OCCURRENCE AND DISTRIBUTION OF URBAN ORGANIC POLLUTANTS IN THE POHICK REGION OF THE POTOMAC RIVER WATERSHED (VIRGINIA, USA)

by

Kevin Joseph Dove II

A Thesis
Submitted to the
Graduate Faculty
of
George Mason University
in Partial Fulfillment of
The Requirements for the Degree
of
Master of Science
Chemistry

Committee:

Gregory O. Foster — Dr. Gregory D. Foster, Thesis Director

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Date: 01/15/2010 — Spring Semester 2010
George Mason University
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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at George Mason University

By

Kevin Joseph Dove II
Bachelor of Science
George Mason University, 2007

Director: Gregory D. Foster, Professor
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Spring Semester 2010
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Fairfax, VA

DEDICATION

This is dedicated to Grandma and Grandpa Horan. Thank you for all of those late nights around the dinner table.

ACKNOWLEDGEMENTS

I would like to thank Ms. Kathleen Housman for her outstanding role as a friend and confidant, and technical advisor. I would especially like to thank Mr. Tom Huff of the Shared Research Instrumentation Facility. Without his help, this project would not be completed. Additionally, without the assistance of Mr. Matt Kershis and Mr. Bradford Pratt, I would still be microwaving fish. Finally, I would like to thank my family and Ms. Emily Slough for assisting me, whenever the need arose.

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ABSTRACT

OCCURRENCE AND DISTRIBUTION OF URBAN ORGANIC POLLUTANTS IN THE POHICK REGION OF THE POTOMAC RIVER WATERSHED (VIRGINIA, USA)

Kevin J. Dove II, M.S.

George Mason University, 2010

Thesis Director: Gregory D. Foster

Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs) and several Endocrine Disrupting Compounds were examined in the Pohick Bay region of the Potomac River, Virginia, USA. Urban Organic Pollutants (UOPs) were found in nanogram/gram quantities in whole fish tissue, bed sediment and suspended sediment. Analytes of interest were extracted from environmental samples using Microwave Assisted Extraction using acetone:hexane as the solvent. Replicate samples from the Pohick Bay region were examined by Gas Chromatography/Mass Spectroscopy. Concentrations of UOPs in the Lower Pohick watershed reveal that the upstream wastewater treatment plant (WWTP) is a possible point source of certain chemicals including triclosan and bisphenol A, PCBs, and PAHs. Loading of creeks and streams from WWTPs that feed into larger water bodies adds to the complexity of modeling a tidal water body such as the Potomac River. Consensus-based Threshold Effect Concentrations (TECs) have also been compared to analyte concentrations of PCBs and

PAHs in bed sediment. Human and watershed health implications, including exposure to endocrine disrupting compounds, should be analyzed to determine possible detrimental effects of utilization of the watershed

INTRODUCTION

Urban organic pollutants (UOPs) are toxic substances derived from anthropogenic sources that are found at the highest concentrations in urban regions and are highly correlated to urban landscapes. Urban organic pollutants of concern in the northern Virginia region include legacy pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), along with emerging pollutants such as endocrine disrupting chemicals (EDCs). Legacy pollutants remain a focus for water quality managers in the Potomac River and Chesapeake Bay. For example, Total Maximum Daily Loads (TMDLs) have only recently been established for PCBs in the Potomac River and Chesapeake Bay [1]. PCBs remain atop the Toxics of Concern List in the Chesapeake Bay Program [2] because of their risk to environmental health, although their concentrations in aquatic environments are slowly declining. PAHs, representing suspected carcinogens [3], are legacy pollutants increasing in the environment because their emissions are linked to ever-expanding fossil fuel consumption and urban development, especially in relation to automobiles, impervious surface coverage, and energy production. PCBs and PAHs have water quality criteria values established for some matrices and homologues [1], which aid in protecting the environment. Emerging pollutants, on the other hand, have little data reported on concentrations in Chesapeake Bay and limited legal enforcement under the Clean Water and Clean Air Acts.

Regulatory policies that better protect water quality will be developed following further studies on the occurrence and distribution of emerging contaminants in the Chesapeake Bay watershed.

The sources of organic pollutants in the urban aquatic environment are complex and varied and arise from many point and nonpoint sources. The prominent nonpoint sources of UOPs include automobile emissions, untreated urban runoff, leaking sewer and septic lines [4-7] and atmospheric deposition. According to the Environmental Protection Agency's National Water Quality Inventory Report to Congress for 2009, atmospheric deposition is the leading source of some pollutants in bays and estuaries in the United States [8]. Prominent point sources include industrial discharges, wastewater treatment plant (WWTP) effluents, and energy utility emissions. Because of the complexity of quantifying multiple source emissions of UOPs to the environment in isolation, aquatic environments such as rivers, lakes and estuaries serve as repositories that enable the levels of UOPs to be correlated with land use, landscapes and identifiable inputs at the scale of a watershed.

One specific source of UOPs in the aquatic environment currently under scrutiny is the WWTP discharge of potentially toxic organic pollutants such as antibiotics, personal care products, therapeutic hormones and materials associated with plastics and coatings [9-16]. WWTPs are thought to be a point source because many UOPs, excluding PCBs, are unregulated and no standards have been established for safe concentrations in effluents. In addition, WWTPs receive very large inputs of contaminants in urban regions, and WWTPs are not designed to remove all trace organic

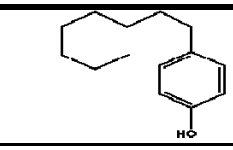
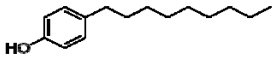
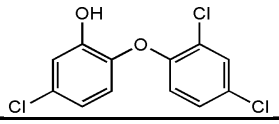
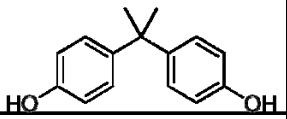
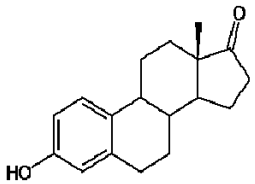
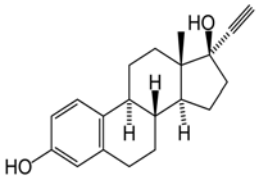
substances in effluents. Many UOPs remain unchanged through the treatment process or partition into multiple phases, including biosolids, during wastewater processing [10, 11, 14-18]. Additionally, many of these compounds, like triclosan, have derivatives or metabolites that are similar in structure and are just as prevalent [19, 20]. Because WWTPs have combined discharge flows similar in magnitude to major rivers in urban regions, the mass fluxes of contaminants into surface waters are substantial even with low concentrations in effluents. Thus, the role of WWTPs in influencing water quality needs further investigation.

Recently, toxicological abnormalities have been observed in the Potomac River vis-à-vis a number of fish species with observed lesions and testicular oocytes (male feminization) [21]. It is postulated that organic contaminants present in water are causing general immuno-suppression in these fish [22]. It is has been shown that endocrine disrupting compounds can have a negative effect on fish immune systems [22-26]. The Pohick Bay region of the Potomac River was chosen as a study location because of fish pathology studies ongoing in Gunston Cove, which includes Pohick and Accotink Bays [27]. Pollutant analysis was conducted in this urban area based on the presence of a large WWTP in one of the small watersheds. By examining the concentrations of organic pollutants in suspended sediment, bed sediment and in fish tissue, it should be possible to correlate the possible source of any toxicological effects to fish in the area.

In this study, several organic contaminants were measured in river particles, bed sediments and fish tissues. The chemical classes investigated included several known endocrine disrupting chemicals (Table 1) and selected PCBs (Table 2), and PAHs (Table

3). These chemicals are of substantial ecotoxicological interest because of public health concerns and media attention [28].

Table 1: List of EDCs Studied

Chemical	Name[a]	Structure[a]	CAS[a] Formula[a] MW[a] Log Kow[b]	Major Use
Octylphenol (OP)	4-(n-octyl)phenol		140-66-9 $CH_3(CH_2)_7C_6H_4OH$ 206.33 5.28	-Detergent Metabolite
Nonylphenol (NP)	4-(n-nonyl)phenol		25154-52-3 $C_9H_{19}C_6H_4OH$ 220.35 5.99	-Detergent Metabolite -Industrial Surfactant
Triclosan (TRI)	5-chloro-2- (2,4-dichlorophenoxy) phenol		3380-34-5 $C_{12}H_7Cl_3O_2$ 289.55 4.66	-Antibacterial
Bisphenol A (BPA)	4,4'-dihydroxy-2,2-diphenylpropane		80-05-7 $C_{15}H_{16}O_2$ 228.28 3.64	-Polycarbonate plastic monomer
Estrone	3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrocyclopenta[a] phenanthren-17-one		53-16-7 $C_{18}H_{22}O_2$ 270.36 3.13	-Estrogenic hormone
17a-Ethinyl Estradiol (EE2)	17-ethynyl-13-methyl-7,8,9,11,12,13,14,15,16,17- decahydro-6H-cyclopenta[a] phenanthrene-3,17-diol		57-63-6 $C_{20}H_{24}O_2$ 296.4 3.67	-Estrogenic hormone

[a]National Institute of Standards and Technology (NIST) Chemistry WebBook

[b] Environmental Protection Agency (EPA) EPI Suite v3.20

Table 2: List of PCBs Studied

PCB Congeners analyzed		
Number of Chlorines	**CAS Structural PCB Number[a]**	**Number of Congeners**
2	4, 5, 6, 7, 8, 9, 10, 12, 15	9
3	16, 17, 18, 19, 20, 22, 24, 25, 26, 27, 28, 29, 31, 32, 33, 34, 37	17
4	40, 41, 42, 33, 44, 45, 46, 47, 48, 49, 52, 56, 59, 60, 63, 64, 66, 67, 69, 70, 71, 74, 77	23
5	82, 83, 84, 85, 87, 91, 92, 93, 95, 97, 99, 101, 104, 105, 107, 110, 114, 115, 118, 119, 123	21
6	128, 129, 131, 132, 134, 135, 136, 138, 141, 144, 146, 147, 149, 151, 153, 156, 157, 158, 164, 167	20
7	170, 171, 173, 174, 178, 177, 178, 179, 180, 183, 185, 187, 189, 190, 191, 193	16
8	194, 195, 196, 197, 199, 203, 206	7
9	206, 207, 208	3
10	209	1
	Total Number of Congeners	**117**

[a] Mills *et al.*, 2007 [29]

[b] IS = Internal Injection Standard

[c] SS = Surrogate Standard

Table 3: List of PAHs Studied

PAH Compounds analyzed [a]				
Number of Rings (number of carbons)	**Compound**	**CAS Number**	**MW**	**Log K_{ow}** [a]
2 (6)	Naphthalene[b]	91-20-3	128.18	3.3
	2-Methylnaphthalene	91-57-6	142.2	3.86
	1-Methylnaphthalene	90.12.0	142.2	3.87
	Biphenyl	92-52-4	154.21	3.76
2(6), 1(5)	Acenaphthylene	208-96-8	152.2	3.94
	Acenaphthene	83-32-9	154.2	4.15
	Fluorene	86-73-7	166.22	4.02
	1-Methylfluorene	1730-37-6	180.25	4.56
3 (6)	Phenanthrene	85-01-8	178.24	4.35
	Anthracene	120-12-7	178.24	4.35
	o-Terphenyl	84-15-1	230.31	5.52
	2-Methylphenanthrene	2531-84-2	192.26	4.89
	2-Methylanthracene	613-12-7	192.26	4.89
	1-Methylphenanthrene	832-69-9	192.26	4.89
	1-Methylanthracene	610-48-0	192.26	4.89
	9-Methylanthracene	779-02-2	192.26	4.89
	9,10-Dimethylanthracene	781-43-1	206.29	5.44
3(6), 1(5)	4,5 Methylenephenanthrene	203-64-5	190.25	4.6
	Fluoranthene	206-44-0	202.26	4.93
4 (6)	Pyrene	129-0-0	202.26	4.93
	Benzo[a]anthracene [c]	56-55-3	228.3	5.52
	Chrysene	218-01-9	228.3	5.52
	Triphenylene	217-59-4	228.3	5.52
4(6), 1(5)	*Benzo[b]fluoranthene*	205-99-2	252.32	6.11
	Benzo[k]fluoranthene	207-08-9	252.32	6.11
5 (6)	Benzo[e]pyrene	192-97-2	252.32	6.11
	Benzo[a]pyrene	50-30-8	252.32	6.11
	Perylene	198-55-0	252.32	6.11
	Dibenz[a,h]anthracene	53-70-3	278.36	6.7
5(6), 1(5)	*Indeno[1,2,3-cd]pyrene*	193-39-5	276.34	6.7
6 (6)	*Benzo[g,h,i]perylene*	191-24-2	276.34	6.7

[a] Environmental Protection Agency (EPA) EPI Suite v3.20

[b] Underlined compounds are on the EPA priority pollutant list [30]

[c] Italicized compounds are known carcinogens [31]

OBJECTIVES

The goal of this study was to determine the spatial distribution, sources, phase distribution and potential links to toxic effects of selected UOPs in surface waters of the northern Virginia aquatic ecosystem. The specific objectives that were addressed are framed by the following questions:

- What are the concentrations and distributions of UOPs in river particles, bed sediment and fish tissues in the vicinity of Pohick Bay and Belmont Bay along the Virginia side of the Potomac River? This region of the Potomac River watershed is highly urbanized with a variety of land uses and sources of organic pollutants. Preliminary observations have shown that fish lesions and deformities occur in this region of the Potomac River watershed.
- Do detected concentrations of UOPs correlate with known sources and land use trends? Increasing impervious surface coverage in the region should enhance mobility of pollutants into the watershed during rain events [4, 5, 7, 30, 31]. A major WWTP is located in one watershed as well as a large military base in another.
- Are exposures to UOPs in fish sufficient to be of concern in relation to toxic effects?

