

Prepared in cooperation with Baltimore City Department of Public Works and  
Maryland Department of the Environment

## Refining Sources of Polychlorinated Biphenyls in the Back River Watershed, Baltimore, Maryland, 2018–2020

Scientific Investigations Report 2022–5012

U.S. Department of the Interior  
U.S. Geological Survey



**Cover:** Herring Run at Sinclair Avenue looking downstream, Baltimore, Maryland. Photograph by Carol Morel, U.S. Geological Survey.



# **Refining Sources of Polychlorinated Biphenyls in the Back River Watershed, Baltimore, Maryland, 2018–2020**

By Emily Majcher, Upal Ghosh, Trevor Needham, Nathalie Lombard, Ellie Foss, Mandare Bokare, Sarahana Joshee, Louis Cheung, Jada Damond, and Michelle Lorah

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## Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
Volume		
cubic meter (m <sup>3</sup> )	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m <sup>3</sup> )	264.2	gallon (gal)

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
cubic decimeter (dm <sup>3</sup> )	0.2642	gallon (gal)
cubic meter (m <sup>3</sup> )	0.0002642	million gallons (Mgal)
cubic centimeter (cm <sup>3</sup> )	0.06102	cubic inch (in <sup>3</sup> )
cubic meter (m <sup>3</sup> )	1.308	cubic yard (yd <sup>3</sup> )
cubic kilometer (km <sup>3</sup> )	0.2399	cubic mile (mi <sup>3</sup> )
cubic meter (m <sup>3</sup> )	0.0008107	acre-foot (acre-ft)
<b>Flow rate</b>		
cubic meter per second (m <sup>3</sup> /s)	70.07	acre-foot per day (acre-ft/d)
cubic meter per year (m <sup>3</sup> /yr)	0.000811	acre-foot per year (acre-ft/yr)
cubic meter per second (m <sup>3</sup> /s)	35.31	cubic foot per second (ft <sup>3</sup> /s)
cubic meter per second per square kilometer ([m <sup>3</sup> /s]/km <sup>2</sup> )	91.49	cubic foot per second per square mile ([ft <sup>3</sup> /s]/mi <sup>2</sup> )
cubic meter per day (m <sup>3</sup> /d)	35.31	cubic foot per day (ft <sup>3</sup> /d)
liter per second (L/s)	15.85	gallon per minute (gal/min)
cubic meter per day (m <sup>3</sup> /d)	264.2	gallon per day (gal/d)
cubic meter per day per square kilometer ([m <sup>3</sup> /d]/km <sup>2</sup> )	684.28	gallon per day per square mile ([gal/d]/ mi <sup>2</sup> )
cubic meter per second (m <sup>3</sup> /s)	22.83	million gallons per day (Mgal/d)
cubic meter per day per square kilometer ([m <sup>3</sup> /d]/km <sup>2</sup> )	0.0006844	million gallons per day per square mile ([Mgal/d]/mi <sup>2</sup> )
<b>Mass</b>		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
metric ton (t)	1.102	ton, short [2,000 lb]
metric ton (t)	0.9842	ton, long [2,240 lb]

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F = (1.8 × °C) + 32.

## Datum

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

## Abbreviations

AEP	annual exceedance probability
BRWWTP	Back River Wastewater Treatment Plant
CSM	conceptual site model
DOC	dissolved organic carbon
DPW	Department of Public Works
EPA	U.S. Environmental Protection Agency
FOG	fat, oil, and grease
GC-ECD	gas chromatography-electron capture detector
LDPE	low-density polyethylene
MDE	Maryland Department of the Environment
ng/g	nanogram per gram or part per trillion in solid phase
ng/L	nanogram per liter or part per trillion in aqueous phase
NPDES	National Pollutant Discharge Elimination System
PCB	polychlorinated biphenyl
pg/L	picogram per liter in aqueous phase
POC	particulate organic carbon
PRC	performance reference compound
SIS	stream impact sampling
SS	suspended solids
SSO	sanitary sewer overflow
TMDL	total maximum daily load
TOC	total organic carbon
TSS	total suspended solids
UMBC	University of Maryland, Baltimore County
USGS	U.S. Geological Survey
v:v	volume/volume
WWTP	wastewater treatment plant
WY	water year



# Refining Sources of Polychlorinated Biphenyls in the Back River Watershed, Baltimore, Maryland, 2018–2020

By Emily Majcher,<sup>1</sup> Upal Ghosh,<sup>2</sup> Trevor Needham,<sup>1</sup> Nathalie Lombard,<sup>2</sup> Ellie Foss,<sup>1</sup> Mandare Bokare,<sup>2</sup> Sarahana Joshee,<sup>2</sup> Louis Cheung,<sup>2</sup> Jada Damond,<sup>2</sup> and Michelle Lorah<sup>1</sup>

## Abstract

Older urban landscapes present unique and complex stressors to urban streams and their habitats through the introduction of legacy and emerging toxic contaminants. Contaminant sources are often associated with various developed land uses such as older residential areas, active and former industrial sites, contaminated sites, and effluents from municipal wastewater treatment plant discharges. These landscapes have a history of legacy contaminant use such as polychlorinated biphenyls (PCBs) resulting in impacts to sediment and water in these complex environments. Despite the ban of PCBs in new commercial use in 1979, PCB contamination is still widespread in the environment, with many fish consumption advisories throughout the Chesapeake Bay region based on elevated PCBs. Several watersheds in the Baltimore region have mandated reductions in PCBs per total maximum daily loads in tidal waters of the watersheds in order to promote compliance with water quality standards. Some of these mandated reductions (for example, regulated watershed runoff) specified in the total maximum daily loads are the responsibility of the local jurisdictions as part of their phase 1 National Pollutant Discharge Elimination System municipal separate storm sewer system permit. In cooperation with the Baltimore City Department of Public Works and Maryland Department of the Environment, the U.S. Geological Survey and University of Maryland, Baltimore County conducted a study from 2018 to 2020 to refine the sources of PCBs from the City of Baltimore into Back River and to use the results to improve the conceptual site model of PCBs in the Back River watershed.

PCB concentrations in the water column of the nontidal streams in Back River watershed are relatively consistent throughout both tributaries, with greater concentrations detected in samples collected from Moores Run but greater loads estimated in samples collected from Herring Run. PCB concentrations measured in the bed sediments and analysis of

the flux between sediment porewater (hereafter porewater) and surface water within the tributaries suggest that there are no stationary legacy sources within the stream channels.

The bulk of PCB mass entering the system from these nontidal tributaries appears to be introduced primarily during storm events. While only one storm event was sampled and concentrations were quantified only in Herring Run, solids captured during the storm were characterized by increases in PCB mass and overall suspended solids concentrations. Although the bioavailability of the PCB-associated sediment is unknown, this mechanism appears to warrant additional attention to better understand how concentrations vary under different storm conditions and temporally. The importance of contaminated stormwater in loading to Herring Run is further supported by the PCB concentrations in storm drain sediments collected near the tributary, which were present in higher concentrations and were characterized by different homolog signatures compared to that in bed sediments.

The observations in the tributaries differed from PCB concentrations and sediment characteristics downstream from the City of Baltimore boundary, in the upper tidal area of the main stem of Back River, particularly at the passive sampler locations BRT-1 and BRT-3. This depositional environment is characterized by higher organic content in sediments and higher concentrations of PCBs in porewater, which result in the possible flux of contaminants from sediment to the water column. This flux is generally opposite of that observed in the nontidal tributaries and the farthest upstream tidal site (BRT-2) and may be a result of the possible settling of sediment particles introduced via suspended solids in stormwater.

Despite an observed considerable reduction in overall PCB mass loading to and from the Back River Wastewater Treatment Plant (BRWWTP) (and similar reductions observed in biosolids) compared to the estimates previously reported from 2015, effluent from the BRWWTP continues to be a primary source of PCBs to Back River. The current study confirmed the likeliness of fat, oil, and grease deposits within the miles of sewer pipe as a source of PCBs to the BRWWTP influent. The differences between PCB concentrations in fat, oil, and grease deposits found in pipes (during replacement) compared to that of the BRWWTP suggest that legacy deposits may contain higher PCB concentrations and may act as a

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source of PCBs to passing sewage, eventually entering the BRWWTP. Variation in freely dissolved concentrations in the sewer system was apparent through the analysis of PCBs in the primary pump stations using passive sampling, with the largest contribution to the influent attributed to a single pump station and associated piping.

The contribution of PCBs to Herring Run and Moores Run via sanitary sewer overflows compared to the BRWWTP effluent is negligible, similar to reports from another large urban wastewater treatment plant. Therefore, decreased occurrence of sanitary sewer overflows is not expected to largely decrease PCB loads.

Results of this study suggest that targeted, sediment-capture best management practices in Back River watershed could be an effective way to reduce PCB mass loading assuming that deposited contaminated sediments are effectively isolated. Recent studies of some common urban best management practices such as bioretention have shown removal of PCBs within the stormwater control structures. In addition, appropriately timed street sweeping practices with appropriate collection equipment may be an effective way to reduce contaminants such as PCBs from road runoff sources. Reductions in concentrations and mass loading within the sewer system measured in this study compared to that estimated 5 years prior reflect the possible success of ongoing gray infrastructure management actions. Reductions may be attributable to enhanced nutrient reduction upgrades to the BRWWTP and extensive capital improvements and maintenance to the sewer system.

This study employed a combined sampling approach and a variety of sampling methods to include low-density polyethylene passive samplers, high-volume water samples, and grab samples of both water and sediment to characterize the PCB inputs to Herring Run, Moores Run, and Back River. Incorporating the passive samplers provided a time-weighted average of the freely dissolved concentration in the surface water, porewater, WWTP influent and effluent, and pump station influent over the deployment period with picogram per liter detection limits. A similar monitoring approach from this study could be implemented within other subwatersheds or municipal separate storm sewer system jurisdictions to assist in refining primary sources of PCBs in order to inform appropriate mitigation approaches.

## Introduction

In cooperation with the Baltimore City Department of Public Works (DPW) and Maryland Department of Environment (MDE), the U.S. Geological Survey (USGS) and University of Maryland, Baltimore County (UMBC) began a study in 2018 to refine the sources of PCBs from the City of Baltimore into Back River and to use the results to improve the conceptual site model (CSM) of polychlorinated biphenyls (PCBs) in Back River watershed. The chemical

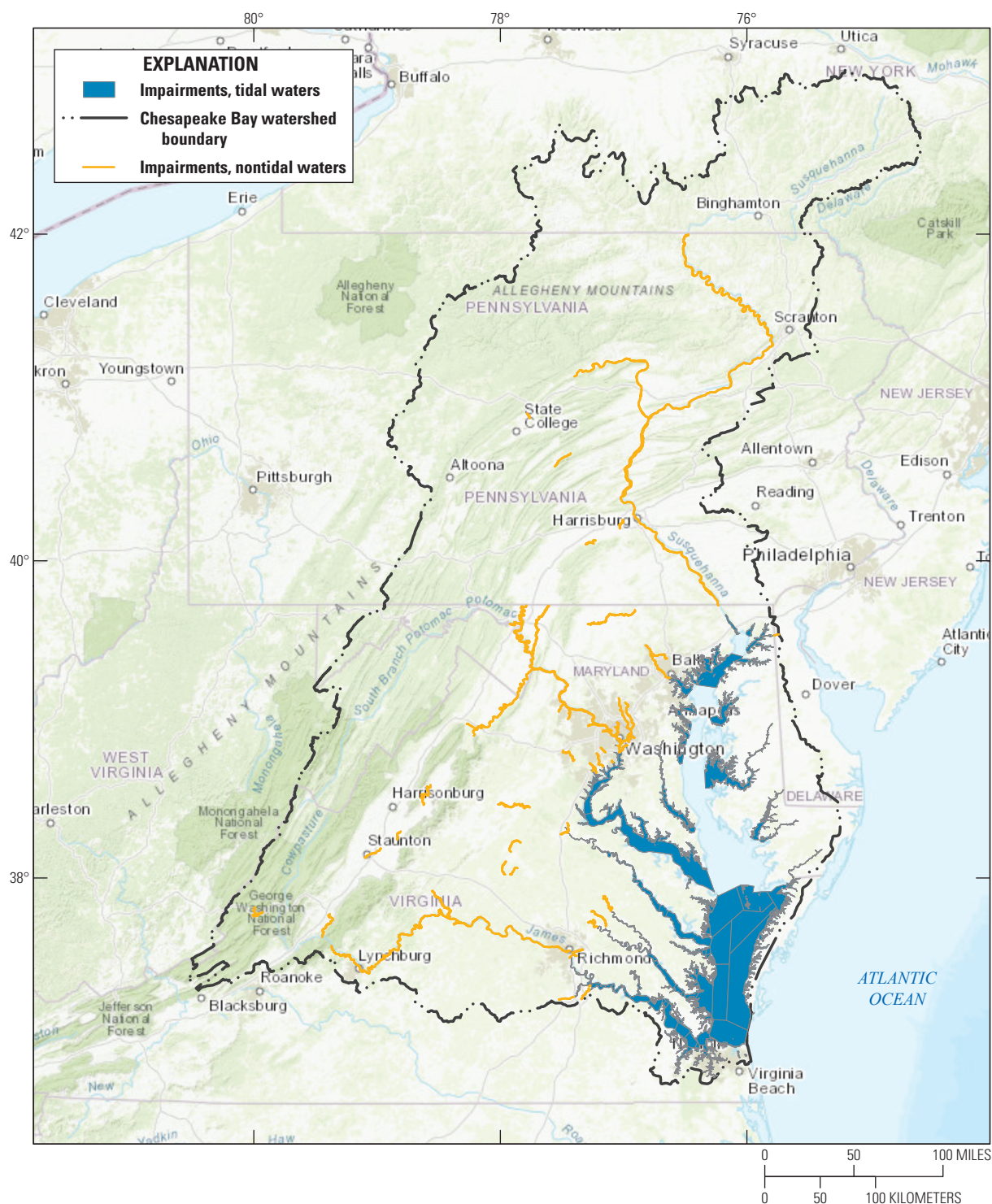
properties of PCBs that make them an ideal flame retardant also enable them to persist in the environment long after their ban in 1979 (U.S. Environmental Protection Agency [EPA], 2021). Specifically, PCBs are hydrophobic, highly stable, nonconductive, chemically inert, and nonflammable. PCBs were originally manufactured in the United States in 1929 and commercially marketed as Aroclor to be used in electrical transformers, hydraulic oils, insulation, flame resistant caulking, paints, and insulation materials (U.S. Environmental Protection Agency, 2021). PCBs are highly lipophilic and therefore bioaccumulate in the lipid fraction of organisms (Gobas and Arnot, 2010). Despite the ban, PCB contamination is still widespread in the environment, resulting in impairments throughout the Chesapeake Bay watershed (fig. 1) and is regulated through establishment of total maximum daily load (TMDL) per requirements of the Clean Water Act (86 Stat. 816) and fish consumption advisories (Maryland Department of the Environment [MDE], 2011, 2020).

Older urban landscapes present unique and complex stressors to urban streams and their habitats through the introduction of legacy and emerging toxic contaminants. Aquatic sediments form the ultimate repositories of past and ongoing discharges of hydrophobic organic compounds such as PCBs. PCBs in sediments can slowly leach into the water column, thereby impairing ecosystems although the manufacturing and new use of these compounds have been stopped (Ortiz and others, 2004). While contaminated legacy sediments continue to be the primary source of PCBs to water bodies and the aquatic food web, contaminated industrial landscapes and wastewater collection systems in urban settings can also serve as ongoing sources.

Contaminant sources are often associated with various developed land uses such as older residential areas, active and former industrial sites, numerous land restoration and brownfield sites, federally regulated contaminated sites (for example, Comprehensive Environmental Response, Compensation, and Liability Act [1980] Superfund sites), and effluent from municipal wastewater treatment plant (WWTP) discharges (King and others, 2004; Capozzi and others, 2019; Needham and others, 2019). While known point sources for these legacy contaminants exist, it is important to note that many of the industrial areas of these older urban landscapes pre-date relevant, current environmental regulations such as the Resource Conservation and Recovery Act (1976) and the Comprehensive Environmental Response, Compensation, and Liability Act (1980), resulting in widespread use and possible misuse and disposal of many of these substances. In addition, the use of PCBs in building materials prior to 1979 increased their prevalence and distribution across older high-density urban areas such as Baltimore, Maryland (King and others, 2004; Jartun and others, 2009; Cao and others, 2019). Ongoing nonpoint source inputs can be difficult to identify and are frequently overlooked in complex urban environments (Brenner and others, 2004; National Research Council, 2008). These ongoing inputs can include uncontrolled terrestrial sources, contaminated stormwater,

and sanitary sewer overflows (SSOs). Stormwater inputs have been identified as major contributors of PCBs and other hydrophobic contaminants to the Chesapeake Bay watershed (Bamford and others, 2002; Hwang and Foster, 2006, 2008).

PCBs in stormwater are found primarily in the suspended-sediment-bound phase because of their hydrophobicity and affinity to organic carbon (Cao and others, 2019).



**Figure 1.** Polychlorinated biphenyl (PCB)-impaired tidal and nontidal waters of the Chesapeake Bay watershed (modified from Williams and Wolf, 2018).



Several watersheds in the Baltimore region have mandated reductions in PCBs per TMDLs in tidal waters in order to promote compliance with water quality standards (Maryland Department of the Environment, 2011). Some of these mandated reductions (for example, regulated watershed runoff) specified in the TMDLs are the responsibility of the local jurisdictions as part of their phase I National Pollutant Discharge Elimination System (NPDES) municipal separate storm sewer system (MS4) permit. In 2011, MDE finalized a TMDL for PCBs within the oligohaline tidal Chesapeake Bay segment of Back River. Although Baltimore city limits do not extend to the tidal portion of Back River, several nontidal streams in the city drain to Back River and are included in the TMDL, including Herring Run and Moores Run (fig. 2). Located outside the city boundary in Baltimore County, Back River Wastewater Treatment Plant (BRWWTP) is owned and operated by the City of Baltimore and treats wastewater from an area inclusive of Baltimore County and the city, across 140 square miles, providing processing for more than 1.3 million residents in the area (Baltimore City Department of Public Works, 2021a). Reductions in PCBs are also mandated for the BRWWTP in the TMDL (Maryland Department of the Environment, 2011). In addition to the TMDL, ongoing actions to improve the sanitary sewer system in the City of Baltimore are a result of a consent decree (entered into in 2002 and modified in 2017) between the city and the EPA, the Department of Justice, and MDE. These consent decree activities include pipe replacement and maintenance cleaning of pipes, pump stations, and cleanout basins to eliminate SSOs.

Since the approval of the TMDL (and since the collection of the data on which the TMDL is based), there have been advances in the understanding of the fate and transport and in the monitoring and mitigation of PCBs (Needham and Ghosh, 2019; Ghosh and others, 2020). More recently, jurisdictions including the City of Baltimore and Baltimore County have developed PCB TMDL implementation plans to begin to address mandates outlined in the TMDL (K. Grove, Baltimore City DPW, written commun., 2018). Better identification and quantification of sources are a critical first step in the TMDL process (Lombard and others, 2019; Majcher and others, 2020). Employing approaches from the environmental cleanup practice to develop and improve the CSM (U.S. Environmental Protection Agency, 2011) can be beneficial to understanding and progressing with complex TMDLs (such as for PCBs). This study in Back River included two main objectives: (1) to refine the identification of both point and nonpoint sources of PCBs from the City of Baltimore into Back River through desktop analysis and field investigations and (2) to use results of the desktop and field analyses to improve the CSM of PCBs in Back River watershed. This report details the field investigations and analysis completed as part of this study and provides an update to the CSM using updated methods and approaches. The goal of the study was to assist the City of Baltimore with an improved understanding of PCBs in Back River watershed that could aid in targeting any additional investigations and

selecting appropriate mitigation approaches. In addition, the methods, approach, and outcomes of the study can be used to assess other similar, complex urban watersheds in the greater Baltimore and broader Chesapeake Bay regions.

## Purpose and Scope

The study was designed to refine the understanding of PCB sources, thereby improving the CSM of PCBs in Back River to focus mitigation efforts. In addition, the study was intended to apply innovative monitoring and analysis techniques that may be expanded to other locations and watersheds following this work. Such methods and approaches are intended to improve efficiency and cost-effectiveness for the monitoring program for source identification in PCB source studies.

Field investigations were conducted within the two primary nontidal streams within the City of Baltimore (Herring Run and Moores Run) the upper tidal zone of Back River (downstream from the City of Baltimore boundary in Baltimore County to the BRWWTP), and within the BRWWTP and all City of Baltimore primary pump stations that provide influent to the BRWWTP. Stationary sources or potential hot spots within each stream were investigated in the field by using low-density polyethylene (LDPE) passive samplers (hereafter passive samplers) in both the water column and sediment porewater (hereafter porewater) in Herring Run, Moores Run, and the upper tidal portion of Back River. Passive samplers provide a time-weighted average of the concentration over the deployment timeframe and reflect the bioavailable portion of PCBs (U.S. Environmental Protection Agency, 2017). During sampler deployment, grab samples for total suspended solids (TSS) and dissolved organic carbon (DOC) were collected since PCBs are typically associated with these phases. Investigation results were used to assess spatial variability of in-stream freely dissolved PCBs and to calculate potential loading of PCBs to the primary tributaries and Back River under low-flow conditions corresponding to the sample deployment timeframe. High-volume sampling was also used to collect surface water during low-flow conditions for PCB analysis, and PCB concentrations were compared with passive sampling values. Stormflow conditions were investigated using high-volume sampling to assess possible mobile, particle-associated sources of PCBs in Herring Run. One storm was sampled and analyzed as a demonstration event, and the event load of PCBs for the single storm was calculated. The storm event was compared to storm magnitude and frequency during the study period, water year 2019 (WY2019). Bed sediments from Herring Run and, later, road materials were collected, extracted, and analyzed for PCBs in March 2020 to supplement the other investigations of the surface waters.

Previous investigations of PCBs in the BRWWTP by Needham and Ghosh (2019) suggested that discharged effluent contributed 5.2 grams of total PCBs per day (g/d) in the form



of dissolved PCBs, a greater than 90 percent mass removal from estimated influent to the plant. Results of this previous study suggested that a legacy source of PCBs may exist within the sanitary sewer system and that the BRWWTP, plays a large role in mass loading to Back River (Needham and Ghosh, 2019). Since the time of this previous study, enhanced nutrient removal (ENR) upgrades have been implemented at the BRWWTP, and considerable capital improvements (for example, pipe replacements, Headworks Project) and operation and maintenance of sanitary sewer lines were performed (for example, physical and chemical cleanouts) as part of the consent decree activities (Baltimore City Department of Public Works, (2021b). Over a 10-month period, passive samplers were deployed within the combined influent and effluent, and grab samples of biosolid cake and pellets were collected and analyzed for PCBs to better define the fate of PCBs through the treatment processes. These data were used to calculate freely dissolved loading entering and exiting the BRWWTP, and results were compared to the Needham and Ghosh study (2019) to determine potential impacts from management activities taken between the studies. Passive samplers were deployed in eight primary pump stations of the City of Baltimore sewer system to quantify PCB concentrations at each pump station and identify potential sources of PCBs to the BRWWTP. The results were used to estimate loading from the sanitary sewer system to the BRWWTP. Freely dissolved concentrations of PCBs in the nearest pump station were used in combination with the MDE-reported SSOs to quantify possible loading in Herring Run and Moores Run over the past 5 years. Fat, oil, and grease (FOG) deposits from within the BRWWTP, pump stations, and pipes replaced were extracted and analyzed for PCB and lipid content to assess FOG as a possible source of freely dissolved PCBs in the influent to the BRWWTP.

Concentrations and estimated loads of PCBs in point and nonpoint sources were compiled to update the CSM for Back River watershed. These loads were used to suggest next steps in understanding and ultimately mitigating PCBs in Back River watershed.

## Description of the Study Area

The Back River watershed is an 8-digit hydrologic unit code watershed (02130901) that encompasses 141.7 square kilometers (km<sup>2</sup>) within the Patapsco River Basin. This study covered the portion of the Back River watershed within the boundaries of the City of Baltimore (about one-third of the Back River watershed, [fig. 2](#)). This portion of the watershed is all nontidal and includes the major tributaries of Herring Run and Moores Run, as well as Chinquapin Run, and several smaller tributaries ([figs. 2 and 3](#)). The west branch of Herring Run is just upstream from the Baltimore city boundary, and Redhouse Creek is downstream from the confluence of Moores Run and Herring Run, in Baltimore County. The portion of Back River watershed within City of Baltimore

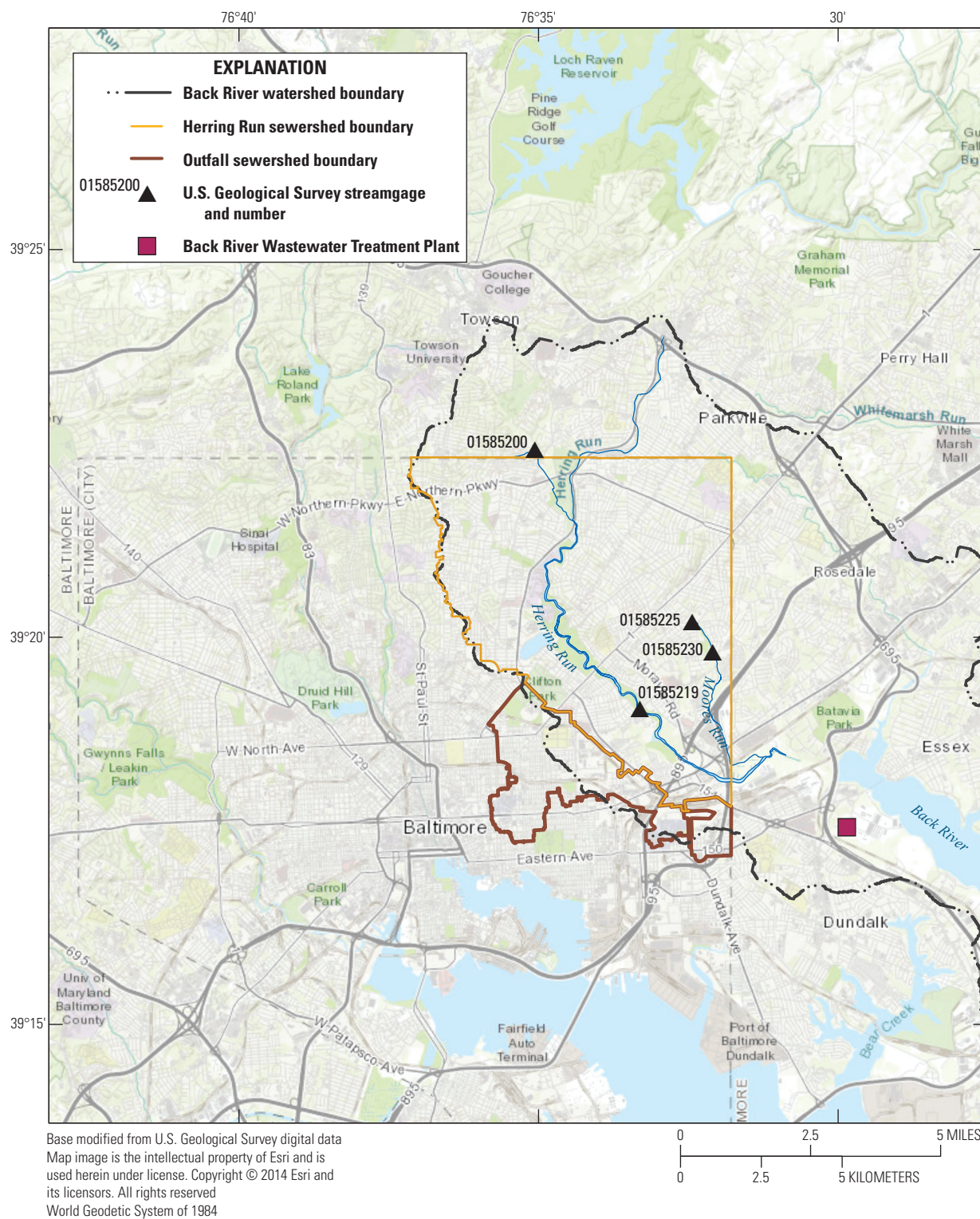
limits is highly urbanized, with greater than 87 percent developed land (National Land Cover Database, 2006) and greater than 35 percent impervious cover (King and others, 2004).

The USGS has four streamflow gages in Back River watershed and all are contained within the study area: USGS 01585200 located along the west branch of Herring Run at Idlewylde (53 water year period of record), USGS 01585219 located along Herring Run at Sinclair Lane (6 water year period of record), USGS 01585230 located along Moores Run at Radecke Avenue (24 water year period of record), and USGS 01585225 located along Moores Run tributary near Todd Avenue (24 water year period of record) ([figs. 2, 3](#)). Hydrologic conditions in the study area can be inferred from these streamflow gages during the study period (U.S. Geological Survey, 2020a,b,c). Annual mean discharge over the periods of record and ranges in discharge during the study period (WY2019, October 2018–September 2019) at three of the four gages are summarized in [table 1](#) (USGS 01585225 was excluded due to consistently low water levels resulting in an inability to sample). These discharge values at the three streamflow gages suggest that WY2019 was wetter than average, with WY2019 annual mean discharge is 1.1–1.6 times greater than the annual mean discharge during the periods of record (6–53 years). Despite a shorter period of record at the Herring Run at Sinclair Avenue gage, annual mean discharge similarly was greater during 2019 compared to the 6-year record.

The USGS program PeakFQ was used to calculate flood frequency discharge thresholds for the 99.5 (one sigma) and 66.67 (two sigma) percent annual exceedance probability (AEP) at the three streamflow gages (Veilleux and others, 2014; England and others, 2019). These discharge thresholds were then used to examine peaks in the record above the base during WY2019 (U.S. Geological Survey, 2020a,b,c). These peaks can be considered the discharge that can be expected each year in the channel (99.5 percent probability) and the bankfull discharge (66.7 percent probability). The bankfull discharge is considered channel-forming flow, as it moves sediment efficiently, and any greater discharge would move water onto the floodplain of the channel (Doheny and Baker, 2018).

