as an insecticide, herbicide, and termiticide until the early 1980s, when most of these uses were restricted in the United States and Canada in response to environmental and safety concerns. In our study, the ratios of TC/CC averaged 0.90 suggested that detected chlordane was historical and weathered residues

365 from commercial sources except at sites GB13, S Brook, BH8, S Lake, NR01, GR3,
366 FR_A (Figure S6) (Bidleman et al., 2002; Yu et al., 2014; Sah et al., 2020). These results
367 were similar with the ratios in rural Great Lakes suggesting tributaries and sediments
368 as likely sources of aged chlordane to the water column (Gouin et al., 2007; Ruge et al.,
369 2018). TN/TC ratio ranged from 0.23 to 2.11, aquatic enrichment of TN in the sites near
370 forest and agricultural land confirming the aged chlordane in the study area, which
371 indicated the volatilization sources from soil containing weathered chlordane residues
372 and deposition into the surface water (Khairy et al., 2014).

373 Technical DDTs contained about 75% of the *p,p'*-isomer, but the *o,p'*-isomer was
374 also present in significant amounts (about 15%). Other compounds having four chlorine
375 atoms, DDE and DDD, made up the balance (Venier & Hites, 2014). DDT degrades
376 into DDE and DDD under aerobic and anaerobic conditions, respectively. After the
377 restrictions in 1972, DDT continued to be used as a synthetic intermediate for the
378 production of dicofol, which contained about 11% of *o,p'*-DDT and was heavily used
379 in U.S. (Qiu et al., 2005; Venier & Hites, 2014). For this study, the average composition
380 of DDTs in this profile was *p,p'*-DDE (54.2%) ＞ *p,p'*-DDD + *o,p'*-DDT (26.8%) ＞
381 *o,p'*-DDD (9.7%) ＞ *p,p'*-DDT (6.0%) ＞ *o,p'*-DDE (3.2%), which was different
382 from the composition of technical DDTs or dicofol. The ratios of DDT/ (DDD + DDE)
383 < 1 (except the site GR184) and DDD/DDE <1 (except the site GR184 and GB7)
384 indicated the biodegradation of past usage and historic contamination of DDT occurs
385 predominantly under aerobic conditions (Figure S6) (Bidleman, 1999; Wang et al.,
386 2018).

387 In addition to the former application to as an antifungal agent in agriculture, HCB
388 is also an unintentionally byproduct of chlorinated compounds from industry. The
389 average concentration of HCB (30 pg L^{-1}) in north urban area was double than it in
390 most south rural area (13 pg L^{-1}, see Figure 2), indicating that anthropogenic inputs
391 other than atmospheric deposition were the dominant sources. α-Endosulfan was used
392 on fruits, vegetables, cotton, tobacco, and trees as insecticide and banned in 2010 in the
393 U.S. α-Endosulfan was the only analyte indicating fresh inputs by runoff and
394 atmospheric deposition of technical-grade endosulfan.

395 Principal component analysis (PCA) of dissolved OCPs distinguished two groups
396 accounting for 84% of total variance, while PCA of sampling sites also extracted two
397 components that captured 81% of total variance (Figure 4). The sampling sites involved
398 in PC-1 were in south rural areas (Q river, S lake, C brook, FR_A), the transition area
399 from north to south (GB13, S Brook), and Bristol Harbor, suggesting these areas had
400 similar sources of legacy OCPs. The continued emissions of racemic chlordane from
401 the transition area (Cluster 1) and aged chlordane from the rural areas (Cluster 2), might
402 be primarily responsible for the current levels of chlordanes in the surface water in the
403 Narragansett watershed-estuary-bay area. The metabolites of heptachlor, endosulfan,
404 HCB, and chlordane presented a potential tendency to degrade in the surface water in
405 Bristol Harbor and south rural area (Cluster 2). The north urban areas represented in
406 PC-2 overlapped with DDTs (Cluster 3), indicating that the secondary sources of past
407 usage and historic contamination were expected to re-enter the surface water via runoff,
408 atmospheric transport, and deposition. These results were consistent with the above

ratio diagnostics results.