- Do legacy and contemporary UOPs obey partitioning and distribution theory in the environment according to physical and chemical properties? A comparison of biota and sediment partitioning constants will show the equilibrium status of the selected UOPs.

The objectives of this study were met by collecting suspended sediment, bed sediment and fish tissue samples for quantitation and analysis of UOPs by gas chromatography-mass spectrometry. Samples consisted of large-volume water grabs (~20 L) as well as bed sediment and fish tissue samples. Water samples were collected and the suspended particulate phase was analyzed and the filtered water discarded. Fish tissue and bed sediment will represent a biological presence (i.e., bioavailability) of the organic contaminants. Biota-sediment accumulation factors (BSAFs) were also analyzed for the selected compounds to determine if there is predictability in their environmental partitioning behavior. This study was collaborative with an ongoing survey of fish health in the Pohick Bay Region of Northern Virginia [27, 32].

MATERIALS AND METHODS

Study Area

The study area encompassed small sub-watersheds in the region of the Potomac River from Mount Vernon at the northern end to Belmont Bay at the southern end as seen in Figure 1. The sampling locations in this study include Upper Pohick Creek (38°42'10.91"N, 77°12'50.24"W) and Lower Pohick Creek(38°40'54.43"N, 77°10'52.47"W), Dogue Creek (38°42'35.86"N, 77° 8'0.76"W), Kane Creek (38°39'18.97"N, 77°11'39.24"W) and Accotink Creek (38°41'28.49"N, 77° 9'37.46"W) of the tidal and non-tidal freshwater Potomac River watershed. This regional Potomac River watershed area incorporates many recreational parks and marinas, an Interstate highway, urban housing developments, a wastewater treatment plant, semi-industrial zones and military districts including Fort Belvoir. The Noman Cole Pollution Control Plant owned by Fairfax County, VA also discharges ~45 million gallons per day of treated wastewater into the Potomac River at Pohick Creek with a maximum capacity of ~67 million gallon per day.

Figure 1: Map of Sampling Area

Land use is a major factor that contributes pollutants to rivers. Urban watersheds are known to release PCBs and PAHs to the aquatic environment during rain events [4]. Land use profiles of the sub-watersheds sampled in this study are illustrated in Table 4 [31]. Impervious surface percentages can be correlated to large volumes of storm runoff that will discharge into the river and thus carrying pollutants with it.

The Kane watershed has 83.8% forested land, therefore PCB and PAH contamination is expected to be low due to less urbanization. The Accotink Creek watershed has approximately 30% impervious surface coverage and should therefore correlate to a large PCB and PAH concentration relative to the other watersheds that were

investigated. However, the Accotink Creek watershed also has within its boundaries Fort Belvoir, a large military installation, which might add to overall loadings of pollutants.

The Dogue Creek watershed is significantly smaller than the Accotink Creek watershed yet has similar land use percentages yet the average percent impervious surface is 10% less. Therefore, if correlations can be made due to square mileage of impervious surface then the Dogue Creek watershed should be approximately 10% lower in PCB and PAH concentration.

The Pohick Creek watershed is similar to the Dogue Creek watershed in that it has a similar average percent impervious surface (~20%) yet the over all square mileage is doubled. The Pohick Creek watershed also contains within its boundaries the Noman Cole Pollution Control Plant which discharges ~67 million gallons per day of treated wastewater. Therefore correlations between Upper Pohick Creek and Dogue Creek pollutant concentrations can be made, but the correlations between the Lower Pohick Creek pollutant concentrations would have to account for the WWTP.

Table 4: Summary of land use profiles [31]

Watershed	Kane	Pohick	Accotink	Dogue
Overall Size (sq mi)	8	34	51.1	12
Land Use Percentages				
Forested	83.81	50.51	37.55	37.03
Field/Pasture	6.73	7.52	5.65	8.36
Low Intensity Residential	2.83	28.73	33.47	31.50
High Intensity Residential	0.00	0.00	0.02	0.03
Commercial/Industrial	0.25	7.26	17.73	7.14
Exposed Land	0.00	2.09	3.23	9.17
Wetlands	4.92	1.98	1.88	5.90
Open Water	1.47	1.98	0.47	0.89
Average Percent Impervious Surface	2.2	~21	~30	~20

The fish species selected for analysis is typical of mid-Atlantic tidal freshwater rivers. The spottail shiner (*Notropis hudsonius*) is the benthivorous species that was selected for analysis due to previous ecological studies in the area [27, 32] as well as PCB and PAH chemical analysis by other research groups [33, 34]. The spottail shiner is classified as a trophic level III species, whose dietary intake includes extensive consumption of benthic organisms such as midge fly larvae (Chironimidae) and oligocheate worms (Oligocheata) [35-37]. This species is an intermediary that is easily analyzed and represents a link between organisms in other tropic levels.

Field Sampling

Field sampling of suspended sediment (river particles) and bed sediment coincided with the collection of spot-tail shiner (*Notropis hudsonius*). This was done to ensure that the geosolids collected were representative of the area where the fish were harvested. Harvesting was conducted over two weeks due to logistical issues in collecting specimens. Fish between 5 to 10 centimeters were collected by electro-shocker and seine net to ensure uniformity in the average age of fish. Fish samples were stored at -4°C wrapped in precleaned aluminum foil and placed in plastic bag until processed. The number of samples collected in each environmental sub-compartment is shown in Table 5.

Table 5: Number of samples collected per site

Sample Sites	***Sample Matrix***		
	Suspended Sediment	**Bed Sediment**	**Fish Tissue**
Lower Pohick	3	3	5
Upper Pohick	3	3	5
Accotink	3	3	5
Dogue	3	4	5
Kane	3	3	5
Total	15	16	25

Large volume (20-L) water samples were collected using a Fultz submersible positive displacement pump (Fultz Inc., Lewistown, PA), fitted with a SP-300 pump head, at an approximate depth of fish habitation. The water samples were collected in pre-cleaned stainless steel Cornelius kegs supplied with air-tight lids. In addition, 1L samples were collected in polyethylene bottles for the analysis of total suspended matter (TSM) in the water samples. The water samples were stored in the 4°C upon arrival in the laboratory prior to the filtration of suspended sediment.

Bed sediment samples at each site were obtained from the top ~5cm and were collected using a Petite Ponar grab sampler (Wildco, Buffalo, NY). The samples were placed in amber glass jars sealed with Teflon-lined lids and stored frozen at -20^{o}C in the analytical laboratory.

Sampling bottles and all glassware used for sample collection and preparation were cleaned by washing with hot soapy tap water, rinsing with distilled water, rinsing with double distilled water (DDW), and then fired at 450°C overnight. All laboratory materials were made of glass, stainless steel or Teflon to avoid sample contamination. The Teflon and stainless steel materials were cleaned with the same procedure as

glassware except for the final firing step and rinsed with methanol and air dried prior to use. DDW was produced in the laboratory using a Corning Megapure still or an Elga Ultrapure 18 MOhm unit with lab-supplied distilled water.

Standards and Reagents

Bisphenol A (BPA), 4-tert-octylphenol (OP), estrone, 17α-ethinylestradiol (EE), triclosan (TRI), nonylphenol (NP) (all of 99% or greater purity) were purchased from Sigma Aldrich (St Louis, MO). The PAHs were purchased from Restek (Bellefonte, PA) neat or in isooctane solution. The PCBs were purchased from AccuStandard Inc., (New Haven, CT) in the form of five prepared congener mixtures dissolved in isooctane. Deuterated PAH standards were purchased from Cambridge Stable Isotopes (Andover, Massachusetts). Internal injection quantitation standards for gas chromatography-mass spectrometry (GC-MS) included 2,4,6-trichlorobiphenyl (PCB 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204) as well as fluorene-d10, anthracene-d10, fluoranthene-d10, and benzo(a)pyrene-d12. Working solutions were made in hexane (Burdick & Jackson, Muskegon, MI) and stored at -4°C. Final calibration standards were also made up in pesticide grade hexane. Surrogate sample spikes (SS) were added to each sample and used for method recovery. Surrogate spikes consisted of 2,2',4,5',6-pentachlorobiphenyl (PCB 103) and 2,2',3,4,4',6'-hexachlorobiphenyl (PCB 140), naphthalene-d8, acenapthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, and bisphenol A-d6. Ultra high purity (carrier grade, 99.9995% pure) nitrogen gas used for N_2 blow down was purchased from Robert's Oxygen Company (Manassas, VA).

Laboratory Sample Processing

PCBs, PAHs, and EDCs were analyzed in filtered river particles, bed sediments and individual spottail shiner using the techniques summarized in Figure 2. Filtration of the suspended sediment was completed within 24 hours to minimize contamination and analyte reaction. Filtration of the 20-L water samples was performed using 293 mm dia., 0.7 μm (nominal) pore size Whatman glass fiber filters (GF/F) (Florham Park, NJ) housed in a 293 mm Millipore stainless-steel filter holder (Billerica, MA). The GF/F filters were precleaned by ashing overnight at 450 °C and sealed in pre-cleaned aluminum foil envelopes until use. Filters, bed sediment grabs and fish were frozen at -4°C prior to analysis.

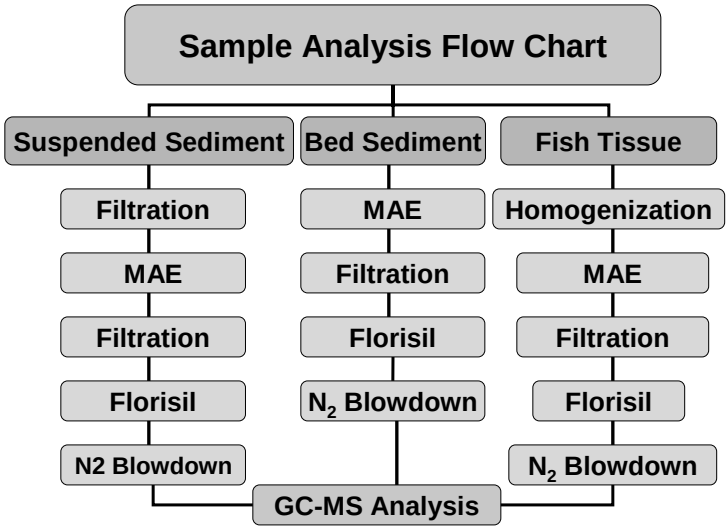


Figure 2: Analytical Flow Chart

Filtered particles and bed sediments were extracted using microwave assisted extraction (MAE) (MARS, CEM Corp., Matthews, NC). The methods were adapted from EPA method 3546 and published reports [38-40]. Sediments were thawed and centrifuged at 1500 rpm (DuPont Sorval RC-5B, New Town, CT) to separate pore water from solids. Filters or ~5 g of bed sediment were added into 100 mL GreenChem extraction vessels along with 15 mL of 3:2 (v/v) acetone:hexane, which functioned as the extraction solvent mixture. The MARS extraction program was found to be optimal at 100 ºC for 15 minutes at 300 W. If four or more vessels were extracted simultaneously the power was increased to 600 W. The acetone:hexane extract was decanted with a disposable glass pipet and filtered through a Whatman GF/F syringe filter (Florham Park, NJ) (0.7 μm nominal dia)to remove residual particles. The extract was then collected in pre-cleaned 50 mL glass centrifuge tubes. The extraction procedure was carried out a total of three times for each sample, and the resulting three extracts were combined and stored overnight in the presence of HCl-activated copper granules (Sigma-Aldrich) to precipitate rhombic sulfur (S_8). Copper activation was performed by treating the copper granules with 1M HCl for 10 minutes then rinsing with DDW and then rinsing with acetone and methanol to remove any water.