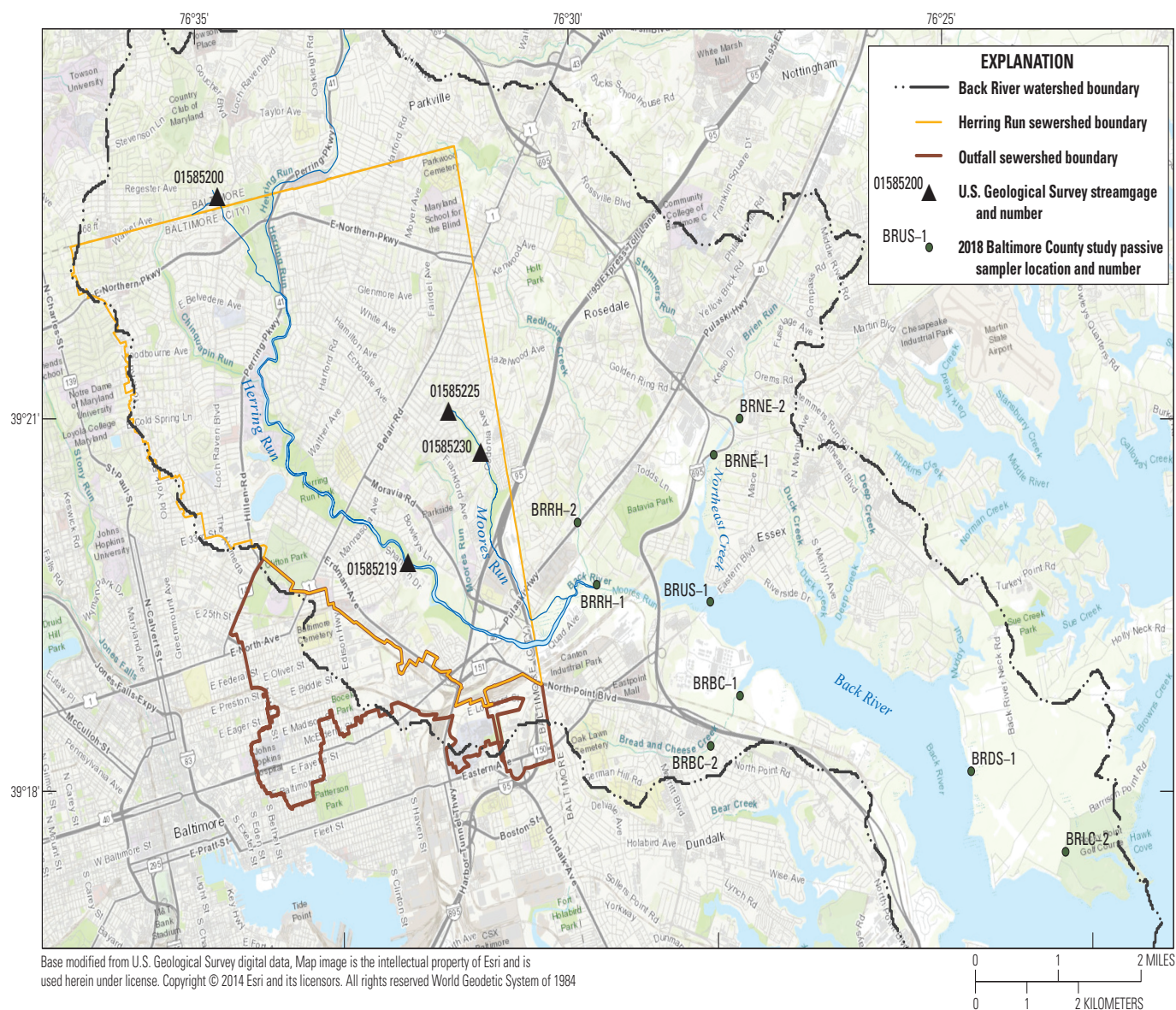
For comparison, the BRWWTP is located just outside the city boundary, in Baltimore County, and discharges to tidal Back River. During calendar year 2019, the average discharge from the BRWWTP was 116 million gallons per day (Mgal/d), or 179.5 cubic feet per second (ft<sup>3</sup>/s) (R. McEachern, Baltimore City DPW, written commun., 2020). Effluent discharge exceeds the maximum daily discharge at both the West Branch Herring Run at Idlewylde gage and the Moores Run at Radecke Avenue gage, as well as the annual mean discharge at all three gages during WY2019.

## 6 Refining Sources of Polychlorinated Biphenyls in the Back River Watershed, Baltimore, Maryland, 2018–2020



**Figure 2.** Study areas of interest, Back River watershed, sewersheds, and U.S. Geological Survey streamflow gages, Baltimore region, Maryland.





**Figure 3.** Locations of Baltimore County passive samplers (adapted from Joshee and others, 2019, 2020) and U.S. Geological Survey streamflow gages in Back River watershed, Baltimore region, Maryland.

**Table 1.** Annual mean discharge over the period of record and for water year 2019, minimum and maximum daily discharge during water year 2019, and minimum daily discharge, maximum daily discharge, and maximum peak flow during water year 2019 measured at U.S. Geological Survey streamflow gages in Back River watershed.

[WY, water year; ft<sup>3</sup>/s, cubic foot per second]

Gage number and name	Annual mean discharge over period of record (WY2019) (ft <sup>3</sup> /s)	Minimum daily discharge during WY2019 (date of measurement) (ft <sup>3</sup> /s)	Maximum daily discharge during WY2019 (date of measurement) (ft <sup>3</sup> /s)	Maximum peak flow WY2019 (date of measurement) (ft <sup>3</sup> /s)
01585200 West Branch Herring Run at Idlewylde	2.89 (4.75)	0.52 (September 27, 2019)	58.9 (March 21, 2019)	1,720 (July 11, 2019)
01585219 Herring Run at Sinclair Lane	50.1 (55.8)	17.4 (September 30, 2019)	509 (November 24, 2018)	4,490 (July 11, 2019)
01585230 Moores Run at Radecke Avenue	4.77 (6.11)	0.41 (September 12, 2019)	112 (March 21, 2019)	1,950 (May 10, 2019)

Relevant Previous and Ongoing Environmental Investigations

Baltimore City DPW conducts ammonia screening (weekly) and stream impact sampling (SIS; monthly, which includes analysis of water samples for metals, nutrients and sediment, bacteria, and other water quality parameters) along Herring Run and Moores Run and in Back River to help identify possible leaky infrastructure and to help meet nutrient, bacteria, and sediment TMDLs (City of Baltimore, 2020a). The MDE conducts periodic fish tissue sampling for PCBs to support fish consumption advisories. A comparison of PCB concentrations in *Ictalurus punctatus* (channel catfish) in Back River from 1999 to 2016 compared to nonurban areas suggest elevated concentrations and may be linked to urban land use (Needham and Sowers, 2018).

Some previous studies have investigated the wastewater and stormwater PCB sources in Back River watershed. Needham and Ghosh (2019) published a survey of PCB material balance through the BRWWTP. The 2015 study demonstrated more than 95 percent removal of PCBs by the BRWWTP and indicated the possibility that legacy sources of PCBs may exist within the sewage collection system (Needham and Ghosh, 2019). A preliminary monitoring effort of Bread and Cheese Creek was conducted in 2012 (Wang and others, 2012), and a source investigation study of many tributaries within Baltimore County including North East branch of Back River, Bread and Cheese Creek, Redhouse Creek, and Long Creek, along with sampling efforts in upstream and downstream sites in the upper tidal portion of Back River, was conducted in 2018 (Joshee and others, 2019, 2020; fig. 3). Freely dissolved concentrations of PCBs during the 2018 study ranged from 0.03 to 2.57 nanograms per liter (ng/L) with the lowest concentrations measured in samples from Longs Creek and the highest concentrations measured in samples from Bread and Cheese Creek (Joshee and others, 2019, 2020). The PCB concentrations measured in samples collected in 2012 in Bread and Cheese Creek (Wang and others, 2012) showed similar total concentrations to the 2018 study (Joshee and others, 2019), though a different homolog distribution was observed. These differences might be linked to methodology or temporal variations.

Methods to Assess PCB Sources in Back River Watershed

A range of tools were used to refine the location and magnitude of PCB sources in Back River watershed. A detailed desktop evaluation of sources identified in the TMDL for the watershed was conducted. Passive samplers were used for *in situ* field sampling in streams, the upper tidal portion of Back River, the BRWWTP, and primary pump stations within the Baltimore city limits. Stream bed and road sediments were collected, extracted, and analyzed for PCBs. In addition, high-volume sampling methods were used to estimate PCB concentrations and loads during storm and low-flow conditions in Herring Run. These field collection and analytical methods are detailed in the following sections.

Desktop Evaluation of Known Sources

A desktop assessment of known sources and inputs from the TMDL development process conducted from 2002 through 2008 was conducted to prepare an up-to-date inventory of known PCB sources in Back River watershed and to select appropriate monitoring sites. This assessment included a review of current and historical permitted discharges in the watershed since TMDL approval (Maryland Department of the Environment, 2021a) and locations of known contaminated sites, both Superfund and State of Maryland Land Restoration Program sites (Maryland Department of the Environment, 2021b). In addition, the reported SSO database (Maryland Department of the Environment, 2021c) was examined, and data were used to determine frequency and location of SSOs in the watershed and sewershed limited to the Quad Avenue pump station. Baltimore City DPW ammonia screening and SIS locations were mapped since these locations include TSS, ammonia, and other nutrient water quality data, and were compiled from the Open Baltimore data portal (City of Baltimore, 2020a).



## Field Sampling Methods

### Passive Sampling

In recent years, passive samplers have become powerful tools to measure the freely dissolved fraction of PCBs in surface water and shallow porewater (Ghosh and others, 2014). The freely dissolved fraction determines the bioavailability of PCBs to the aquatic food web and is the link between contaminated sediments and the benthic organisms that reside in the sediment and the fish in the surface water. The freely dissolved fraction measured by passive samplers provides a conservative method to estimate bioaccumulation to fish that will approach thermodynamic equilibrium with their environment (U.S. Environmental Protection Agency, 2012). Additionally, passive sampling provides a time-weighted average of the freely dissolved concentration within a flowing system, such as surface water or municipal wastewater, that is difficult to measure by other means.

### Herring Run, Moores Run, and Tidal Back River

Elevated concentrations or hot spots in bed sediments could result in PCB exposure to organisms in streams under low-flow conditions. Sample locations in Herring Run and Moores Run were selected based on field reconnaissance, previous MDE sample locations for TMDL development, and Baltimore City SIS sample locations, as well as other TMDL considerations such as outfall locations for NPDES-permitted locations, contaminated sites, and wastewater treatment outfalls (fig. 4, table 2). Passive samplers were also placed near USGS streamflow gages to facilitate the calculation of low flow loading during the deployment timeframe (at three locations; fig. 4). Passive samplers were placed in the upper tidal portion of Back River from the confluence of Redhouse Creek and Back River near the BRWWTP (fig. 4, table 2).

A recently published guidance document on passive sampling (U.S. Environmental Protection Agency, 2017) was followed to measure freely dissolved concentrations of PCBs in surface water. The sampling method entails preparation of LDPE passive sampling strips with performance reference compounds (PRCs), placement at the selected locations after encasing in deployment devices, and retrieval after a period of deployment, followed by extraction and analysis for PCBs. Upon retrieval, samplers were cleaned onsite by using Kimwipes (Kimberly Clark Professional, Roswell, Georgia) and deionized water to remove surface contamination, placed into precleaned 40-milliliter (mL) closed glass vials, and placed into a cooler for delivery to the University of Maryland, Baltimore County (UMBC) laboratory. Samples were stored at  $-4$  degrees Celsius ( $^{\circ}\text{C}$ ) in closed glass vials until extraction, which was completed within 1 month of sample collection. For each deployment, a set of three passive samplers loaded with PRCs (not deployed) were extracted and measured to determine the initial concentration of the PRCs

and any background contamination. The loss of PRCs during the deployment period was used to correct for nonequilibrium as described in Fernandez and others (2009).

For stream and river sites, LDPE sheets of 50.8-micron ( $\mu\text{m}$ ) thickness (Husky, Bolton, Ontario, Canada) were used as passive samplers. To account for nonequilibrium between the passive sampler and surface water or porewater, the LDPE strips were spiked with known concentrations of PRCs in a methanol:water mixture (80:20 volume:volume [v:v]) (Booij and others, 2002). Four PCBs (congeners 29, 69, 155, and 192) were chosen as PRCs, as they are not prevalent in the environment. This mixture was left on a shaker for 15 days to 1 month at room temperature, and then the passive samplers were submerged in deionized water overnight to remove the methanol. The samplers were dried and encased in stainless steel mesh (fig. 5A). The prepared samplers were then wrapped in aluminum foil and stored in a freezer until deployment (U.S. Environmental Protection Agency, 2017). For water column measurements in the streams, the mesh-encased samplers were secured into cinder blocks with zip ties (fig. 5B).

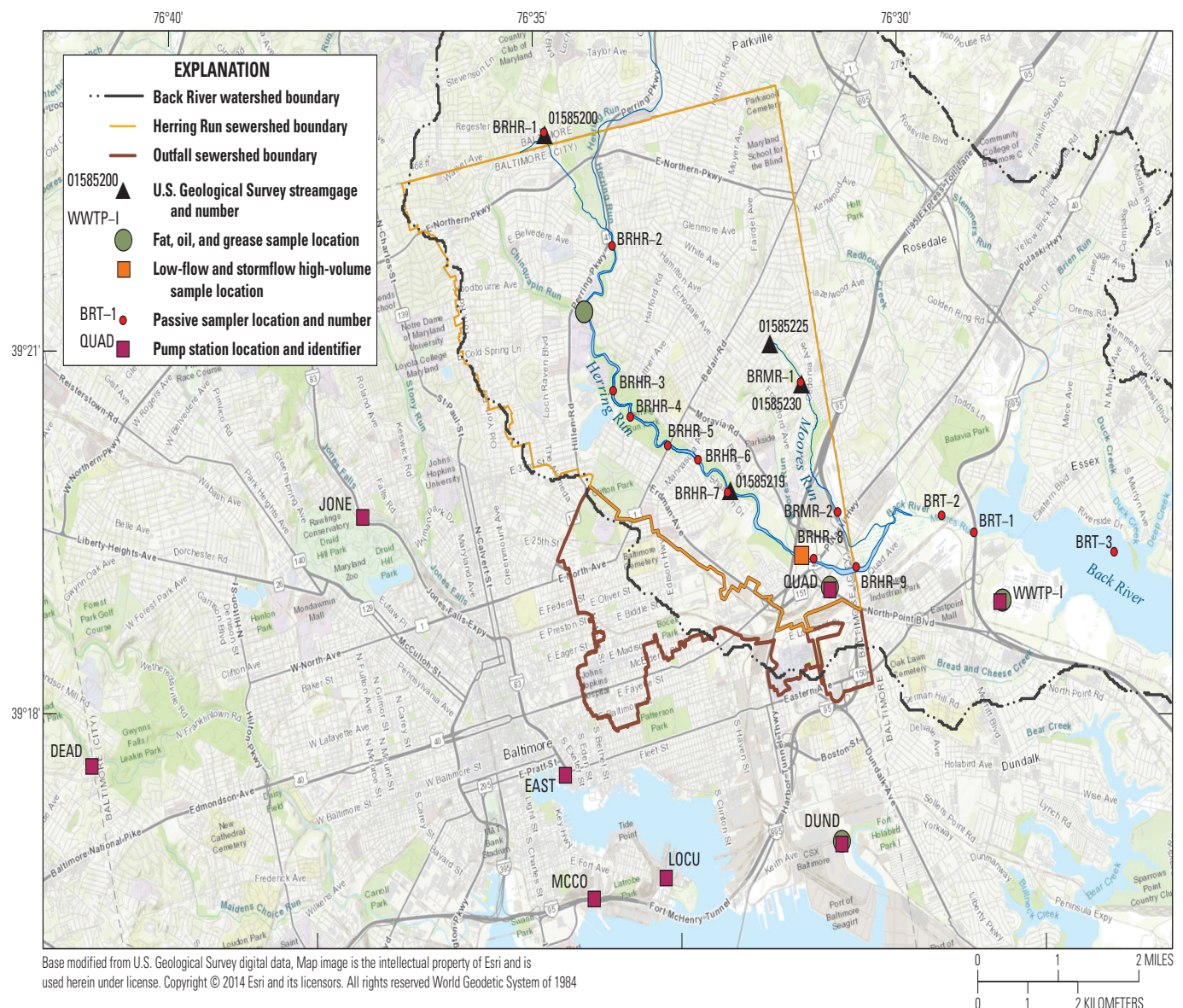
Passive samplers deployed within the nontidal stream portions of Herring Run and Moores Run consisted of two samples to measure the porewater and surface water at each site. For porewater measurements at the nontidal stream sites, the passive sampler was secured onto a stainless-steel frame inserted vertically into the sediment, which was then attached to the cinder block system with a braided polypropylene rope (fig. 5C, sampler installed and not visible). A second passive sampler was included within the center hole of the cinder block to sample the surface water. The system was then attached to a metal stake to anchor it in place. The anchoring method for porewater sampling in tidal Back River sites required a different sampler construction and deployment because of the water depth. Stainless-steel frames for porewater passive samplers at these sites were drilled onto the sides of a cinder block (fig. 5D). Then, the sampler along with a float was secured to a rope, which was connected to the cinder block (fig. 5D). This mechanism allowed for a passive sampler to be submerged in the sediment bed while allowing a second passive sampler to be suspended in the water column. Images of passive samplers during recovery are shown in figure 6A and B.

Passive samplers were deployed at various locations in two tributaries, Herring Run and Moores Run, and in the main stem of Back River (fig. 4, table 2). Construction work at site BRHR-9 prevented retrieval of the sampler, and therefore no results are presented for that site. The planned single deployment from May to August 2019 was modified to several shorter deployments in response to storms at the nontidal streams that resulted in lost samples (table 3). Seasonality was assumed to be negligible and therefore not expected to impact results.

During deployment 1, the peak discharge of the year occurred on July 11, 2019 (tables 1, 3), resulting in the loss of several samplers in Herring Run. Samplers in Moores Run

and the upper tidal portion of Back River were not affected by the July 11 event. Remaining samplers from deployment 1 in Herring Run were retrieved, and new samplers were deployed at the end of July (deployment 2, table 3) for an additional 32 days at all Herring Run locations (except BRHR–9, which was inaccessible because of construction work) with additional anchoring of the cinder blocks to riparian trees. All deployment 2 samples were collected on August 26, 2019, except at BRHR–5, where the anchoring rope was found cut and the samplers were not located. To complete the Herring Run freely dissolved concentration dataset, additional samplers were deployed at BRHR–5, BRHR–6, and BRHR–8, (deployment 3, table 3). The additional samplers were deployed on September 18, 2019, and retrieved on October 30, 2019.

At deployment, and at multiple times during deployment, water samples were collected for TSS and DOC analysis at all sample locations in Herring Run, Moores Run, and the upper tidal portion of Back River. TSS grab samples were collected in 1-liter (L) glass bottles as described in Ghosh and others (2020). In summary, the bottles were rinsed at least twice, filled with the sample, and refrigerated at 4 °C until analysis at the UMBC laboratory. For DOC samples, 40-mL baked glass vials were filled. TSS and DOC analyses were completed within one week of sample collection.



**Figure 4.** Study sample locations in nontidal streams, in the upper tidal portion of Back River, and in wastewater, and locations of U.S. Geological Survey streamflow gages.



**Table 2.** Locations of low-density polyethylene passive samplers in the study area.

[USGS, U.S. Geological Survey; TMDL, total maximum daily load; SIS, Baltimore City Department of Public Works stream impact sampling location; BRWWTP, Back River Wastewater Treatment Plant]

Sample name	Latitude	Longitude	Location details
BRHR-1	39.3736	76.5844	Herring Run, adjacent to USGS streamflow gage 01585200 West Branch Herring Run at Idlewyld
BRHR-2	39.3567	76.5728	Herring Run, downstream from confluence of Chinguapin Run, near TMDL site WQX352
BRHR-3	39.3336	76.5766	Herring Run, downstream from Montebello Lake outfall, site WQX353
BRHR-4	39.3301	76.5708	Herring Run, near Harford Road
BRHR-5	39.3264	76.5677	Herring Run, near Belair Road (SIS Belair Road)
BRHR-6	39.3235	76.5614	Herring Run, near SIS Brehms Lane North outfall, structural overflow
BRHR-7	39.3180	76.5550	Herring Run, adjacent to USGS streamflow gage 01585219 Herring Run at Sinclair Lane, SIS Sinclair Lane
BRHR-8	39.3054	76.5386	Herring Run, near SIS Pulaski, near high volume sample location
BRHR-9	39.3029	76.5292	Herring Run, near Baltimore city boundary, downstream from Interstate-95 overpass
BRMR-1	39.3304	76.5348	Moore's Run, adjacent to USGS streamflow gage 01585230 Moore's Run at Radecke Avenue, near TMDL site WQX362
BRMR-2	39.3097	76.5309	Moore's Run, near TMDL site WQX361
BRT-1	39.3027	76.4997	Upper tidal zone, Back River, near Interstate 695 overpass
BRT-2	39.3061	76.5053	Upper tidal zone, Back River, upstream from trash boom between Route 40 and I-95
BRT-3	39.2960	76.4700	Upper tidal zone, Back River, pier on eastern bank of Back River

**Table 3.** Sampling events using low-density polyethylene passive samplers in Herring Run, Moore's Run, and the upper tidal Back River.

Sampling event	Sample location	Deployment date	Period of deployment	Media sampled	Number of samplers deployed and retrieved
Deployment 1	Herring Run, Moore's Run, Back River tidal	May 2019	58 days (Herring Run), 89–90 days (Moore's Run and Back River tidal)	Surface water, porewater	Deployed 32, retrieved 17
Deployment 2	Herring Run	July 2019	32 days	Surface water, sediment	Deployed 9, retrieved 8
Deployment 3	Select locations in Herring Run (BRHR-5, BRHR-6, BRHR-8)	September 2019	42 days	Surface water, porewater	Deployed 9, retrieved 9



**Figure 5.** Low-density polyethylene passive samplers *A*, encased in stainless steel mesh, *B*, secured to cinder block with zip tie for nontidal surface water measurements, *C*, deployed for nontidal surface water and porewater (not visible, subsurface) measurements, and *D*, encased in stainless steel mesh drilled onto sides of cinder block for porewater measurements, with float attached. Photographs by Nathalie Lombard, University of Maryland, Baltimore County.





**Figure 6.** A, Passive sampler retrieved from a Back River tidal site, August 2019, and B, buildup of biofouling on the stainless steel mesh casing around a passive sampler, August 2019. Photographs by Nathalie Lombard, University of Maryland, Baltimore County.

### BRWWTP and Associated Pump Stations

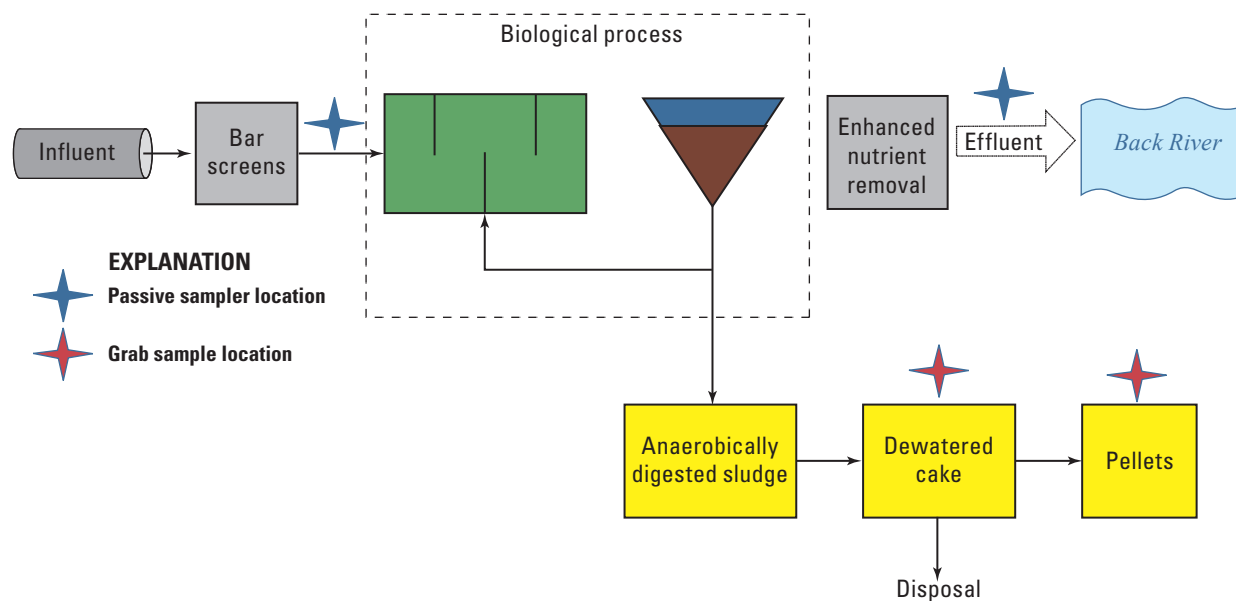
Passive samplers were deployed in the BRWWTP (figs. 4, 7) to measure freely dissolved concentrations of PCBs. Influent (fig. 8A–C) and effluent (fig. 8D) of the BRWWTP were measured in duplicate during spring, summer, and fall (table 4). Effluent samplers detached from their anchors during the summer deployment and were replaced June 17, 2019, reducing the deployment time from at least 90 to 51 days.

Using similar methodology and approaches, commercially available passive samplers (SiREM SP3, Toronto, Ontario, Canada) were deployed in the eight primary pump stations (fig. 4) to assess potential areas of concern (or “hotspots”) within the city sewershed of the BRWWTP. Like the previously described method, LDPE sheets were spiked with PRCs PCB 14, PCB 36, PCB 104, PCB 121, PCB 142, PCB 155, PCB 184, PCB 192, and PCB 204. The LDPE sheets were then secured with copper mesh to a stainless-steel frame prior to shipment to the USGS. Samplers included one trip blank to correct for PRC loss and possible contamination during the deployment process. Commercially available samplers were deployed in wet wells within the pump stations and down a manhole access point for the weir at Dead Run (fig. 9A). Samplers were secured using braided polypropylene rope and an 8-pound (3,628.74-gram) lead fishing sinker to keep the sampler within the flow. Samplers were deployed from June 12, 2019, to July 15, 2019 (table 4).

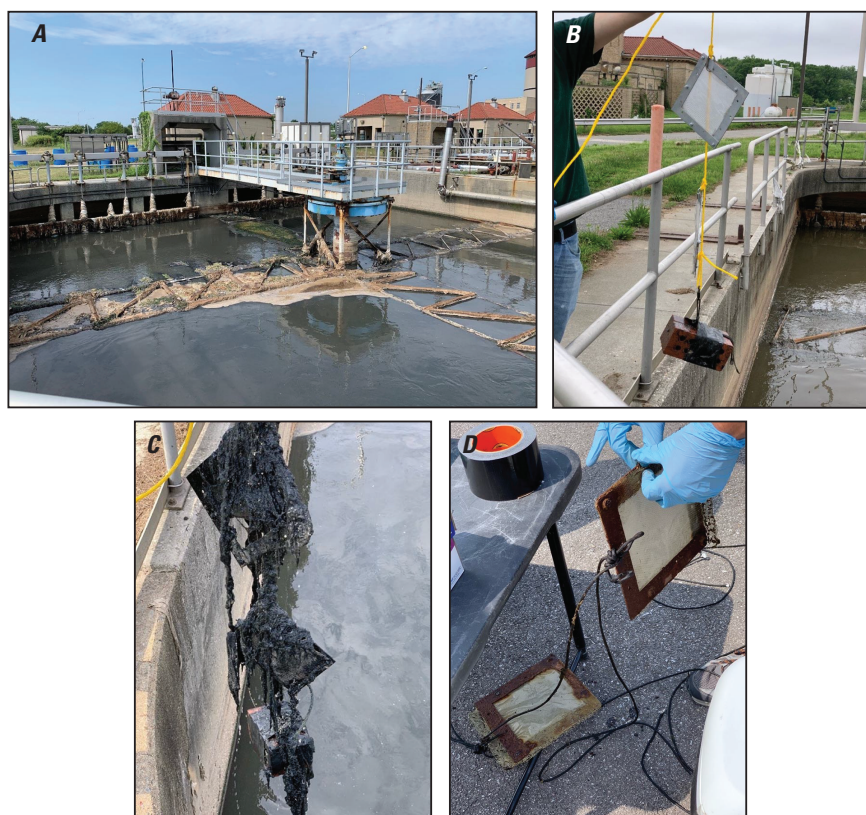
After deployment, the sampler associated with the Jones Falls pump station was lost: the steel frame was damaged and was not retrieved. The retrieved samplers were collected (fig. 9B, C), stored on ice, and then shipped overnight to Eurofins TestAmerica (Knoxville, Tennessee) for processing and analysis. PCB analysis was conducted according to method 1668A by HRGC/HRMS (U.S. Environmental Protection Agency, 2003). Freely dissolved PCB concentrations (in picograms per liter) were reported to the USGS by SiREM based on laboratory results and PCB partitioning coefficients and were corrected for disequilibrium on the basis of PRC loss.

### Cake, Pellet, and Bed Sediment Sampling

Biosolids produced during wastewater treatment were collected as grab samples in the BRWWTP in the forms of cake (anaerobically digested sludge conditioned with polymeric coagulant and dewatered in a solid bowl centrifuge) and pellet (biosolids that were further dewatered and reduced in volume through additional thermal treatment, performed by a Pelletech facility [Synagro Technologies, Inc.] located in the BRWWTP) (figs. 7, 10) when the passive samplers were retrieved from the plant (table 4). The grab sampling was carried out by BRWWTP and Synagro Technologies, Inc. personnel for biosolids and pellets, respectively (fig. 10A, B). Samples collected were transported in a cooler to the UMBC laboratory and stored at  $-4^{\circ}\text{C}$  until sample processing.



**Figure 7.** Schematic of sample locations at Back River Wastewater Treatment Plant (BRWWTP), February through November 2019 (modified from Needham and Ghosh, 2019).



**Figure 8.** Passive samplers at Back River Wastewater Treatment Plant (BRWWTP) A, in influent, B, before deployment, tied to a polypropylene rope and anchored by a brick weight, C, after recovery from influent, and D, after recovery from the effluent after being deployed for approximately 50 days in summer 2019. Photographs by Ellie Foss, U.S. Geological Survey.





**Figure 9.** Commercially available low-density polyethylene (LDPE) passive samplers (SiREM SP3) *A*, before deployment into a manhole access point for Dead Run as part of the pump station investigation, June 2019, *B*, upon retrieval from a pump station after a deployment period of 33 days, and *C*, after retrieval and cleaning with deionized water, July 2019. Photographs by Ellie Foss, U.S. Geological Survey.

**Table 4.** Sampling events at the Back River Wastewater Treatment Plant and pump stations.

[BRWWTP, Back River Wastewater Treatment Plant; NA, not applicable]

Sampling event	Deployment date	Period of deployment	Media sampled	Anchoring mechanism	Number of samplers deployed and retrieved
BRWWTP deployment 1	February 2019	92 days	Wastewater	Zip ties, rope, brick	Deployed 8, retrieved 8
BRWWTP deployment 2	May 2019	89 days (influent)	Wastewater	Zip ties, rope, brick, duct tape	Deployed 8, retrieved 8 (including redeployed effluent samplers)
BRWWTP effluent redeployment (part of deployment 2)	June 2019	51 days (effluent)	Wastewater	Zip ties, rope, brick, duct tape	Deployed 2, retrieved 2
BRWWTP deployment 3	August 2019	99 days	Wastewater	Zip ties, rope, brick, duct tape	Deployed 8, retrieved 8
BRWWTP cake/pellet sample 1	May 2019	NA (grab)	Cake and pellet	NA	NA
BRWWTP cake/pellet sample 2	August 2019	NA (grab)	Cake and pellet, liquid cake (sludge)	NA	NA
Pump station deployment 1	June 2019	33 days	Wastewater	Zip ties, rope, brick, duct tape, lead fishing sinker	Deployed 8, retrieved 7

Bed sediments were collected from eight Herring Run locations corresponding to passive sampler locations BRHR–1 through BRHR–8 (fig. 4). A clean trowel was used to collect grab samples from the bed sediments. The samples were grabbed within 0–6 inches of the sediment bed and transferred to wide-mouth glass jars. All samples were transported in a cooler to the UMBC laboratory and then refrigerated at 4 °C until further processing.



**Figure 10.** Biosolid pellet sample at the Back River Wastewater Treatment Plant (BRWWTP). Photograph by Nathalie Lombard, University of Maryland, Baltimore County.

## Fat, Oil, and Grease Deposit Sampling

FOG samples were collected in 2019 at four different locations (figs. 4, 11; table 5). The first FOG sample was collected on March 13, 2019, at the BRWWTP (fig. 11A). This sample was collected from primary settling tank number 6 by using a glass jar to scoop the sample and was transported to the UMBC laboratory for extraction method testing (table 5).