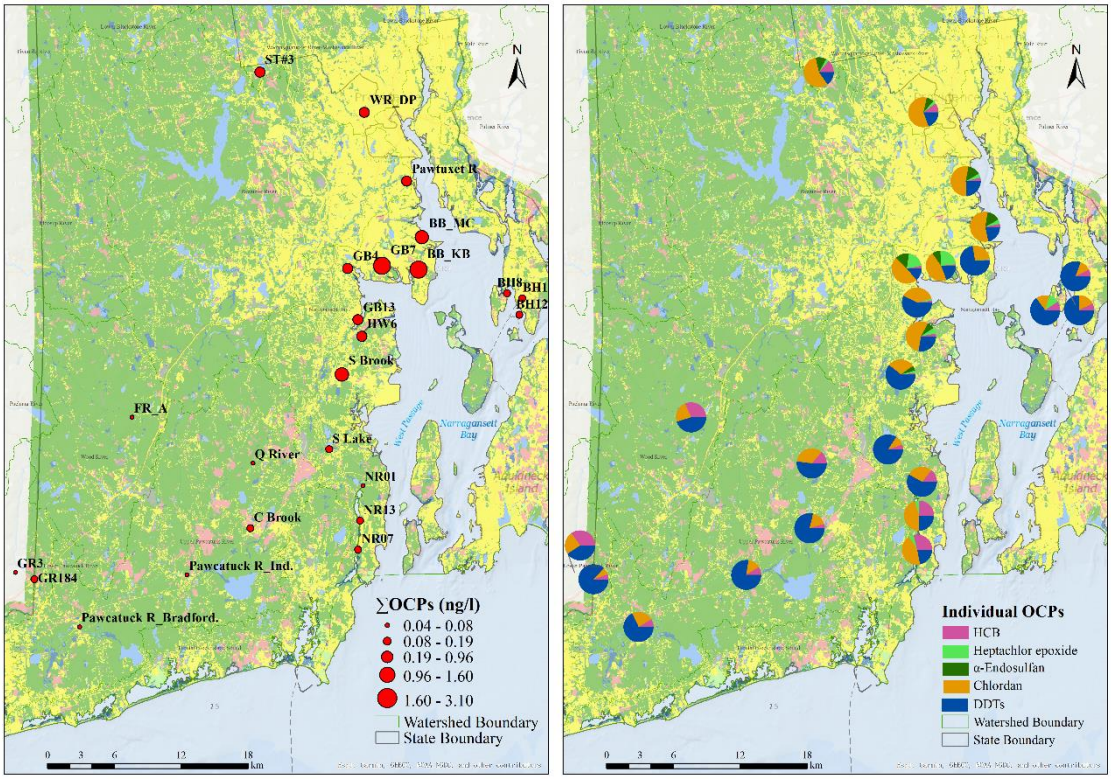


Figure 3 Dissolved $\sum_{22}$OCP and individual OCP in Narragansett watershed-coastal area. Dissolved OCP concentrations in north urban area were significantly greater than it in most south rural area, and were dominated by DDTs, followed by chlordanes, and HCB. For land use pattern, please refer to Figure S1.

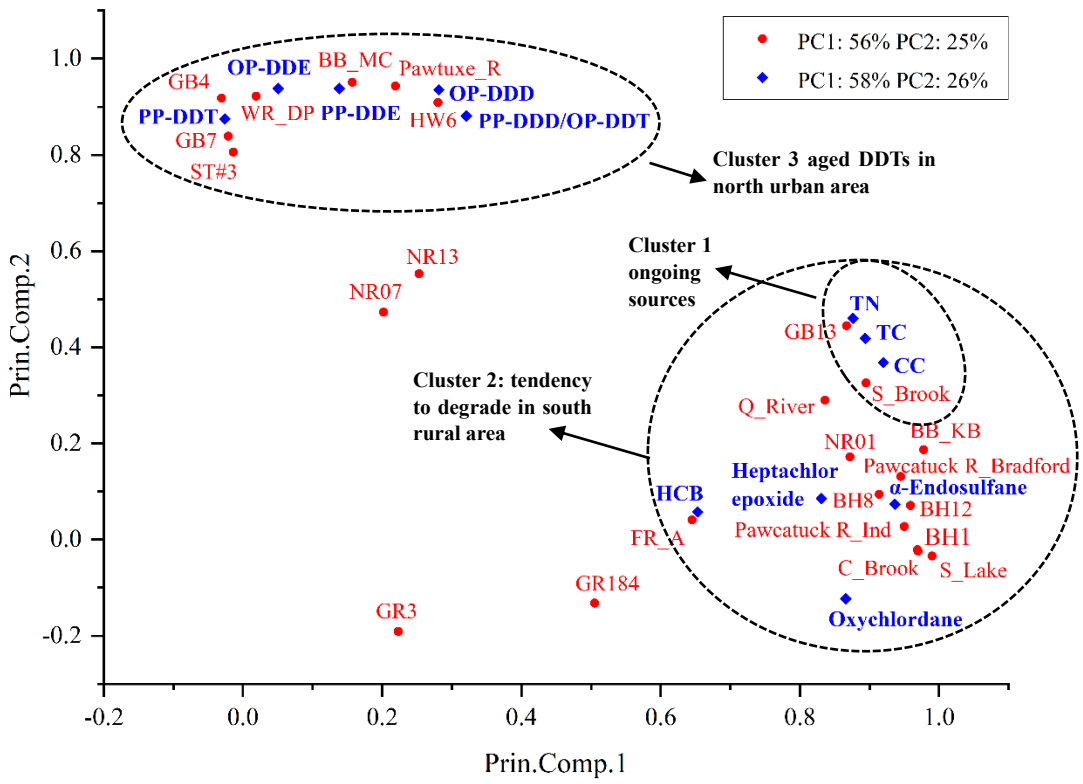


Figure 4 Principal component analysis (PCA) of Dissolved ΣOCPs. Three clusters represented the ongoing emissions and historical residues of legacy OCPs in different sections of Narragansett watershed-estuary-bay area.