Individual whole fish (1.5 to 3.0 g) were completely homogenized in a mortar and pestle using 2 g of anhydrous sodium sulfate as an abrasive and desiccant. Homogenized fish were extracted using MAE with the same solvents and procedures as was used for the filter and bed sediments extractions. Good extraction efficiencies using MAE have been previously reported [38].

All the MARS extracts were cleaned-up by using Florisil chromatography to remove interfering substances prior to GC-MS analysis. The Florisil clean-up procedure was adapted from EPA method 3620C [41]. The sample extracts were concentrated to approximately 10 mL utilizing a using an N-VAP model 112 nitrogen evaporator (Organomation Associates Inc., Berlin, MA). The concentrated extracts were subjected to column chromatography clean-up using 4 g of 2% (v/w) water-deactivated Florisil (J.T. Baker, Phillipsburg, NJ), sandwiched between layers of 3 g of sodium sulfate, packed in a pre-fired (450 ^{o}C) stoppered glass chromatography column. The Florisil column was first rinsed with several bed volumes of hexane, followed by loading the sample on top of the Florisil column. Analytes were eluted from the column with 60 mL of hexane into two separate 50 mL glass centrifuge tubes, which were later combined during solvent volume reduction. The combined eluent was concentrated to 250 μL under a gentle stream of N_2 gas and vialed along with the internal injection standard.

For the determination of TSM, ~200 mL of water was filtered using a Millipore vacuum filtration apparatus, which contained a pre-weighed 47 mm Whatman (Florham Park, NJ) glass fiber filter (GF/F; 0.70 μm nominal pore size). The volume of water passing through the filter was measured with a graduated cylinder, and the GF/F filters were dried to a constant mass overnight at 50 °C in a drying oven. TSM was then determined to be the mass of sediment (mg) per volume of water filtered (L). Filters used for TSM analysis were then subjected to ignition at 475 °C (48 hrs) to determine the organic matter content (OM). This loss on ignition technique was used to gravimetrically

determine the amount of organic material [42]. The remaining material was considered non-combustible inorganic matter.

Instrumental Analysis

All extracts were analyzed and quantitated using an Agilent 7890 gas chromatograph (GC) mated with an Agilent 5875C XL quadrapole MSD (New Haven, CT). The GC-MS was equipped with an Agilent 7890 series autoinjector programmed to introduce 2 μL injections into a pulsed splitless inlet at 300 °C having the pulse pressure at 25 psi until 0.5 min post-injection and purge flow to the split vent at 50 mL/min for 1.25 min post-injection. The septum purge flow was set for 3 mL/min in standard purge flow mode with total inlet pressure at 12 psi. Column flow was set for 1.2 mL/min to the detector. The MS transfer line was heated to 230° C, and the MS source was heated to 150° C to prevent condensation of analytes inside the detector. The electron multiplier voltage was set to 2400 Volts and the filament voltage set at 70 eV.

Columns were changed and oven programs varied to suit the polarity of the compounds and to maximize chromatographic separation. The GC column used for PCBs was a RTX-1 (Restek, Bellefonte, PA) capillary column, 30m x 0.25 mm (id) with a stationary film thickness of 0.25 μm of 100 % dimethylpolysiloxane using He as the carrier gas. The column was subjected to the following thermal gradient upon injection: 100 °C (2 min), 100 to 135 °C at 10 °C/min (0 min), 135 to 235 °C at 1.3 °C/min (0 min), and 235 to 260 °C at 10 °C/min (0 min), making the total run time 83.7 minutes per

sample. The oven was programmed for a column backflush at 300 °C for 15 minutes to ensure proper removal of residual analytes to avoid sample cross contamination.

The column utilized for PAH and EDC analysis was an Agilent J&W DB-5 (New Haven, CT) capillary column, 30m x 0.18 mm (id) with a stationary film thickness of 0.25 μm of 95 % dimethylpolysiloxane and 5%-phenyl-methylpolysiloxane using He as the carrier gas.

The column was subjected to the following thermal gradient upon injection for EDC analysis: 100 °C (1 min), 100 to 200 °C at 10 °C/min (0 min), 200 to 280 °C at 5 °C/min (0 min), and 280 to 300 °C at 10 °C/min (10 min), making the total run time 38 minutes per sample. The column was held at 300°C for 10 min to remove heavier molecular weight contaminants.

The column was subjected to the following thermal gradient upon injection for PAH analysis: 100 °C (2 min), 100 to 200 °C at 15 °C/min (0 min), 200 to 275 °C at 3 °C/min (0 min), and 275 to 300 °C at 10 °C/min (20 min), making the total run time 57.17 minutes per sample. The column was held at 300°C for 20 min to remove heavier molecular weight contaminants.

Quality Assurance

Quality assurance measures included laboratory blanks, surrogate standard spikes, and detection limit determinations. Laboratory blanks were performed for all analytes in suspended sediments. Suspended sediment blanks were performed by adding 20-L DDW which had no previous contact with the Fultz pump, into a clean, hexane-rinsed 20-L keg,

filtering it, and extracting the filter in the same fashion as environmental samples. A total of five lab blanks were analyzed for total PCBs, PAHs, and EDCs. Three field blanks were employed on each day of sampling for a total of six field blanks. Field blanks consisted of transporting two kegs of DDW to the sampling site and passing DDW through the Fultz pump and returning to a fresh pre-cleaned keg. The field blank was then returned to the lab and analyzed for total PCBs, PAHs, and EDCs following the same methods as an environmental sample. Field blank concentrations ranged from 0.21 to 0.33 ng/L for total EDCs, <IDL to 1.06 ng/L for total PAHs, and 0.91 to 6.08 ng/L for PCBs.

Surrogate standards (PCB 103, PCB 140, bisphenol A-d6 (BPA-d6), naphthalene-d8, acenaphthene-d10, phenanthrene-d10, cChrysene-d12 and perylene-d12) were introduced to all samples prior to extraction as a measure to test method performance (Table 6 and 7).

Table 6: List of Internal and Surrogate Standards for PCB analysis

Quality Assurance Congeners	
Number of Chlorines	**CAS Structural PCB Number and Structural Name[a]**
3	IS[a] 30 (2,4,6-Trichlorobiphenyl)
5	SS[b] 103 (2,2',4,5',6-Pentachlorobiphenyl)
6	SS 140 (2,2',3,4,4',6'-Hexachlorobiphenyl)
8	IS 204 (2,2',3,4,4',5,6,6'-Octachlorobiphenyl)

[a] "IS" = Internal Standard
[b] "SS" = Surrogate Standard
[c] Mills *et al.*, 2007 [29]

Table 7: List of Internal and Surrogate Standards for PAH analysis

Quality Assurance Compounds		
Compound	**CAS Number**	**MW**
Naphthalene-d8 SS	1146-65-2	136.22
Acenaphthene-d10 SS	15067-26-2	164.27
Phenanthrene-d10 SS	1517-22-2	188.29
Chrysene-d12 SS	1719-03-5	240.36
Perylene-d12 SS	1520-96-3	264.38
Fluorene-d10 IS	81103-79-9	176.28
Anthracene-d10 IS	1719-06-8	188.29
Fluoranthene-d10 IS	93951-69-0	212.31
Benzo(a)pyrene-d12 IS	63466-71-7	264.38

[a] "IS" = Internal Standard
[b] "SS" = Surrogate Standard

Recoveries of the individual PCB 103 and 140 congeners spiked in suspended sediment samples ranged from 64% to 111%, from 79% to 109% in bed sediment and from 69% to 107% in fish tissue (Table 8).

Naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 were used as surrogates for PAH analysis. Compound recovery ranges and average percent recoveries are presented in Table 8. The lowest PAH surrogate recovery was observed for acenaphthalene-d10 in fish tissue at 41% and the highest observed surrogate recovery was that of chrysene-d12 in fish tissue at 124%. The highest and lowest average percent recoveries were chrysene-d12 with 90±17% in bed sediments and phenanthrene-d10 in suspended sediments at 58±11%, respectively.

Bisphenol A-d6 was used as the surrogate standard in EDC determinations. Recoveries of BPA-d6 spiked in suspended sediment samples ranged from 66% to 90%, from 80% to 97% in bed sediment and from 48% to 84% in fish tissue. Percent recoveries

(mean ± standard deviation) were 77 ± 8% for suspended sediment, 86 ± 6% for bed sediment and 63 ± 10% for fish tissue.

Table 8: Method surrogate recoveries

Matrix	Surrogate Compound (Class used for)	Range[a] (%)	Average[b] (%)	*n*[c]
Suspended Sediment	PCB 103 (PCB)	79 - 109	95 ± 8	12
	PCB 140 (PCB)	64 - 111	94 ± 12	12
	Bisphenol A-d6 (EDC)	66 - 90	77 ± 8	11
	Naphthalene-d8 (PAH)	47 - 107	64 ± 12	13
	Acenaphthene-d10 (PAH)	43 - 96	74 ± 12	13
	Phenanthrene-d10 (PAH)	45 - 96	58 ± 11	13
	Chrysene-d12 (PAH)	59 - 94	81 ± 9	13
	Perylene-d12 (PAH)	54 - 94	74 ± 8	13
Bed Sediment	PCB 103 (PCB)	80 - 98	88 ± 8	16
	PCB 140 (PCB)	79 - 109	90 ± 12	16
	Bisphenol A-d6 (EDC)	80 - 97	86 ± 6	7
	Naphthalene-d8 (PAH)	59 - 87	70 ± 12	15
	Acenaphthene-d10 (PAH)	61 - 87	73 ± 11	15
	Phenanthrene-d10 (PAH)	51 - 92	74 ± 15	15
	Chrysene-d12 (PAH)	74 - 115	90 ± 17	15
	Perylene-d12 (PAH)	71 - 90	81 ± 8	15
Fish Tissue	PCB 103 (PCB)	69 - 106	95 ± 9	18
	PCB 140 (PCB)	77 - 107	91 ± 9	18
	Bisphenol A-d6 (EDC)	48 - 84	63 ± 10	10
	Naphthalene-d8 (PAH)	49 - 105	68 ± 16	22
	Acenaphthene-d10 (PAH)	41 - 115	84 ± 18	22
	Phenanthrene-d10 (PAH)	54 - 102	80 ± 15	22
	Chrysene-d12 (PAH)	44 - 124	87 ± 21	22
	Perylene-d12 (PAH)	42 - 115	85 ± 18	22

[a]Range of % recoveries

[b]Average and standard deviation of % recovery

[c] Number of samples used in range and average

Method detection limits (MDL) were determined by multiplying the standard deviation of 10 replicate calibration samples by the Student t Test for the 95% confidence interval [43]. The MDL was then divided by the approximate sample mass to determine the Estimated Method Detection Limit (EMDL) in ng/g units. Approximate sample masses are two (2) grams for fish tissue, five (5) grams for bed sediment and three (3) grams for suspended sediment. This produces an average EMDL (mean ± standard deviation) of 0.16±0.01 ng/g for fish tissue, 0.06 ± 0.01 ng/g for bed sediment and 0.09 ± 0.04 ng/g for suspended sediment. A summary of the EMDL data is presented in Table 9. Complete EMDL data is presented in Appendix B.

Table 9: Summary of Estimated Method Detection Limit for PCBs, PAHs, and EDCs

Compound Class	Method Detection Limit	Estimated Method Detection Limit		
	MDL (ng)	Fish (ng/g)	Bed Sediment (ng/g)	Suspended Sediment (ng/g)
PCBs	0.31	0.15	0.04	0.04
PAHs	0.30	0.15	0.06	0.10
EDCs	0.34	0.17	0.07	0.11
Average	0.32	0.16	0.06	0.09
Standard Dev	0.02	0.01	0.01	0.04

Biota-Sediment Accumulation Factor (BSAF)

To evaluate UOP distribution behavior and bioavailability, the biota-sediment accumulation factor (BSAF) was estimated for each chemical or chemical class. Compounds with high K_{ow} values are known to partition into the biota lipids as well as the organic carbon portion of sediments [44]. The BSAF assesses partitioning behavior by comparing the concentrations of the compounds found in these two sub-

compartments. Analysis of the BSAF leads to the ability to predict the concentration of any given UOP from only one variable, either the biota concentration or the sediment concentration.