Following the passive sampler deployments at eight pump stations in the City of Baltimore, FOG samples were collected from two of the pump stations during passive sampler retrieval in July 2019. The first pump station FOG sample was collected on July 15, 2019, from the side of the concrete wall in the deep well at the Dundalk pump station. A plastic jar attached to a polyvinyl chloride pipe was used to scrape the concrete wall in the deep well. Approximately 200 mL of FOG was collected in the jar; it was capped, labeled, and transported to the UMBC laboratory for further processing and analysis. At the laboratory, the FOG sample was stored at –4 °C until extraction could be performed. The second pump station FOG sample was also collected on July 15, 2019, during passive sampler retrieval at the Quad Avenue pump station. Unlike at the Dundalk pump station, there was not a safe way to collect a FOG sample from inside the Quad Avenue pump station. However, upon retrieval of the passive sampler, large clumps of FOG were observed to be attached to the passive sampler rope. These FOG clumps were



removed and placed in a plastic jar (fig. 11B) and transported to the UMBC laboratory, where the sample was stored at  $-4^{\circ}\text{C}$  until extraction could be performed.

The final FOG sample was collected at the end of November 2019 from a concrete sanitary sewer pipe that was being removed from the sewer system and subsequently

crushed. The pipe was located near the confluence of Chinquapin Run and Herring Run (fig. 4). On November 25, 2019, a city worker was provided a jar to scrape the wall of the pipe to collect the FOG material present inside the pipe into the jar. The sample was then transported to the UMBC laboratory and stored at  $-4^{\circ}\text{C}$  until extraction could be performed.



**Figure 11.** Fat, oil, and grease (FOG) samples collected *A*, at Back River Wastewater Treatment Plant (BRWWTP) and *B*, from pipe located near the confluence of Chinquapin Run and Herring Run. Photographs by Ellie Foss, U.S. Geological Survey.

**Table 5.** Sampling events for fat, oil, and grease deposits.

[BRWWTP, Back River Wastewater Treatment Plant; FOG, fat, oil, and grease]

Location	Collection date	Method of sampling
BRWWTP	March 2019	Collected FOG grab sample from accumulation atop primary settling tank 6 and placed in glass jar
Dundalk pump station	July 2019	Collected FOG grab sample from FOG attached to concrete wall in deep well and placed in glass jar
Quad Avenue pump station	July 2019	Collected FOG grab sample from passive sampler rope and placed in glass jar
Pipe near confluence of Chinquapin Run and Herring Run	November 2019	Collected FOG grab sample from pipe and placed into glass jar

## High-Volume Sampling

High-volume samples were collected during low-flow conditions on December 11, 2018, through streamside filtration near BRHR-8, approximately 1 mile downstream from streamflow gage 01585219 Herring Run at Sinclair Lane along Route 40 (fig. 4, table 6). Methods of sample collection were adapted from Wilson (2020). Two inlet lines were connected to peristaltic pumps placed in the stream (fig. 12A). The intake lines were placed about 15 centimeters (cm) above the stream bottom and oriented 60 degrees from the downstream direction of flow. The water depth did not exceed 50 cm and may have declined slightly throughout the day. The water was passed through a glass fiber canister filter (Advantec MF, Inc., GF-75, 293-millimeter [mm] diameter, nominal pore size 0.3  $\mu\text{m}$ , Dublin, California), collected, weighed, and then passed through a large plate filter, and a sum weight was totaled through both filters. For most of the sampling duration, the pumping and the total filtering rate was 6 liters per minute, which was proportional to the streamflow during low-flow conditions at the time it was sampled.

Five filters from the left pump line and four filters from the right pump line were collected over a sampling period of 7 hours. In total, 1,031 L of water were filtered to collect the solids. A field equipment blank consisting of 4 L of high-performance liquid chromatography (HPLC) grade-water was passed through a filter in the field before the stream water was filtered. A second blank consisted of an unused filter pad. Bed sediment at this site appeared to be dominated by sand and fine gravel with few fine particles, resulting in difficulty quantifying the solid mass after drying.

Particulate organic carbon (POC) samples were collected in 1-L plastic autosampler bottles during low-flow conditions. The bottles were capped and transported in coolers to the USGS laboratory. After processing, nine suspended solids (SS) samples and eight POC samples were submitted to the UMBC laboratory for analysis.

Stormflow samples were collected in April and May 2019 at the same location at which the low-flow samples were collected previously in December 2018 (fig. 4, table 6). Stormflow samples were collected on April 19–20, 2019, which despite elevated turbidity did not yield enough sediment for analysis. A second set of stormflow samples was collected on May 5, 2019. Methods described in Wilson (2020) were adapted for Herring Run stormflow sample collection for both dates. During the May 2019 storm, a total volume of 31 L was collected in the field in a mobile sampling trailer outfitted with the automated sampler (fig. 12B). Once samples were collected and transported to the USGS laboratory, three glass-fiber filters (Advantec MF, Inc., GF-75, 293-mm diameter, 0.3  $\mu\text{m}$ , Dublin, California) were used to obtain sediment from the large-volume storm samples, and the wet tared weights were recorded. In addition, one equipment blank was prepared from HPLC grade water, and the wet filter weight was recorded for the blank. Overall, 3 sediment filters from low-volume sampling, 1 equipment blank, and 5 unused

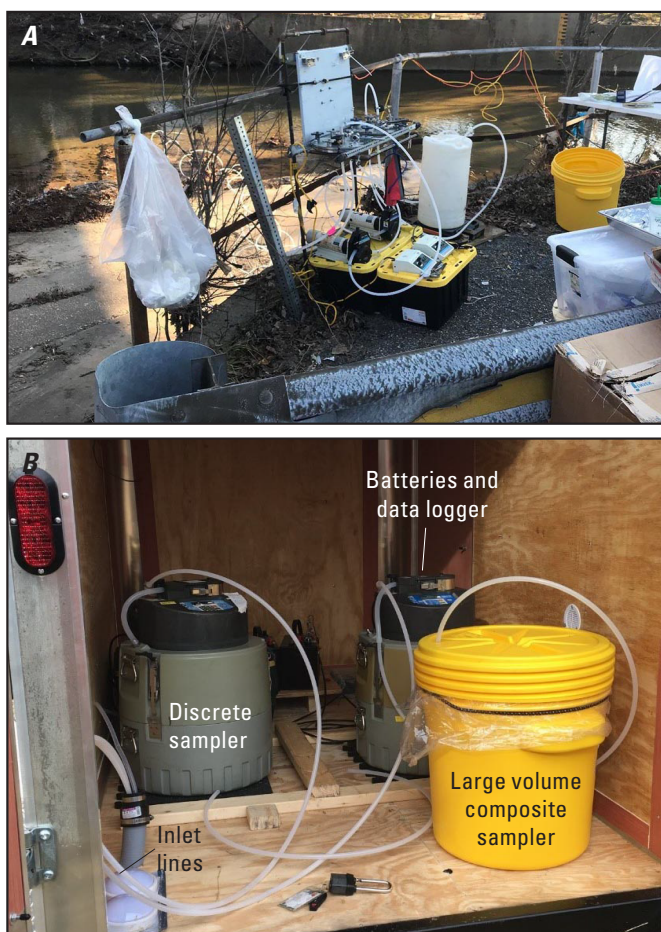
glass fiber filters were stored at  $-4^{\circ}\text{C}$ , and 14 SS bottles were capped, sealed, and marked with the water level prior to analysis at the UMBC laboratory.

Each TSS sample was subsampled for POC. POC samples were passed through glass fiber filters (Advantec GF-75, 25-mm diameter, 0.3  $\mu\text{m}$ , Dublin, California). Three filters were used for each sample, and the samples were wrapped in aluminum foil, bagged in plastic bags, and stored at  $-4^{\circ}\text{C}$  until analysis.

**Table 6.** High-volume surface water sampling events in Herring Run (near BRHR-8) during low-flow and stormflow conditions.

[SS, suspended solids; POC, particulate organic carbon]

Sampling event	Date	Number of samples
Low-flow sampling	12/11/2018	9 SS samples, 8 POC samples
Stormflow sampling	5/5/2019	14 SS and 14 POC samples



**Figure 12.** High-volume sampling setup during A, low-flow conditions (December 11, 2018) and B, stormflow conditions (April 19–20, 2019). Photographs by Timothy Wilson, U.S. Geological Survey.



## Road Material Sampling

Three road material samples were collected from three storm drain locations along Herring Run and Moores Run within Baltimore city boundaries on February 27, 2020 (table 7). These sites were identified from satellite imagery and were located as close as possible to the associated passive sampler location for that site. The SD–BRHR–2 road material sample was collected from a storm drain grate at the intersection of Woodbourne Avenue and Pioneer Drive, about 90 ft from the location of the passive samplers at BRHR–2 (fig. 4). The SD–BRHR–7 road material sample was collected from a storm drain grate on an overpass above where passive samplers for BRHR–7 (fig. 4) were deployed in the stream, about 85 ft away. The SD–BRMR–1 road material sample was collected from a storm drain grate on a residential road about 113 ft from the BRMR–1 passive sampler site (fig. 4). Each sample was collected using a metal spatula to scoop sediment stuck in between the drain grates into a 60-mL amber glass 40-mL vial. One full tube was collected for each sample.

## Laboratory Analytical Methods

Methods for extraction and analysis of PCBs for all portions of the study except for the passive sampling at the primary pump stations are detailed in this section and in the corresponding data release (Foss and others, 2022) and data quality assurance-quality control is discussed in Appendix 1. Commercially available passive samplers (SiREM SP3, Guelph Ontario, Canada) used for sampling the primary pump stations were analyzed by Eurofins TestAmerica (Knoxville, Tennessee).

## Passive Sampler PCB Extraction

Immediately after retrieval, passive samplers were cleaned onsite with Kimwipes (Kimberly Clark Professional, Roswell, Georgia) and deionized water. The PE samplers were stored in 40-mL glass vials and transported to the UMBC laboratory for further processing. PCBs were extracted according to extraction and cleanup methods reported by Needham and Ghosh (2019). In summary, sample extract cleanup was based on EPA methods 3660B (activated copper) (U.S. Environmental Protection Agency, 1996a) and 3630C (deactivated silica gel) (U.S. Environmental Protection Agency, 1996b).

## Solid Sample Extraction

Sediment samples were homogenized, sieved (1 mm) to remove detritus and gravel, and freeze-dried for at least 24 hours prior to extraction. Similarly, biosolid and road material samples were homogenized and freeze-dried for at least 24 hours prior to extraction. At least 1 gram of dry mass of solids was extracted using a hexane:acetone mixture (1:1 v:v). Sediment and road material extract cleanups consisted of EPA methods 3660B (activated copper cleanup) (U.S. Environmental Protection Agency, 1996a) and 3630C (silica gel cleanup) (U.S. Environmental Protection Agency, 1996b) as reported by Ghosh and others (2020). Biosolid (cake and pellet sample) cleanups were based on EPA SW–846 methods 3665A (sulfuric acid cleanup due to possible interferences from oil and grease) (U.S. Environmental Protection Agency, 1996c), 3660B (activated copper cleanup) (U.S. Environmental Protection Agency, 1996a), and 3630C (silica gel cleanup) (U.S. Environmental Protection Agency, 1996b).

FOG samples were processed similarly to the other solid samples but omitting the freeze-drying step. Because of the high lipid content of the FOG samples, additional sample cleanup was required. A modified EPA method 3620C (U.S. Environmental Protection Agency, 2014) was used for a packed column cleanup using Florisil (U.S. Silica, Katy, Texas) and acidified silica gel, generally used for biological tissue cleanups as reported by Fadaei and others (2015).

## High-Volume Filter Extraction

After solid material mass was quantified and SS mass was estimated, filters from high-volume sampling were extracted using Soxhlet extraction according to EPA method 3540C (U.S. Environmental Protection Agency, 1996d). Because of the limited space in the Soxhlet sample container, each filter was split in half, extracted separately, and recombined after extraction was completed.

Final combined sample extracts were evaporated to approximately 10 mL by using nitrogen blowdown evaporation, transferred to clean vials, and then concentrated to 1 mL. This concentrated sample extract sample was exchanged to hexane, and then clean up procedures described for solid samples (sediment and road materials) in the previous section were conducted.

**Table 7.** Collection events for road material samples from storm drain grates along Herring Run and Moores Run.

[EST, eastern standard time]

Location	Latitude	Longitude	Date, time collected	Approximate distance from passive sampler location (feet)
Near BRHR–2 (intersection of Woodbourne Avenue and Pioneer Drive)	39.355755	76.572756	2/27/2020, 10:50 a.m. EST	90
Near BRHR–7 (along overpass)	39.317994	76.555106	2/27/2020, 11:17 a.m. EST	85
Near BRMR–1 (on residential road)	39.330362	76.534614	2/27/2020, 11:30 a.m. EST	113

## PCB Analysis

All PCB analysis performed by the UMBC laboratory used gas chromatography with electron capture detection according to an adapted version of EPA SW-846 method 8082A and described in Beckingham and Ghosh (2011). PCB standards for calibration were purchased as hexane solutions. Internal standards 2,4,6-trichlorobiphenyl (PCB 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204) were added to all samples. Solvent blanks were run after every five samples, and calibration check standards were run at the beginning and end of each analysis to confirm calibration. A total of 119 PCB congeners were measured either as single congeners or as congener groups. PCB calibration standards were composed of a mixture of Aroclor 1232, Aroclor 1248, and Aroclor 1262, the dominant congeners found in the environment (Mullins and others, 1984). Individual congeners or coeluting groups were then summed by homolog group and total PCB concentration by mass. Method detection limits (appendix) were used to correct measurements after chromatogram peak identification.

## Total Suspended Solids and Total Organic Carbon

During the deployment time of the passive samplers, grab samples were collected to estimate TSS and total organic carbon (TOC). During high-volume sampling, TSS and DOC were measured and are detailed in this section.

### Grab Sample TSS

Analysis for TSS at the UMBC laboratory was performed by vacuum filtration, by filtering raw water samples through pre-weighed glass fiber filters (particle retention 1.6  $\mu\text{m}$ ) under vacuum. Before filtering the samples, the filter papers were rinsed with deionized water under vacuum in a filter flask. Rinsed filter papers were then baked at 500 °C in an oven for at least 2 hours to remove any traces of organic carbon, and then filter papers were stored in the oven at 110 °C until use. The total volume of water filtered was measured with a graduated cylinder and recorded. The wet filters were then dried in the oven at 110 °C for at least 1 hour. The filters were removed from the oven and placed for 20 minutes in a desiccator containing calcium sulfate desiccant. The weight of the filter was determined on an electronic weighing scale. This procedure was repeated as required until the difference between consecutive weights of the filter paper was less than 0.5 milligram (mg) (or a minimum of two additional times).

TSS (in milligrams per liter) was calculated as follows:

$$TSS = \frac{A - B}{V} \quad (1)$$

where

$A$  is the weight of the filter and residue (in milligrams),

$B$  is the weight of the filter (in milligrams), and  
 $V$  is the volume of sample filtered (in liters).  
 $TSS$  is the concentration of total suspended sediment (in milligrams per liter)

The solids collected on the filters were then analyzed for carbon content by catalytic oxidation at 900 °C and measurement of carbon dioxide released. The TOC analyzer was calibrated by using 5, 12.5, 25, 37.5, and 50 mg of anhydrous dextrose, which corresponds to 2, 5, 10, 15, and 20 mg of carbon, respectively. The POC concentration in milligrams per liter was calculated by dividing the amount of carbon measured in the SS by the volume of water that was filtered to obtain the sample.

### High-Volume Sample TSS

Estimates of mass of TSS were performed through the collection of high-volume samples during low-flow and stormflow conditions in Herring Run by measuring the SS accumulated on the filters. Upon receipt in the laboratory, all filters were frozen and freeze-dried to remove any moisture present in the sample. Following freeze-drying, the number of filters per sample and total mass of the sample were recorded to calculate the mass of solids collected per sample:

$$m(SS) = m_1(\text{filter} + SS) + m_2(\text{filter} + SS) + \dots + m_n(\text{filter} + SS) - n \times m(\text{filter blank}) \quad (2)$$

where

$m$  is the mass (in milligrams), and  
 $n$  is the number of filters.

These results were compared with a second approach to estimate the mass of SS by using the TSS measurements from each event and the volume of water sample filtered as follows:

$$m(SS) = [TSS] \times V(\text{water filtered}) \quad (3)$$

where

$[TSS]$  is the concentration of TSS measured per event (in milligrams per liter), and  
 $V(\text{water filtered})$  is the volume of water filtered to collect the SS to be analyzed for PCBs (in liters).

## DOC Analyses

Within 24–48 hours of stormflow sample collection, samples were filtered in the laboratory with 0.45- $\mu\text{m}$  nylon filters, acidified with hydrochloric acid to a pH of 3, and stored in a refrigerator at 4 °C until analysis as described by Ghosh and others (2020). Stormflow samples were analyzed for DOC within 3 weeks of collection. Analysis was performed using a TOC analyzer in the nonpurgeable organic carbon mode, and detection was performed with a nondispersive infrared detector. The instrument was calibrated before each set of

measurements with standard solutions of potassium hydrogen phthalate containing 1, 5, 10, and 20 milligrams per liter (mg/L) of carbon. A DOC reference standard was run with every set of measurements. Results for the samples were reported only if the DOC of the reference standard was within the specified limits.

## Data Analysis Methods

### Passive Sampling Calculation of Freely Dissolved PCBs

PCB concentrations were normalized by LDPE mass and corrected for nonequilibrium by using PRC loss. PCB 29, PCB 69, PCB 155, and PCB 192 were used as PRCs to correct for PCB concentrations. Methods adapted from Perron and others (2013) were used to estimate the freely dissolved concentrations in the water column:

$$C_w = \frac{C_{pe,t}}{(1 - e^{-k_e t}) \times K_{pew}} \quad (4)$$

where

- $C_w$  is the water column concentration (in nanograms per liter),
- $C_{pe,t}$  is the target compound concentration in the polymer at time  $t$  (in nanograms per liter),
- $k_e$  is the mass transfer coefficient (per day),
- $t$  is the deployment time (in days), and
- $K_{pew}$  is the partition coefficient of the target compound between water phase and polymer.

The mass transfer coefficient ( $k_e$ ) is calculated as follows:

$$-k_{e,PRC} - \ln \left( \frac{C_{pe,prc,t}}{C_{pe,prc,ini}} \right) \frac{1}{t} \quad (5)$$

where

- $C_{pe,prc,t}$  is the concentration of a PRC compound in polymer at time  $t$  (in nanograms per gram),
- $C_{pe,prc,ini}$  is the initial concentration of a PRC compound in polymer (in nanograms per gram), and
- $t$  is the time of deployment (in days).

For all target congeners,  $k_e$  was extrapolated from the linear correlation between  $\log k_{e,PRC}$  and  $\log$  of the octanol-water partitioning coefficient ( $K_{ow}$ ). The fractional equilibrium constant ( $f_{eq}$ ) was then calculated for all target analytes as follows:

$$f_{eq} = 1 - e^{-k_e t} \quad (6)$$

Polymer partitioning coefficients for PCBs were based on published consensus values published in Ghosh and others (2014).

The diffusive flux of chemicals between sediments and water was calculated based on freely dissolved concentration gradients by a Fickian diffusion model previously used for PCB congeners and legacy pesticides and metabolites in riverine and coastal shelf sediments (Beckingham and Ghosh, 2013; Fernandez and others, 2014).

## Summary of Known PCB Sources to Back River

Back River was identified as an impaired waterway in 1998 because of elevated levels of PCBs within sediment and in 2008 because of fish tissue PCB concentrations (Maryland Department of the Environment, 2011). In addition to PCBs, TMDLs were approved for chlordane, nutrients, and zinc for Back River estuary or its tributaries because of impairments to water quality. In 2011, MDE finalized a TMDL for PCBs within the oligohaline tidal Chesapeake Bay segment of Back River (based on sample locations shown in [fig. 13.4](#)) to reduce the risk to human health through fish consumption and to protect ecological resources (that is, benthic communities). The goals outlined in the TMDL include endpoints for the water column and sediment that are protective of the fishing designated use at 0.57 ng/L and 21.6 micrograms per kilogram ( $\mu\text{g/kg}$ ), respectively. This water column endpoint for total PCBs is lower than the established criteria that are protective of human health (0.64 ng/L) and freshwater and saltwater aquatic life (14 and 30 ng/L, respectively) (Maryland Department of the Environment, 2011). Similarly, the sediment endpoint goal is lower than the effects range median of the sediment quality guideline (180  $\mu\text{g/kg}$ ) (Maryland Department of the Environment, 2011). The TMDL for Back River identifies regulated stormwater as contributing 48 percent of the total annual load of PCBs to the river, approximately 18 percent of which is attributed to City of Baltimore. To meet TMDL requirements, City of Baltimore and Baltimore County need to reduce PCB loads in stormwater by more than 50 percent (Maryland Department of the Environment, 2011). The BRWWTP was estimated to contribute 14 percent of the total annual load of PCBs to Back River. The TMDL requires a reduction in loads from BRWWTP by more than 60 percent (Maryland Department of the Environment, 2011).

Two primary sources of PCBs evaluated in the TMDL included industrial NPDES permitted discharges and contaminated sites. Since the time the TMDL was drafted in 2011, these sources were revisited at the onset of this study to evaluate any updates or new sources. In addition, SSOs, a major target of the consent decree efforts, were evaluated as a source of PCB loading that was not included in the original TMDL assessment of sources.



## Industrial NPDES Permitted Discharges and Contaminated Sites

Upstream portions of the study area are dominated by residential land use. Areas downstream of Pulaski Highway and to the west of Herring Run downstream from Sinclair Avenue are dominated by heavy industrial land use. Industrial land use in this area dates to the 1800s, with landfills and incinerators in operation back to the early 1900s (Edds and Gross, 2003), predating environmental regulations. This continues to be a largely industrial area of Baltimore that is likely to remain in this land use into the future (Edds and Gross, 2003).

The prevalence of industrial sites within the watershed and sewershed boundaries has resulted in the continued issuance of numerous NPDES permitted stormwater discharges (fig. 13B). Land restoration sites are numerous and include former incinerators, landfills, dumps, and chemical companies (fig. 13C). Since the TMDL was approved, several new stormwater discharge permits (9) were issued under the general permit, and one was issued under municipal permit for a total of 10 within the City of Baltimore (Maryland Department of the Environment, 2021a). Activities conducted under these new permits include operation of refuse systems, maintenance, primary repair and salvage, automotive recycling, and manufacturing of concrete products based on associated standard industrial classification (SIC) codes. Monitoring of stormwater for PCBs is not currently a requirement of the general permit.

Superfund contaminated sites (fig. 13C) were considered in the development of the TMDL and were included in the baseline load estimate, comprising less than 1.5 percent of the overall PCB loading to Back River in Baltimore city and county combined (Maryland Department of the Environment, 2011). The areal coverage of these sites is a small portion of the overall watershed. In addition to these federal cleanup sites, some State of Maryland land restoration program sites within the study area have reported PCBs in soils or sediment, including the Pulaski Incinerator Facility, located along the eastern banks of Herring Run, and the 68th Street Dump/Industrial Enterprises complex, downstream from the Baltimore City boundary and in the tidal portion of the study area (Maryland Department of the Environment, 2021b). While there are many other industrial facilities in the study area, no other sites report PCBs in soils or sediment that could provide contaminated stormwater to Back River or its tributaries (Maryland Department of the Environment, 2021b).

## SSOs and FOG

Despite the separate sanitary and stormwater sewer system in Baltimore the age of the infrastructure (built in 1907; Baltimore City Department of Public Works, 2021a) results in considerable infiltration and inflow of water into

the sanitary sewer system. For example, average daily flow at the BRWWTP was 116 Mgal/d during the current study; however, flows as high as 253 Mgal/d were measured (the design capacity of the plant is 180 Mgal/d). Deposits of FOG are a recurrent problem in aging sanitary sewer pipes; these deposits result in pipe blockages and have been reported to be the cause of as much as 50 percent of SSOs (He and others, 2017). FOG deposits form in pipes primarily because of inappropriate disposal of fats and grease from restaurants and homes. Characterization of FOG from sewer collection systems is a highly adhesive material that is high in total fat content (dominated by palmitic fatty acid) and calcium (likely a result of a combination of soap and concrete weathering), which combine to form hardened deposits (He and others, 2017). Baltimore has recently had SSOs attributed to FOG deposits, such as one discovered blocking more than 85 percent of a sewer main (Wells, 2017).

Reducing the number of SSOs is a critical component of the consent decree (as described in the “Introduction” section). Areas of Moores Run were highlighted as areas of concern (because of elevated *Escherichia coli* concentrations) during the 2019 consent decree public meeting (Baltimore City Department of Public Works, written commun., 2019). The high fat content of FOG deposits in sewer pipes makes it a potential sink for hydrophobic organic compounds, such as PCBs. While PCBs have been banned from use since 1979, it is possible that industrial wastewater and stormwater, leaks from transformers, or other sources of legacy PCBs could have entered the sanitary sewer system (for example, through cracks, leaks, or incorrect disposal) and partitioned into the FOG. The long-term presence of PCBs in FOG deposits in the sanitary sewer system may result in an ongoing loading of PCBs to liquid sewage, which then enters the WWTP via the influent water and SS.

If the source of some of the PCBs in the BRWWTP influent is FOG, SSOs that occur near streams may discharge PCBs directly into those streams (fig. 13D). SSOs within the study area reported to MDE by Baltimore City DPW were tabulated from the public database (Maryland Department of the Environment, 2021c). Because investigative methods to identify and quantify SSO discharges has improved over time, only the SSOs during the last 5 years were examined for locations and discharge volumes. The number of records and an estimate of the volume discharged during 2015–19 are summarized in tables 8 and 9. Within the study area during this time period, numerous SSOs occurred in the area of Herring Run near Belair Road (near study site BRHR–5, fig. 13D).

In addition to the reported SSOs, four suspected discharges were identified in 2016 as part of the Baltimore illicit discharge determination and elimination program (City of Baltimore, 2020b). All four discharge locations were within Herring Run, between Belair Road and Sinclair Avenue.

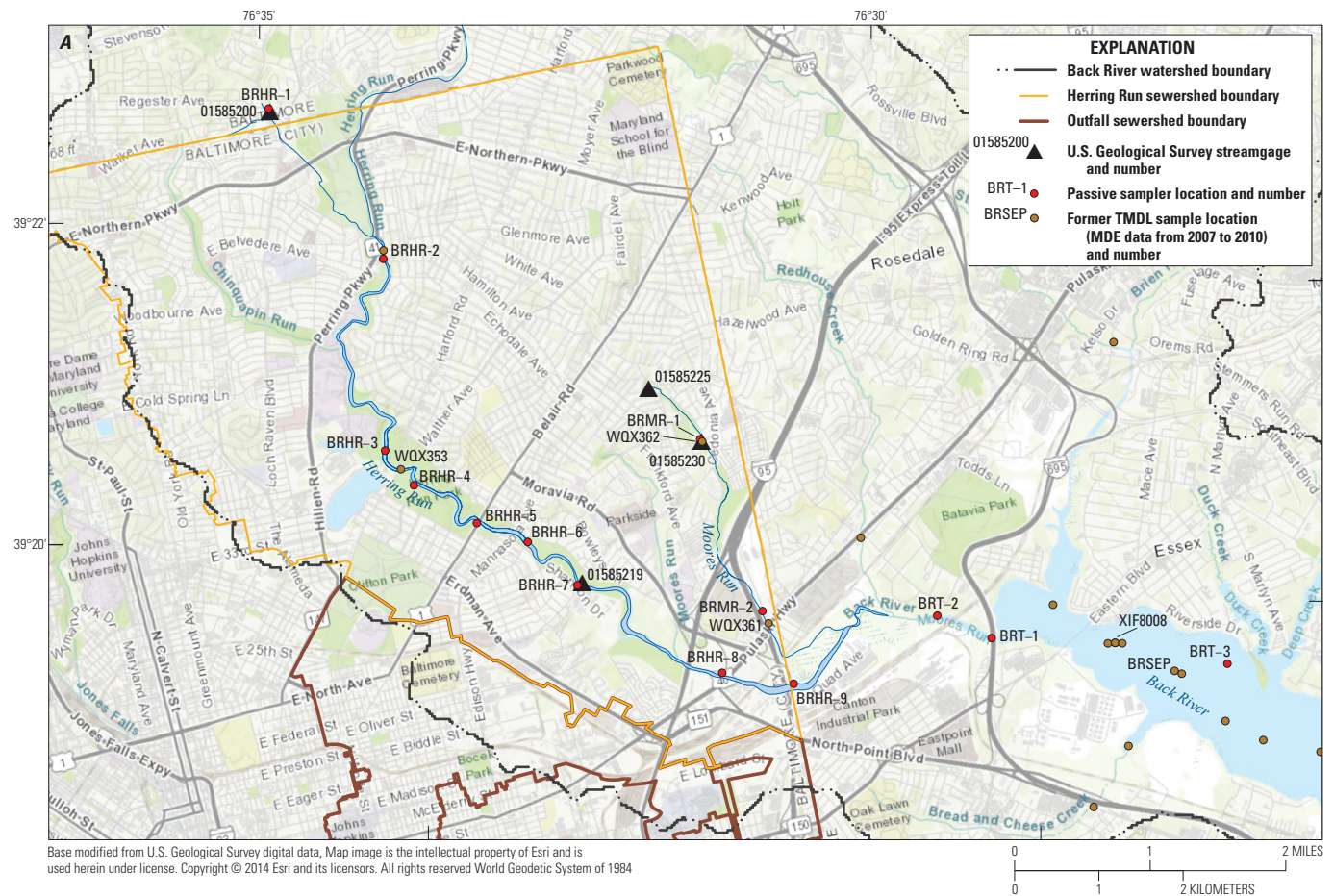
**Table 8.** Total sanitary sewer overflow records for drainage areas of U.S. Geological Survey streamflow gages in Back River watershed by year, 2015–19. Data from Maryland Department of the Environment (2021c).

Year	Number of records
2015	533
2016	487
2017	420
2018	544
2019	363
Total	2,347

**Table 9.** Estimated volumes reported in sanitary sewer overflows expressed in number of records and percent of total records, 2015–19.