Correlations of human activities and freely dissolved concentrations

The effect of the land use patterns on the spatial distribution of dissolved PCBs and OCPs was investigated using a Land-use regression (LUR) (Table S10). Population density, roads, buildings, and residential areas within 2 km radius explained 36-73% of PCB variability (Table 1). Decreasing residential coverage and increasing population density might lead to greater amounts of PCBs' entering the environment, especially for penta-, hexa-, and hepta-CBs. Furthermore, there was a positive correlation existing

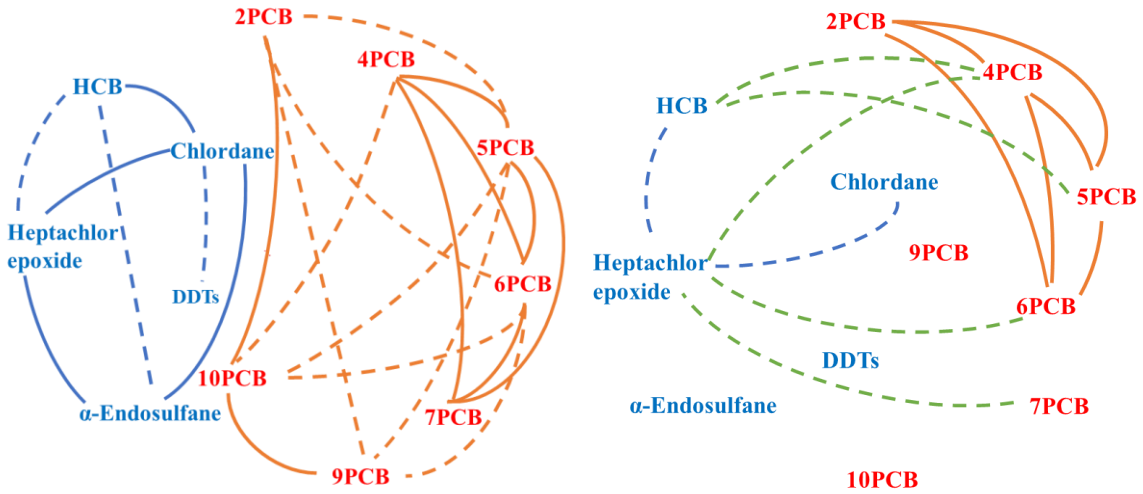
between buildings and tetra-CBs. Hence, we can infer that legacy PCB levels in the surface water might be associated with PCBs used in building and equipment materials like sealants, paints, adhesives, etc. (Kohler et al., 2005; Liu et al., 2016; Marek et al., 2017), which could still release with building aging (Demirtepe et al., 2019).

Correlations between PCB congeners varied between north urban area and south rural area (Figure 5). In the north urban area, correlation between di-PCB (CB-11) and deca-CB(CB-209) was significant and strong ($p < 0.01$), indicating the potential sources of unintentionally produced PCBs coming from inadvertent production during paint, colorant, and pigment manufacturing or other industrial activities (Jahnke & Hornbuckle, 2019; Mao et al., 2021). While correlations among di-CB and penta-PCBs (CB-101, -123, -118, -105), hexa-CBs (CB-128, -138, -156, -153, -169), nona-CB (CB-206) were also significant but relatively weaker ($p < 0.05$), suggesting similar ways of these contaminants entering the surface water, such as stormwater discharging and volatilization, and further supporting the results of PMF model. On the other hand, dissolved concentrations of di-CB and tetra-CBs (CB-52, -44, -66), penta-CBs, and hexa-CBs correlated significantly ($p < 0.01$) in south rural area, possibly related to their vapor pressor and presented similar environmental transport from north to south area.

Urban areas within 2 km radius were major predictors of increased concentrations of chlordanes, DDTs, and heptachlor epoxide in the Narragansett watershed-coast area (Table 1 & S9). The apparent urban signal further indicated volatilization of past OCPs use from urban soil could be emitted to the Narragansett watershed (Sun et al., 2006; Venier & Hites, 2009). Agricultural areas within 5 km radius accounting for ~30-35%

of the total variability in the dissolved concentrations of HCB and α-Endosulfane. The correlation coefficients were negative which suggested the application of endosulfan and HCB might decrease, and the changes of agricultural area surrounding each site could affect its spatial distribution pattern in a certain extent (Khairy et al., 2014).