The BSAF is expressed as a lipid normalized chemical concentration divided by the organic carbon normalized sediment concentrations. By factoring in the lipid mass of the fish and the organic carbon content of the geosolids, concentrations of the UOPs are normalized to minimize biological and geochemical variability among the compared sites. The ratio of normalized fish/sediment UOP concentrations should provide ratios between 1-10 as predicted by partitioning theory [44]. Organic contaminants have a slightly greater preference for lipids relative to sediment organic matter. BSAF values outside this range challenge the existence of equilibrium partitioning between the two compartments, such as through metabolism in biota.

To calculate the BSAF, the concentration of the analyte in the fraction of organic carbon and the lipid fraction of biota were obtained. The fraction of organic carbon (f_{oc}) was estimated in each bed sediment sample based on the thermal gravimetric analysis of replicates determinations of %OM. The percentage of total organic matter was converted to the percentage of total organic carbon (OC) by dividing OM by 1.85 as shown in equation 1. This conversion factor was derived through the regression of direct OC measurements (performed using elemental analysis) with ignition-based OM measurements on Potomac River sediments in a previous study (%OM = 1.85 x %OC, Foster unpublished data).

$$f_{oc} = \frac{\%OC}{100} = \frac{\%OM}{1.85} \div 100 \qquad \text{Eq.1}$$

The sediment portion of the BSAF is the average of the measured chemical concentrations of an analyte in dry sediment (C_s) in ng/g units and divided by the average fraction of organic carbon present in the sample (f_{oc}) as shown in equation 2. The average concentration is obtained by dividing the sum of the sediment concentrations by the number of replicates (*n*). The average fraction of organic carbon was determined the same way but by dividing the sum of the percent organic carbon measurements by the number of replicate measurements (*m*).

$$C_{oc} = \frac{\left(\sum C_s\right)/n}{\left(\sum f_{oc}\right)/m} \qquad \text{Eq.2}$$

The biota portion of the BSAF is the average of the chemical concentration of an analyte on a wet tissue weight basis (C_{fish}) in ng/g units and divided by the average fraction of lipid present in the sample (f_{lipid}) as shown in equation 3. The average concentration is obtained by dividing the sum of the fish concentrations by the number of replicates (*n*). The average fraction of lipid was determined the same way but by dividing the sum of the percent lipid measurements by the number of replicate measurements (*m*).

$$C_l = \frac{\left(\sum C_{fish}\right)/n}{\left(\sum f_{lipid}\right)/m} \qquad \text{Eq.3}$$

Combining equations 2 and 3 yields the formula below in the estimation of the BSAF for each of the selected chemicals at the various sites (equation 4).

$$BSAF = \frac{C_{fish(ave)} / f_{lipid}}{C_{s(ave)} / f_{oc}} = \frac{C_l}{C_{oc}} \qquad \text{Eq.4}$$

Compounds analyzed in this study all have K_{ow} values greater than 3, which suggest that preferred binding is within organic carbon or tissue lipid phases and not the polar aqueous or mineral phases. This assumption is only valid with non-ionic organic compounds. However, several of the EDCs have appreciable dissociation in surface waters (Ka's) because of dissociable hydrogen atoms on carboxyl or hydroxyl functional groups, which can substantially effect environmental partitioning. Chemicals carrying formal charges will have different binding characteristics to particles and biota relative to the neutral species [44].

The theoretical BSAF value was determined by a Linear Free Energy Relationship (LFER) to determine the ratio of K_{lipid} to $K_{organic\ carbon}$ [45]. The K_{lipid} was determined from the K_{ow} of the compound raised to the 0.91 power and multiplied by 3.2.

The same LFER that was used to determine K_{lipid} for PCBs was used for PAHs and EDCs.

The $K_{organic\ carbon}$ for PCBs was determined from the K_{ow} of the compound raised to the 0.74 power and multiplied by 1.4. The $K_{organic\ carbon}$ for PAHs was determined from the K_{ow} of the compound raised to the 0.98 power and multiplied by 0.73. The LFER used for the EDC compounds was the same as the LFER used for PAHs. This was done to determine theoretical BSAF values for the EDCs since little LFER data is available from published data. The theoretical range was then determined by multiplying and dividing the theoretical BSAF by two. The theoretical range for PCBs was between 1.5 to 6.5, PAHs were between 2.0 to 8.0 and EDCs were between 1.9 to 8.1.

RESULTS AND DISCUSSION

Polychlorinated Biphenyl (PCB) Concentrations

PCBs were found at varying concentrations in all compartments (bed sediments, suspended sediment and fish) at each of the five sites (Figure 3). For this study, total-PCBs (tPCBs) consisted of the sum of all 117 individual congeners including co-eluters. The tPCB concentrations appeared to increase among compartments at each site from suspended sediments (ranging from 1.29 to 2.18 ng/g dry wt) to bed sediments (ranging from 2.67 to 19.8 ng/g dry wt) and finally the highest concentrations observed were in fish tissues (ranging from 12.8 to 38.1 ng/g wet wt). Greater tPCB concentrations were observed in suspended sediment, bed sediments, and fish collected at the Lower Pohick site when compared to samples collected at the other four other sites in this study, including samples collected at Upper Pohick site (Figure 3). The Lower Pohick site shows approximately 18 ng/g dry wt tPCBs in suspended sediments in comparison to approximately 2 ng/g dry wt tPCBs observed at all the other sites. Bed sediment collected at the Lower Pohick site was the most concentrated in PCBs (19.8 ± 1.4 ng/g dry wt), followed by Kane Creek (14.5 ± 0.13 ng/g dry wt), the Upper Pohick site (7.29 ± 0.4 ng/g dry wt), Accotink Creek (3.56 ± 0.4 ng/g) then finally Dogue Creek (2.67 ± 0.13 ng/g). With regards to PCBs in fish tissue, 38.1 ± 4.6 ng/g wet wt tPCBs was found at the

Lower Pohick site as compared to ~15 ng/g wet wt tPCBs for the other sites. Of the three sampled matrices, fish tissue was found to be the most concentrated in PCBs.

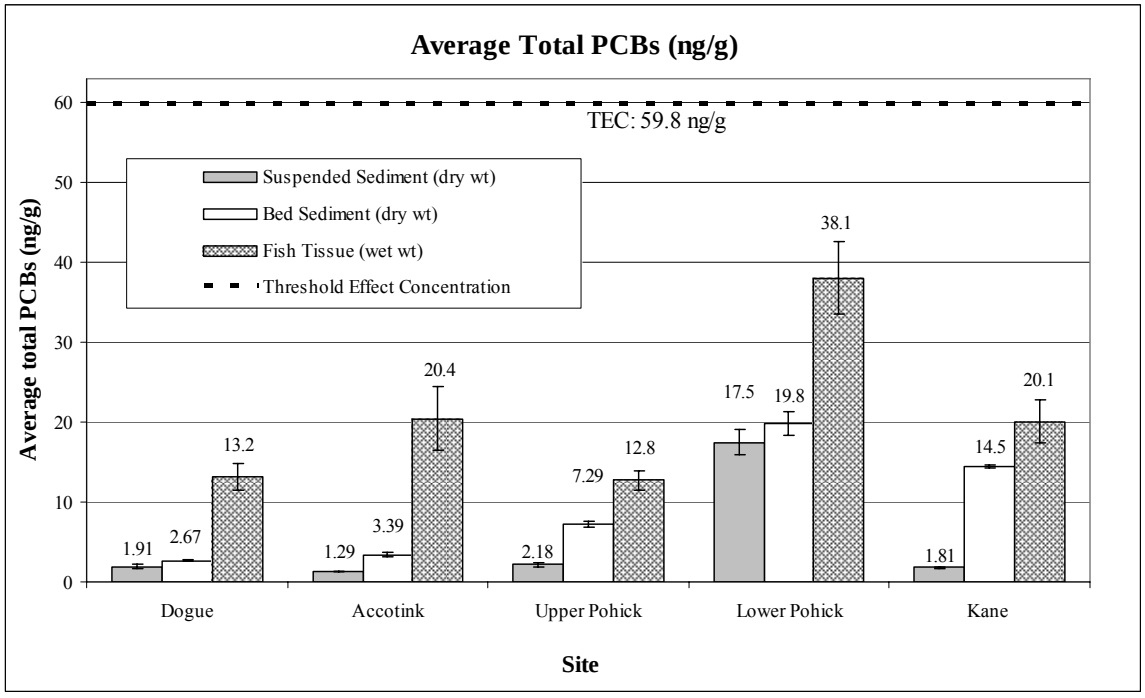


Figure 3: Mean total-PCB concentrations (± 1 sd) by site.

A one-way analysis of variance (ANOVA) was performed at the 95% confidence level to determine if significant differences existed in mean concentrations of tPCBs among all sites for each compartment separately. The ANOVA test results with a p value of less than 0.05 are considered to be significantly different. Statistical comparisons were not made among sub-compartments (i.e., bed sediment vs. suspended sediment vs. fish) at individual sites except for the Upper and Lower Pohick site. The ANOVA revealed that significant differences exist between the means of bed sediment concentrations (p =

0.000) at the various sites. Fish tissue concentrations ($p = 0.000$) as well as suspended sediment concentrations ($p = 0.024$) are also significantly different among the various sites.

Among the sub-compartments at the Lower Pohick site, the ANOVA test shows significantly different mean concentrations between the bed sediment and fish tissue sub-compartments ($p = 0.001$), as well as between the suspended sediment and fish issue sub-compartments ($p = 0.001$). However, the mean concentrations between the suspended sediment and bed sediment sub-compartments are not significantly different ($p = 0.126$).

Among the sub-compartments at the Upper Pohick site, the ANOVA test shows significantly different mean concentrations between the bed sediment and fish tissue sub-compartments ($p = 0.023$), as well as between the suspended sediment and fish issue sub-compartments ($p = 0.000$ and between the suspended sediment and bed sediment sub-compartments ($p = 0.000$). The implications of these results are elaborated upon in the *PCB Homologue Profiles* section of this document.

A Tukey's test was further applied to determine which tPCB mean concentrations differed from each other between the various sites. The Tukey's test values are shown in Table 10 as a matrix to compare the significant differences. This matrix shows the significant differences of the sites in the first column as they compare to the first row. The direction of the arrow denotes the site with the relatively greater tPCB concentration.

Table 10: Matrix of Tukey's range test results for tPCBs

Site	Accotink	Dogue	Kane	Lower Pohick
Dogue	F↓			
Kane	F↓, S↑	S↑		
Lower Pohick	F↑, S↑	F↑, P↑, S↑	F↑, S↑	
Upper Pohick	F↓, S↑	S↑	S↓	F↓, P↓, S↓

Arrows denote which compartment is significantly greater at the site in the first column in relation to the first row

F: fish tissue P: particles (suspended sediment) S: bed sediment

Missing letters (F,P,S) denote no significant difference at that site in the sub-compartment

The statistical evaluation of the concentrations of tPCBs in sediments, suspended sediment and fish tissue yielded the following relative order from largest to smallest. For tPCBS in bed sediment: Lower Pohick Creek > Kane Creek > Upper Pohick Creek > Accotink Creek ≈ Dogue Creek. For tPCBs in suspended sediment: Lower Pohick Creek > Upper Pohick Creek ≈ Accotink Creek ≈ Dogue Creek ≈ Kane Creek. For tPCBs in fish tissue: Lower Pohick Creek > Accotink Creek ≈ Kane Creek > Upper Pohick Creek ≈ Dogue Creek

A very notable trend is the Lower Pohick Creek site has the greatest tPCB concentrations in all sub-compartments. The Dogue Creek site had consistently one of the lowest significantly different concentrations in all sub-compartments. This is interesting due to the highly urban characteristics of the Dogue Creek watershed as compared to the Kane Creek watershed that is more rural and undeveloped. Possible tidal fluctuations, above normal levels, of the Potomac River at Belmont Bay into the Kane Creek watershed accounts for the increased tPCB concentrations at that sampling location.

It was observed in Figure 3 that the concentrations of tPCBs in the suspended sediment sub-compartment are lower than the bed sediment sub-compartment except for the Lower Pohick site where the concentrations are not statistically different. The depositional history of PCBs in an area can be measured by bed sediment sampling most often by core samples. This is because as sediment settles out of the water column containing bound PCB residues, a layering effect occurs as the depth of the now bed sediment increases.