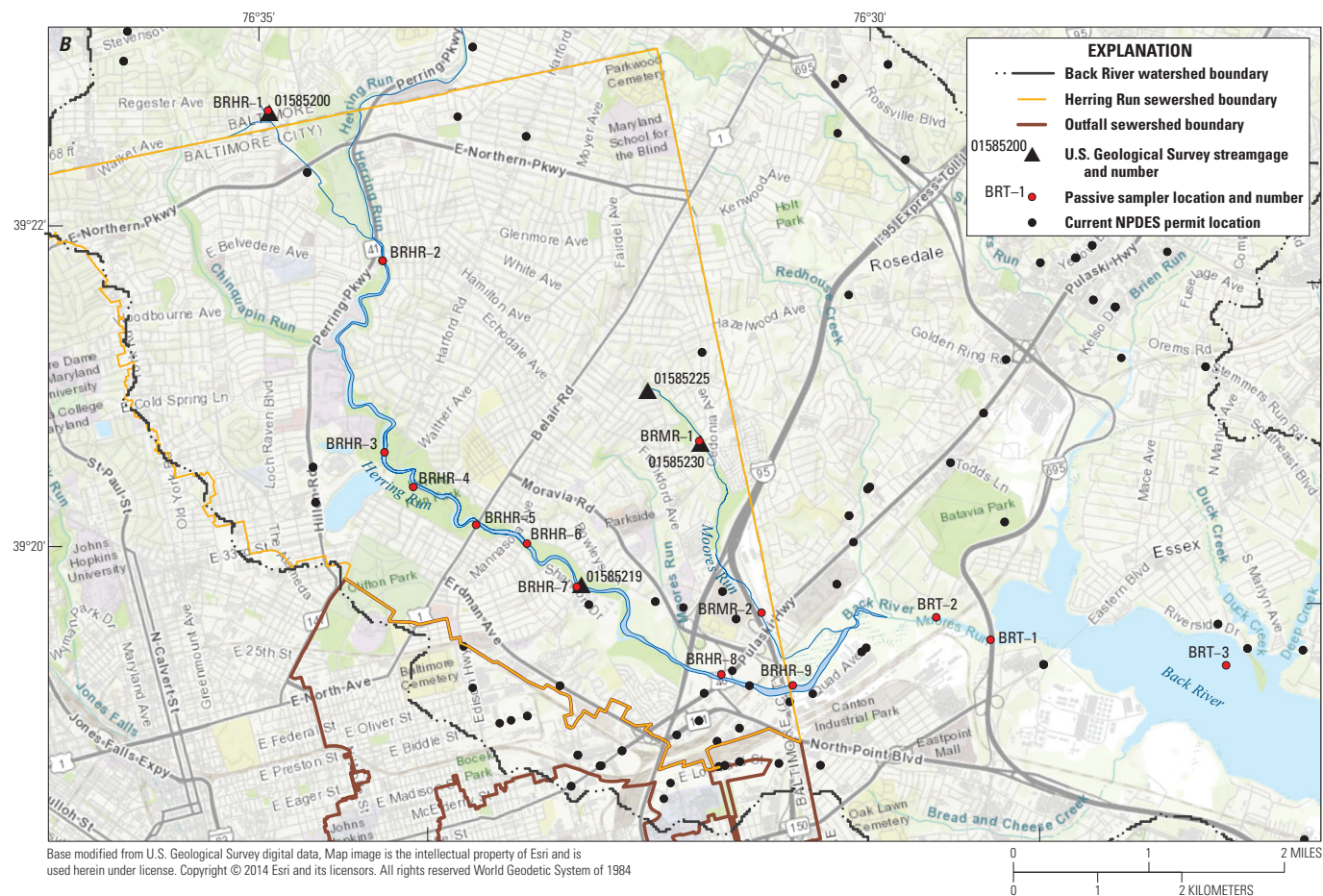
[<, less than]

Volume in gallons (cubic foot)	Number of records	Percent of total (2,347) records in 2015–19
<100 (13.4)	1,261	54
<1,000 (134)	1,694	72
<10,000 (1,340)	2,031	87
<100,000 (13,400)	2,162	92
<1,000,000 (134,000)	2,246	96
<10,000,000 (1,340,000)	2,310	98
<100,000,000 (13,400,000)	2,318	99



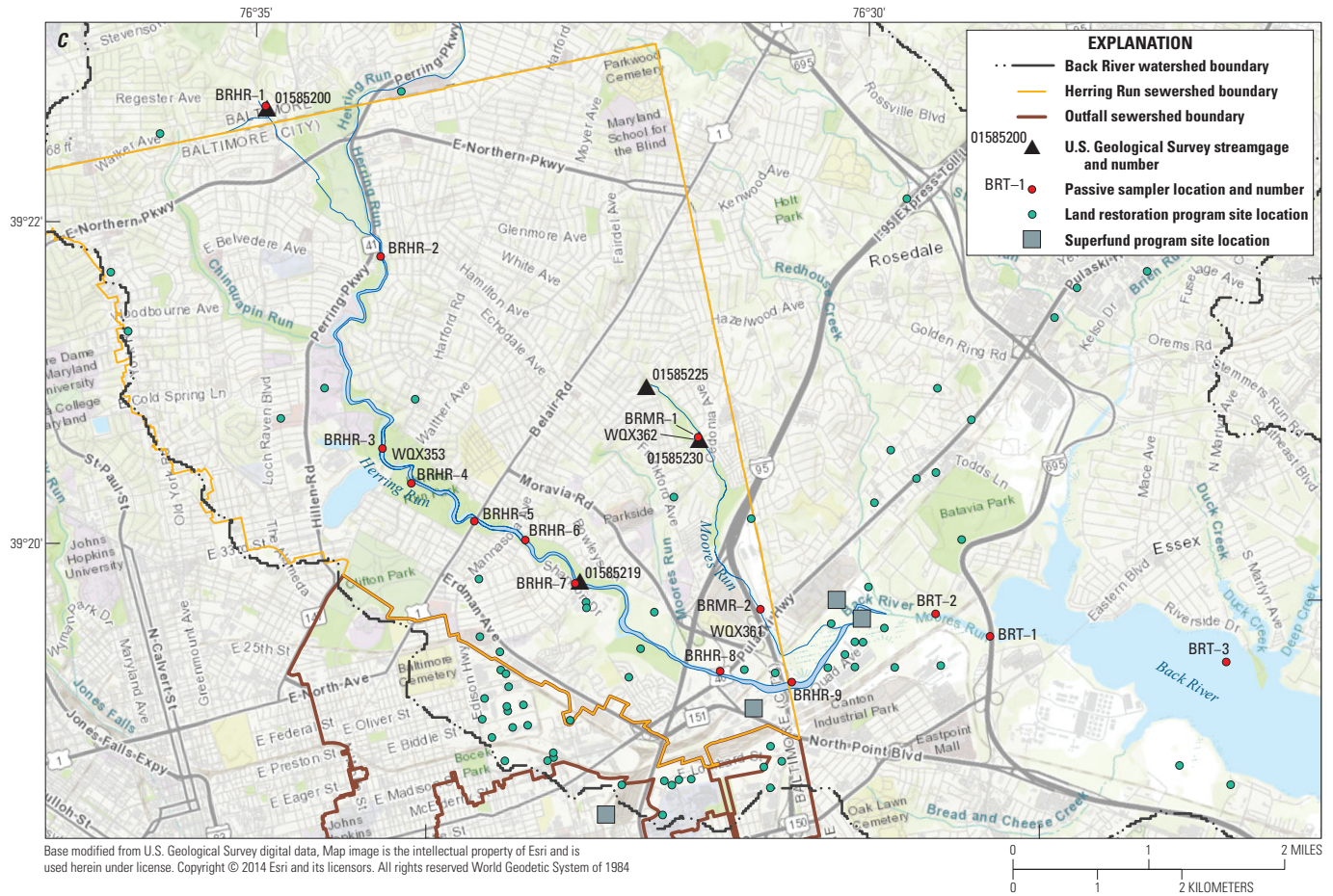
**Figure 13.** Locations of U.S. Geological Survey streamflow gages, current study passive samplers, and A, former total maximum daily load (TMDL) samples (adapted from Maryland Department of the Environment [MDE], 2011), B, 2018 National Pollutant Discharge Elimination System (NPDES) permits (MDE, 2021a), C, State of Maryland land restoration program and Federal Superfund sites (MDE, 2011, 2021b), and D, sanitary sewer overflows (SSOs) from 2015 to 2019 (MDE, 2021c).





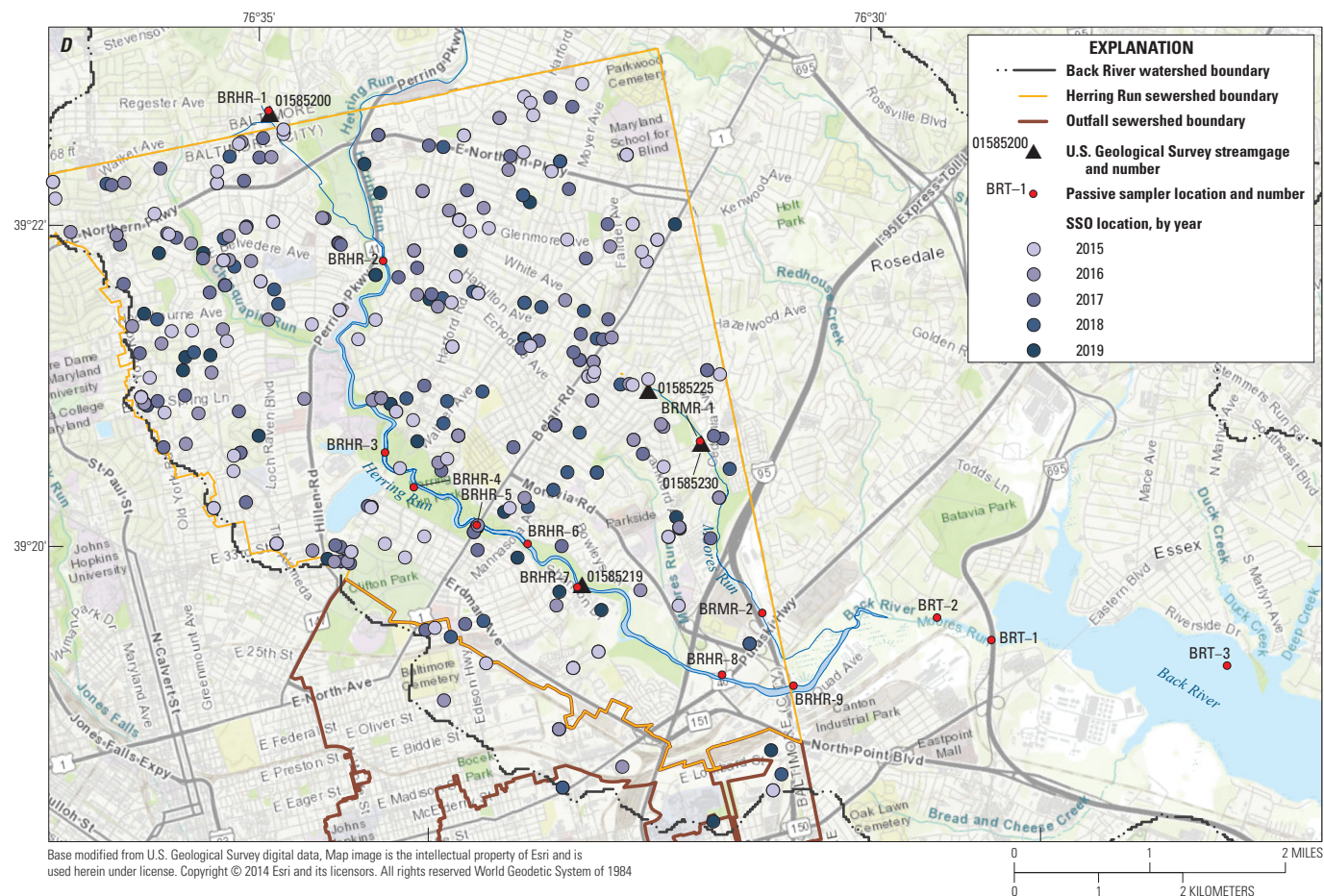
**Figure 13.** Locations of U.S. Geological Survey streamflow gages, current study passive samplers, and *A*, former total maximum daily load (TMDL) samples (adapted from Maryland Department of the Environment [MDE], 2011), *B*, 2018 National Pollutant Discharge Elimination System (NPDES) permits (MDE, 2021a), *C*, State of Maryland land restoration program and Federal Superfund sites (MDE, 2011, 2021b), and *D*, sanitary sewer overflows (SSOs) from 2015 to 2019 (MDE, 2021c).—Continued





**Figure 13.** Locations of U.S. Geological Survey streamflow gages, current study passive samplers, and *A*, former total maximum daily load (TMDL) samples (adapted from Maryland Department of the Environment [MDE], 2011), *B*, 2018 National Pollutant Discharge Elimination System (NPDES) permits (MDE, 2021a), *C*, State of Maryland land restoration program and Federal Superfund sites (MDE, 2011, 2021b), and *D*, sanitary sewer overflows (SSOs) from 2015 to 2019 (MDE, 2021c).—Continued





**Figure 13.** Locations of U.S. Geological Survey streamflow gages, current study passive samplers, and *A*, former total maximum daily load (TMDL) samples (adapted from Maryland Department of the Environment [MDE], 2011), *B*, 2018 National Pollutant Discharge Elimination System (NPDES) permits (MDE, 2021a), *C*, State of Maryland land restoration program and Federal Superfund sites (MDE, 2011, 2021b), and *D*, sanitary sewer overflows (SSOs) from 2015 to 2019 (MDE, 2021c).—Continued

## Assessment of PCBs Under Low-Flow Conditions

Both passive sampling and high-volume sampling were used to assess PCB presence under low-flow conditions in the nontidal streams and upper tidal reaches of Back River and are described in this section of the report. These approaches were compared, an assessment of flux between the sediment and water column using the passive sampling results was calculated and loading to Back River from these areas was estimated for the timeframe of sample deployment.

### Surface Water

Freely dissolved PCB concentrations in the water column ranged from 0.50–1.9 ng/L in Herring Run, 2.4–2.8 ng/L in Moores Run, and 1.0–1.2 ng/L in the upper reaches of tidal Back River (fig. 14). The average freely dissolved PCB concentrations in Herring Run and the tidal portion of

Back River were approximately 1.0 ng/L, while the average concentration in Moores Run was 2.6 ng/L. Concentrations detected in Moores Run being twice that measured in Herring Run or Back River samples may reflect a different or more accessible source in the Moores Run drainage area or may reflect the lower streamflow discharge compared to Herring Run. Maximum concentrations in both Herring and Moores Run were detected in the most upstream sites, which may suggest the presence of watershed sources.

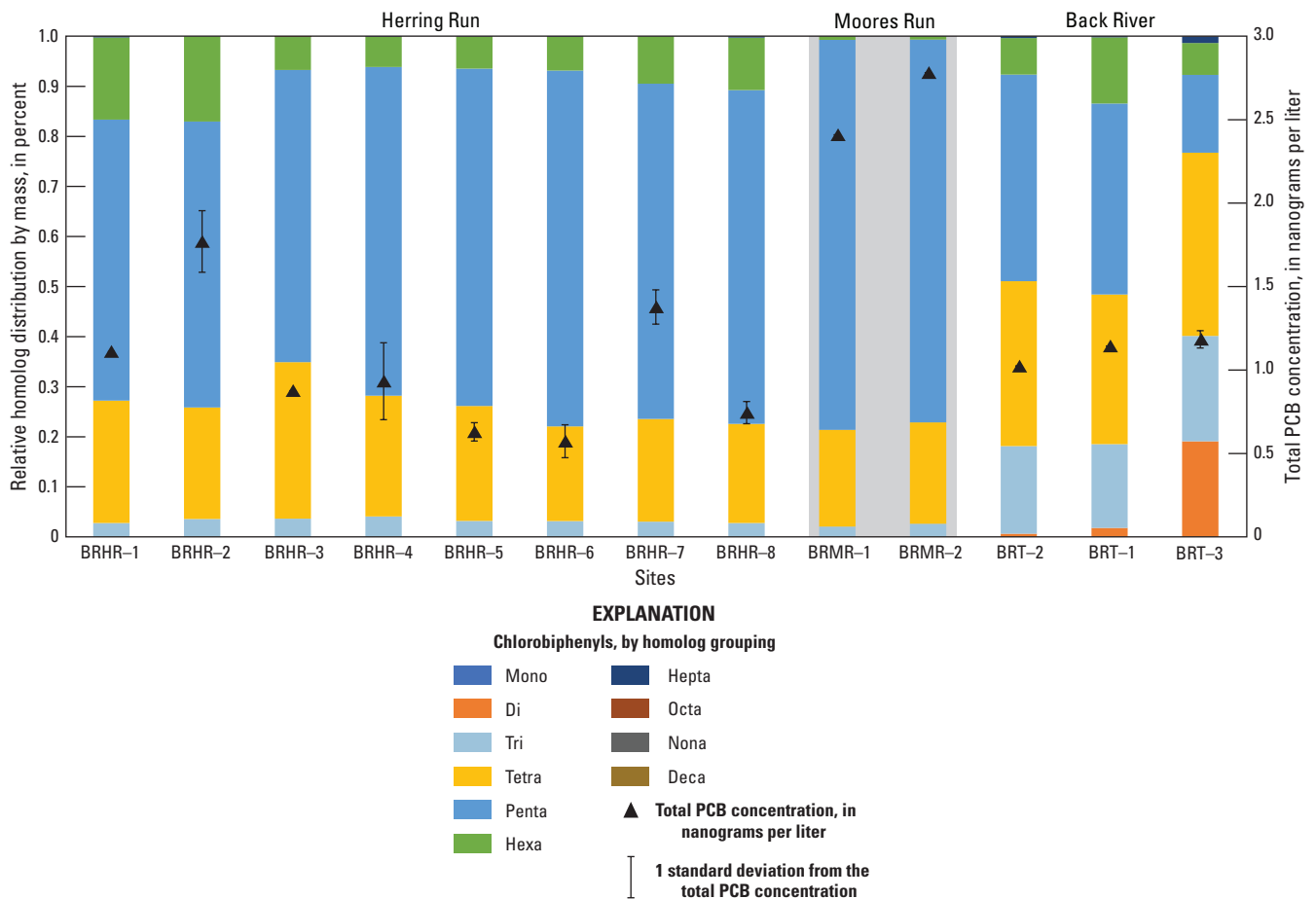
Homolog distributions are generally similar among all sites in Herring Run and Moores Run, both dominated by pentachlorobiphenyls (fig. 14). However, samples from the upper tidal area of Back River showed an increase in di- and trichlorobiphenyls compared to the nontidal tributaries. The freely dissolved concentration and dichlorobiphenyls increased from the most upstream site (BRT–2) to the most downstream site (BRT–3).

Results of this study were compared to the 2018 Baltimore County tributary study (Joshee and others, 2019) since similar sampling and analysis methods were used

(fig. 15). Concentrations detected in samples from the tidal Back River in this study (about 1 ng/L) were similar in magnitude to PCBs detected in 2018 at the upstream part of Back River (BRUS) (0.99 ng/L). In general, PCB concentrations detected in nontidal streams in the County in 2018 were similar to concentrations detected in nontidal streams in the City of Baltimore as part of this study, with the exception of concentrations detected in Longs Creek (BRLC\_2) that is located near the confluence of Back River and Chesapeake Bay (fig. 3). Homolog distribution profiles in the two studies were similar among Herring Run, Moores Run, a northeast Branch of Back River (BRNE\_1, BRNE\_2), and Redhouse Creek (BRRH\_1, BRRH\_2). The most downstream location sampled in Bread and Cheese Creek (BRBC\_1) also had a higher proportion of dichlorobiphenyls than the upstream site (BRBC\_2) and was similar to the concentration measured and homolog patterns found in BRT-3 of the current study.

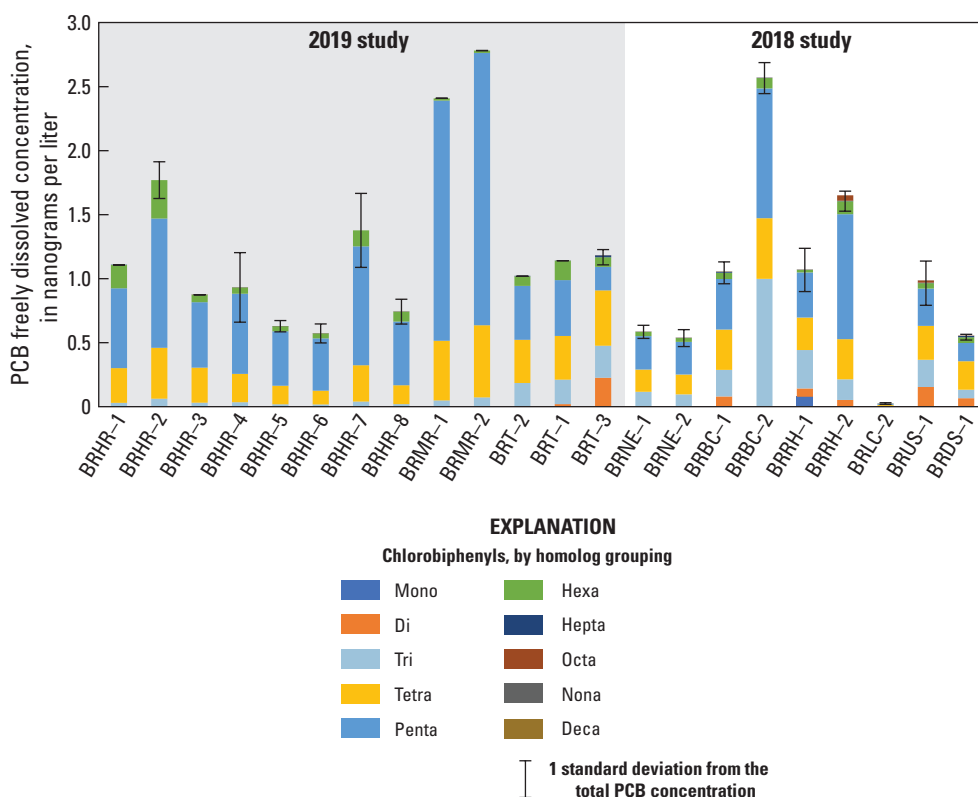
Water column concentrations reported in the TMDL were not directly comparable to the freely dissolved PCB concentrations reported here since different sampling and analysis methods were used (grab samples versus time-integrated measurements and dissolved versus freely dissolved in the TMDL and current study, respectively); however, relative comparisons can be made at the common sites sampled in 2000 and 2001 and the present study.

In general, maximum concentrations were detected in samples collected upstream within the study area (as observed in WQX352 and BRHR-2) and declined downstream (as observed in WQX353 and BRHR-3, figs. 4, 13A, table 2). Average PCB concentrations detected in samples collected in Moores Run were consistent across the stream in both studies (B362 and BRMR-1, B361 and BRMR-2, table 2) (Maryland Department of the Environment, 2011). Similarities between the two studies were also observed in the tidal portion of Back River where PCB concentrations were elevated upstream compared to the downstream sampling areas.



**Figure 14.** Freely dissolved concentration and relative homolog distribution of polychlorinated biphenyls (PCBs) measured from the water column at various locations in Herring Run, Moores Run, and tidal Back River. PCB, polychlorinated biphenyl; BRHR, Back River Herring Run; BRMR, Back River Moores Run; BRT, Back River tidal; error bars represent standard deviation.





**Figure 15.** Water column concentrations and homolog distribution comparing studies from 2019 (current study in City of Baltimore) and 2018 (Baltimore County, Joshee and others, 2019, 2020) in the Back River watershed. BRHR, Back River Herring Run; BRMR, Back River Moores Run; BRT, Back River tidal; BRNE, northeast branch of Back River, BRBC, Back River Break and Cheese Creek; BRRH, Back River Redhouse Creek; BRUS, Back River Mainstem upstream; BRDS, Back River Mainstem downstream; BRLC, Back River Longs Creek; PCB, polychlorinated biphenyl; error bars represent standard deviation.

## Porewater

Porewater PCB concentrations ranged from 0.66–3.5 ng/L, with the minimum concentration detected at BRHR–6 and the maximum concentration detected at BRT–3 (fig. 16). Porewater concentrations and homolog distributions for all sites in Herring Run and Moores Run were similar to their respective water column concentrations as shown in figure 16. The highest porewater concentration detected in the nontidal streams was at location BRMR–1, similar to the concentration detected in the water column at that location. This similarity between porewater and water column concentration at this location suggests that the net flux of PCBs between porewater and the water column is small. The similarities in concentrations between porewater and surface water concentrations was consistent with the sandy texture of the bed sediment observed in Herring Run and Moores Run. PCB concentrations detected in sediment were low and ranged from 1.4 nanogram per gram (ng/g) dry sediment at BRHR–7 to 10 ng/g dry sediment at BRHR–1) (fig. 17). These results suggest that the surface bed sediment of

Herring Run and Moores Run are likely not the source for the elevated freely dissolved PCB concentrations measured in the water column.

As seen in figure 16 the highest porewater concentrations were detected in tidal Back River at the most downstream site, BRT–3 (3.5 ng/L). PCB concentrations detected in the porewater of the two most downstream sites (BRT–1 and BRT–3) were two- to three-times higher than concentrations detected in the water column, which suggests that porewater may act as a PCB source to the overlying water column at these locations. The most upstream site in the tidal portion of Back River, BRT–2, had the lowest porewater concentration of the three BRT sites that was like the surface water concentration at these sites.

## Flux and Loading Estimates

Flux plots were created using methods adapted from Apell and others (2018) for each site with colocated water column and porewater measurements using passive samplers as seen in figure 18. Net fluxes ranged

from -73 to 233 nanograms per meter square per day (ng/m<sup>2</sup>/d) in Herring Run, -382 to -113 ng/m<sup>2</sup>/d in Moores Run, and 36 to 772 ng/m<sup>2</sup>/d in the tidal Back River. The high positive flux observed at the tidal Back River indicated that the bed sediment may be a PCB source to the water column. Positive fluxes (upward) at these sites were driven by higher porewater PCB concentrations as opposed to lower water column PCB concentrations. In contrast, the negative (downward) fluxes at the two Moores Run sites were driven by relatively high water-column PCB concentrations despite relatively high porewater PCB concentrations. Among the Herring Run sites, fluxes were relatively low (below 150 ng/m<sup>2</sup>/d), suggesting that these sites are probably in equilibrium, except at BRHR-1 where higher positive net flux (233 ng/m<sup>2</sup>/d) was observed. This site, BRHR-1, had one of the highest water column concentrations measured, the highest porewater concentration, and the highest PCB concentration in bed sediment from all Herring Run sites. This positive flux from bed sediment to water column was unexpected considering the sandy/pebble texture of shallow sediment visually observed and the low organic content observed in these sediments (0.06 percent and below MDL; Foss and others, 2022).

To further understand the contribution of PCBs to the Back River from the nontidal streams in the City of Baltimore, loading estimates were conducted using streamflow data during low-flow conditions for the relevant deployment dates. PCB loads to the Back River from Herring Run and Moores Run were calculated based on the freely dissolved PCB concentrations, DOC measurements, POC measurements, and streamflow data from gages in the watershed (U.S. Geological Survey, 2020a,b) for all necessary deployment periods.

The freely dissolved PCB concentrations measured in passive samplers nearest to the streamflow gages, BRHR-7 and BRMR-1, were used for the loading estimates.

Calculations of low-flow loads from Herring and Moores Run during the passive sampler investigation were estimated as time-weighted averages for the timeframe corresponding to the deployment window according to the following series of equations to account for the freely dissolved, and DOC- and POC-associated fractions:

$$C_{DOC} = [C_{Free} \times 106] \times [DOC] \times K_{DOC} \quad (7)$$

where

- $C_{free}$  is the freely dissolved concentration (in nanograms per liter),
- $DOC$  is the dissolved organic carbon concentration (in milligrams per liter), and
- $C_{DOC}$  is the concentration associated with the DOC-fraction (in milligrams per liter).

$$\log K_{DOC} = 0.71 \log K_{ow} - 0.5 \quad (8)$$

where

- $K_{ow}$  is the octanol-water partitioning coefficient (unitless), and

- $K_{DOC}$  is the dissolved organic carbon coefficient (unitless).

$$C_{POC} = C_{Free} \times f_{OC} \times C_{SS} \times K_{OC} \times \quad (9)$$

(unit conversion factor)

where

- $f_{OC}$  is the fraction organic carbon (unitless),
- $K_{OC}$  is the organic carbon partitioning coefficient (in liters per kilogram),
- $C_{SS}$  is the concentration of suspended solids collected during the deployment period (in milligrams per liter), and
- $C_{POC}$  is the concentration associated with the POC-fraction (in milligrams per liter).

These fractions were summed to provide an estimate of total PCB concentration,

$$C_{Total} = C_{Free} + C_{DOC} + C_{POC} \quad (10)$$

where

- $C_{total}$  is the total PCB concentration (in milligrams per liter).

The low-flow load was calculated as shown in [equation 11](#) using the total PCB concentration during the low-flow sampling timeframe in [equation 10](#) and the low-flow discharge measured at the nearest streamflow gage.

$$L_{LF} = C_{total} \times Q_{LF} \times \text{(unit conversion factor)} \quad (11)$$

where

- $Q_{LF}$  is the low-flow discharge (in liters per second), and
- $L_{LF}$  is the low-flow load (in grams per day).

The low-flow load from Herring Run was estimated to be 0.163 g/d for the deployment period, with 82, 2, and 16 percent associated with the freely dissolved, DOC, and POC fractions, respectively. Moores Run had a load of 0.024 g/d, with 90, 2, and 8 percent associated with the freely dissolved, DOC, and POC fractions, respectively. Even though higher freely dissolved PCB concentrations were observed in Moores Run compared to Herring Run, low-flow loading to Back River was about one fifth that of Herring Run due to much lower measured discharge. Extrapolated across the year as a generalized estimate, PCB loading in Herring Run and Moores Run would be 59.50 and 8.76 grams/year, respectively.

Similarly, concentrations from BRHR-1 (West Branch Herring Run at Idlewylde) were used to estimate loading entering Herring Run at the City of Baltimore northern boundary. Despite the higher concentration at BRHR-1 compared to other downstream sites in Herring Run, the load was estimated to be 0.01g/day, with 100 percent associated with the freely dissolved fraction. Extrapolated to an annual basis, this would be approximately 3.65 grams/year entering Herring Run from Baltimore County.

## High-Volume, Low-Flow PCB Sampling Challenges

Due to the low SS concentrations during low-flow, high-volume sampling and possible mass loss from the glass fiber filter during the sample collection process, an accurate mass of the SS accumulated on the filter could not be measured. TSS was, however, measured concurrently from grab samples at the same location and ranged between 0.87 and 2.75 mg/L with an average concentration of 1.56 mg/L ( $\pm 0.57$ ,  $n=8$ ). The POC concentration ranged between 7 and 17 percent with an average value of 12 percent ( $\pm 4$ ,  $n=8$ ). The total volume of filtered water was 1,031 L, collected over a 7-hour period on December 11, 2018 (fig. 19A).

A total of four whole filters were extracted for PCBs, and the total mass of PCBs extracted from these filters was 1.05 micrograms ( $\mu\text{g}$ ). The homolog distribution was primarily tri- (29 percent), tetra- (26 percent), and pentachlorobiphenyl (35 percent) (fig. 20). The estimated mass of solids collected on filters during the low-flow sampling was 1.61 g based on the volume of water filtered and the TSS measured in grab samples taken during the low-flow sampling. This sampling method assumes that only PCBs bound to the SS were sequestered by the glass fiber filter and that nearly all PCBs in the freely dissolved phase passed through the filter. Using the estimated mass of solids collected, the TSS grab sample concentration would result in a calculated total PCB concentration of 652 ng/g by dry weight. This calculated concentration exceeded the range of all observed concentrations for all solids samples collected during this study. It is suspected that due to the large volume of surface water needed to capture a measurable quantity of solids, PCBs from other phases within the bulk water were also accumulated by the filter, as described by others (Maske and Garcia-Mendoza, 1994; Karl and others, 1998).