No correlation was found among OCPs and PCBs, implying the declined impact of past indoor uses of OCPs for indoor insect control in north urban area. However, we found significant correlations among HCB, heptachlor epoxide and PCBs (tetra-, penta-, hexa-, and hepta-CBs) in south rural area, possibly indicating the historical residues of byproducts during the synthesis of chlorinated pesticides, including HCB and PCB mixtures (Figure 5 & Table S11-12).



a) north urban area

b) south rural area

Figure 5 Spearman correlation results between OCPs and PCBs. Solid lines represents $p < 0.01$, dotted lines represents $p < 0.05$. There was declining impact of past pesticide usage in north urban area, while historical residues of byproducts during the synthesis of chlorinated pesticides still existed in south rural area.

Table 1. Correlation Coefficients and Significant Variables for Multiple Linear Regression Analysis

Compound	Variable (squared partial correlation coefficient)						Adjusted	Standard
	ln(A+1)	ln(B+1)	ln(C+1)	ln(D+1)	ln(E+1)	ln(F+1)	R^2	Error
ln(ΣPCB+1)	0.67	/	/	/	/	/	0.42	1.09
ln(2PCB+1)	1.58	-1.14	/	/	/	/	0.36	1.16
ln(4PCB+1)	/	/	-1.79	2.42	/	/	0.73	0.68
ln(5PCB+1)	1.65	/	-1.11	/	/	/	0.49	0.98
ln(6PCB+1)	1.62	/	-1.08	/	/	/	0.49	0.89
ln(7PCB+1)	1.54	/	-0.91	/	/	/	0.55	0.85
ln(HCBz+1)	/	/	/	/	/	-0.62	0.35	0.62
ln(Heptachlor epoxide+1)	/	/	/	/	0.72	/	0.50	1.39
ln(α-Endosulfane+1)	/	/	/	/	/	-0.58	0.30	1.88
ln(Chlordane+1)	/	/	/	/	0.71	/	0.48	1.19
ln(ΣDDTs+1)	/	/	/	/	0.58	/	0.30	0.96

A = population density within 2 km; B = roads within 2 km； C = residential areas within 2 km; D = buildings within 2 km; E = urban areas (including residential, commercial and industrial, recreation areas and facilities & institutes) within 2 km； F = agricultural areas within 5 km.
2PCB: di-CB (CB11); 4PCB: tetra-CBs (CB-52, -44, -66); 5PCB: penta-PCBs (CB-101, -123, -118, -105); 6PCB: hexa-CBs (CB-128, -138, -156, -153, -169); 7PCB: hepta-PCBs (CB-187, -180, -170)
The p values for these multiple regression equations were less or equal to 0.001.

Water quality concerns and potential ecological risk assessment

As a result, freely dissolved PCB concentrations from the current study were much greater than the U.S. EPA National recommended water quality criteria for the protection of human health from the consumption of fish and water (64 pg/L) (USEPA, 2002) and the NYSDEC standards for the consumption of water and fish (1.0 pg/L). The dioxins' toxicity equivalents (TEQs) for DL-PCBs were assessed based on the toxicity equivalence factor (TEF) (Vanden Berg et al., 2006). The WHO-TEQ (2005) values of Σ_5PCBs were 8.6E-03 pg/L in water (Table S4). The lowest WHO-TEQ (2005) values in surface water were estimated for PCB-123, whereas the highest values were estimated for PCB-169.

For OCPs, the total risk quotients (∑RQs) of north urban area were higher

compared with the south rural area (Figure S7). Among all pesticides, DDE showed a RQ > 0.01 at all monitored sites and had medium to high ecological risks near Pawtuxet River (Pawtuxet R), Buckeye Brook (BB_MC, BB_KB), Greenwich Bay (GB7, GB13), and Sand hill Brook (S Brook). Furthermore, DDD, DDT and α-Endosulfane also showed medium to low risks at the majority sites in north area, while chlordane, HCBz, oxychlordane, and heptachlor epoxide showed low to negligible risks in all zones.

Conclusions and Implications

This work represented the extended research of dissolved PCBs and OCPs using passive samplers around the Narragansett Bay watershed, deployed by a long-running volunteer network. It further confirmed that LDPE passive sampling could easily and accurately detect the active portion of trace contaminants (e.g., freely dissolved PCBs and OCPs) to help determine time-integrated exposure in aquatic environments. We tracked the potential stormwater/wastewater inputs of PCBs to the surface water combing the sampling technology and PMF model. There were still several sites contaminated with Aroclor 1260 and ongoing chlordane. Surprisingly, several sites in north area still displayed medium to high toxic effects based on the presence of DDE, DDD, DDT and α-Endosulfane long after their use stopped. The sampling approach should be applied to more worldwide areas and environment reservoirs to build routine monitoring programs.