Often, due to increased river flow causing turbulent conditions in the water column, resuspension of bed sediment will show an increased suspended sediment tPCB concentration. However, it was observed in this study, due to homologue variances between suspended sediment and bed sediment (especially at the Lower Pohick site), tPCB concentrations the source of tPCBs is considered different. Additionally, the TSM at the Lower Pohick site was the lowest measured in this study (251.45 mg/L) suggesting that resuspension of bed sediment is unlikely. This is discussed further in the *PCB Homologue Profiles* section of this document.

An interesting perspective can be established by subtracting the concentrations of tPCBs found at the Lower Pohick site from the Upper Pohick site to identify possible PCB loadings from the Noman Cole WWTP. The concentration difference for the Lower Pohick site was +12.5 ± 1.5 ng/g for bed sediment, +15.3 ± 1.5 ng/g for suspended sediment and +25.3 ± 4.8 ng/g for fish tissue. These positive concentration differences suggest a substantial loading of PCBs from the treatment plant.

None of the mean tPCB concentrations found in any sub-compartment were above the consensus-based Threshold Effect Concentration (TEC) of 59.8 ng/g for tPCBs compiled by MacDonald (2000a) as shown in Figure 3. The Lower Pohick site, having the largest tPCB concentrations detected in bed sediments in this study, was 21 ng/g below the sediment quality guideline. It is therefore unlikely that any adverse acute effects will be noticed in benthic organisms arising solely from PCB exposure [46].

The measured tPCB concentrations found in this study were comparable to those measured by other research groups investigating tPCBs in the same geographic area (Table 11). The Virginia Department of Environmental Quality (VA DEQ 2008) sampled the same area approximately four months prior to the current study and found comparable data to the current study with regards to bed sediment (15 ng/g dry wt) and fish tissue (10-20 ng/g wet wt in Pohick Bay and 9-27 ng/g wet wt in Accotink creek) concentrations[47]. The VA DEQ sample values shown are a composite of several species including bluegill sunfish (*Lepomis macrochirus*) and yellow perch (*Perca flavescens*). These species are considered trophic level III fish and consume similar benthic organisms as the spottail shiner [48]. This relation should remove variability in diet as these organisms consume the same benthic biota but does not remove variability in physiology and metabolism.

Research done by Housman (2009) found PCBs at the Potomac River estuarine turbidity maximum (ETM) zone at concentrations ranging from 16 to 54 ng/g dry wt for bed sediments on various days of sampling in May 2008 and May 2009. Concentrations of tPCBs in suspended sediment ranged from 21 to 530 ng/g dry wt. This increased

concentration is due to large storm events where the total suspended material (TSM) ranged from 9.6 to 325 mg/L [49]. To compare another site upstream of the ETM, Housman (2009) analyzed sediment from the Washington Ship Channel, which is located at the fork of the Potomac and Anacostia rivers in an area known for having very high PCB concentrations in sediments [1, 50]. Additionally, Foster et al. (2008) found bed sediment concentrations ranging from 0.2 to 104 ng/g dry wt with an average of 12 ng/g dry wt in bed sediments from the Potomac River basin [50]. McEachern (2005) found PCB concentrations in bed sediments in the Potomac River ETM region at Nanjemoy Creek, MD, Mathias Point, VA, the 301 Bridge, MD, and Dahlgren, VA at 158, 63.4, 40.4 ng/g dry wt, and 55.8 ng/g dry wt, respectively [51].

Table 11: Concentrations (ng/g) of PCBs in suspended sediment, bed sediment and fish tissue from various locations in the Potomac River region

Potomac River PCB concentrations

Sampling Locale	Date	Fish Tissue	Bed Sediment	Suspended Sediment		# congeners	Reference
		ng/g	ng/g	ng/g	ng/L		
Upper Pohick Creek		11-13	7-14	2.1			
LowerPohick Creek		32-42	18-21	19			
Accotink Creek	Dec 8, 2008	16-25	3-4	1.3	nr[a]	117	Current Study
Kane Creek		17-23	14-15	1.8			
Dogue Creek		12-15	2-3	1.9			
Pohick Bay, VA	Sept 4, 2008	10-20[c]	nr	nr	nr	nr	VA DEQ (2008)
Accotink Creek, VA		9-27[c]	15				
Potomac River ETM	Mar. 30, 2008		26-41	21-530	1.6-5.6		
	May 21, 2008	nr	16-54	83-471	1.6-7.2	117	Housman (2009)
	May 8, 2009		22-35	21-66	1.3-14		
Potomac River Basin, VA and MD	May and Dec. 2000	nr	12 (0.2-104) 104[b]	nr	nr	75	Foster *et al.* (2008)
Nanjemoy Creek, MD			158				
Mathias Point, VA		nr	63.4	nr	nr	90	McEachern (2005)
301 Bridge, MD			40.4				
Dahlgren, VA			55.8				
Anacostia River Washington Ship Channel	Spring 2009	nr	222-256	nr	nr	117	Housman (2009)

[a] "nr"= not reported

[b] Sample from the Anacostia River Washington Ship Channel

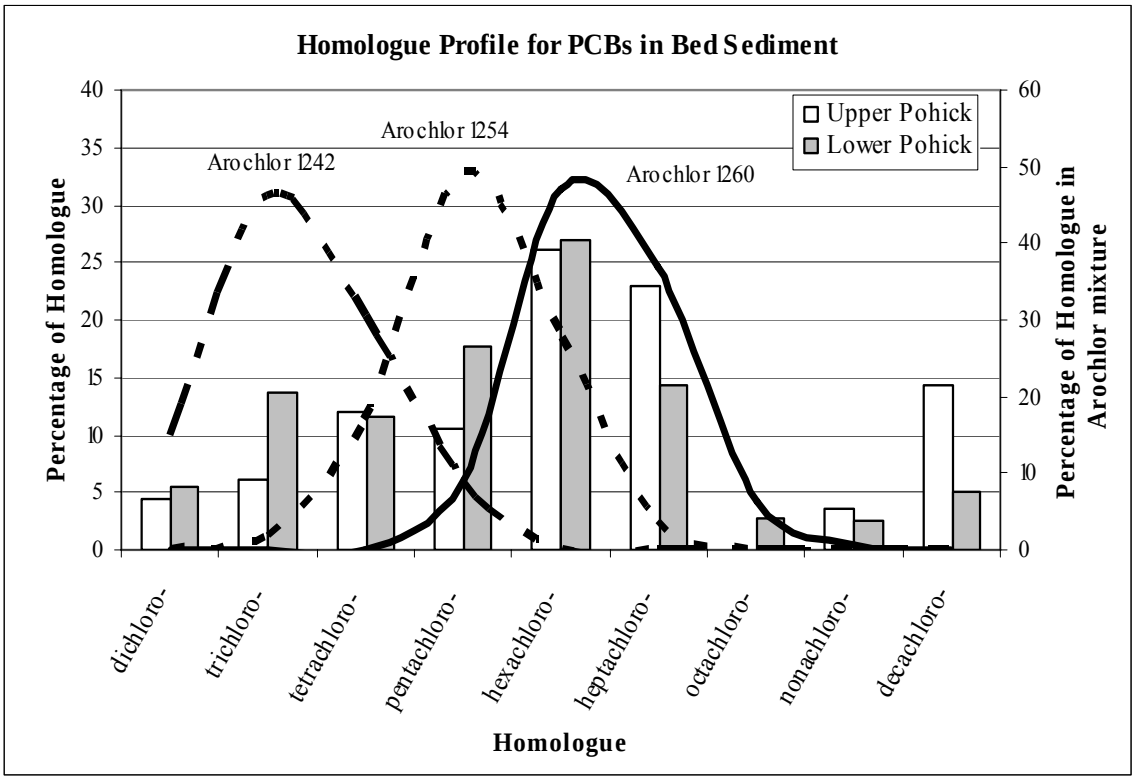
[c] Obtained from Yellow Perch and Bluegill Sunfish (trophic level III fish)

PCB Homologue Profiles

The molecular composition of PCBs lends information on sources, aging, reactions, diagenesis, fractionation and depositional trends and processes [52]. The predominant source of PCBs in United States waterbodies is considered to be derived from Arochlor mixtures, in which 640,000 tons were manfactured by the Monsanto Company (St Louis, MO, USA), for 47 years until production was banned in the US in 1979 [53, 54]. These compounds were used as the coolant and dielectric fluids in transformers, capacitors and other electrical systems [55]. Additionally, PCB usage included applications in paints and plasticizers, and hydraulic fluids. These mixtures include Arochlor 1242, Arochlor 1254, and Arochlor 1260. These mixtures were created reacting biphenyl with anhydrous chlorine in the presence of a catalyst of iron fillings or ferrous chloride [53]. By separating the 117 individual PCB congener concentrations into their respective chlorine substitution homologue groups (i.e., sum of dichloro-, trichloro-, tetrachloro-biphenyls, etc.), comparisons of the sources and environmental processing of PCBs can be made [55-57].

The homologue profile for PCBs in bed sediment is shown in Figure 4. At the Upper and Lower Pohick site the hexachloro- homologue is dominant. However, from the relative profile of the homologues Arochlors 1242, 1254 and 1260 appear to be represented in bed sediments. The percentages of each homologue with relation to site can give clues to possible sources of PCBs. With regards to percent abundances, trichloro-, and pentachloro-, homologues are present in bed sediment in a much lesser abundance at the Upper Pohick site than the Lower Pohick site. The heptachloro- and

decachloro-PCBs are present in a much greater abundance at the Upper Pohick site than the Lower Pohick site. The tetrachloro-, hexachloro-, and nonachloro-PCBs are approximately equivalent in abundance. This pattern shows that the lower molecular weight PCBs are more abundant at the Lower Pohick site and the higher molecular weight PCBs more abundant at the Upper Pohick site in bed sediment. This pattern is also present in Accotink Creek, Dogue Creek, and Kane Creek bed sediment where the dominant homologues are tetrachloro-, pentachloro, and hexachloro-PCBs.



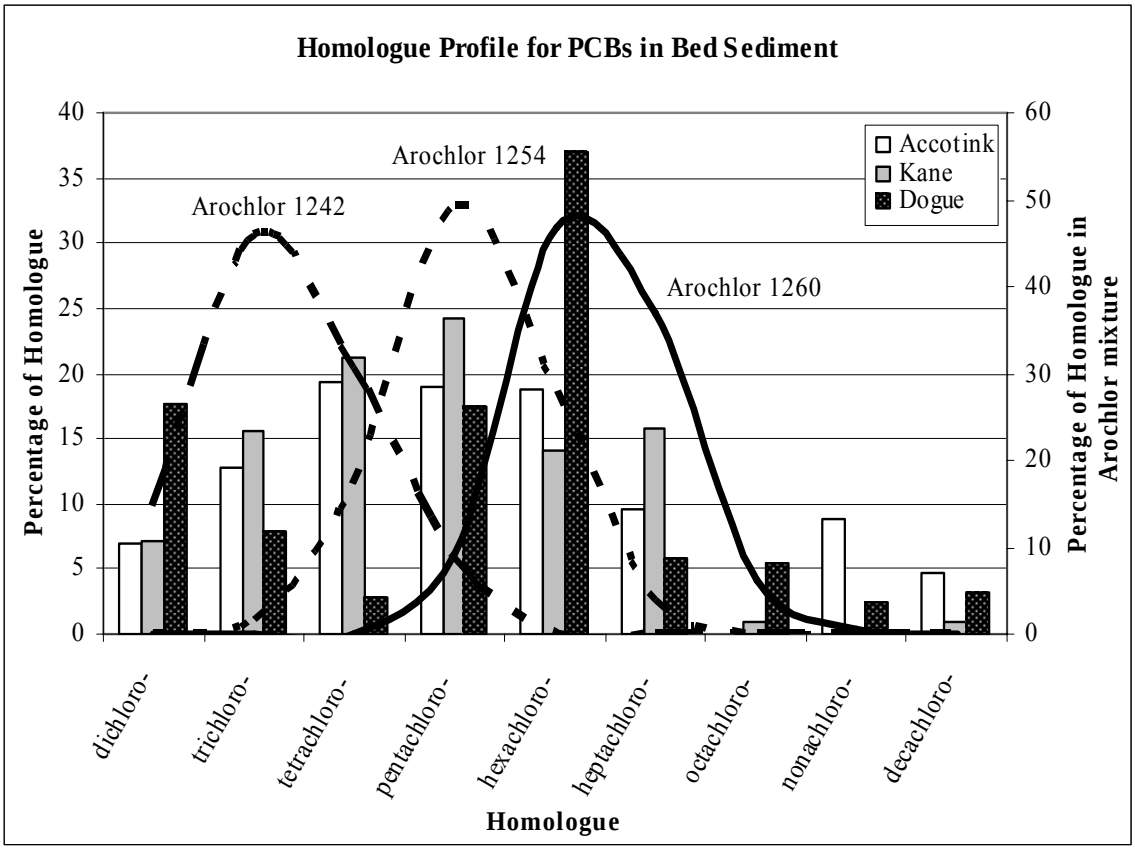


Figure 4: Composite homologue percent profile for PCBs in bed sediment

Homologue profiles in suspended sediment are shown in Figure 5. The dominant group for the Lower Pohick suspended sediment sub-compartment is the tetrachloro-, and pentachloro-PCB homologues. Additionally, the trichloro-, and lower molecular weight homologues are dominant in the Upper Pohick Creek site. The lower molecular weight homologues are present in greater abundance at the Upper and Lower Pohick site as compared to the Accotink, Dogue and Kane Creek sites.