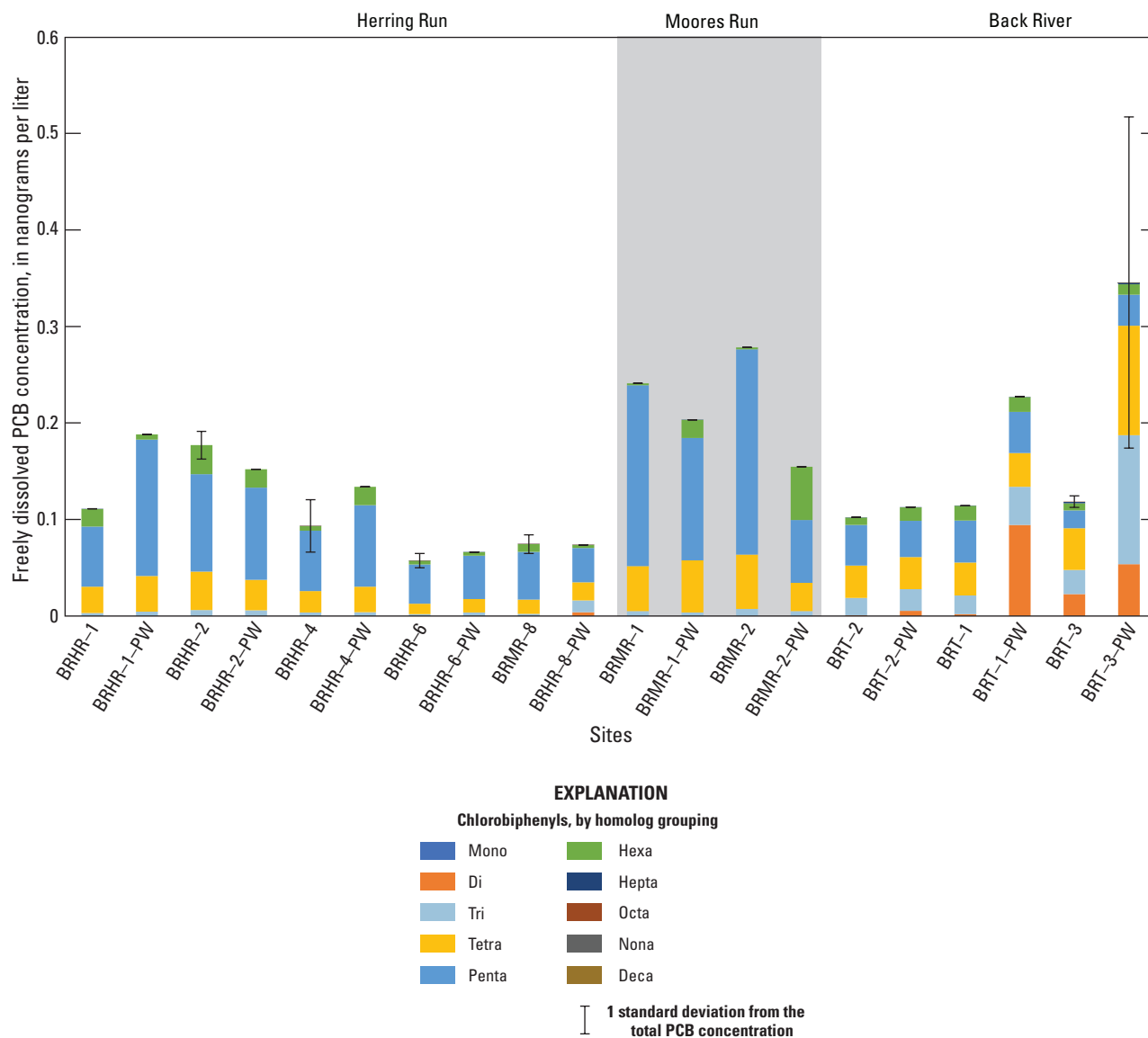
For comparison, the bulk water concentration was estimated from the freely dissolved concentration measured from the nearest upstream passive sampler location (BRHR–8). The bulk water consisted of all phases within the surface water column to include TSS, DOC, and the freely dissolved fractions. Using this method, the PCB concentration of the bulk water was estimated at BRHR–8 to be 0.85 ng/L total PCBs with the freely dissolved fraction contributing the largest portion of the mass. If it is assumed that the mass extracted from the filters represents the total PCBs within the

bulk water, then the bulk water concentration measured by the low-flow sampling can be estimated by the total mass of PCBs extracted from the filters (1.61 g) divided by the total volume of water filtered (1,031 L). This resulted in a bulk water PCB concentration of 1.02 ng/L total PCBs, which is within 20 percent of the concentration measured through passive samplers. Due to uncertainty in the low-flow, high-volume sampling results, the low-flow loading was calculated using the passive sampler results only and is not presented for the low-flow, high-volume method. These results suggest that the passive sampler approach may more appropriately represent the PCB concentrations and loading under low-flow conditions and can address a larger footprint within the study area.

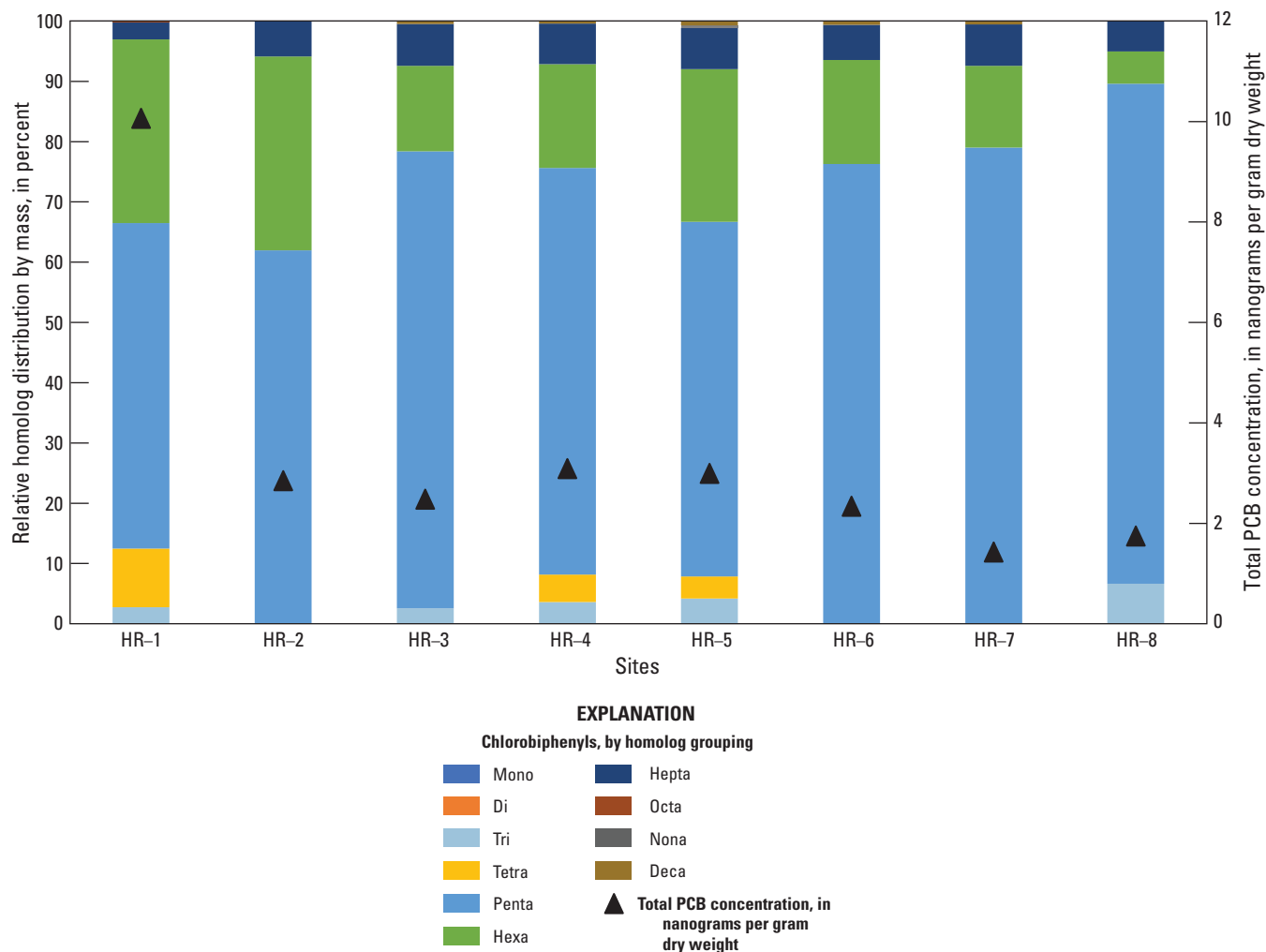
## TSS in Herring and Moores Run

Since the current study of Herring Run included a single low-flow and single stormflow, high-volume sampling event in different seasons, and passive sampling was integrated over several months of one water year, it is valuable to look at the historical data record for TSS in Herring and Moores Run to understand how representative these events are in the period of record for the various SIS sites. TSS concentrations can influence PCB loading over time since at least a portion of the PCB load is associated with TSS in the system. Mean TSS throughout Herring Run (four sites between BRHR–2 and BRHR–8; 1,170 total records collected between 1997 and 2019) was 4.72 mg/L with a maximum detected concentration of 287 mg/L (City of Baltimore, 2020a). During 2019, the mean TSS concentration of all measurements at SIS Pulaski (nearby BRHR–8) was 5.4 mg/L; however, some seasonal variation was observed as shown in figure 21A. Sample collection during this study occurred in the fall and summer seasons for the low-flow, high-volume and passive sampling field efforts, respectively. Despite 2019 having greater discharge compared to annual mean discharge records for the streamflow gages in the watershed (table 1), the measured TSS appears to be generally lower during this study compared to the long-term records. Similar patterns were noted in Moores Run (SIS Radecke Avenue, BRMR–1), as shown in figure 21B.

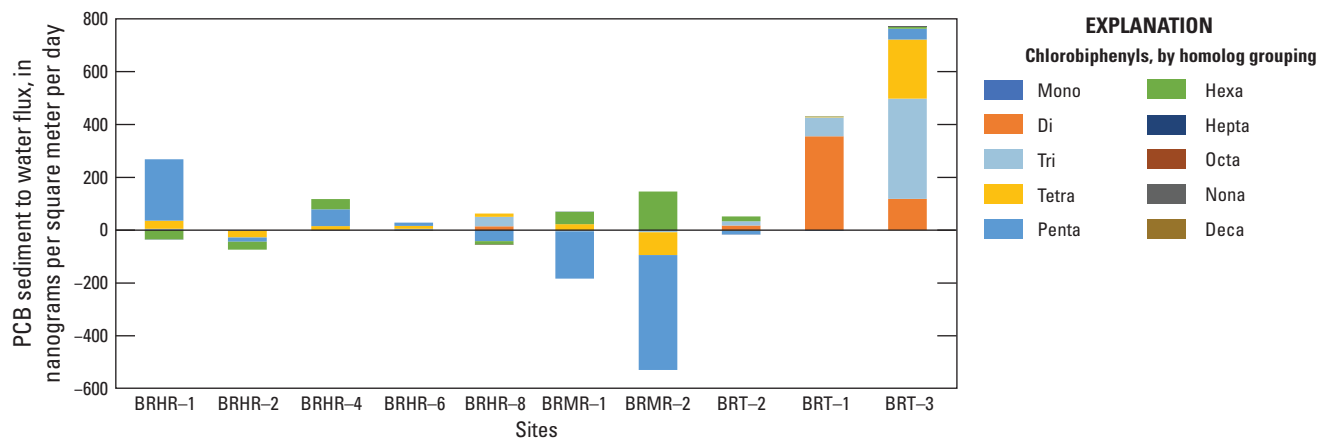




**Figure 16.** Freely dissolved concentrations and homolog distribution in water column and co-located porewater at select sample locations in Herring Run, Moores Run, and tidal Back River. BRHR, Back River Herring Run; BRMR, Back River Moores Run; BRT, Back River tidal; PCB, polychlorinated biphenyl; PW, porewater passive sampler; no PW and number only, water column passive sampler; ng/L, nanograms per liter; error bars represent standard deviation.

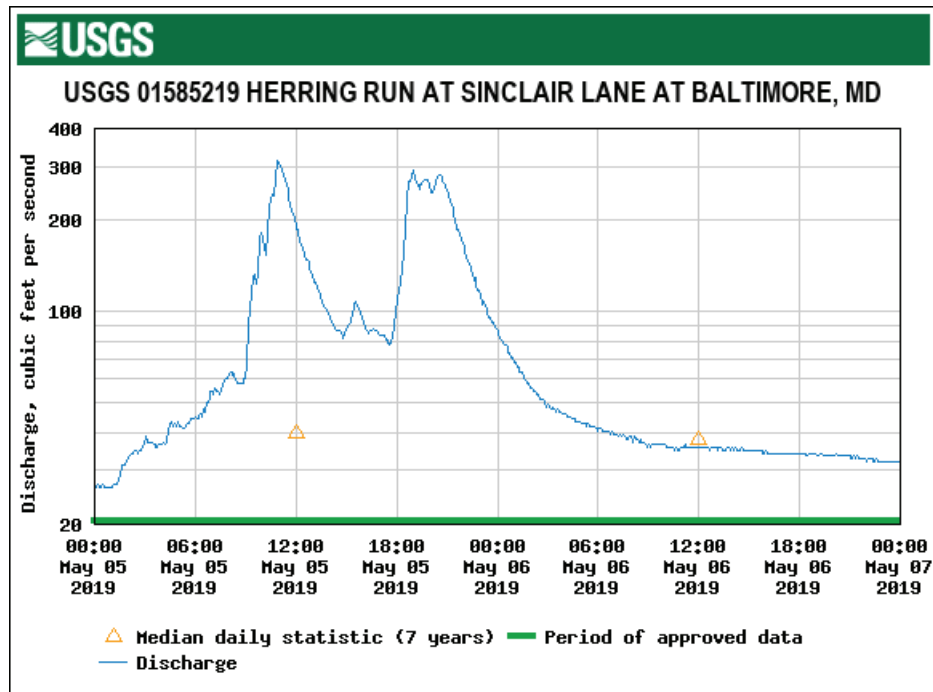


**Figure 17.** Polychlorinated biphenyl (PCB) concentration and relative homolog distribution in bed sediments in Herring Run, normalized per dry weight extracted. HR, Herring Run.

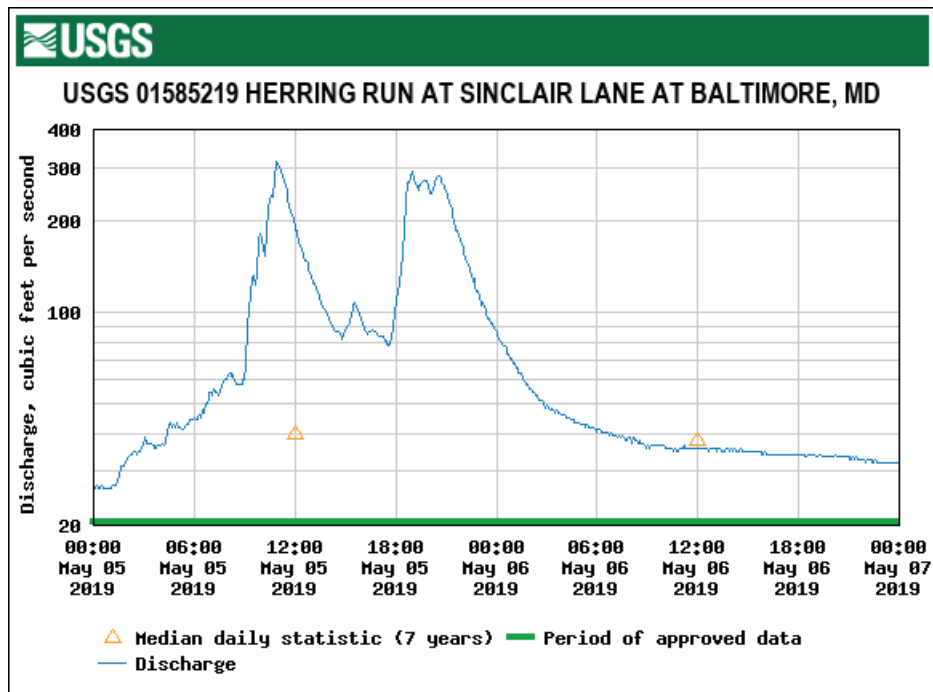


**Figure 18.** Polychlorinated biphenyl (PCB) flux between sediment and water column for select sites in Herring Run (BRHR), Moores Run (BRMR), and tidal Back River (BRT).

A

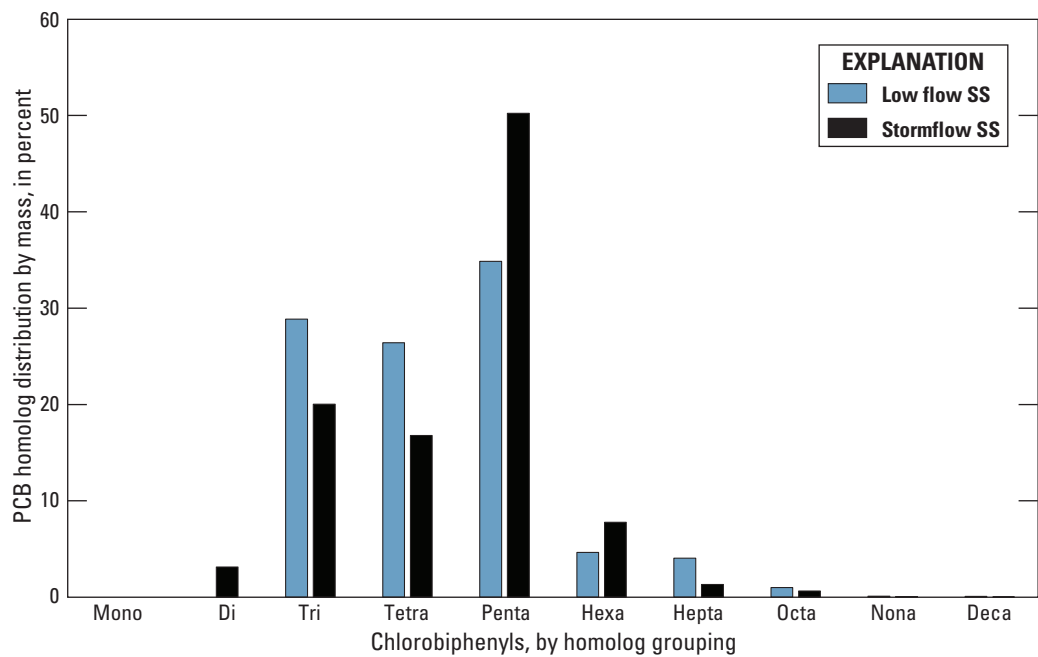


B

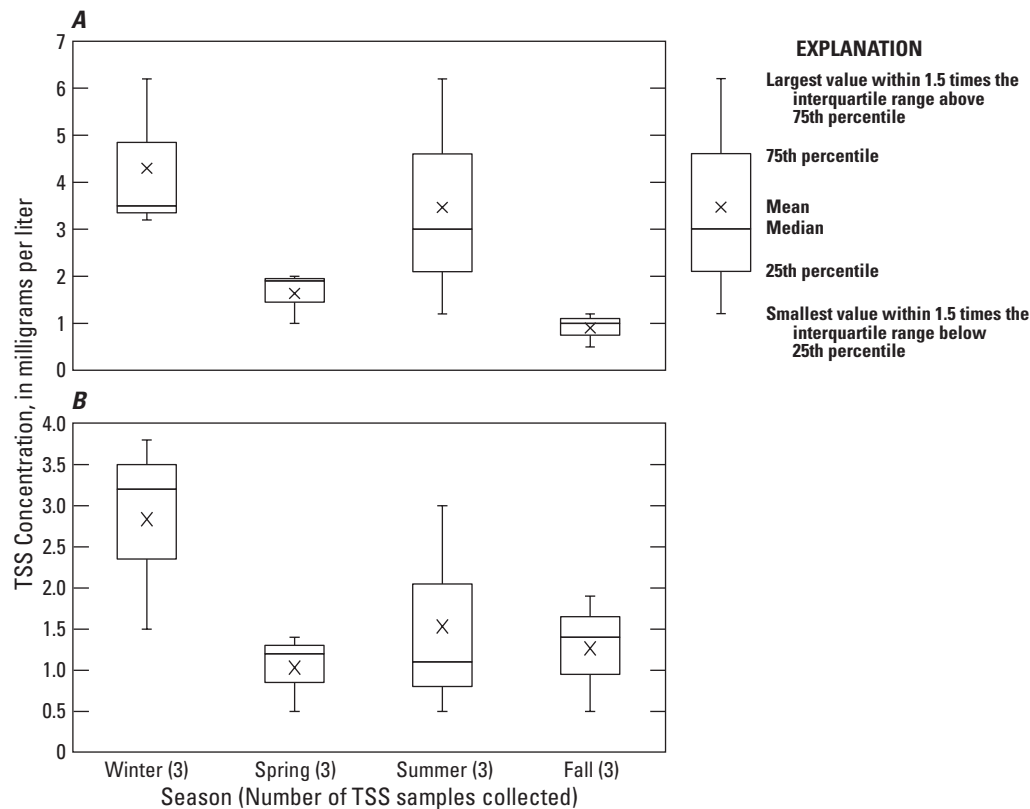


**Figure 19.** Hydrographs (discharge in cubic feet per second) from Herring Run at Sinclair U.S. Geological Survey (USGS) streamflow gage during A, low-flow sampling event, and B, stormflow sampling event (USGS, 2020b). MD, Maryland.





**Figure 20.** Percent polychlorinated biphenyl (PCB) homolog distribution by mass for high-volume, low-flow and stormflow, filtered samples collected from Herring Run (December 2018, May 2019). SS, suspended solids.



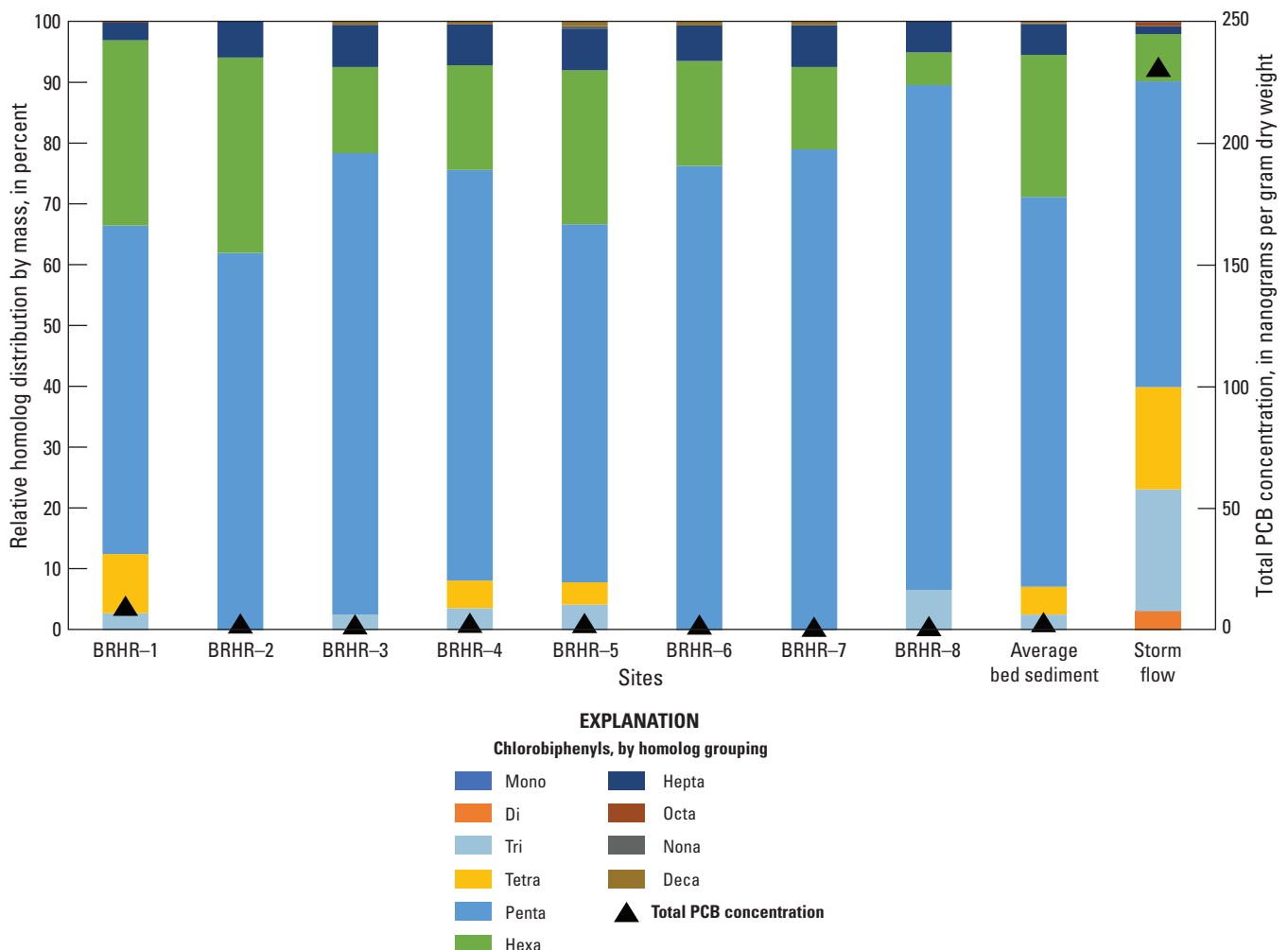
**Figure 21.** Total suspended solids (TSS) concentration collected as part of City of Baltimore Stream Impact Sampling (SIS) during 2019 study period from A, SIS Pulaski (nearby BRHR–8), and B, SIS Radecke (nearby BRMR–1) (City of Baltimore, 2020a).

## Assessment of PCBs Under Stormflow Conditions

### Herring Run Stormflow Concentrations

Stormflow sampling was conducted on May 5, 2019, from approximately 09:48 to 23:55, to capture the rising limb and crest of the storm hydrograph (fig. 19B). Less water (31 L) was required to filter a measurable quantity of sediment for analysis compared with low-flow sampling (greater than 1,000 L). Sediment collected on the filter was estimated from the 14 TSS grab samples collected between 08:30 and 12:49, completely overlapping the large volume collection period on that day. The TSS concentration of these grab samples was  $336 \pm 38$  mg/L with a  $f_{OC}$  of  $3.2 \pm 0.8$  percent. Approximately 10.4 g of solids were extracted from three glass fiber filters. Filters were extracted following the solid extraction method

described in the previous sections. The particle-associated PCB concentration in solid material extracted from the filters was 231 ng/g, significantly higher than the bed sediment concentration (average  $3.4 \pm 2.8$  ng/g,  $n=8$ ) collected from Herring Run (fig. 22). In addition, the particle-associated PCBs collected from the stormwater sample had relatively more di-, tri-, and tetrachlorinated biphenyls compared to the bed sediment samples. Pentachlorobiphenyl is the dominant homolog group in all the sediments analyzed with the dominant congener from a co-eluting group of PCB 84/89/92. For consistency with the low-flow measurements, the total mass of PCBs extracted from the filters was used to determine a bulk water concentration during stormflow. Using the 31 L filtered for the sample and a total PCB mass of 2407 ng; the bulk water concentration was calculated as 77.65 ng/L, which is an order of magnitude greater than concentrations detected in the nontidal streams of Back River during low-flow conditions.



**Figure 22.** Polychlorinated biphenyl (PCB) concentration and relative homolog distribution by mass in Herring Run bed sediments and stormflow, filtered solids collected using high-volume sampling. BRHR, Back River Herring Run.

Herring Run PCB Stormflow Event Load

The storm event load of PCBs to Herring Run was calculated based on [equation 12](#),

$$L_{SF} = Q_t \times C_{PCB} \tag{12}$$

where

- $Q_t$  is the discharge measure by USGS streamflow gage 01585219 (U.S. Geological Survey, 2020b) (in cubic feet per second over the storm event timeframe),
- $C_{PCB}$  is concentration of PCBs in bulk stormwater measured from filters (in grams and surface water filtered in liters), and
- $L_{SF}$  is PCB storm event load (in grams per day).

The PCB load associated with the storm event over the 14-hour sampling period is 16.6 g. The load calculation assumes that the mass of PCBs collected on the filters represents an average concentration over the sampling period. Given the low concentrations observed in the bed sediment and the surface water during low-flow conditions, the elevated concentrations in the stormflow suggest inputs from surrounding drainage areas to Herring Run. Stormwater sewers in the surrounding old industrial and residential area drain stormwater and its contents into Herring Run. The age of the surrounding building and industrial sites coincides with the commercial widespread use of PCBs from 1950 to 1978 which could be found in materials such as caulks, paints, and cooling oils (U.S. Army Corps of Engineers, 2012; Klosterhaus and others, 2014). The PCB load associated with the sampled storm event was two orders of magnitude greater than the daily low-flow loading, approximately 29 percent of the total annual PCB load coming from low flow in a single event. During WY2019, 27–33 storm events defined as peaks above discharge (99.5 percent annual exceedance probability [AEP]) were observed, with one event being bankfull discharge (or 66.67 percent AEP). Although the event measured met the criteria for sampling (greater than 75th percentile annual discharge), it was below the base discharge for the 99.5 percent AEP; therefore, this storm is likely a conservative estimate of a more typical event load during the

WY ([table 10](#)). The bankfull, channel forming event was an order of magnitude greater discharge than what was measured during the calculated PCB event load. Using the PCB event load as a conservative estimate for events during WY2019, the annual load during storm flow in 2019 would likely exceed 400 grams/year.

Solid materials accumulated on the road next to storm-water drains were sampled to identify potential sources of PCBs associated with stormwater runoff. The elevated levels of PCBs observed during the stormflow sampling and low PCB concentrations found in the bed sediments of Herring Run and Moores Run (1.4–10 ng/g) are consistent with another source of particle-associated PCBs to stormflow (assuming similar masses from both sources). The two Herring Run stormwater drain samples contained 34 ng/g dw total PCBs and the Moores Run stormwater drain contained 19 ng/g dw total PCBs, all higher than PCB concentrations in bed sediments from these streams ([fig. 17](#)). In addition, the homolog distribution between the samples varied as illustrated in [figure 23](#). The sample collected in the upstream section of Herring Run (SD–BRHR–2) contained the highest relative percentage of lower chlorinated congeners as mono-(32 percent), di-(2 percent), and trichlorobiphenyl (14 percent) by mass. The downstream sample collected at BRHR–7, contained higher relative percentages of higher chlorinated congeners as octa- (21 percent) and nonachlorobiphenyl (9 percent) by mass. The sample collected from Moores Run (SD–BRMR–1) was dominated by the mid-range congeners tetra-(18 percent), penta-(18 percent), hexa-(19 percent), and heptachlorobiphenyl (19 percent) by mass.

The differences in PCB homolog relative abundance among the three stormdrain material samples may reflect different sources. Atmospheric PCB inputs, because they are likely homogenous on this small spatial scale, can probably be ruled out as a major source to these samples. In contrast, aging building materials that are expected to be more heterogeneously located in the study area might explain the differing homolog profiles in storm drain materials. Additional information and sampling are needed to determine the source(s) and influence this type of soils have on the stormwater loading to Back River. Sediment source fingerprinting coupled with PCB congener profiles may provide additional source tracking capabilities to identify areas of concern to reduce stormwater PCB loads.