Combining passive sampling with land-use regressions in Narragansett watershed-bay area enabled the identification the emission sources of legacy PCBs and OCPs from

various human activities. Results presented here suggested that the spatial variability of PCBs and OCPs concentrations and potential land-based sources were related to the land use pattern and population distribution in the urbanized estuary's watershed. The contaminant contents in the urban and built-up regions were higher than those from the other areas, indicating that influences of anthropogenic activities with land use change were the major reasons for this distribution pattern. Land-use regression models could also be used to better understand sources, distributions of pollutants with the aim of reducing emissions, and guide sampling site selection (Melymuk et al., 2013). It is important to pay a continued attention to the potential emissions of legacy contaminants and their relationship with changes in land use and human activities by applying this method in future work.

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573

574 *Appendix A. Supplementary data*

575 Additional details relating to sampling locations, chemical analysis, and dissolved

576 concentrations of PCBs and OCPs are available free of charge via the Internet at ….

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578 **References**

579 Anezaki, K., Nakano, T., Kashiwagi, N., 2016. Estimation of polychlorinated biphenyl
580 sources in industrial port sediments using a bayesian semifactor model considering
581 unidentified sources. Environ. Sci. Technol. 50(2), 765-771.
582 https://doi.org/10.1021/acs.est.5b03501.

583 Antweiler, R.C., Taylor, H.E., 2008. Evaluation of statistical treatments of left-censored
584 environmental data using coincident uncensored data sets: I. Summary statistics.
585 Environ. Sci. Technol. 42(10), 3732-3738. https://doi.org/10.1021/es071301c.

586 Basu, I., Arnold, K.A., Venier, M., Hites, R.A., 2009. Partial pressures of PCB-11 in air
587 from several Great Lakes sites. Environ. Sci. Technol. 43(17), 6488-6492.
588 https://doi.org/10.1021/es900919d.

589 Baqar, M., Sadef, Y., Ahmad, R.S., Mahmood, A., Qadir, A., Aslam, I., Li, J., Zhang,
590 G., 2017. Occurrence, ecological risk assessment, and spatio-temporal variation of
591 polychlorinated biphenyls (PCBs) in water and sediments along River Ravi and its
592 northern tributaries, Pakistan. Environ. Sci. Pollut. Res.e 24(36), 27913-27930.
593 https://doi.org/10.1007/s11356-017-0182-0.

594 Barbiero, R. P., Lesht, B. M., Hinchey, E. K., Nettesheim, T. G., 2018. A brief history
595 of th US EPA Great Lakes National Program Office's water quality survey. J. Great
596 Lakes Res. 44, 539-546. https://doi.org/10.1016/j.jglr.2018.05.011.

597 Bidleman, T.F., Jantunen, L.M.M., Helm, P.A., Brorström-Lundén, E., Juntto, S., 2002.
598 Chlordane enantiomers and temporal trends of chlordane isomers in arctic air.
599 Environ. Sci. Technol. 36(4), 539-544. https://doi.org/10.1021/es011142b.

Briggs, D.J., Collins S., Ellott, P., Fischer, P., Kingham, S., Lebret, E., Pryl, K., Reeuwijk, H.V., Smallbone, K., Veen, A.V. D., 1997. Mapping urban air pollution using gis: a regression-based approach. Int. J. Geogr. Inf. Sci. 11(7), 699-718. https://10.1080/136588197242158

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(8), 1157-1161. https://doi.org/10.1016/S0045-65350(01)00200-4

Booij, K., Smedes, F., 2010. An improved method for estimating in situ sampling rates of nonpolar passive samplers. Environ. Sci. Technol. 44(17), 6789-6794. https://doi.org/10.1021/es101321v

Cantwell, M.G., King, J., Burgess, R.M., 2006. Temporal trends of Aroclor 1268 in the Taunton River estuary: Evidence of early production, use and release to the environment. Mar. Pollut. Bull. 52(9), 1105-1111. https://doi.org/10.1016/j.marpolbul.2006.05.019.

Choi, H.D., Pagano, J.J., Milligan, M.S., Hopke, P.K., Skubis, S., Holsen, T.M, 2010. Polychlorinated biphenyls (PCB) and dichlor odiphenyltrichloroethane (DDE) air concentrations in the Lake Ontario region: Trends and potential sources. Atmos. Environ. 44(26), 3173-3178. https://doi.org/10.1016/j.atmosenv.2010.05.031.

Demirtepe, H., Melymuk, L., Diamond, M. L., Bajard, L., Vojta, Š., Prokeš, R., Sáňka, O., Klánová, J., Murínová, Ľ.P., Richterová, D., Rašplová, V., Trnovec, T., 2019. Linking past uses of legacy SVOCs with today's indoor levels and human exposure. Environ. Int. 127, 653-663. https://doi.org/10.1016/j.envint.2019.04.001.