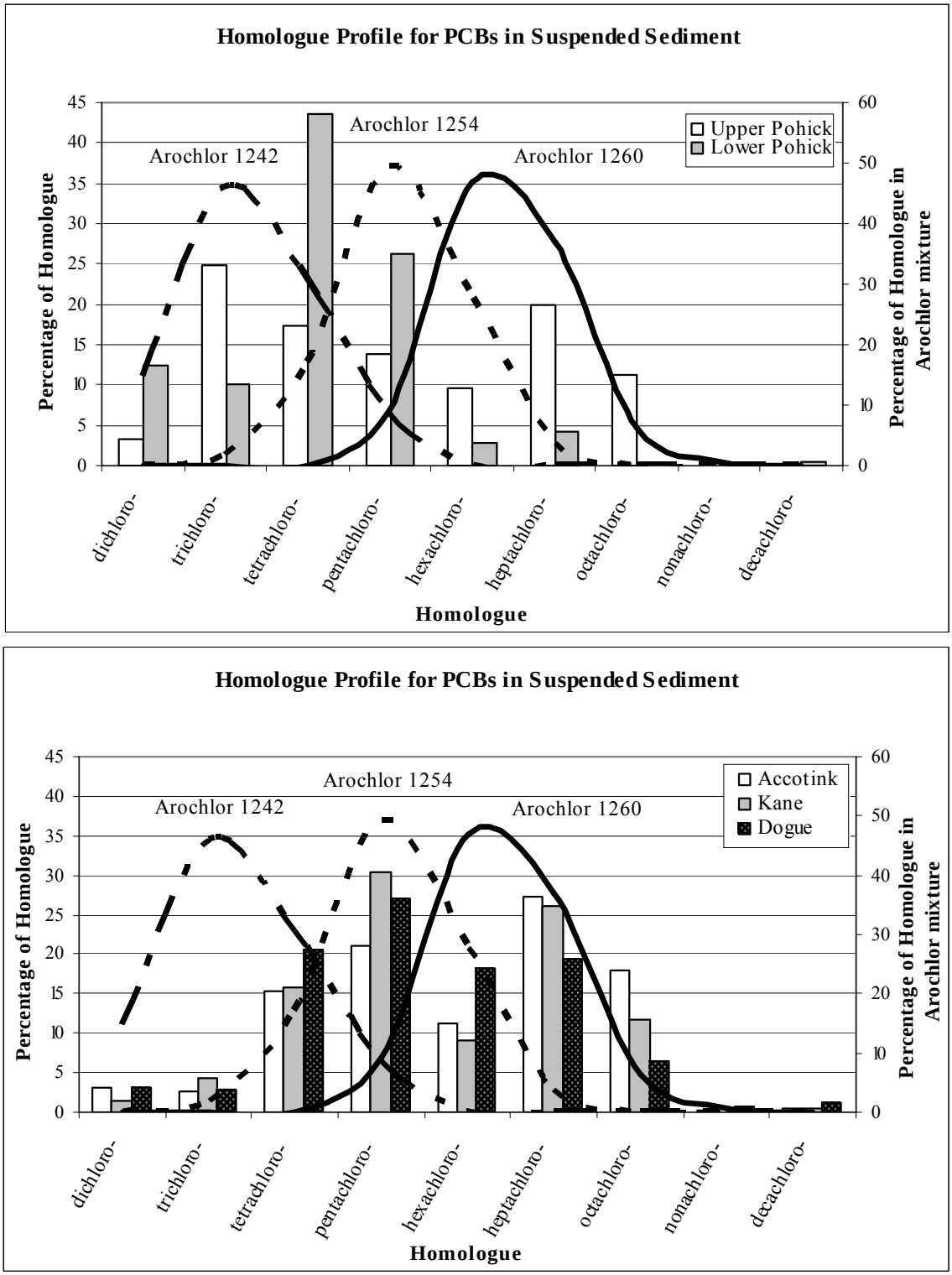
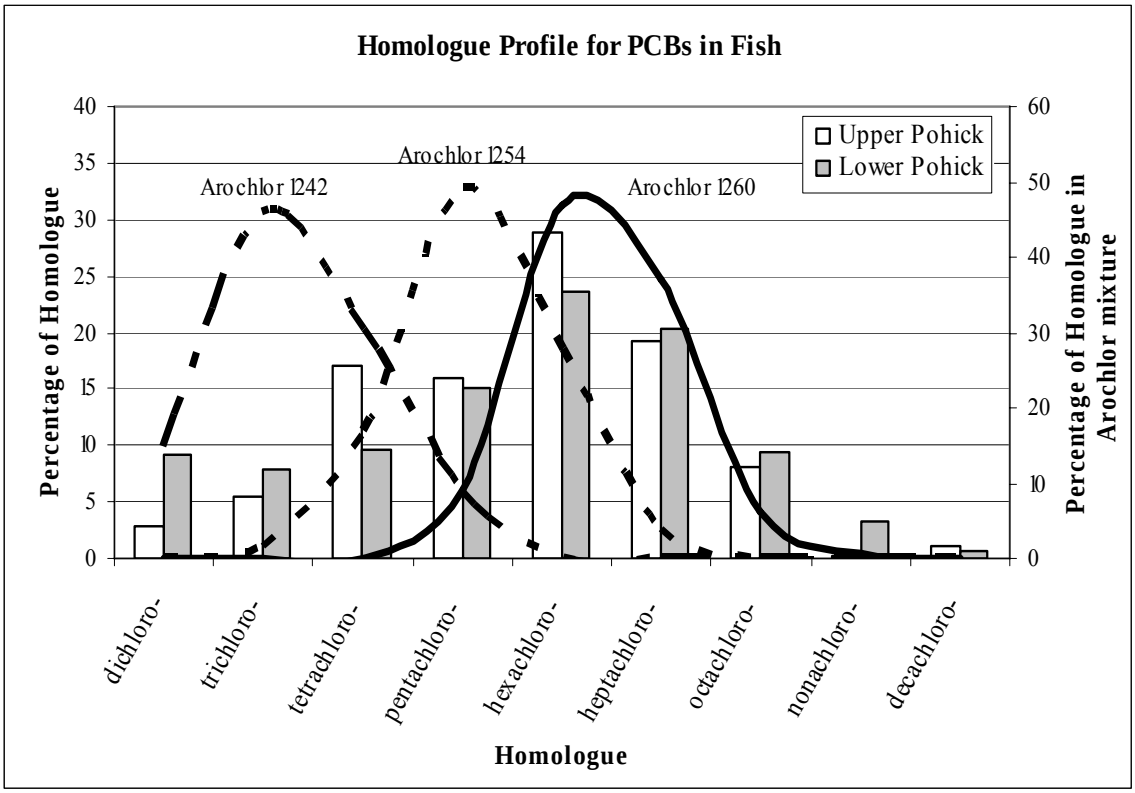


Figure 5: Composite homologue percent profile for PCBs in suspended sediment

The homologue profile for fish tissue is shown in Figure 6. The pentachloro-PCB congeners were dominant in the Dogue and Kane Creek sites and a relatively low percentage was present in the hexachloro-PCB form. The different homologue profiles found in Dogue Creek, Kane Creek and Accotink Creek sites suggest that the tPCBs are derived from different sources than the Upper and Lower Pohick sites. This argument is developed below.



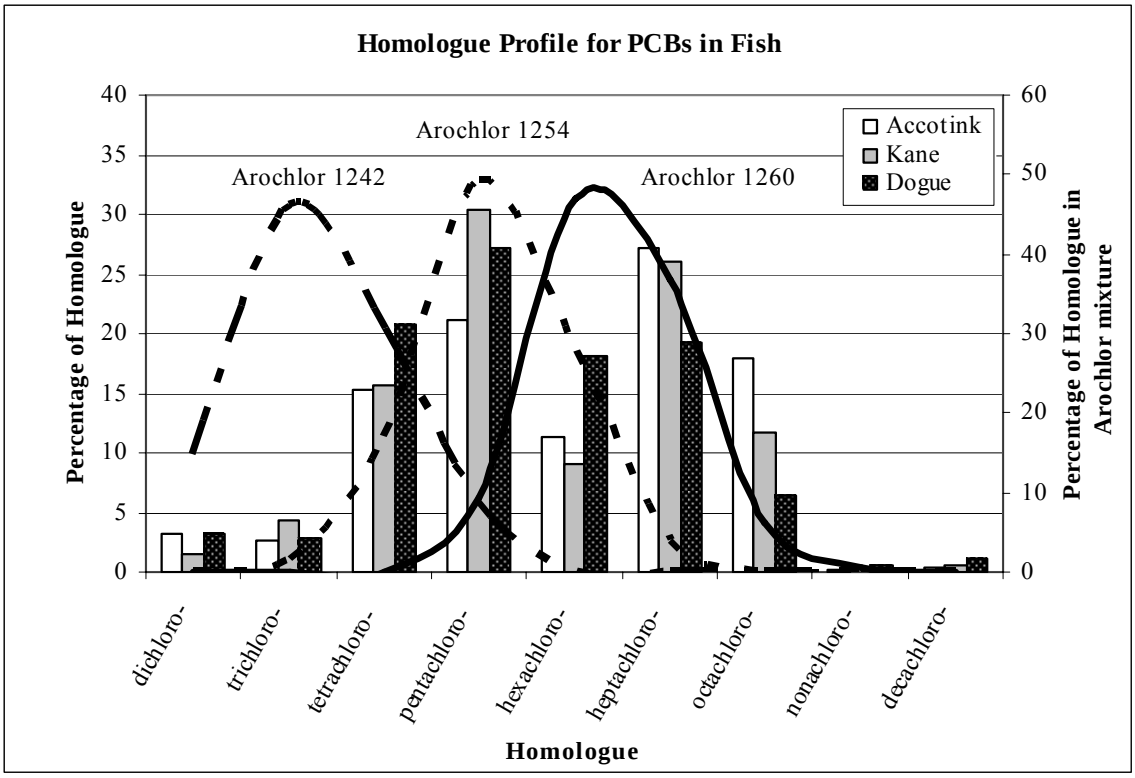


Figure 6: Composite homologue percent profile for PCBs in fish tissue

Further analysis of the Lower Pohick Creek homologue percent profiles as they compare to the sub-compartments show distinct patterns (Figure 7). The suspended sediment sub-compartment shows much higher lower molecular weight percent abundance than the fish tissue and bed sediment sub-compartment. The bed sediment and fish tissue sub-compartment shows percent abundances that represent higher molecular weight PCBs. This difference in homologue profiles suggests that the suspended sediment is not resuspension of bed sediment but rather an input from upstream. The homologue profiles for bed sediment and fish tissue are very similar and this reinforces that the fish are obtaining tPCBs from the sediment as they are benthivorous organisms.