**Table 10.** Annual exceedance probability discharge and number of peaks exceeding discharge during water year 2019.

[AEP, annual exceedance probability; ft<sup>3</sup>/s, cubic foot per second; WY, water year]

Gage number/name	Discharge 99.5 percent AEP (ft <sup>3</sup> /s)	Number of peaks above 99.5 percent AEP (WY2019)	Discharge 66.67 percent AEP (ft <sup>3</sup> /s)	Number of peaks above 66.67 percent AEP
01585200 West Branch Herring Run at Idlewylde	110.9	33	665.1	9
0158519 Herring Run at Sinclair Avenue	551.7	27	4,185	1
01585230 Moores Run at Radecke Avenue	570.7	10	1,795	1



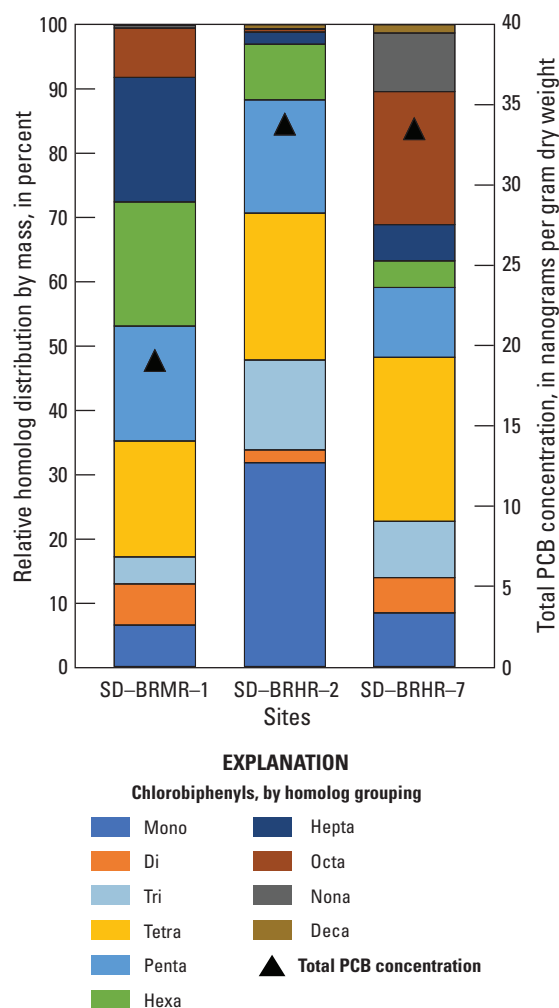
## Stream and Watershed Sources Summary

PCB concentrations in the water column of both nontidal streams were relatively consistent throughout both tributaries with the exception of upstream porewater sample in Herring Run (BRHR-1). Nearly all sample concentrations in the water column exceeded the human health target compliance endpoint of 0.57 ng/L but were below the freshwater aquatic life concentration threshold of 14 ng/L established in the TMDL (Maryland Department of the Environment, 2011). Examination of shallow bed sediment grab samples in Herring Run and porewater PCB concentrations in both tributaries did not reveal shallow, stationary, legacy sources remaining in the streams (with flux from sediment to water only present possibly in the farthest upstream location at BRHR-1). Bed sediments in Herring Run were low in organic carbon content and had a sandy, cobbly texture, and relatively low PCB concentrations (less than 4 ng/g), except at BRHR-1, which was closer to 10 ng/g. These concentrations were below the target compliance sediment endpoint that is protective of the benthic organisms (6.9 ng/g; Maryland Department of the Environment, 2011) except near BRHR-1.

The bulk of PCB mass entering the system from these nontidal tributaries appears to be primarily introduced through particle-associated delivery during storm events. While only one storm event was sampled and concentrations quantified, solids captured during the storm were characterized by elevated PCB concentrations and overall SS concentrations (fig. 22). While this sampling methodology does not assess the bioavailability of the PCBs associated with these storm sediments, this mechanism appears to warrant additional attention to better understand how concentrations vary temporally and under different storm conditions. Storm drain materials near the tributary had considerably higher PCB concentrations than stream bed sediments and may have contributed to total PCB storm loads (figs. 22 and 23). The Back River watershed has a high percentage of impervious surface and many storm drains that discharge into Herring Run through overpasses and channels. Gellis and others (2020) have shown the transport of sediment from pavement into open channels, particularly in areas with abundant developed land use and impervious surfaces, as a potential vector for the introduction of particle-bound, urban contaminants. Sediment source tracking during storm events could help elucidate the origin of sediments moving through tributaries during storms. Coupling this with an ex-situ assessment of PCB bioavailability could inform the potential impact of storm-deposited PCBs.

The observations in the tributaries were contrasted with PCB concentrations and sediment characteristics downstream of the City of Baltimore boundary, in the upper tidal area of Back River (between BRT-2 and BRT-3). An accumulation of sediments at the upper tidal area is apparent, as navigation in this portion of Back River is limited due to shallow water. This depositional environment was characterized by higher organic content and higher

concentrations of PCBs in porewater, which resulted in a predicted flux of contaminants from porewater to the water column. This flux is different than what was observed in the nontidal tributaries and may be driven by the settling of sediment particles introduced via SS in stormwater.



**Figure 23.** Polychlorinated biphenyl (PCB) concentration and relative homolog distribution by mass in storm drain materials collected nearby Herring Run and Moores Run. SD, storm drain materials; BRHR, Back River Herring Run; BRMR, Back River Moores Run.

## Assessment of PCBs in Wastewater

In urban areas, wastewater effluent can be a major driver of stream impairments. As such the BRWWTP has specific goals in the PCB TMDL (Maryland Department of the Environment, 2011). This study looked at PCBs in wastewater in the plant itself, in the primary pump stations of the City of Baltimore, and in the FOG deposits accumulating in the sanitary sewer system.

## BRWWTP

The sampling efforts at BRWWTP during this study consisted of passive samplers deployed in 3-month periods at the influent (after the city and county influent is mixed) and effluent discharge, and grab samples of the biosolids in the form of dewatered cake and pellets at the end of each 3-month period (fig. 7). Sampling the biosolids and effluent in the current study provided a point of comparison to the 16-month study previously published by Needham and Ghosh (2019) using similar methods to determine if the PCB concentrations or loading from the plant has significantly changed since 2015.

During the sampling periods in 2019, the freely dissolved concentration of PCBs in the influent ranged from 0.8 to 3.2 ng/L with the maximum concentration measured in samples recovered in November 2019 (fig. 24A). The average influent freely dissolved PCB concentration across the three deployments was 1.57 ng/L. Effluent PCB freely dissolved concentrations ranged from 1.67 to 4.93 ng/L, with the maximum measured in samples recovered in November 2019. Average effluent concentration measured during the three deployments was 2.83 ng/L (fig. 24A). The increase in effluent concentration was due to the increase of lower molecular weight, more soluble congeners, dichlorobiphenyls (homolog distribution not shown), likely from microbially mediated dechlorination of more highly chlorinated congeners occurring during anaerobic digestion of the sludge, along with decreased total solids due to the treatment process (Needham and Ghosh 2019). These results were consistent with the congener profiles reported by Rodenburg and others (2010) for a WWTP in the Delaware River Valley. Many of the lower chlorinated PCBs in the effluent were primarily found in the freely dissolved (aqueous) phase due to the removal of solids and the low DOC content of the treated wastewater. However, the freely dissolved phase of the influent represented only a small fraction of the total PCBs entering the plant due to the high quantities of organic carbon in untreated wastewater. When both the solids and the freely dissolved phases were measured in 2015, the solid phase contributed 120 times more PCBs than the freely dissolved phase (Needham and Ghosh, 2019). Concentration of PCBs in both the influent and effluent were reduced compared to 2015, by 40 and 70 percent, respectively, suggesting that management actions both up the pipe from the BRWWTP and within the BRWWTP itself may have reduced PCBs to and from the plant (fig. 24A). Since a grab sample of the influent was not collected as part of this study, a total mass balance on PCBs in the plant was not estimated; however, the load of freely dissolved PCBs between 2015 and 2019 was compared using the following calculations:

$$L_{free} = C_{free} \times Q_{event} \times (\text{unit conversion factor}) \quad (13)$$

where

- $C_{free}$  is the freely dissolved PCB concentration (in nanograms per liter),
- $Q_{event}$  is the discharge during the deployment period

(in liters per second), and  
 $L_{free}$  is the freely dissolved PCB load (in grams per day).

Similar to the pattern observed in PCB influent concentrations, influent freely dissolved PCB loads were lower in this study compared to 2015 (fig. 24B). Concentrations in effluent, which contained mainly freely dissolved PCBs since the solids and DOC have been removed by design, were used to calculate freely dissolved effluent PCB loads using flow data from the BRWWTP. The effluent load decreased from 4.6 g/d (2015) to  $1.4 \pm 0.6$  g/d (2019) in the freely dissolved phase (fig. 24B).

Most of the PCBs leaving the plant were determined to be associated with the biosolids in the 2015 study, as expected due to the hydrophobicity of PCBs and their affinity for organic carbon material (Needham and Ghosh, 2019). In the current study, post-centrifuged cake samples from the three WWTP deployments had PCB concentrations ranging from 279 to 285 ng/g dw. Dry pellet sample concentrations ranged from 197 to 249 ng/g dw. These concentrations are lower than the average  $760 (\pm 160)$  ng/g dry weight measured in 2015 (Needham and Ghosh, 2019). The homolog distributions were generally consistent among all biosolids samples except for the cake sample collected in May 2019 showing a higher proportion of dichlorobiphenyls (data not shown, Foss and others, 2022). The slight decrease in concentration from cake to pellet samples, along with absence of dichlorobiphenyls in pellets, can be attributed to the drying of biosolids resulting in volatilization of lower chlorinated PCBs. The total mass of PCBs leaving the plant in the form of dewatered cake or pellets was determined based on the measured concentration in the grab samples and the average quantity produced during the month the grab sample was collected (R. McEachern, Baltimore City Department of Public Works, written commun., January 2020). The total mass of PCBs and the concentration by dry weight in the solid phase are shown in figure 25A, were calculated as follows.

$$C_{BiosolidsTotal} = C_{cake} + C_{pellets} \quad (14)$$

where

- $C_{cake}$  is the concentration by dry weight in dewatered cake (in nanograms per gram),
- $C_{pellets}$  is the concentration by dry weight in pellets (in nanograms per gram), and
- $C_{BiosolidsTotal}$  is the concentration by dry weight of dewatered cake plus pellets (in nanograms per gram).

$$L = C_{BiosolidsTotal} \times Q_{WWTP} \quad (15)$$

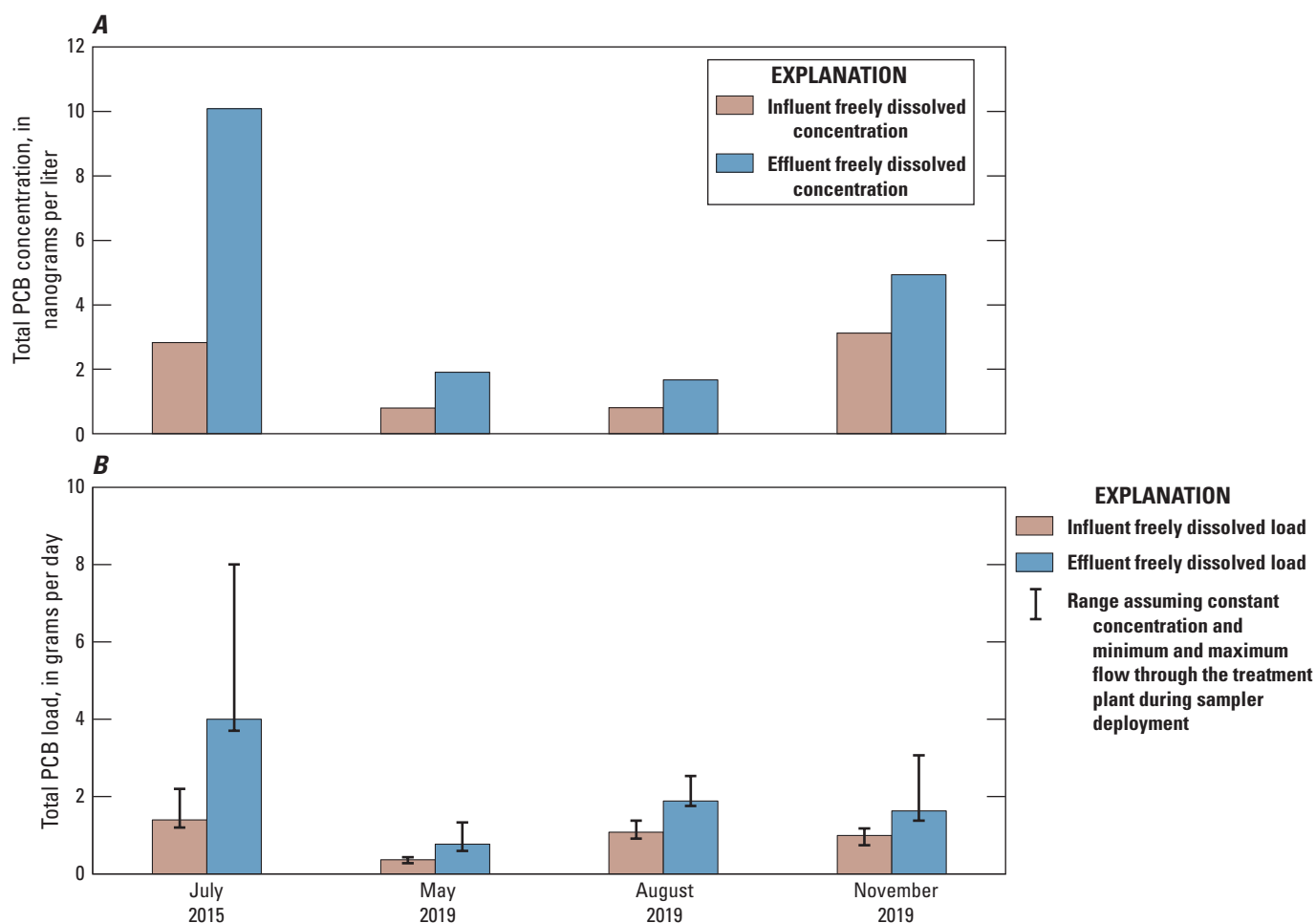
where

- $Q_{WWTP}$  is the average monthly flow through the plant during sampler collection (in liters per day), and
- $L$  is the total PCB concentration in biosolids (in grams per day).

The average load of PCBs in the cake and pellets during the 2019 sampling was  $28 \pm 3$  g/d. (fig. 25B) A comparison of the two studies shows both the total PCBs by mass and the concentration within the biosolids decreased from 2015 to 2019 (fig. 25B; Needham and Ghosh, 2019). Since 2015, as noted previously, numerous capital improvements occurred as part of the consent decree efforts in addition to ENR upgrades to the BRWWTP itself. The reduction in both the concentration and total mass of PCBs in the influent, effluent, and biosolids from 2015 to 2019 provide evidence that the load of PCBs to BRWWTP have decreased. Of note, during the 16-month sampling efforts by Needham and Ghosh (2019) from 2014 to 2015, no reductions in biosolid concentrations were observed.

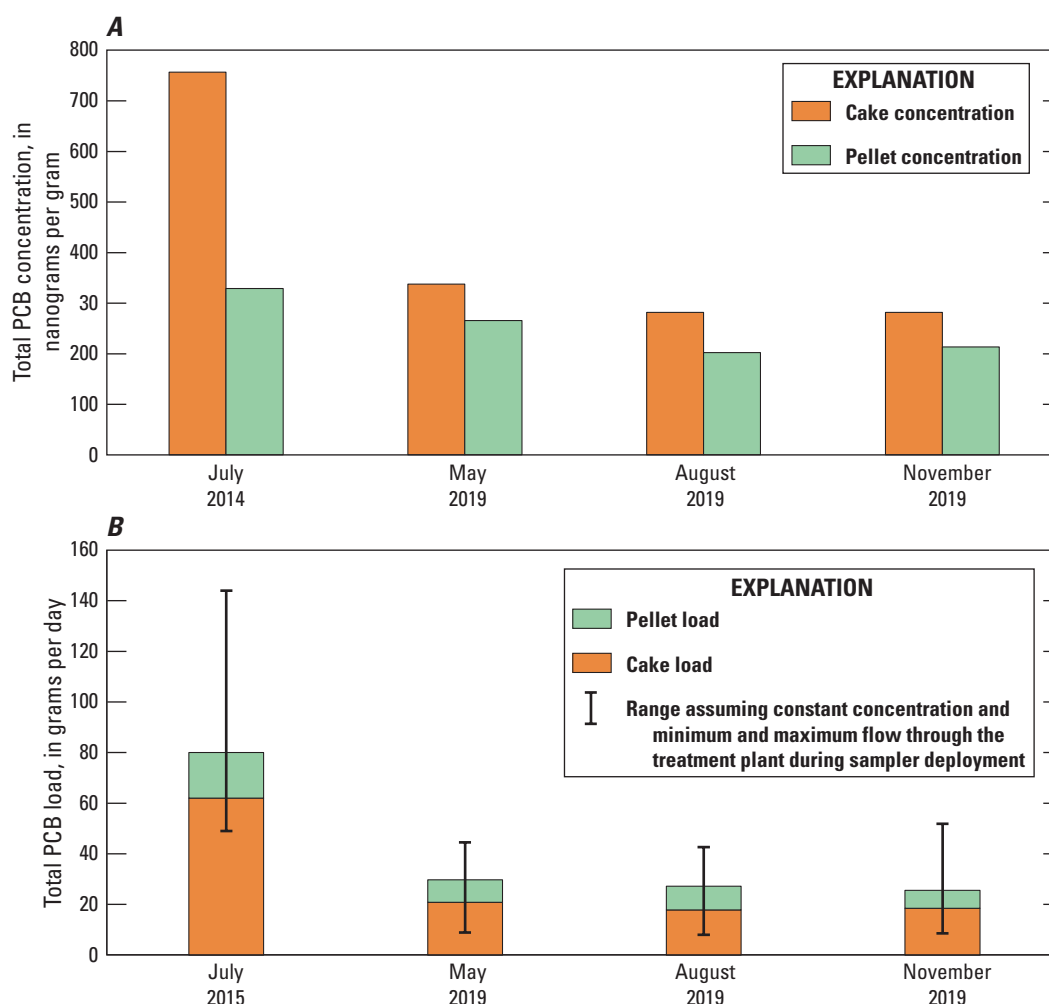
Specifically, Baltimore's improvements to the sanitary sewer system within the city likely removed legacy PCB sources to the BRWWTP.

The homolog distribution in samples collected from effluent at the BRWWTP was similar to that of tidal Back River (Foss and others, 2022, data not shown), which might indicate the BRWWTP having an impact on the water column. Specifically, there was an increase in proportion of dichlorobiphenyls from the most upstream points (as measured in BRT-2, BRT-1) to the most downstream point (BRT-3). Furthermore, the freely dissolved concentration for the BRWWTP effluent during the spring season deployment was similar to the total PCB concentration measured at BRT-3.



**Figure 24.** Total polychlorinated biphenyl (PCB) *A*, concentration and *B*, load in the influent and effluent associated with the freely dissolved phase measured by PE passive samplers at the Back River Wastewater Treatment Plant in 2019 compared to the previous study in 2015 (adapted from Needham and Ghosh, 2019). Error bars represent range assuming constant concentration and minimum and maximum flow through the treatment plant during sampler deployment.





**Figure 25.** Total polychlorinated biphenyl (PCB) *A*, concentration and *B*, load associated with the biosolids produced as pellets and dewatered cake, measured in 2019 compared to the previous study in 2015 (adapted from Needham and Ghosh, 2019). Error bars represent range assuming constant concentration and minimum and maximum flow through the treatment plant during sampler deployment.

## Primary Pump Stations in the City of Baltimore

PCB homolog distribution and loading within the BRWWTP sewer shed was assessed based on the freely dissolved PCB concentrations measured using commercially available passive samplers (SiREM SP3, Guelph, Ontario, Canada) in primary pump stations in the City of Baltimore. One of the recommendations for future actions by Needham and Ghosh (2019) was to identify areas of concern within the sewer collection system to determine if a targeted approach may be possible for reducing loads to the BRWWTP. Similar efforts have been effective in other municipalities such as the City of Camden, New Jersey (Belton and others, 2005). Freely dissolved concentration by dominant congeners or congener groups at the pump stations can be found in [table 11](#). While this mass represents only a fraction of the PCB mass in the system since it is a measurement of the freely dissolved concentration, it is helpful to infer differences between the different pump

stations and the BRWWTP influent (WWTP-1). The PCB concentration in the freely dissolved phase was greatest in Eastern Avenue Pump Station (529 pg/L, [fig. 26](#)) located in Baltimore's Inner Harbor and is one of the original structures of the sewer system installed in 1912. The Eastern Avenue Pump Station has the highest daily flow of the pump stations sampled (approximately 20 Mgal/d) and therefore dominates the system. The lowest freely dissolved concentration was observed at the Quad Avenue Pump Station (36 pg/L, [fig. 26](#)), which services the sanitary sewer system within the Herring Run watershed studied in this report. Results of the freely dissolved concentrations indicated differences in homolog distributions, and patterns were observed between the different locations of the sewer shed. The differences in the congener distributions may be the result of different sources, such as different Aroclor blends, or differential degradation and weathering of common sources within the sanitary sewer. In addition, processes such

as microbial dechlorination will shift congener profiles from higher chlorinated congeners to lower chlorinated congeners (Abramowicz, 1995).

The homolog distribution in the Eastern Pump Station was dominated by tetrachlorobiphenyls (table 12, fig. 27) and was similar to the biosolids homolog distribution observed by for BRWWTP in 2015 (Needham and Ghosh, 2019). PCB congeners 47, 49, 51, and 52 comprised 9 percent by mass of the total PCB concentration within the biosolids and 51 percent by mass of the total tetrachlorobiphenyls in the 2015 study. Biosolids sampled in August 2019 from BRWWTP contained similarly high distributions of these congeners with a 9.7 percent by mass (Foss and others, 2022). While a direct comparison of pump station and treatment plant concentrations was not possible due to the different laboratories and EPA methods used for analysis and differences in coeluting congeners, it is important to note that the tetrachlorobiphenyl congeners PCB 47, 49, 51, and 52 along with the coeluting congeners presented in table 11 represent a significantly higher fraction of the freely

dissolved concentration at Eastern Avenue Pump station (accounting for 49 percent of the total). The passive sampler deployed at BRWWTP during the same deployment window (June through August 2019) also measured elevated levels of PCBs 47 (16.2 percent), PCB 49 (6.3 percent), PCB 51 (12.2 percent), and PCB 52+42 (4.5 percent) of the freely dissolved concentration. These four PCB congeners have been reported as terminal dechlorination products of Aroclor 1260 in Baltimore Harbor sediments (Fagervold and others, 2007). Similarly, Rodenburg and others (2010) identified PCB coeluting congeners 44+47+65 and 45+51 as intermediate dechlorination product found in over 40 WWTP within the Delaware River Basin. Within the sewershed, the distributions of these congeners varied between 0 and 20.8 percent of the total PCBs in the aqueous concentration consistent with values reported by Rodenburg and others (2010). These results provide evidence that microbial degradation may be occurring within the sewer collection system. The presence of these potential dechlorination products did not appear to directly correlate with elevated freely dissolved concentrations.

**Table 11.** Dominant polychlorinated biphenyl (PCB) congeners expressed as percent of mass measured in primary pump stations of City of Baltimore.

[%  $C_{free}$ , percent by mass in concentration in the freely dissolved phase; BRWWTP, Back River Wastewater Treatment Plant]

Location	Dead Run	Dundalk	Eastern Avenue	Locust Point	McComas Street	Quad Avenue	BRWWTP influent
PCB congeners	% $C_{free}$	% $C_{free}$	% $C_{free}$	% $C_{free}$	% $C_{free}$	% $C_{free}$	% $C_{free}$
PCB 43+73	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PCB 44+47+65	9.1	5.6	20.8	13.6	4.9	11.8	12.7
PCB 49+69	0.0	3.0	5.3	5.2	4.1	11.0	5.4
PCB 45+51	0.0	0.0	18.9	0.0	0.0	8.8	8.6
PCB 52	12.9	7.2	4.0	11.5	6.0	9.6	6.7
Subtotal	22.0	15.8	49.0	30.3	15.0	41.3	33.3

**Table 12.** Freely dissolved concentrations of polychlorinated biphenyl (PCB) summed by homolog group at seven primary pump stations in the City of Baltimore.

[pg/L, picogram per liter; BRWWTP, Back River Wastewater Treatment Plant]

Location	Dead Run	Dundalk	Eastern Avenue	Locust Point	McComas Street	Quad Avenue	BRWWTP influent
Homolog group	$C_{free}$ (pg/L)	$C_{free}$ (pg/L)	$C_{free}$ (pg/L)	$C_{free}$ (pg/L)	$C_{free}$ (pg/L)	$C_{free}$ (pg/L)	$C_{free}$ (pg/L)
Mono	0	0	0	0	0	0	0
Di	0	0	0	0	0	0	0
Tri	7	65	146	19	267	7	22
Tetra	24	33	320	37	103	21	148
Penta	26	23	47	18	11	6	97
Hexa	9	4	14	7	5	2	38
Hepta	1	0	2	1	0	0	9
Octa	0	0	0	0	0	0	0
Nona	0	0	0	0	0	0	0
Deca	0	0	0	0	0	0	0
<b>Total PCBs</b>	67	124	529	81	386	36	315

Passive samplers provided an average concentration in the freely dissolved phase for PCBs and were useful in determining potential areas of concern. The freely dissolved or aqueous phase for hydrophobic contaminants such as PCBs accounted for a very small fraction of the total due to high organic material and lipid that was found in the solid material within raw wastewater. Higher chlorinated compounds have a higher affinity for organic matter and have a lower concentration in the aqueous phase. A more extensive targeted sampling effort at each pump station that would include multiple grab samples and passive sampling would be required to generate a more accurate load estimate for each pump station. However, using the PCB load associated with the solid and freely dissolved fraction from the 2015 plant mass balance (Needham and Ghosh, 2019), influent concentration can be used to estimate a load for the pump stations based on the measured freely dissolved concentration. Needham and Ghosh (2019) report mass in the solids was 120 times higher than the mass in the freely dissolved phase. This estimate assumes the composition did not change significantly since 2015 and that the composition is uniform within the collection system. This assumption affects the accuracy of the estimate since the composition of wastewater will change throughout the collection system based on the different inputs from the areas serviced and would influence PCB loads in the solids. A simplistic equation (16) estimates the total PCB load:

$$PCB_{total} = Q_{ave} \times C_{free} \times 120 \quad (16)$$

where

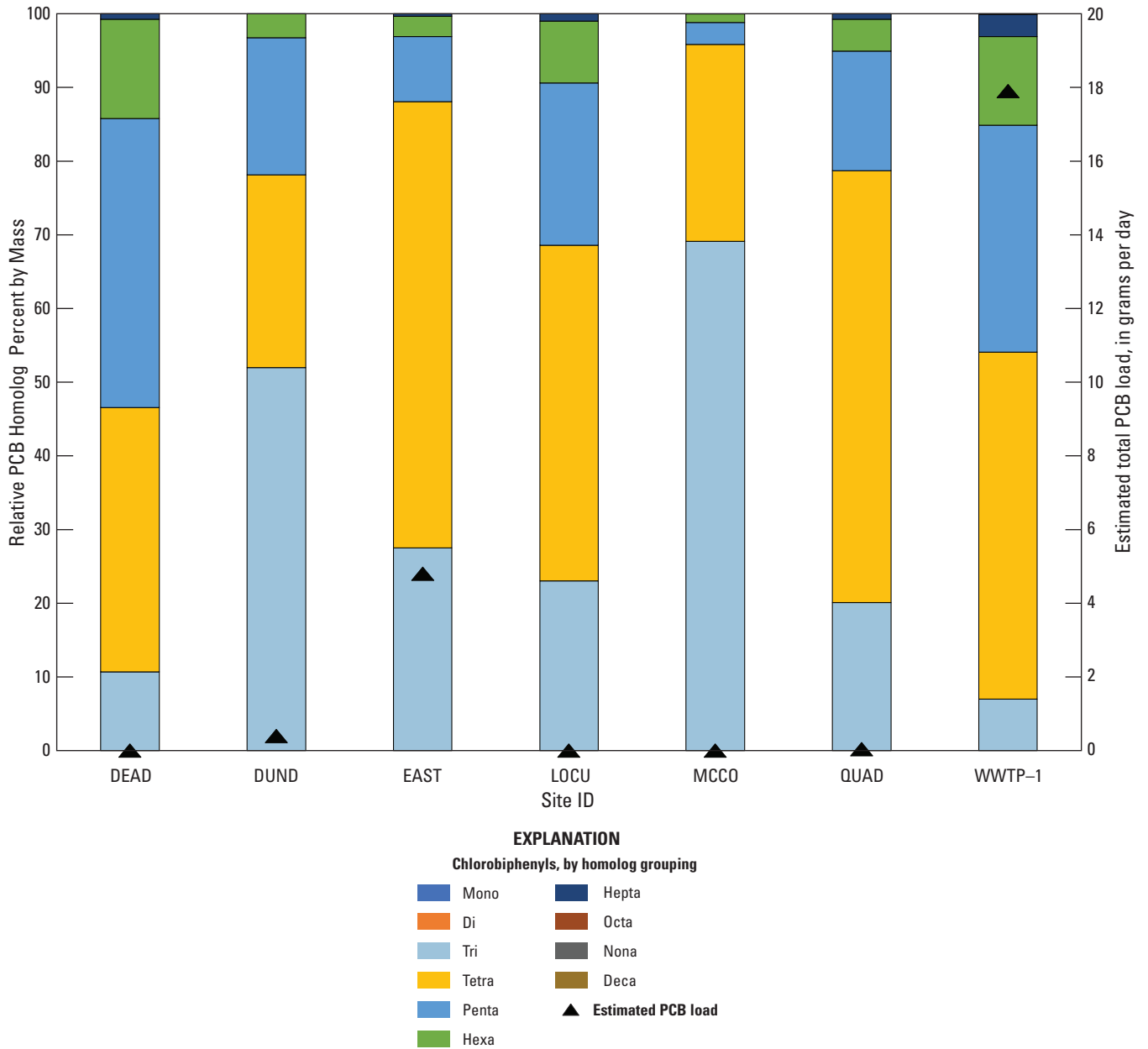
$Q_{ave}$  is the average flow during passive sampler deployment (in liters per day),

120 is the multiplier to estimate total PCBs from freely dissolved, based on Needham and Ghosh (2019).

$PCB_{total}$  is the estimated total PCB load (in grams per day) and 120

The average flow for the pump stations and weir were provided by the City of Baltimore (C. Stielper, Baltimore Department of Public Works, written commun., January 2020). Based on this estimate the portion of the sewer systems serviced by the Eastern Avenue Pump Station contributed the highest load of PCBs to BRWWTP, 4.8 g/d (fig. 26). Due to the lower flows and lower concentrations measured at the other sites, the total relative contribution to the plant from these other sites was negligible, totaling an additional 0.45 g/day or less than 10 percent of the total. It is important to note that the pump stations within the collection system provided necessary access and flow data to investigate differences in loading for this study but do not represent all inputs to BRWWTP. Additional sampling would be necessary to provide a more comprehensive assessment and mass balance. These additional inputs could include portions of the sewer system from Baltimore County and other sections of the system that do not require a pump station to reach BRWWTP. These results demonstrate that differences within the collection system exist, and targeted approaches to reduce PCB loading to the treatment plant is feasible based on these differences.





**Figure 26.** Freely dissolved total polychlorinated biphenyl (PCB) concentration, homolog distribution, and estimated total PCB loads associated with primary pump stations in City of Baltimore and in wastewater influent. DEAD, Dead Run; DUND, Dundalk; EAST, Eastern; LOCU, Locust Point; MCCO, McComas; QUAD, Quad Avenue; WWTP-I, influent at Back River Wastewater Treatment Plant.

## SSOs

SSO data were queried for the entire period of record, from 2005 to 2019, and pulled from the Maryland Reported Sewer Overflow Database (Maryland Department of the Environment, 2021c). The database records were searched using specific criteria, such as type of overflow (SSOs), year (all years), and county (City of Baltimore). The criteria were later expanded to include additional records reported from Baltimore City DPW and others within the study area. The query produced results that included information from the SSO record such as the year, date, and time the overflow was discovered, volume overflowed, and the address that was reported for the SSO location. Latitudes and longitudes were created from the reported addresses and were plotted in GIS as the date and volume released for that location (fig. 13D).