Desbonnet, A., Lee, V., 1991. Historical trends: water quality and fisheries Narragansett Bay. University of Rhode Island Graduate School of Oceanography, Narragansett, RI, RIU-T-91-001.

Du, S., Belton, T.J., Rodenburg, L.A., 2008. Source apportionment of PCBs in the Tidal Delaware River. Environ. Sci. Technol. 42(11), 4044-4051. https://doi.org/10.1021/es400375e.

629 Gouin, T., Jantunen, L., Harner, T., Blanchard, P., Bidleman, T., 2007. Spatial and
630 temporal trends of chiral organochlorine signatures in Great Lakes air using
631 passive air samplers. Environ. Sci. Technol. 41(11), 3877-3883.
632 https://doi.org/10.1021/es063015r.
633 Häder, D.P., Banaszak, A.T., Villafane, V.E., Maine, A.N., Raúl, A.G., Helbling, E.W.,
634 2020. Anthropogenic pollution of aquatic ecosystems: Emerging problems with
635 global implications. Sci. Total Environ. 713, 136586.1-136586.10.
636 https://doi.org/10.1016/j.scitotenv.2020.136586.
637 Hartmann P.C., Quinn J.G., Cairns R.W., King J.W, 2005. Depositional history of
638 organic contaminants in Narragansett Bay, Rhode Island, USA. Mar. Pollut. Bull.
639 50(4), 388-395. https://doi.org/10.1016/j.marpobul.2004.11.020.
640 Holma-Suutari A., Ruokojärvi P., Komarov A.A., Makarov D.A., Ovcharenko V.V.,
641 Panin A.N., Kiviranta H., Laaksonen S., Nieminen M., Viluksela M., Hallikainen
642 A., 2016. Biomonitoring of selected persistent organic pollutants (PCDD/Fs,
643 PCBs and PBDEs) in Finnish and Russian terrestrial and aquatic animal species.
644 Environ. Sci. Eur. 28(1), 5. https://doi.org/10.1186/s12302-016-0071-z.
645 Hu, D., Martinez, A., Hornbuckle, K.C., 2008. Discovery of non-aroclor PCB (3,3′-
646 dichlorobiphenyl) in Chicago air. Environ. Sci. Technol. 42(21), 7873-7877.
647 https://doi.org/10.1021/es901855r.
648 Hu, L.Q., Lou, D., Wang, L.M., Yu, M., Zhao, S.Z., Wang, Y.J., Mei, S.R., Zhang, G.,
649 2020. Levels and profiles of persistent organic pollutants in breast milk in China
650 and their potential health risks to breastfed infants: A review. Sci. Total Environ.
651 753, 142028. https://doi.org/10.1016/j.scitotenv.2020.142028.
652 Jahnke, J.C., Hornbuckle, K.C., 2019. PCB emissions from paint colorants. Environ.
653 Sci. Technol. 53(9), 5187-5194. https://doi.org/10.1021/es9b01087.
654 Suarez-Lopez, J.R., Clemesha, C.G., Porta, M., Gross, D.M., Lee, D.H., 2018.
655 Organochlorine pesticides and polychlorinated biphenyls (PCBs) in early
656 adulthood and blood lipids over a 23-year follow-up. Environ. Toxicol. Phar. 66,
657 24-35. https://doi.org/10.1016/j.etap.2018.12.018.