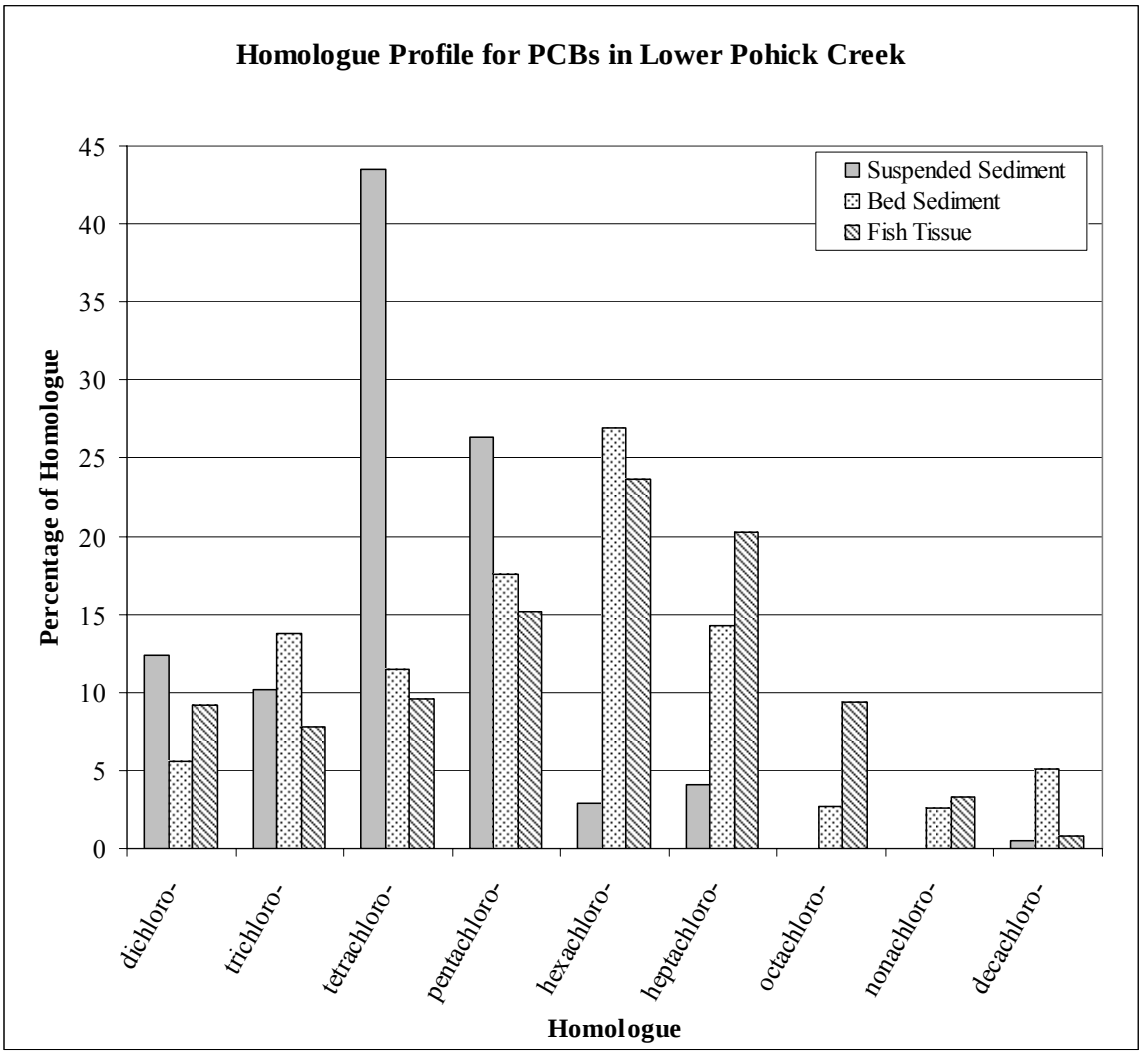


Figure 7: Homologue profile for PCBs in Lower Pohick Creek

Homologue profiles for the Upper Pohick site differentiate from the Lower Pohick site in that the suspended sediment more resembles the bed sediment and fish tissue suggesting that the source of PCBs is resuspension of bed sediments (Figure 8). There is a visible increase in trichloro-PCBs in the suspended sediment sub-compartment however, and shows a different source of PCBs from upstream.

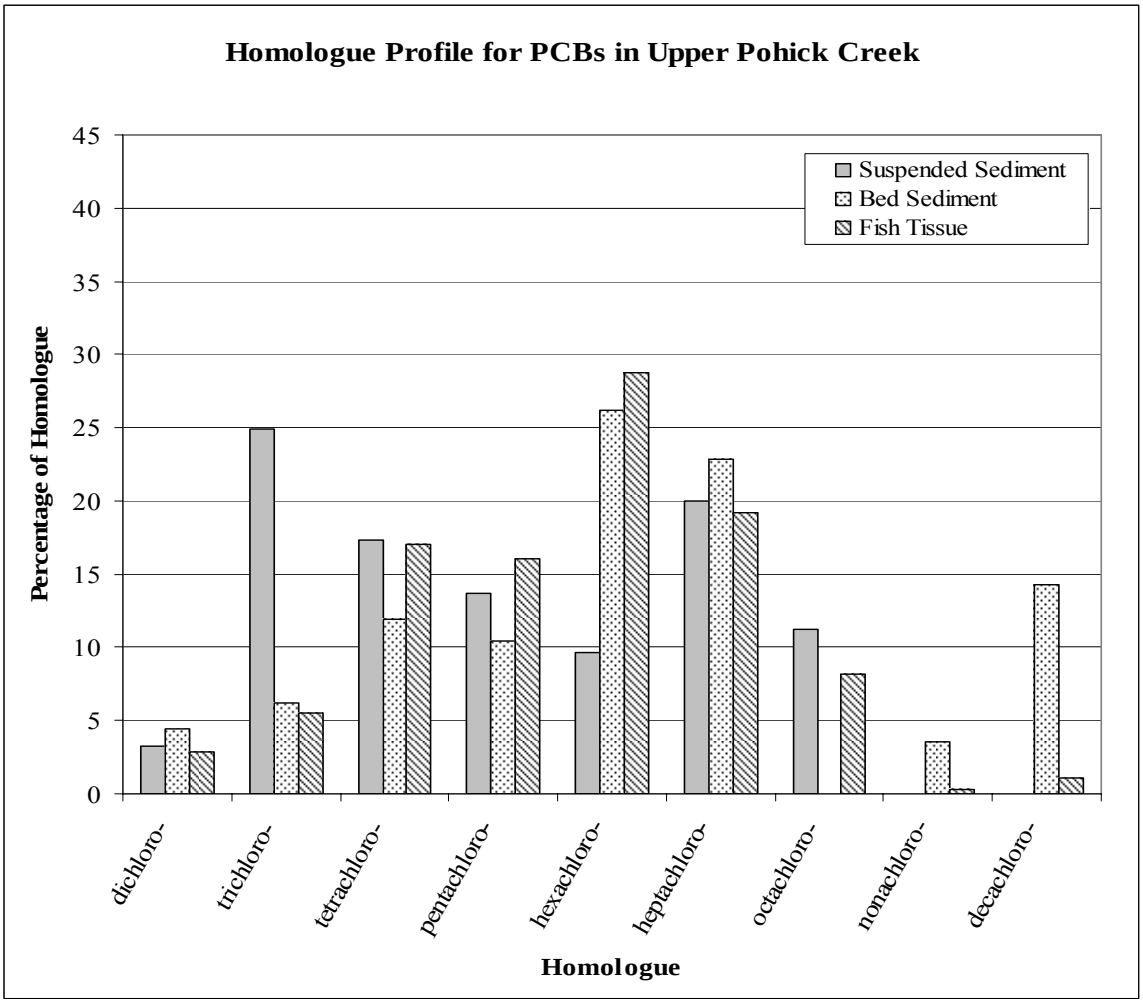


Figure 8: Homologue profile for PCBs in Upper Pohick Creek

The homologue profiles for tPCBs in Kane Creek suggest that the all sub-compartments show similar patterns of percent abundance. This shows that the sub-compartments are closely inter-related with respect to PCB partitioning and there is not an evident source of PCBs it relates to sub-compartment

The homologue profiles for Accotink Creek show that the fish tissue and suspended sediment are closely related with respect to PCB percent abundance (Figure

9). The bed sediment sub-compartment does not resemble the other sub-compartments in homologue pattern. The Accotink Creek site consists largely of sandy soil with very few areas of soil containing large amounts of organic matter and this absence of soils that retain PCBs suggest that fish receive available PCBs from the suspended sediment rather than bed sediment.

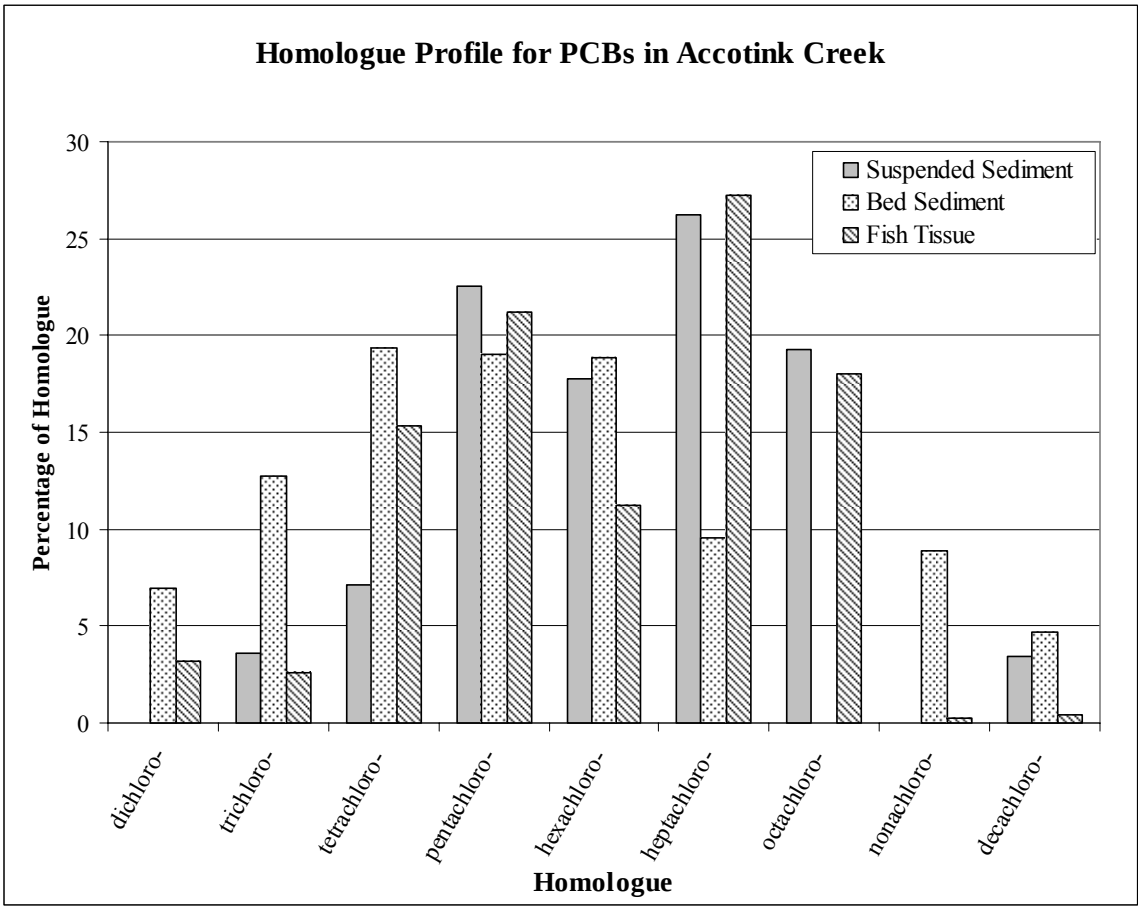


Figure 9: Homologue profile for PCBs in Accotink Creek

Dogue Creek shows a similar homologue profile to the Accotink Creek homologue profile in that the suspended sediment sub-compartment closely resembles the fish tissue sub-compartment in percent abundances (Figure 10). However, the Dogue Creek site has very different soil conditions in that it is not as sandy. The TSM for this site was the highest measured at 931.9 mg/L. This TSM concentration correlates to a very high PCB concentration for the suspended sediment sub-compartment but also allows mobility of PCBs to fish tissue at a faster rate due to increased bioavailability.