Based on the locations of the SSOs, loads to Herring Run, Moores Run, and Back River were calculated. GIS was used to map all SSO records available within the criteria specified and narrowed to include records from 2015 to 2019. SSOs within the drainage boundaries of the USGS gages in the study area were tabulated (records per year, table 8). This allowed separate contribution calculations to be made for Herring Run and Moores Run. The distribution in volume for all records is shown in table 9.

Loading was estimated using methods similar to the pump station estimates using the appropriate location, flow reported, the freely dissolved PCB concentration measured at the Quad Avenue pump station, and a factor of 120 to account for solids partitioning (eq. 16). Total PCB loading to Back River from SSOs in 2019 was estimated to be 0.47 grams/year, all originating from Herring Run. Mass loading to Moores Run was insignificant in previous years (2015–18), and no SSOs were reported in 2019 (Maryland Department of the Environment, 2021c). While these were only estimates and may be biased low since flow of some SSOs may be estimated and not measured, it was apparent that loading from SSOs was not a significant source of PCBs to Back River and was considerably less than total loading that occurs under low-flow conditions, in storms, and from BRWWTP effluent.

## Role of FOG

FOG samples showed a high variability of water content among samples, ranging from 55 percent (Quad Avenue and Dundalk pump stations) to 94 percent (in-pipe sample at Chinquapin Run), and therefore were reported on a dry weight basis. Furthermore, because PCBs partition with lipids in the FOG matrix, samples were also reported on a lipid-normalized basis. Lipid concentration of the FOG matrix was measured using a gravimetric method previously reported by Harvey and others (1987). Lipid content ranged from 11 to 47 percent with the lowest lipid content from the in-pipe sample at Chinquapin Run ( $11 \pm 4$  percent,  $n=3$ ) and the highest content at the BRWWTP ( $47 \pm 6$  percent,  $n=3$ ). FOG

sampled at the Quad Avenue and Dundalk pump stations had lipid content of 28 and 23 percent, respectively. FOG from the in-pipe sample at Chinquapin Run produced a very thick emulsion that prevented complete recovery of the lipid extract. Lipid content for that location might be underestimated, and therefore lipid normalized PCB concentration at that location might be overestimated. Although all four samples were analyzed, the Dundalk pump station sample PCB results were not reported due to significant interferences in the chromatogram despite additional clean-up steps.

The total PCB concentrations normalized for dry weight ranged from 92 ng/g (Quad Avenue pump station sample) to 380 ng/g (in-pipe Chinquapin Run sample, fig. 27). FOG from the BRWWTP had a concentration of 164 ng/g, which might reflect the different inputs from the City of Baltimore sewer system. The total PCB concentrations normalized per lipid content are as follows: 349 nanogram PCB per gram lipid (ng PCB/g lipid) for the BRWWTP sample, 3,405 ng PCB/g lipid for the Chinquapin Run in-pipe sample, and 333 ng PCB/g lipid for the Quad Avenue pump station sample (fig. 27). Samples from the BRWWTP and Quad Avenue pump station had similar range of PCB concentration normalized per lipid while FOG from the Chinquapin Run in-pipe sample was measured as about 10 times greater in normalized concentration.

PCBs are lipophilic compounds and will accumulate in fat tissues of organisms in the environment (Fadaei and others, 2015). FOG is a common material within sewer systems due to improper disposal of materials resulting in large build ups (He and others, 2017). This build-up of lipid material has been proposed as a potential ongoing source for PCBs within the sewer system (Needham and Ghosh, 2019). Releases of legacy PCBs to the collection system would preferentially accumulate in the FOG material and slowly release to newer sewage following equilibrium partitioning if it is assumed that freely dissolved PCBs declined over time after commercial use ceased. FOG buildups within some sewer systems, including Baltimore, can result in large buildups from many years of legacy deposition (Ratcliffe, 2015; Wells, 2017). The mobile FOG collected from the BRWWTP and attached to the passive sampler at Quad Avenue pump station was believed to be younger or more recently released into the collection system, whereas the immobilized FOG collected from within the pipe at Chinquapin Run and attached to the wet well walls of the Dundalk pump station were believed to be older legacy materials.

To assess if the FOG material could be a potential source within the system now, the influent freely dissolved concentration measured by passive samplers was used to predict a FOG concentration (ng/g lipid) assuming equilibrium (eq. 22). Concentrations measured in the influent were selected for this comparison because the analytical method was similar to the method used to measure the FOG samples. While passive samplers were also deployed at the various pump stations, these samplers were analyzed by a different laboratory (Eurofins TestAmerica, Knoxville, Tennessee) using a different analytical method, and combining the results may introduce

additional error and biases. The octanol-water partitioning coefficients ( $K_{ow}$ ) for PCBs is an approximation for the partitioning coefficient of lipid.

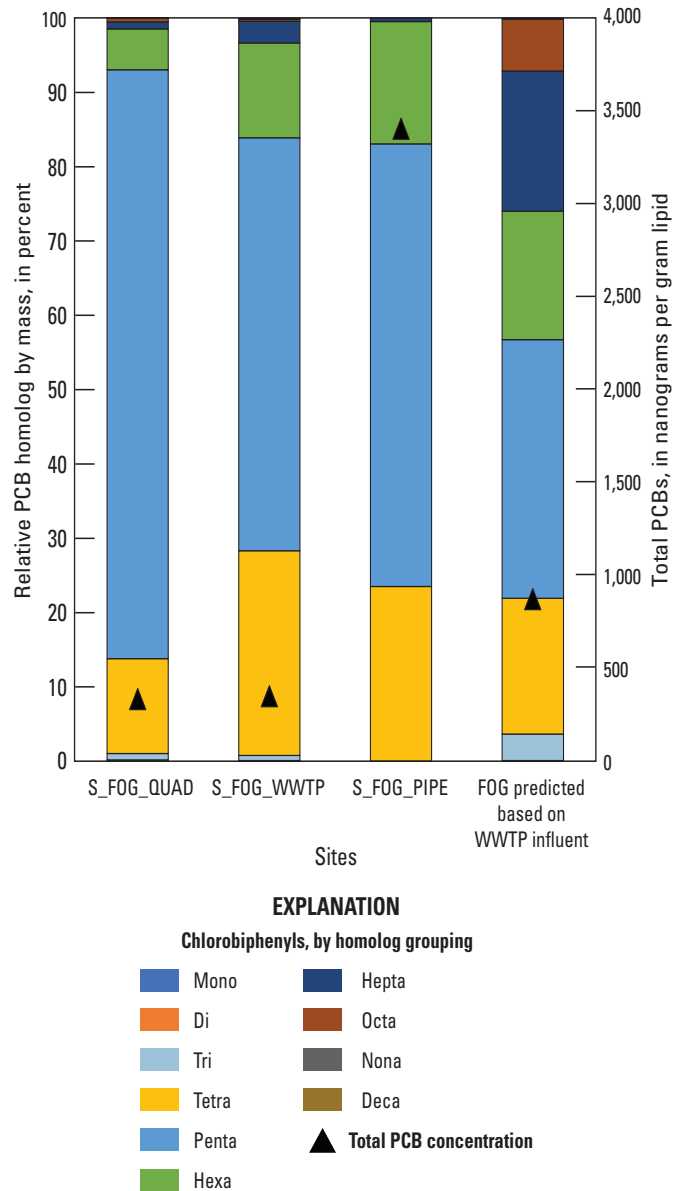
$$C_{PCB-lipid} = C_{free} \times K_{ow} \quad (17)$$

where

$K_{ow}$  is the octanol-water partitioning coefficient, used as an approximate for  $K_{lipid-water}$  (in nanogram per gram per nanogram per liter), and

$C_{PCB-lipid}$  is the concentration of PCBs in lipid (in nanogram per gram).

Using equation 17, the resulting PCB concentration in lipid, based on the BRWWTP influent freely dissolved PCB concentration, was estimated to be 1,136 ng PCB/g lipid. Figure 27 shows the homolog distribution by mass of the measured and predicted FOG samples along with the predicted total PCB concentration in lipid. The predicted total PCB concentration in lipid is greater than the PCB concentrations measured in the mobile FOG samples (Quad Avenue pump station and BRWWTP). This discrepancy suggests that the mobile (younger) FOG would accumulate PCBs to reach equilibrium with the freely dissolved concentration in the influent and does not appear to be a source for PCBs within the system. The lower concentration also supports that the FOG was either newly deposited and not yet at equilibrium; or was coming from an area with a lower concentration of PCBs in the freely dissolved phase. In contrast, the FOG collected from within the pipe section at Chinquapin Run contained higher levels of measured PCBs than the predicted value based on the BRWWTP influent freely dissolved concentration. The measured, higher concentration indicates that the immobile older FOG material could be a source of PCBs resulting in a flux from the FOG to wastewater. Although the freely dissolved concentration measured at Quad Avenue pump station was not used to predict the PCB concentration in lipid, it is important to note that the freely dissolved PCB concentration measured in the Quad Avenue pump station was considerably lower than what was measured in the WWTP influent and therefore estimates were conservative. Results from the FOG sampling support the hypothesis that FOG could act as a possible source of PCBs for areas of higher PCB loading and concentration measured in the freely dissolved phase such as at the portions of the system served by the Eastern Avenue pump station. The in-pipe FOG sample at Chinquapin Run was collected from within a section of pipe being replaced as part of the improvements to the sewer collection system by Baltimore City. Replacing this section of pipe and similar efforts to remove build up within the system have the potential to reduce legacy PCB mass within the system.



**Figure 27.** Polychlorinated biphenyl (PCB) homolog distribution by mass normalized to lipid for measured fat, oil, and grease (FOG) samples and predicted lipid concentrations in FOG (based on the wastewater treatment plant influent freely dissolved PCB concentration). S\_FOG\_QUAD, FOG from sampling device in Quad Avenue pump station; S\_FOG\_WWTP, FOG from sampling device in wastewater treatment plant influent; S\_FOG\_PIPE, FOG from pipe being replaced near confluence of Chinquapin Run and Herring Run.

## Summary of Sanitary Sewer System Sources

This study further supports conclusions reached in Needham and Ghosh (2019) that the sanitary sewer system plays a primary role in mass loading of PCBs to the Back River. Despite an observed considerable reduction in overall



mass loading to and from the plant compared to the estimates previously reported from 2015 (Needham and Ghosh, 2019), effluent from the BRWWTP continues to be a primary source of PCB mass to Back River.

Variation in freely dissolved concentrations in the sewer system was apparent through the analysis of PCBs in the primary pump stations using passive samplers, with the largest contribution to the influent attributed to the Eastern Avenue pump station and its associated piping. By contrast, the concentration and mass loading in the Quad Avenue pump station, which is nearest the Back River and within the Herring Run and Outfall sewersheds, was negligible compared to Eastern Avenue. In addition to the variation in concentration, homolog distribution suggests the presence of differing sources and can provide a roadmap to investigations associated with particular pump stations, similar to approaches taken in Camden, New Jersey (Belton and others, 2005). The passive methods employed during the pump station investigation provided an effective approach to identify areas of concern within the system.

Despite the potential under-estimate of total loading from SSOs, the contribution of PCB mass to Herring and Moores Run via SSOs compared to the wastewater effluent is negligible, similar to findings reported at another large urban WWTP (Jing and others, 2019). Therefore, decreased occurrence of SSOs (as mandated in the Consent Decree) is not expected to measurably decrease PCB loads into Back River.

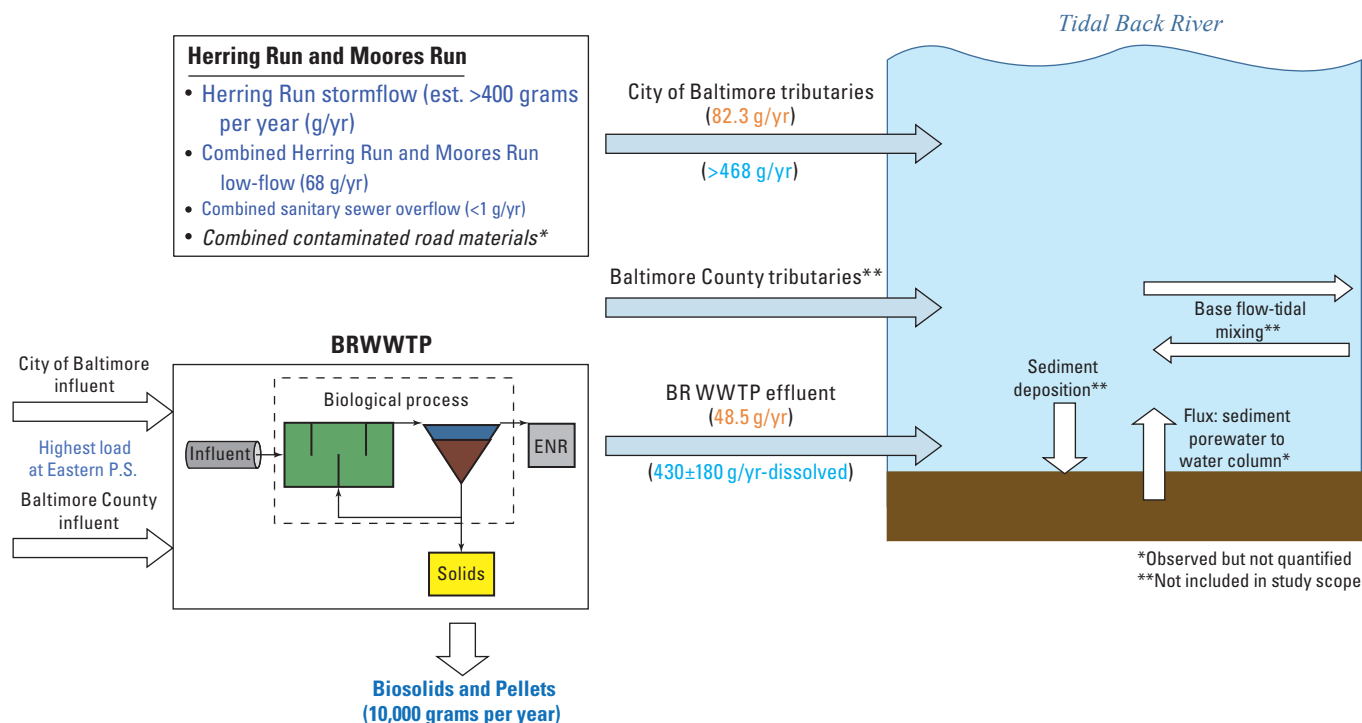
The study further confirmed the likeliness of FOG deposits within the miles of sewer pipe as a source of PCBs to the BRWWTP influent, which was speculated for BRWWTP (Needham and Ghosh, 2019) and has been confirmed elsewhere (Albright and others, 2014). In sewer systems in South Carolina, grease interceptors and their contents were contaminated by unauthorized disposal of PCBs in the sewer system resulting in PCBs detected in biosolids and effluent (Albright and others, 2014). The combined age of the sewer systems of Baltimore and the possibility of PCB contaminated FOG cannot be discounted as a possible source of PCBs to influent via PCB waste introduced to the system during the period of PCB commercial use, either by unauthorized disposal or inflow and infiltration from surrounding areas. The differences between PCB concentrations in FOG found in pipes (during replacement) compared to the BRWWTP suggests that legacy deposits may contain higher PCB concentration and act as a source of PCBs to passing raw sewage, eventually entering the BRWWTP.

During the 5 years since the previous study (Needham and Ghosh, 2019), ENR enhancements to the BRWWTP and capital improvements to the sewer system have taken place (City of Baltimore, 2021 b). Reductions in PCB concentrations and loads in the sewer system observed in this study compared to that estimated 5 years prior may reflect the possible impact of ongoing gray infrastructure management actions.

## Conceptual Model of PCBs in Back River and Implications for Management

Investigations were conducted as part of this study to better understand primary sources of PCBs in the nontidal tributaries within the City of Baltimore and its wastewater system to the Back River. A generalized schematic outlines these sources in [figure 28](#). While the quantified loads summarized in the figure should be considered generalized estimates only, comparisons between them are reasonable and can be used to consider further refinement of source and to consider possible management actions with the greatest potential for mass reductions. Based on the study, in the nontidal tributaries of the City of Baltimore, storm loads ([fig. 28](#)) possibly driven by introduction of contaminated SS introduced in stormwater ([fig. 28](#)), appear to contribute the most input to the Back River from Herring Run. Recent studies of some common urban best management practices such as bioretention have shown removal of PCBs within the stormwater control structures (David and others, 2015, Majcher and others, 2020). In addition, PCBs have been detected in street sweeping materials at concentrations in the 200–400 µg/kg range in studies outside the Baltimore region (Donner and others, 2015).

In the tidal portion of the Back River, the effluent from the BRWWTP was the primary source of PCB mass loading to the water body, estimated to be larger than tributary loads associated with storms. The BRWWTP, acting as a collection system, was highly efficient at sequestering and removing PCB mass, largely by concentrating it in the biosolids (Needham and Ghosh, 2019). Nonetheless, the mass loading from the effluent was still a primary source of PCBs to the Back River ([fig. 28](#)). While the study suggests a potential source in the system near the Eastern Avenue pump station, the pump station investigation did not account for all PCB mass or flow volume to the influent, and further consideration of other sources to the treatment plant influent could be considered (for example, Baltimore County pump stations and other parts of the sanitary sewer system not connected to the primary pump stations). Reductions observed between effluent loading in this study and in the previous investigation in 2015 (Needham and Ghosh, 2019) may be a result of ENR upgrades within the plant and capital improvements to the sewer system piping to the plant itself (possibly due to removal of legacy FOG deposits and other build ups). Continued maintenance and completion of gray infrastructure projects may continue to result in a decline in loads “up the pipe” to the plant. Continued efforts to implement BMPs both in the watershed (as part of MS4 requirements) and continued capital improvements and maintenance of the sanitary sewer system (as part of Consent Decree activities) may provide the potential for additional reductions in PCB loading to Herring Run, Moores Run, and Back River.



**Figure 28.** Conceptual model of polychlorinated biphenyls in Back River. BRWWTP, Back River Wastewater Treatment Plant; est., estimated; >, greater than; g/year, grams per year; P.S., pump station; ENR, enhanced nutrient removal; orange values are waste load allocations in the total maximum daily load (Maryland Department of the Environment, 2011).

## Conclusions and Summary

While not designed to explicitly quantify yearly loads, this study employed a variety of methods that yielded relative load estimates and helped identify driving sources of PCBs to receiving waters more than ten years after the TMDL approval. As such, this study provides baseline information to inform additional investigations or mitigation to help reach TMDL goals. Based on a single event, the loading to the nontidal tributaries of the Back River in the City of Baltimore was dominated by storm events, possibly as a result of contaminated stormwater, although this estimate does not reflect bioavailability of the sediment-bound PCBs. PCBs measured in the water column under low-flow conditions were fairly consistent and ubiquitous, with no apparent hot spots within the shallow stream bed. Net fluxes between the porewater in bed sediments and overlying water were generally small except at the most upstream site in a residential area outside the City of Baltimore boundary. PCB concentrations in water and sediment measured in this study were generally comparable or somewhat lower than concentrations measured in the studies used for setting the TMDL, suggesting there are likely no newly introduced sources in the streams or to the Back River during this timeframe.

SS captured and measured during the December 2019 storm did not appear to be from the shallow stream bed. Sediment accumulation in the upper tidal area of Back River

is visible by satellite imagery and creates a shallow area with sediments composed of finer materials compared to upstream stream beds. The porewater concentration measured in this area was higher than the co-located surface water, indicating a potential flux from sediment to surface water. The elevated PCB concentrations measured during the storm sampling and elevated concentrations in the porewater suggest that contaminated materials may move rapidly through the nontidal tributaries and deposit in the tidal mixing zone downstream. PCB concentration in bed sediment was lower than the concentration measured in SS during storm flow. Thus, SS likely came from sources with relatively higher PCB concentrations. Additional investigation of stormwater and source materials in storm drains and culverts and associated PCB concentrations could provide a more quantitative estimate of loading and source. The heterogeneity of preliminary samples of road materials and measured variability in concentrations suggested potential differing sources. Any additional investigation of this material and the bioavailability of the PCBs contained in it could provide insight into where sediment capture management could be most helpful in the watershed.

Both deposition of SS into the tidal area and effluent from the BRWWTP dominated mass loading to Back River. The study confirmed the presence of PCBs within FOG were consistent, indicating that the material is a likely source of PCBs to the BRWWTP influent, which was previously speculated for BRWWTP (Needham and Ghosh, 2019) and confirmed elsewhere (Albright and others, 2014). Further

delineation of areas of concern within the sanitary sewer system that contribute mass to the BRWWTP influent was achieved through sampling of the primary pump stations in the City of Baltimore; however, data gaps remain in the system indicating there are additional sources that have not been delineated to date. Approximately 25 percent of measured PCB loading could be attributed to water processed through the Eastern Avenue pump station, which indicates this may be an area of concern for further investigation.

Apparent dominant sources of PCBs in this study indicate that both gray and green infrastructure improvements are necessary to reduce loading to Back River, which is consistent with other studies of urban areas and water quality management actions (Reisinger and others, 2018; Majcher and others, 2020). BMPs that are planned or are being implemented already as part of MS4 and Chesapeake Bay TMDL requirements (Baltimore City Department of Public Works, 2021b), include sediment reduction strategies. BMPs planned in the watershed, particularly those designed for sediment capture, could be considered for their capacity to remove PCBs if PCB sources are identified. In addition to watershed BMPs, capital and maintenance projects may continue to reduce PCB loads to WWTPs. Based on the concentrations of PCBs measured in the SS in this study, any BMP designed to trap sediments will involve removal and proper disposal of the PCB-contaminated sediments in the BMPs.

This study employed a combined sampling approach and a variety of sampling methodologies to include passive samplers, high-volume water samples, and grab samples of both water and sediment to characterize the PCB inputs to Herring Run, Moores Run, and Back River. Incorporating passive samplers provided a time-weighted average of the freely dissolved concentration in the surface water and porewater over the deployment period with picogram per liter detection limits. Multiple passive samplers were deployed simultaneously within a watershed over a period of weeks to months, unlike traditional high-volume sampling or grab sampling that provide a measurement at a given time and location only. PCB concentrations associated with the other phases within the bulk water can be calculated from the freely dissolved concentration measured with the passive sampler using the DOC, TSS, and TOC. Calculated bulk water concentrations based on passive sampler measurements were within 20 percent of those measured with the traditional low-flow high-volume (1,000 L) sample from this study. Similar implementation of the methodology and sampling approach from this study could be implemented within other MS4 jurisdictions to assist in refining primary sources of PCBs and to inform appropriate mitigation approaches. Passive samplers were also used to assess changes in the influent and effluent of the BRWWTP and in primary pump stations. While concentrations in other bulk water phases could not be determined from these measurements (particularly for the BRWWTP influent and primary pump stations where organic carbon and SS was not known), estimates were made based on previously published studies using a correlation factor (Needham and

Ghosh, 2019). These measurements provided an assessment of the areas of concern and allowed for a comparison with past studies. These passive samplers could provide an effective way to assess changes in PCB mass loading while capital improvement projects and maintenance in the sewer system continues through the consent decree efforts.

## References Cited

- Abramowicz, D.A., 1995, Aerobic and anaerobic PCB biodegradation in the environment: Environmental Health Perspectives, v. 103, no. 5, p. 97–99. [Also available at <https://doi.org/10.1289/ehp.95103s497>.]
- Albright, R.A., Smith, H.H., and Huddleston, M., 2014, PCBs—Old chemicals present new challenges, *in* South Carolina Water Resources Conference, Columbia, S.C., October 15–16, 2014, Proceedings: Clemson, S.C., Clemson University, South Carolina Water Resources Center, 6 p.
- Apell, J.N., Shull, D.H., Hoyt, A.M., and Gschwend, P.M., 2018, Investigating the effect of bioirrigation on in situ porewater concentrations and fluxes of polychlorinated biphenyls using passive samplers: Environmental Science & Technology, v. 52, no. 8, p. 4565–4573.
- Baltimore City Department of Public Works, 2021a, Back River Wastewater Treatment Plant: City of Baltimore web page, accessed September 7, 2021, at <https://publicworks.baltimorecity.gov/pw-bureaus/water-wastewater/wastewater/back-river>.
- Baltimore City Department of Public Works, 2021b, MS4 annual report—Reporting period—July 1, 2019 to June 30, 2020: Baltimore City Department of Public Works web page, accessed December 9, 2021, at <https://publicworks.baltimorecity.gov/sites/default/files/FY%202020%20MS4%20Annual%20Report%20for%20Website.pdf>.
- Bamford, H.A., Ko, F.C., and Baker, J.E., 2002, Seasonal and annual air–water exchange of polychlorinated biphenyls across Baltimore Harbor and the northern Chesapeake Bay: Environmental Science & Technology, v. 36, no. 20, p. 4245–4252. [Also available at <https://doi.org/10.1021/es0206893>.]
- Beckingham, B., and Ghosh, U., 2011, Field-scale reduction of PCB bioavailability with activated carbon amendment to river sediments: Environmental Science & Technology, v. 45, no. 24, p. 10567–10574. [Also available at <https://doi.org/10.1021/es202218p>.]



- Beckingham, B., and Ghosh, U., 2013, Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field: *Chemosphere*, v. 91, no. 10, p. 1401–1407.
- Belton, T., Stevenson, E., Lippincott, L., England, R., Ruppel, B., Botts, J., and Cavallo, G., 2005, Trackdown of polychlorinated biphenyls (PCBs) in a municipal sewer system—Pilot study at the Camden County Municipal Utility Authority (CCMUA), in *Water Environment Federation TMDL 2005 Specialty Conference*, Philadelphia, Pa., June 26–29, 2005, Proceedings: Water Environment Federation, 18 p. [Also available at <https://doi.org/10.2175/193864705783966990>.]
- Booij, K., Smedes, F., and van Weerlee, E.M., 2002, Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers: *Chemosphere*, v. 46, no. 8, p. 1157–1161. [Also available at [https://doi.org/10.1016/S0045-6535\(01\)00200-4](https://doi.org/10.1016/S0045-6535(01)00200-4).]
- Brenner, R.C., Magar, V.S., Ickes, J.A., Foote, E.A., Abbott, J.E., Bingler, L.S., and Crecelius, E.A., 2004, Long-term recovery of PCB-contaminated surface sediments at the Sangamo-Weston/Twelvemile Creek/Lake Hartwell superfund site: *Environmental Science & Technology*, v. 38, no. 8, p. 2328–2337. [Also available at <https://doi.org/10.1021/es030650d>.]
- Cao, S., Capozzi, S.L., Kjellerup, B.V., and Davis, A.P., 2019, Polychlorinated biphenyls in stormwater sediments—Relationships with land use and particle characteristics: *Water Research*, v. 163, p. 114865.
- Capozzi, S.L., Jing, R., Rodenburg, L.A., and Kjellerup, B.V., 2019, Positive matrix factorization analysis shows dechlorination of polychlorinated biphenyls during domestic wastewater collection and treatment: *Chemosphere*, v. 216, p. 289–296. [Also available at <https://doi.org/10.1016/j.chemosphere.2018.10.151>.]
- City of Baltimore, 2020a, Open Baltimore surface water quality data since 1995: City of Baltimore web page, accessed September 30, 2020, at <https://data.baltimorecity.gov/datasets/surface-water-quality-data-since-1995/-/explore>.
- City of Baltimore, 2020b, Baltimore illicit discharge detection and elimination map: City of Baltimore web page, accessed September 30, 2020, at <https://mangomap.com/pesturm/maps/38636/baltimore-illicit-discharge-detection-and-elimination-map#>.
- David, N., Leatherbarrow, J.E., Yee, D., and McKee, L.J., 2015, Removal efficiencies of a bioretention system for trace metals, PCBs, PAHs, and dioxins in a semiarid environment: *Journal of Environmental Engineering*, v. 141, no. 6, p. 04014092. [Also available at [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0000921](https://doi.org/10.1061/(ASCE)EE.1943-7870.0000921).]
- Doheny, E.J., and Baker, S.M., 2018, Geomorphic characteristics of Tenmile Creek, Montgomery County, Maryland, 2014–16: U.S. Geological Survey Scientific Investigations Report 2018–5098, 34 p. [Also available at <https://doi.org/10.3133/sir20185098>.]
- Donner, S., Frost, B., Goulet, N., Hurd, M., Law, N., McGuire, T., Selbig, B., Shafer, J., Stewart, S., and Tribo, J., 2015, Recommendations of the expert panel to define removal rates for street and storm drain cleaning practices, final report (September 18, 2015): Chesapeake Bay Program Office, 68 p. [Also available at [https://www.chesapeakebay.net/documents/FINAL\\_APPROVED\\_Street\\_and\\_Storm\\_Drain\\_Cleaning\\_Expert\\_Panel\\_Report\\_-\\_Complete2.pdf](https://www.chesapeakebay.net/documents/FINAL_APPROVED_Street_and_Storm_Drain_Cleaning_Expert_Panel_Report_-_Complete2.pdf).]
- Edds, R., and Gross, R., 2003, Industrial land use analysis, City of Baltimore, Maryland (November 23, 2003): Baltimore Development Corporation report, prepared by Bay Area Economics, Randall Gross Development Economics, HNTB Corporation, Milestone Associates, and Woodley Appraisal Group, Inc., 142 p.
- England, J.F., Jr., Cohn, T.A., Faber, B.A., Stedinger, J.R., Thomas, W.O., Jr., Veilleux, A.G., Kiang, J.E., and Mason, R.R., Jr., 2019, Guidelines for determining flood flow frequency—Bulletin 17C (ver. 1.1, May 2019): U.S. Geological Survey Techniques and Methods, book 4, chap. B5, 148 p. [Also available at <https://doi.org/10.3133/tm4B5>.]
- Fadaei, H., Watson, A., Place, A., Connolly, J., and Ghosh, U., 2015, Effect of PCB bioavailability changes in sediments on bioaccumulation in fish: *Environmental Science & Technology*, v. 49, p. 12405–12413. [Also available at <https://doi.org/10.1021/acs.est.5b03107>.]
- Fagervold, S.K., May, H.D., and Sowers, K.R., 2007, Microbial reductive dechlorination of Aroclor 1260 in Baltimore Harbor sediment microcosms is catalyzed by three phylotypes within the phylum chloroflexi: *Applied and Environmental Microbiology*, v. 73, no. 9, p. 3009–3018. [Also available at <https://doi.org/10.1128/AEM.02958-06>.]
- Fernandez, L., Harvey, C., and Gschwend, P., 2009, Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals: *Environmental Science and Technology*, v. 43, no. 23 p. 8888–8894. [Also available at <https://doi.org/10.1021/es901877a>.]
- Fernandez, L.A., Lao, W., Maruya, K.A., and Burgess, R.M., 2014, Calculating the diffusive flux of persistent organic pollutants between sediments and the water column on the Palos Verdes Shelf Superfund site using polymeric passive samplers: *Environmental Science & Technology*, v. 48, no. 7, p. 3925–3934. [Also available at <https://doi.org/10.1021/es404475c>.]