658 Khairy, M., Muir, D., Teixeira, C., Lohmann, R., 2014. Spatial trends, sources, and air-
659 water exchange of organochlorine pesticides in the great lakes basin using low
660 density polyethylene passive samplers. Environ. Sci. Technol. 48(16), 9315-9324.
661 https://doi.org/10.1021/es501686a.
662 Khairy, M., Muir, D., Teixeira, C., Lohmann, R., 2015. Spatial distribution, air-water
663 fugacity ratios and source apportionment of polychlorinated biphenyls in the lower
664 great lakes basin. Environ. Sci. Technol. 49(23), 13787-13797.
665 https://doi.org/10.1021/acs.est.5b00186.
666 Kohler, M., Tremp, J., Zennegg, M., Seiler, C., Minder-Kohler, S., Beck, M.,
667 Lienemann, P., Wegmann, L., Schmid, P., 2005. Joint sealants: an overlooked
668 diffuse source of polychlorinated biphenyls in buildings. Environ. Sci.Technol.
669 39(7), 1967-1973. https://doi.org/10.1021/es048632z.
670 Latimer J.S., Quinn J.G., 1996. Historical Trends and Current Inputs of Hydrophobic
671 Organic Compounds in an Urban Estuary: The Sedimentary Record. Environ. Sci.
672 Technol. 30(2), 623-633. https://doi.org/10.1021/es950367h.
673 Litten, S., Fowler, B., Luszniak, D., 2002. Identification of a novel PCB source through
674 analysis of 209 congeners by US EPA modified method 1668. Chemosphere. 46,
675 1457-1459. https://doi.org/10.1016/S0045-6535(01)00253-3
676 Liu, X., Guo, Z., Krebs, K. A., Greenwell, D.J., Roache, N.F., Stinson, R.A., Nardin,
677 J.A., Pope, R.H., 2016. Laboratory study of PCB transport from primary sources
678 to building materials. Indoor. Built. Environ. 25(4), 635-650.
679 https://doi.org/10.1177/1420326X15623355.
680 Liu, Y., Wang, S.Y, McDonough, C.A., Khairy, M., Muir, D.C.G., Helm, P.A., Lohmann,
681 R., 2016. Estimation of uncertainty in air-water exchange flux and gross
682 volatilization loss of PCBs: A case study based on passive sampling in the lower
683 great lakes. Environ. Sci. Technol. 50(20), 10894-10902.
684 https://doi.org/10.1021/acs.est.6b02891.
685 Magar, V.S., Johnson, G.W., Brenner, R.C., Quensen, J.F., Foote, E.A., Durell, G., Ickes,
686 J.A., McCarthy, C.P., 2005. Long-term recovery of PCB-contaminated sediments
687 at the Lake Hartwell superfund site: PCB dechlorination. 1. End-member

688 characteristics. Environ. Sci. Technol 39, 3538-3547.
689 https://doi.org/10.1021/es048622y.
690 Mao, S., Liu, S., Zhou, Y., An, Q., Zhou, X., Mao, Z., Wu, Y., Liu, W., 2021. The
691 occurrence and sources of polychlorinated biphenyls (PCBs) in agricultural soils
692 across China with an emphasis on unintentionally produced PCBs. Environ. Pollut.
693 271, 116171. https://doi.org/10.1016/j.envpol.2020.116171.
694 Marek, R.F., Thorne, P.S., Herkert, N.J., Awad, A.M., Hornbuckle, K.C., 2017.
695 Airborne PCBs and OH-PCBs inside and outside urban and rural U.S. schools.
696 Environ. Sci. Technol. 51(14), 7853-7860.
697 https://doi.org/10.1021/acs.est.7b01910.
698 Mcdonough, C.A., Khairy, M.A., Muir, D.C., Lohmann, R., 2014. Significance of
699 population centers as sources of gaseous and dissolved PAHs in the lower Great
700 Lakes. Environ. Sci. Technol. 48(14), 7789-7797. https://doi.org/10.1021/es501074r.
701 Melymuk, L., Robson, M., Helm, P. A., Diamond, M. L., 2013. Application of land use
702 regression to identify sources and assess spatial variation in urban SVOC
703 concentrations. Environ. Sci. Technol. 47 (4), 1887-1895.
704 https://doi.org/10.1021/es3043609.
705 Montuori, P., Rosa, E.D., Sarnacchiaro, P., Duca, F.D., Provvisiero, D.P., Triassi, M.,
706 2020. Polychlorinated biphenyls and organochlorine pesticides in water and
707 sediment from Volturno River, Southern Italy: occurrence, distribution and risk
708 assessment. Environ. Sci. Eur. 32(1), 123. https://doi.org/10.1186/s12302-020-
709 00408-4.
710 Morgan, E.J., Lohmann, R., 2010. Dietary Uptake from Historically Contaminated
711 Sediments as a Source of PCBs to Migratory Fish and Invertebrates in an Urban
712 Estuary. Environ. Sci. Technol. 44(14), 5444-5449. https://doi.org/10.1021/es100450f.
713 Paatero, P., Tapper, U., 1994. Positive matrix factorization: a non-negative factor model
714 with optimal utilization of error estimates of data values. Environmetrics. 5(2),
715 111-126. https://doi.org/10.1002/env.3170050203.