- Foss, E.P., Lombard, N., Joshee, S., Bokare, M., Ghosh, U., Needham, T.P., and Majcher, E.H., 2022, Polychlorinated biphenyl (PCB) concentrations of passive samplers, solids, fat, oil, and greases (FOG), and road sediments; and dissolved organic carbon (DOC), total suspended solids (TSS), and particulate organic carbon (POC) concentrations in the Back River watershed, Baltimore City, Maryland, 2018–2020: U.S. Geological Survey data release, <https://doi.org/10.5066/P9WFDIBM>.
- Gellis, A.C., Fuller, C.C., Van Metre, P.C., Mahler, B.J., Welty, C., Miller, A.J., Nibert, L.A., Clifton, Z.J., Malen, J.J., and Kemper, J.T., 2020, Pavement alters delivery of sediment and fallout radionuclides to urban streams: *Journal of Hydrology (Amsterdam)*, v. 588, p. 124855. [Also available at <https://doi.org/10.1016/j.jhydrol.2020.124855>.]
- Ghosh, U., Kane Driscoll, S., Burgess, R., Jonker, M.T.O., Reible, D., Gobas, F., Choi, Y., Apitz, S.E., Maruya, K.A., Gala, W.R., Mortimer, M., and Beegan, C., 2014, Passive sampling methods for contaminated sediments—Practical guidance for selection, calibration and implementation: *Integrated Environmental Assessment and Management*, v. 10, no. 2, p. 210–223.
- Ghosh U., Lombard N., Bokare M., R., Yonkos L., and Pinkney F., 2020, Passive samplers and mussel deployment, monitoring, and sampling for organic constituents in Anacostia River tributaries, 2016–2018: Department of Energy and Environment Final Report, 344 p.
- Gobas, F. and Arnot, J., 2010, Food web bioaccumulation model for polychlorinated biphenyls in San Francisco Bay, California, USA: *Environmental Toxicology and Chemistry*, v. 29, no. 6, p. 1385–1395. [Also available at <https://doi.org/10.1002/etc.164>.]
- Harvey, H.R., Eglinton, G., O'Hara, S.C.M., and Corner, E.D.S., 1987, Biotransformation and assimilation of dietary lipids by *Calanus* feeding on a dinoflagellate: *Geochimica et Cosmochimica Acta*, v. 51, no. 11, p. 3031–3040.
- He, X., de los Reyes, F.L., III, and Ducoste, J.J., 2017, A critical review of fat, oil, and grease (FOG) in sewer collection systems—Challenges and control: *Critical Reviews in Environmental Science and Technology*, v. 47, no. 13, p. 1191–1217. [Also available at <https://doi.org/10.1080/10643389.2017.1382282>.]
- Hwang, H.-M., and Foster, G.D., 2006, Characterization of polycyclic aromatic hydrocarbons in urban stormwater runoff flowing into the tidal Anacostia River, Washington, DC, USA: *Environmental Pollution*, v. 140, no. 3, p. 416–426. [Also available at <https://doi.org/10.1016/j.envpol.2005.08.003>.]
- Hwang, H.-M., and Foster, G.D., 2008, Polychlorinated biphenyls in stormwater runoff entering the tidal Anacostia River, Washington, DC, through small urban catchments and combined sewer outfalls: *Journal of Environmental Science and Health, Part A, Toxic/Hazardous Substances & Environmental Engineering*, v. 43, no. 6, p. 567–575.
- Jartun, M., Ottesen, R.T., Steinnes, E., and Volden, T., 2009, Painted surfaces—Important sources of polychlorinated biphenyls (PCBs) contamination to the urban and marine environment: *Environmental Pollution*, v. 157, no. 1, p. 295–302. [Also available at <https://doi.org/10.1016/j.envpol.2008.06.036>.]
- Joshee, S., Bokare, M., Schmidt, W., Brittingham, K., and Ghosh, U., 2019, PCB levels in the surface water, sediment porewater, and benthic organisms in Back River watershed, in Chesapeake-Potomac Regional Chapter of the Society of Environmental Toxicology and Chemistry, 2019 Spring meeting, Davis, W. Va., April 7–8, 2019, program and abstracts: Chesapeake Potomac Regional Chapter, Society of Environmental Toxicology and Chemistry, p. 22. [Also available at [https://cprcsetac.files.wordpress.com/2019/04/cprc-setac-abstracts-and-program-2019\\_final.pdf](https://cprcsetac.files.wordpress.com/2019/04/cprc-setac-abstracts-and-program-2019_final.pdf).]
- Joshee, S., Bokare, M., Schmidt, W., Brittingham, K., Lombard, N., and Ghosh, U., 2020, PCB levels in the surface water, sediment porewater, and benthic organisms in Back River watershed in Chesapeake-Potomac Regional Chapter of the Society of Environmental Toxicology and Chemistry, 2020 Fall virtual meeting, September 23, 2020, program and abstracts: Chesapeake Potomac Regional Chapter, Society of Environmental Toxicology and Chemistry. [Also available at <https://cprcsetac.files.wordpress.com/2020/08/meeting-program-draft-2020-08-31.pdf>.]
- Jing, R., Fusi, S., Chan, A., Capozzi, S., and Kjellerup, B.V., 2019, Distribution of polychlorinated biphenyls in effluent from a large municipal wastewater treatment plant—Potential for bioremediation?: *Journal of Environmental Sciences (China)*, v. 78, p. 42–52. [Also available at <https://doi.org/10.1016/j.jes.2018.06.007>.]
- Karl, D.M., Hebel, D.V., Björkman, K., and Letelier, R.M., 1998, The role of dissolved organic matter release in the productivity of the oligotrophic North Pacific Ocean: *Limnology and Oceanography*, v. 43, no. 6, p. 1270–1286.
- King, R.S., Beaman, J.R., Whigham, D.F., Hines, A.H., Baker, M.E., and Weller, D.E., 2004, Watershed land use is strongly linked to PCBs in white perch in Chesapeake Bay subestuaries: *Environmental Science & Technology*, v. 38, no. 24, p. 6546–6552.
- Klosterhaus, S., McKee, L.J., Yee, D., Kass, J.M., and Wong, A., 2014, Polychlorinated biphenyls in the exterior caulk of San Francisco Bay area buildings, California, USA: *Environment International*, v. 66, no. May, p. 38–43.

- Lombard, N., Bokare M., and Ghosh U., 2019. Getting a grip on toxic pollutant inputs to the Anacostia River: Society of Environmental Toxicology and Chemistry, Chesapeake Potomac Regional Chapter Newsletter (Fall 2019), v. 27, no. 2, p. 7–9.
- Majcher, E., Smalling, K., Blaney, L., Harvey, A., Phillips, S.L., Blazer, V., Pickney, A., Brosch, C., and Allen, G., 2020. Integrating science and developing approaches to inform management for contaminants of concern in agricultural and urban settings, Chesapeake Bay Scientific and Technical Advisory Committee Workshop Report, Baltimore, Md., May 22–23, 2019, [Proceedings]: Scientific and Technical Advisory Committee [STAC], STAC Publication 20–001, 51 p. [Also available at [https://www.chesapeakebay.net/channel\\_files/41733/final\\_stac-report\\_contaminants-of-concern.pdf](https://www.chesapeakebay.net/channel_files/41733/final_stac-report_contaminants-of-concern.pdf).]
- Maryland Department of the Environment, 2011, Total maximum daily load of polychlorinated biphenyls in back river oligohaline tidal Chesapeake Bay segment, Maryland (September 2011): Maryland Department of the Environment, Final Report, 79 p. [Also available at [https://mde.maryland.gov/programs/Water/TMDL/DocLibBackRiver02130901/BackRiver\\_PCB\\_TMDL\\_100212\\_Final.pdf](https://mde.maryland.gov/programs/Water/TMDL/DocLibBackRiver02130901/BackRiver_PCB_TMDL_100212_Final.pdf).]
- Maryland Department of the Environment, 2020, Maryland fish consumption advisory map: Maryland Department of the Environment web page, accessed September 30, 2020, at <https://mdewin64.mde.state.md.us/WSA/FCA/index.html>.
- Maryland Department of the Environment, 2021a, Wastewater permits interactive search portal: Maryland Department of the Environment web page, accessed September 7, 2021, at <https://mes-mde.mde.state.md.us/WastewaterPermitPortal/>.
- Maryland Department of the Environment, 2021b, MDE—LRP map: Maryland Department of the Environment web page, accessed September 7, 2021, at <https://mdewin64.mde.state.md.us/LRP/index.html>.
- Maryland Department of the Environment, 2021c, Maryland reported sewer overflow database: Maryland Department of the Environment web page, accessed September 7, 2021, at <https://mde.maryland.gov/programs/water/compliance/pages/reportedseweroverflow.aspx>.
- Maske, H., and Garcia-Mendoza, E., 1994, Adsorption of dissolved organic matter to the inorganic filter substrate and its implications for  $^{14}\text{C}$  uptake measurements: *Applied and Environmental Microbiology*, v. 60, no. 10, p. 3887–3889.
- Mullins, M.D., Pochini, C.M., McCrindle, S., Romkes, M., Safe, S.H., and Safe, L.M., 1984, High-resolution PCB analysis—Synthesis and chromatographic properties of all 209 PCB congeners: *Environmental Science & Technology*, v. 18, no. 6, p. 468–476. [Also available at <https://doi.org/10.1021/es00124a014>.]
- National Land Cover Database, 2006, NLCD 2006 land cover—CONUS: Multi-Resolution Land Characteristics Consortium web page, accessed September 30, 2020, at <https://www.mrlc.gov/data/nlcd-2006-land-cover-conus>.
- National Research Council, 2008, Urban stormwater management in the United States: Washington, D.C., National Academies Press, 610 p.
- Needham, T., and Sowers, K., 2018, From miracle chemical to environmental hazard—Legacy of the PCB problem in the Baltimore regions and possible solutions: Baltimore, Md., Institute of Marine and Environmental Technology Public Lecture Series, November 13, 2018.
- Needham, T.P., and Ghosh, U., 2019, Four decades since the ban, old urban wastewater treatment plant remains a dominant source of PCBs to the environment: *Environmental Pollution*, v. 246, p. 390–397. [Also available at <https://doi.org/10.1016/j.envpol.2018.12.016>.]
- Needham, T.P., Payne, R.B., Sowers, K.R., and Ghosh, U., 2019, Kinetics of PCB microbial dechlorination explained by freely dissolved concentration in sediment microcosms: *Environmental Science & Technology*, v. 53, no. 13, p. 7432–7441. [Also available at <https://doi.org/10.1021/acs.est.9b01088>.]
- Ortiz, E., Luthy, R.G., Dzombak, D.A., and Smith, J.R., 2004, Release of polychlorinated biphenyls from river sediment to water under low-flow conditions—Laboratory assessment: *Journal of Environmental Engineering* (February 2004), v. 130, no. 2, 10 p.
- Perron, M.M., Burgess, R.M., Suuberg, E.M., Cantwell, M.G., and Pennell, K.G., 2013, Contaminants of concern, part 1—Performance of passive samplers for monitoring estuarine water column concentrations: *Environmental Toxicology and Chemistry*, v. 32, no. 10, p. 2182–2189.
- Ratcliffe, R., 2015, 10-tonne fatberg removed from west London sewer: London, *Guardian*, April 22, 2015, accessed September 7, 2021, at <https://www.theguardian.com/uk-news/2015/apr/21/huge-10-ton-fatberg-removed-chelsea-sewer-london>.
- Reisinger, A.J., Woytowitz, E., Majcher, E., Rosi, E., Belt, K., Duncan, J., Kaushal, S., and Groffman, P.M., 2018, Changes in long-term water quality of Baltimore streams are associated with both gray and green infrastructure: *Limnology and Oceanography*, v. 64, no. S1, p. 1–17. [Also available at <https://doi.org/10.1002/lno.10947>.]
- Rodenburg, L.A., Du, S., Fennell, D.E., and Cavallo, G.J., 2010, Evidence for widespread dechlorination of polychlorinated biphenyls in groundwater, landfills, and wastewater collection systems: *Environmental Science & Technology*, v. 44, no. 19, p. 7534–7540.



- U.S. Army Corps of Engineers, 2012, PCBs in caulk and paint: Washington, D.C., Department of the Army, Public Works Technical Bulletin (December 31, 2012), no. 200–1–126, 32 p.
- U.S. Environmental Protection Agency, 1996a, Method 3660B Sulfur cleanup, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d. ed., rev. 2, December 1996): U.S. Environmental Protection Agency publication SW–846, 6 p.
- U.S. Environmental Protection Agency, 1996b, Method 3630C—Silica gel cleanup, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 3, December 1996): U.S. Environmental Protection Agency publication SW–846, 15 p.
- U.S. Environmental Protection Agency, 1996c, Method 3665A—Sulfuric acid/permanganate cleanup, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 1, December 1996): U.S. Environmental Protection Agency publication SW–846, 5 p.
- U.S. Environmental Protection Agency, 1996d, Method 3540C—Soxhlet extraction, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 3, December 1996): U.S. Environmental Protection Agency publication SW–846, 8 p.
- U.S. Environmental Protection Agency, 2007a, Method 3500C—Organic extraction and sample preparation, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 3, February 2007): U.S. Environmental Protection Agency publication SW–846, 19 p.
- U.S. Environmental Protection Agency, 2007b, Method 3550C—Ultrasonic extraction, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 3, February 2007): U.S. Environmental Protection Agency publication SW–846, 17 p.
- U.S. Environmental Protection Agency, 2003, Method 1668A, Chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS: U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (August 2003), EPA–821–R–07–004, 127 p.
- U.S. Environmental Protection Agency, 2011, Environmental cleanup best management practices—Effective use of the project life cycle conceptual site model: U.S. Environmental Protection Agency, Office of Solid Waste Emergency Response (July 2011), EPA 542–F–11–011, 12 p.
- U.S. Environmental Protection Agency, 2012, Guidelines for using passive samplers to monitor organic contaminants at Superfund sediment sites: U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation and Office of Research and Development (December 2012), OSWER Directive 9200.1–110 FS, 32 p.
- U.S. Environmental Protection Agency, 2014, Method 3620C—Florisol cleanup, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 4, July 2014): U.S. Environmental Protection Agency publication SW–846, 28 p.
- U.S. Environmental Protection Agency, 2017, Laboratory, field, and analytical procedures for using passive sampling in the evaluation of contaminated sediments—User’s manual: Washington, D.C., U.S. Environmental Protection Agency, Office of Research and Development, no. EPA–600–R–16–357, 167 p.
- U.S. Environmental Protection Agency, 2021, PCBs in building materials—Determining the presence of manufactured PCB products in buildings or other structures: U.S. Environmental Protection Agency Fact Sheet (May 2021), 7 p.
- U.S. Geological Survey, 2020a, USGS 01585200 West Branch Herring Run at Idlewylde, MD: U.S. Geological Survey National Water Information System database, accessed September 30, 2020, at [https://waterdata.usgs.gov/md/nwis/uv/?site\\_no=01585200&PARAMeter\\_cd=00065,00060,62615,62620](https://waterdata.usgs.gov/md/nwis/uv/?site_no=01585200&PARAMeter_cd=00065,00060,62615,62620).
- U.S. Geological Survey, 2020b, USGS 01585219 Herring Run at Sinclair Lane at Baltimore, MD: U.S. Geological Survey National Water Information System database, accessed September 30, 2020, at [https://waterdata.usgs.gov/md/nwis/uv/?site\\_no=01585219&PARAMeter\\_cd=00065,00060,62615,62620](https://waterdata.usgs.gov/md/nwis/uv/?site_no=01585219&PARAMeter_cd=00065,00060,62615,62620).
- U.S. Geological Survey, 2020c, USGS 01585230 Moores Run at Radecke Avenue at Baltimore, MD: U.S. Geological Survey National Water Information System database, accessed September 30, 2020, at [https://waterdata.usgs.gov/md/nwis/uv/?site\\_no=01585230&PARAMeter\\_cd=00065,00060,62615,62620](https://waterdata.usgs.gov/md/nwis/uv/?site_no=01585230&PARAMeter_cd=00065,00060,62615,62620).
- Veilleux, A.G., Cohn, T.A., Flynn, K.M., Mason, R.R., Jr., and Hummel, P.R., 2014, Estimating magnitude and frequency of floods using the PeakFQ 7.0 program: U.S. Geological Survey Fact Sheet 2013–3108, 2 p. [Also available at <https://doi.org/10.3133/fs20133108>.]
- Wang, B., Paul, P., and Ghosh, U., 2012, Passive sampler measurement of PCB concentrations in sediment porewater and overlying water in three Maryland streams: Baltimore, Md., Maryland Department of Environment by Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, 36 p.

- Wells, C., 2017, “Fatberg” of congealed fat, wet wipes and waste discovered under Baltimore's streets, causing sewer overflows: Baltimore Sun, September 26, 2017, accessed September 30, 2020, at <https://www.baltimoresun.com/maryland/baltimore-city/bs-md-ci-fatberg-20170925-story.html>.
- Williams, M., and Wolf, J., 2018, PCBs in the Chesapeake Bay watershed: Chesapeake Bay Program web page, accessed September 30, 2020, at <https://chesbay.maps.arcgis.com/apps/MapSeries/index.html?appid=704ecbbb9f5943eca87d59b349edf1ab>.
- Wilson, T.P., 2020, Sediment and chemical contaminant loads in tributaries to the Anacostia River, Washington, District of Columbia, 2016 -17: U.S. Geological Survey Scientific Investigations Report 2019 -5092, 146 p., accessed September 30, 2020, at <https://doi.org/10.3133/sir20195092>.

## Appendix 1. Quality Assurance-Quality Control Discussion of Results

The purpose of this section is to discuss the effects of quality assurance-quality control (QA-QC) procedures on the data and interpretation of results performed by the laboratory at University of Maryland, Baltimore County (UMBC). Specifically, this section will discuss the method detection limit (MDL), performance reference compound (PRC) correction, surrogate recoveries, solid phase sample procedure blanks, replicate samples, and U.S. environmental Protection Agency (EPA) Method comparisons. EPA guidance for QA-QC procedures outlined in modified EPA method 8082A (Beckingham and Ghosh, 2011) and method 8000D were followed (U.S. Environmental Protection Agency, 2018). Any modifications to the specified QA-QC procedures or exceedance of any QA-QC limits are discussed in this appendix.

### Polychlorinated Biphenyl (PCB) Instrumental Analysis and Method Detection Limits for Modified Method 8082A

PCB analysis by UMBC was performed on a gas chromatography-electron capture detector (GC-ECD). Calibration of the GC was verified with a standard check solution at the beginning of every run and recalibrated if the concentration detected deviated more than 20 percent from expected concentration. Further manual identification was required to fine-tune the retention time windows so that interfering peaks (identified as phthalates on GC-mass spectrometry [MS]) were not included in the PCB analysis. For passive sampler data the targeted analyte group 172+197 was removed from analysis due to significant co-elution with the performance reference compound (PRC) 192, and thus was indicated as “—” (no value provided) in the data file. The MDL is defined as “the minimum measured concentration of a substance that can be reported with 99 percent confidence that the measured concentration is distinguishable from method blanks results” (U.S. Environmental Protection Agency, 2016). Seven samples spiked at the lowest level of the calibration were run, and the standard deviation of the measured concentrations ( $S_s$ ) was calculated. An MDL based on spiked samples ( $MDL_s$ ) was first determined by using the following equation:

$$MDL_s = t_{(n-1, 1-\alpha=0.99)} \times S_s \quad (1.1)$$

where

$t_{(n-1, 1-\alpha=0.99)}$  is the student's t-value appropriate for a single tailed 99th percentile t statistic, and  
 $S_s$  is the standard deviation estimate with  $n-1$  degrees of freedom.

The  $MDL_s$  was either used as the “initial MDL” if none of the methods blanks (that is, procedure blanks in this document) gave numerical results, or the initial MDL was updated with the results from the method blanks if numerical value was measured for individual analytes (U.S. Environmental Protection Agency, 2016). If some but not all methods blanks gave numerical results, the MDL for blanks ( $MDL_b$ ) was set equal to the highest method blank results. If all method blanks gave numerical results, the standard deviation ( $S_b$ ) of the replicates results was calculated and the  $MDL_b$  was determined as follows:

$$MDL_b = t_{(n-1, 1-\alpha=0.99)} \times S_b \quad (1.2)$$

The greater of  $MDL_s$  or  $MDL_b$  was selected as the MDL. PCB congeners below the MDL were flagged with a “J” identifier and reported as less than the MDL value (Foss and others, 2022). PCB congeners that were not detected were reported as less than the MDL value.

### PRC Correction for Method 8082A

PRC initial concentration in the sampler was measured from two pieces of passive samplers weighing between 0.5 and 1.0 g for each deployment batch. A total of six batches were deployed, three batches for the BRWWTP and three batches for the Back River watershed tributaries. Deployment dates are indicated in the Field Sampling Methods section of this report (tables 3, 4). PCB PRC initial concentration (in ng/g) had a relative standard deviation from 0 to 5 percent for all deployment batches considered.

PRC final concentration in samplers was measured and PRC loss was used to estimate a mass transfer coefficient  $k_c$  (from PE to water) or partition constant  $K_d$  (from sediment matrix to water) for each compound by drawing a linear regression of  $\log k_c$ - $\log K_{ow}$  or  $\log K_d$ - $\log K_{ow}$ . The linear regression for PCB PRCs had a correlation ( $r^2$ ) averaging 0.94 for Back River watershed passive samples and 0.86 for the BRWWTP passive samples.

The fractional equilibration estimated from PRC loss was used to correct for nonequilibrium conditions. Due to the uncertainty associated with high correction factors (above 10), concentrations for PCB congeners with fractional equilibration below 0.1 were flagged with an “E” modifier and not used for total PCB concentration calculation. It is important to note that these compounds were present, and given sufficient deployment time to reach equilibrium, they could be accurately quantified. The fractional equilibration is a function of deployment time (longer deployment time will allow reaching concentrations closer to equilibrium) and the waterbody discharge (higher flow rate allow faster diffusion). Lower fractional equilibration is usually observed for higher



molecular weight compound (octa- to decachlorobiphenyls) with higher hydrophobicity and lower diffusivity. Those highly hydrophobic compounds are usually not relevant in total PCB freely dissolved water concentration calculation as these compounds are sparingly soluble and therefore in very low concentration in the water phase. These higher hydrophobic compounds become more important when estimating total loads for a waterbody since the more hydrophobic compounds increase in partitioning to organic carbon material such as DOC. Therefore, the resulting load estimates based on the freely dissolved phase may be biased low due to the exclusion of the higher chlorinated congeners.

After the loss of some samplers in Herring Run, replacement samplers were only deployed for 32 to 58 days, which precluded equilibration for the more highly chlorinated PCBs (hepta- to decachlorobiphenyls). In some instances, hexachlorobiphenyls also did not reach equilibrium (porewater of BRHR-1 and BRHR-2, water column of BRHR-4 (one replicate), BRHR-7, BRMR-1 and BRMR-2). Fractional equilibration correction led to freely dissolved water concentration correction by a factor 1.18 (BRT-1, 89-day deployment) to 3.46 (BRHR-5, 42-day deployment). Surprisingly high correction factors (from 2.2 to 4.8) were applied to data from Moores Run, despite the full 90-day deployment. This might be due to lower discharge compared to Herring Run.

## Surrogate Recovery for Method 8082A

PCB surrogates 3,5-dichlorobiphenyl (PCB 14) and 2,3,5,6-tetrachlorobiphenyl (PCB 65) were added to all samples prior to sample extraction. The purpose of these surrogates was to quantify any potential losses during the extraction procedure, clean-up steps, and transfers during the sampler preparation prior to analysis. The separate internal standards added to the sampler prior to analysis on the GC-ECD are used to account for any variations in the instrument response. A low surrogate recovery would indicate that the reported values may be biased low due to losses during sample preparation. Samples originating from specific sites (for example, Moores Run, Herring Run site BRHR-7, and BRWWTP effluent), had surprisingly high surrogate recovery (>150 percent) for one or both surrogates. Of the 52 samples analyzed, one sample (BRHR-8\_PW) had a surrogate recovery less than 50 percent and was removed from analysis. The high surrogate recoveries observed throughout the sampling area were the result of a co-eluting an unknown environmental contaminant that shares similar physiochemical properties to the surrogates and could not be removed during the clean-up process or differentiated by retention time. The co-contamination was not detected in any of the method blanks and was therefore not an environmental contaminant from the laboratory. In addition, the method blank analysis performed showed that 89 to 100 percent of the targeted analytes were not detected or were below the MDL.

PCB 14 and PCB 65 were selected as surrogates since they are not found in commercial Aroclor mixes and do not co-elute with the congeners analyzed for using the modified method 8082A as described in Beckingham and Ghosh (2011). Losses associated with the sample preparation could not be quantified due to the inability to differentiate between the surrogate and the co-contaminant. Therefore, PCB concentrations and subsequent calculations within this report may be biased low.

## Solid Phase Extraction Blanks and Surrogate Recovery

Solid phase samples were processed in batches along with procedure blanks to certify the absence of contamination during the processing of samples in accordance with methods 3500C and 3550C (U.S. Environmental Protection Agency, 2007a,b). The procedure blank analysis showed that 92 to 98 percent of the targeted analytes were not detected or were below the MDL. Few targeted analytes (seven) were detected in the procedure blank of cake and pellet batches, with two targeted analytes having higher concentration than that detected in samples, and a data qualifier was added to the results. Similarly, two targeted analytes were detected in the procedure blank of bulk sediment at concentrations higher than that of some bulk sediment and were therefore set to zero. Surrogate recovery averaged 88 percent (77–95 percent) for the bulk sediment and reached 80 percent (67–109 percent) for the cake and pellet.

## Replicate Analysis

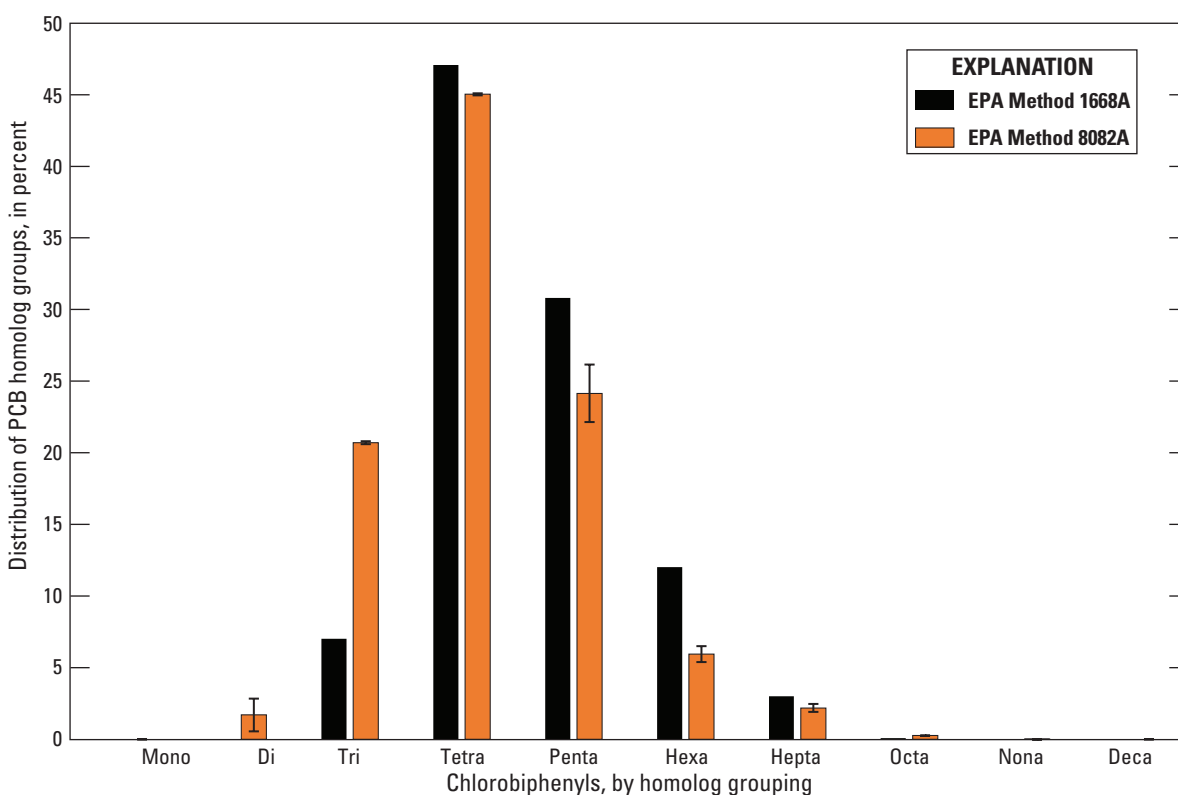
Replicate analysis of environmental samples was performed on 11 passive samplers, 1 pellet sample from BRWWTP, and 3 FOG samples. Average relative percent difference for congeners using passive samplers was 39 percent ( $\pm 38$  percent standard deviation). Average relative percent difference for congeners was  $29 \pm 22$  percent for the pellet sample and  $67 \pm 44$  percent for FOG samples.

## EPA Methods Comparison

The primary analytical method used for PCB analysis in the study was a modified EPA method 8082A using a GC-ECD as described in the Methods section of this report. This method is sensitive for semi-volatile chlorinated organic compounds and relies on retention time to identify compounds. The passive samplers deployed in the pump stations were commercially available (SiREM SP3, Guelph, Ontario, Canada) and used EPA Method 1668A with a high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS, Eurofins Test America, Knoxville, Tennessee). A

passive sampler prepared and analyzed by UMBC and a commercially available passive sampler were co-deployed in the BRWWTP influent during overlapping periods. The UMBC passive sampler was deployed for 89 days while the commercially available passive sampler was deployed for 33 days overlapping days. Both passive samplers used LDPE but included different masses of LDPE sheets of different thickness, and different PRCs used to correct for equilibrium. The average freely dissolved PCB concentrations using passive sampling methods was 748 pg/L (method 8082A) and 315 pg/L (method 1668A). A total of 106 PCB congeners were detected by method 8082A, and a total of 72 PCB congeners could be detected in the sample analyzed by method 1668A.

The higher concentration measured by using the UMBC sampler may be the result of lower MDL due to the larger mass of LDPE used in the sampler and the longer deployment time to reach equilibrium, resulting in a larger number of congeners or congener groups detected. As shown in [figure 1.1](#), the homolog distribution measured between the two passive samplers is similar. A direct comparison of individual congeners is not possible due to different co-elution patterns between the two methods. For consistency and for comparison between samples, the results presented in this report did not combine results from different methods; however, the similarities between the results of the two methods from two different laboratories provides additional confidence in the data.



**Figure 1.1.** A comparison of the percent distribution of polychlorinated biphenyls (PCBs) by homolog groups measured by two separate analytical methods in the Back River Wastewater Treatment Plant influent. EPA, U.S. Environmental Protection Agency.

## References Cited

- Beckingham, B., and Ghosh, U., 2011, Field-scale reduction of PCB bioavailability with activated carbon amendment to river sediments: *Environmental Science & Technology*, v. 45, no. 24, p. 10567–10574. [Also available at <https://doi.org/10.1021/es202218p>.]
- Foss, E.P., Lombard, N., Joshee, S., Bokare, M., Ghosh, U., Needham, T.P., and Majcher, E.M., 2022, Polychlorinated biphenyl (PCB) concentrations of passive samplers, solids, fat, oil, and greases (FOG), and road sediments; and dissolved organic carbon (DOC), total suspended solids (TSS), and particulate organic carbon (POC) concentrations in the Back River watershed, Baltimore City, Maryland, 2018–2020: U.S. Geological Survey data release, <https://doi.org/10.5066/P9WFDIBM>.
- U.S. Environmental Protection Agency, 2007a, Method 3500C—Organic extraction and sample preparation, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 3, February 2007): U.S. Environmental Protection Agency publication SW-846, 19 p.
- U.S. Environmental Protection Agency, 2007b, Method 3550C—Ultrasonic extraction, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 3, February 2007): U.S. Environmental Protection Agency publication SW-846, 17 p.
- U.S. Environmental Protection Agency, 2016, Definition and procedure for the determination of the method detection limit (rev. 2, December 2016): U.S. Environmental Protection Agency, Office of Water, EPA 821-R-16-006, 6 p.
- U.S. Environmental Protection Agency, 2018, Method 8000D—Determinative chromatographic separations, final update III *in* Test methods for evaluating solid waste, physical/chemical methods (3d ed., rev. 5, March 2018): U.S. Environmental Protection Agency publication SW-846, 56 p.

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