716 Praipipat, P., Rodenburg, L.A., Cavallo, G.J., 2013. Source apportionment of
717 polychlorinated biphenyls in the Tidal Delaware River. Environ. Sci. Technol.
718 47(9), 4277-4283. https://doi.org/10.1021/es400375e.
719 Qiu, X.H., Zhu, T., Yao, B., Hu, J.X., Hu, S.W., 2005. Contribution of dicofol to the
720 current DDT pollution in China, Environ. Sci. Technol. 39(12), 4385-4390.
721 https://doi.org/10.1021/es050342a.
722 Rodenburg, L.A.; Du, S.; Fennell, D.E.; Cavallo, G.J., 2010. Evidence for widespread
723 dechlorination of polychlorinated biphenyls in groundwater, landfills, and
724 wastewater collection systems. Environ. Sci. Technol. 44(19), 7534-7540.
725 https://doi.org/10.1021/es1019564.
726 Rodenburg, L.A., Hermanson, M.R., Summer, A.L., 2019. Sources of polychlorinated
727 biphenyl blank contamination and their impact on fingerprinting. Environ.
728 Forensics. 21(1), 99-112. https://doi.org/10.1080/15275922.2019.1694098.
729 Ruge, Z., Muir, D., Helm, P., Lohmann, R.,2018. Concentrations, trends, and air-water
730 exchange of PCBs and organochlorine pesticides derived from passive samplers
731 in Lake Superior in 2011. Environ. Sci. Technol. 52(24), 14061-14069.
732 https://doi.org/10.1021/acs.est.8b04036.
733 Sacks, V.P., Lohmann, R., 2012. Freely dissolved PBDEs in water and porewater of an
734 urban estuary. Environ. Pollut. 162(5), 287-293.
735 https://doi.org/10.1016/j.envpol.2011.11.028.
736 Sah, R., Baroth, A., Hussain, S.A.,2020. First account of spatio-temporal analysis,
737 historical trends, source apportionment and ecological risk assessment of banned
738 organochlorine pesticides along the Ganga River. Environ. Pollut. 263, 114229.
739 https://doi.org/10.1016/j.envpol.2020.114229.
740 Stringer. R., Johnston. P., 2001. PCBs (polychlorinated biphenyls). In: Stringer, R.,
741 Johnston, P. (Eds.), Chlorine and the Environment: An Overview of the Chlorine
742 Industry. Springer, Dordrecht, 277-304.
743 Sun, P.; Blatnchard, P.; Brice, K.; Hites, R.A., 2006. Atmospheric organochlorine
744 pesticide concentrations near the Great Lakes: Temporal and spatial trends.
745 Environ. Sci. Technol. 40(21), 6587-6593. https://doi.org/10.1021/es060858+.

746 Van den Berg, M., Birnbaum, L.S., Denison, M.S., Vito, M.D., Farland, W., Feeley,
747 M., Fiedler, H., Håkansson, H., Hanberg, A., Haws, L.C., Rose, M., Safe, S.,
748 Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N.,
749 2006. The 2005 World Health Organization reevaluation of human and
750 mammalian toxic equivalency factors for dioxins and dioxin-like compounds.
751 Toxicol. Sci. 93(2), 223-241. https://doi.org/10.1093/toxsci/kfl055.
752 Venier, M.; Dove, A.; Romanak, K.; Backus, S.; Hites, R., 2014. Flame retardants and
753 legacy chemicals in the Great Lakes' water. Environ. Sci. Technol. 48(16), 9563-
754 9572. https://doi.org/10.1021/es501509r.
755 Venier, M.; Hites, R. A., 2009. Regression model of partial pressures of PCBs, PAHs,
756 and organochlorine pesticides in the Great Lakes' atmosphere. Environ. Sci.
757 Technol. 44(2), 618-623. https://doi.org/10.1021/es902804s.
758 Venier, M., Hites, R.A., 2014. DDT and HCH, two discontinued organochlorine
759 insecticides in the Great Lakes region: Isomer trends and sources. Environ. Int. 69,
760 159-165. https://doi.org/10.1016/j.envint.2014.03.028.
761 Venier. M., Salamova. A., Hites. R.A., 2016. Temporal trends of persistent organic
762 pollutant concentrations in precipitation around the Great Lakes. Environ. Pollut.
763 217, 143-148. https://doi.org/10.1016/j.envpol.2016.01.034.
764 Wang, Y.Z., Zhang, S.L., Cui, W.Y., Meng, X.Z., Tang, X.Q., 2018. Polycyclic aromatic
765 hydrocarbons and organochlorine pesticides in surface water from the Yongding
766 River basin, China: seasonal distribution, source apportionment, and potential risk
767 assessment. Sci. Total Environ. 618, 419-429.
768 https://doi.org/10.1016/j.scitotenv.2017.11.066.
769 Yang, Y.Y., Xie, Q.L., Liu, X.Y., Wang, J., 2015. Occurrence, distribution and risk
770 assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in
771 nine water sources. Ecotox. Environ. Safe. 115, 55-61.
772 https://doi.org/10.1016/j.ecoenv.2015.02.006.
773 Yu, Y., Li, Y.X., Shen, Z.Y., Yang, Z.F., Mo, L., Kong, Y.H., Lou, I., 2014. Occurrence
774 and possible sources of organochlorine pesticides (OCPs) and polychlorinated

biphenyls (PCBs) along the Chao River, China. Chemosphere. 114, 136-143. https://doi.org/10.1016/j.chemosphere.2014.03.095

Zhao, W.L., Cai, M.G., 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. Environ. Pollut. 238, 573-580. https://doi.org/10.1016/j.envpol.2018.02.057.