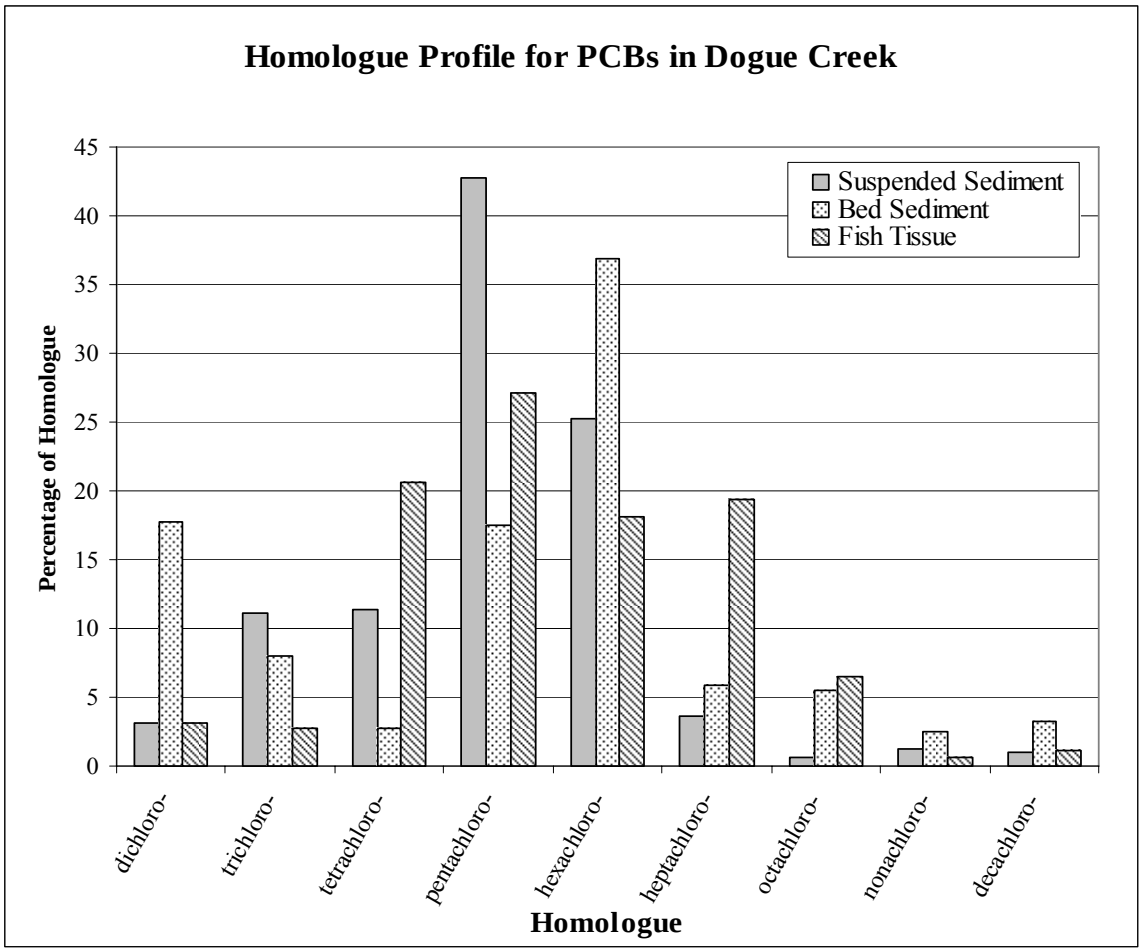


Figure 10: Homologue profile for PCBs in Dogue Creek

Polycyclic Aromatic Hydrocarbons (PAH) Concentrations

Detected concentrations of total-PAHs (tPAHs) are shown in Figure 11. Suspended sediment and fish tissue show comparable concentrations ranging from 60 to 170 ng/g (wet or dry weight). The largest concentrations of tPAHs can be found in bed sediment for all sites. The largest concentration of tPAHs was found at the Lower Pohick site in bed sediment with 2350 ± 290 ng/g dry wt. The next lowest value for tPAHs was found at the Upper Pohick site in bed sediment with 1250 ± 160 ng/g dry wt. Bed sediments at the Dogue Creek, Accotink Creek and Kane Creek sites were 375 ± 88 ng/g, 583 ± 46 ng/g and 285 ± 27 ng/g dry weight, respectively. The Dogue Creek and Kane Creek sites were very similar in tPAH concentration trends in that the suspended sediment concentration was less than the fish tissue concentrations, which, in turn, was less than the bed sediment concentrations.

A one-way ANOVA (95% probability level) determined that the mean tPAH concentrations in fish tissue are not significantly different ($p > 0.05$) among the sites. However, the mean concentrations for tPAHs in the suspended sediment and bed sediments were significantly different ($p < 0.05$ in both instances).

Within the Lower Pohick site, the suspended sediment and fish tissue mean tPAH concentrations were not significantly different ($p > 0.05$). However, the bed sediment compared to the fish tissue and suspended sediment tPAH concentrations were significantly different ($p < 0.05$ in both instances).

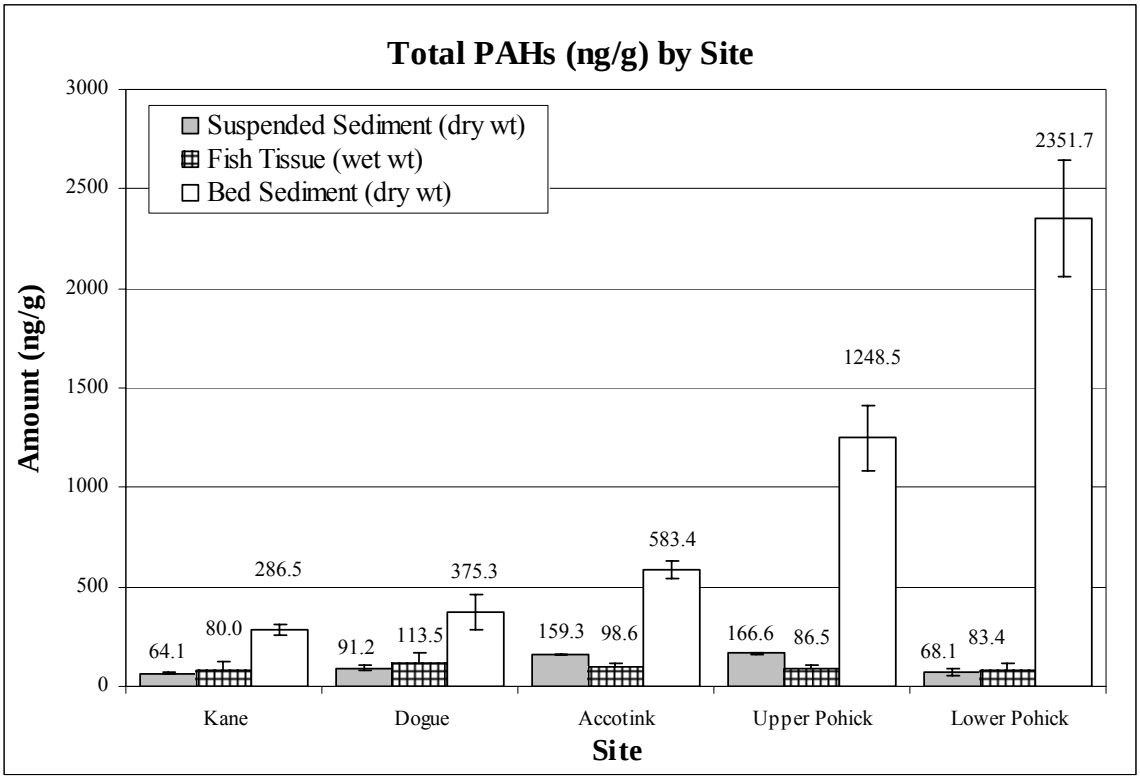


Figure 11: Total PAH concentration in ng/g by site and sub-compartment

A Tukey's range test was then necessary to determine significant statistical differences between the tPAH concentrations in the individual bed sediment and suspended sediment samples. Since the ANOVA showed that there were no significant differences among the means in the fish tissue sub-compartment the Tukey's range test was not done for this data set. The Tukey's range test values are shown in Table 12 as a matrix to compare the significant differences. This matrix shows the significant differences of the sites in the first column as they compare to the first row.

Table 12: Matrix of Tukey's range test results for tPAHs

	Accotink	Dogue	Kane	Lower Pohick
Dogue	P↓			
Kane	P↓			
Lower Pohick	P↓, S↑	S↑	S↑	
Upper Pohick	S↑	S↑, P↑	S↑, P↑	S↓, P↑

Arrows denote which compartment is significantly greater at the site in the first column in relation to the first row

P: particles (suspended sediment) S: bed sediment

Missing letters (P and S) denote no significant difference at that site in the sub-compartment

The statistical evaluation of the concentrations of tPAHs in sediments, suspended sediment and fish tissue yielded the following relative order from largest to smallest. For tPCBS in bed sediment: Lower Pohick Creek > Upper Pohick Creek > Accotink Creek ≈ Dogue Creek ≈ Kane Creek. For tPCBs in suspended sediment: Upper Pohick Creek ≈ Accotink Creek < Dogue Creek ≈ Lower Pohick Creek ≈ Kane Creek. Implications of these mean tPAH concentrations are further evaluated below in the *Watershed Evaluation* section of this document.

The Threshold Effect Concentration (TEC) as noted by MacDonald (2000a) is 1610 ng/g as shown in Figure 12 [58]. The TEC for the PAHs utilizes 11 individual PAH compounds for the consensus-based concentration values, therefore, the data in Figure 11 shows a composite of those 11 PAHs, as extracted from this study. The TEC value for the 11 PAHs is expressed as tPAHs. The Lower Pohick concentration is below this concentration threshold by 292 ng/g with a concentration value of 1320 ± 140 ng/g dry wt. Below this threshold effect level harmful effects are unlikely to occur, however, above this concentration toxicological effects might be observed. The Lower Pohick site is the closest to meeting the Threshold Effect Concentration value. Due to this elevated

concentration, the tPAH concentration in the Lower Pohick site should be monitored to determine if this concentration is increasing or decreasing or will soon approach the TEC.

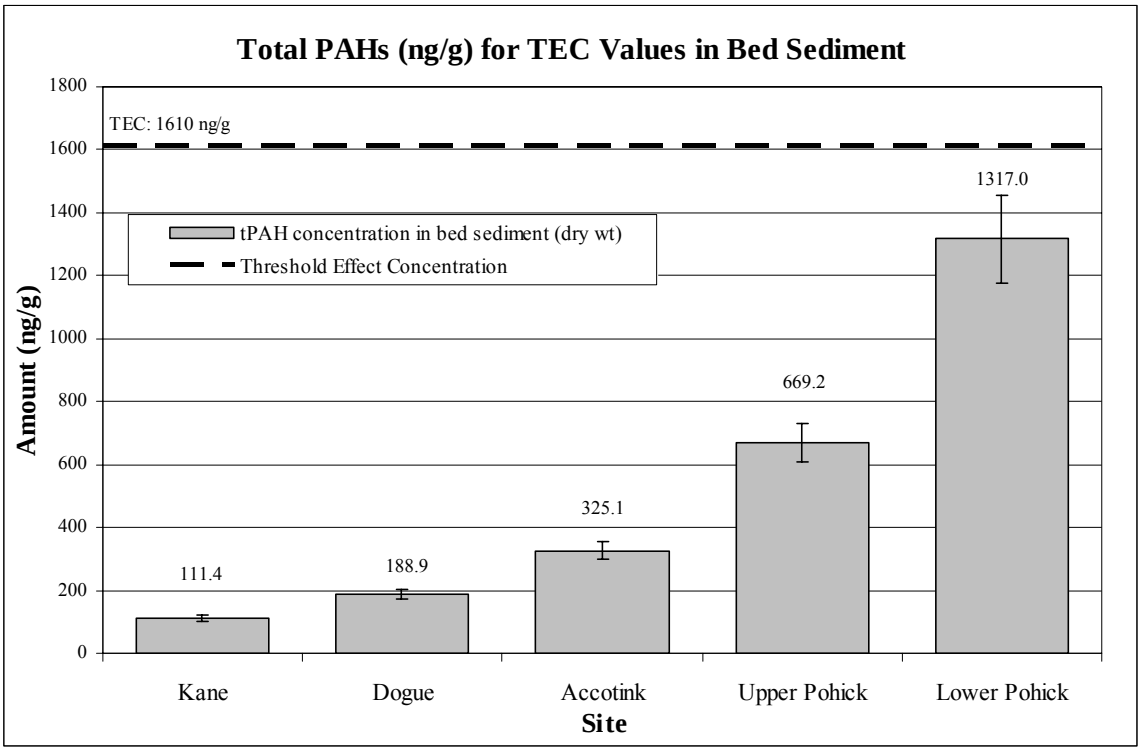


Figure 12: Total PAH concentration values versus TEC

TEC values are also given by MacDonald (2000) for eleven (11) individual PAH compounds. Only two of the individual compounds, pyrene (259 ± 16 ng/g dry weight) and benzo[a]anthracene (158 ± 12 ng/g dry weight), are above the TEC of 195 ng/g and 108 ng/g, respectively (Figure 13) [58]. Both of these compounds are on the EPA's toxics of concern list and are above the consensus-based TEC values [8]. Ecological and histological studies need to be completed to determine if these compounds have effect on

the biota at the Lower Pohick site since negative effects are possible based on the predictive ability of the TEC values.

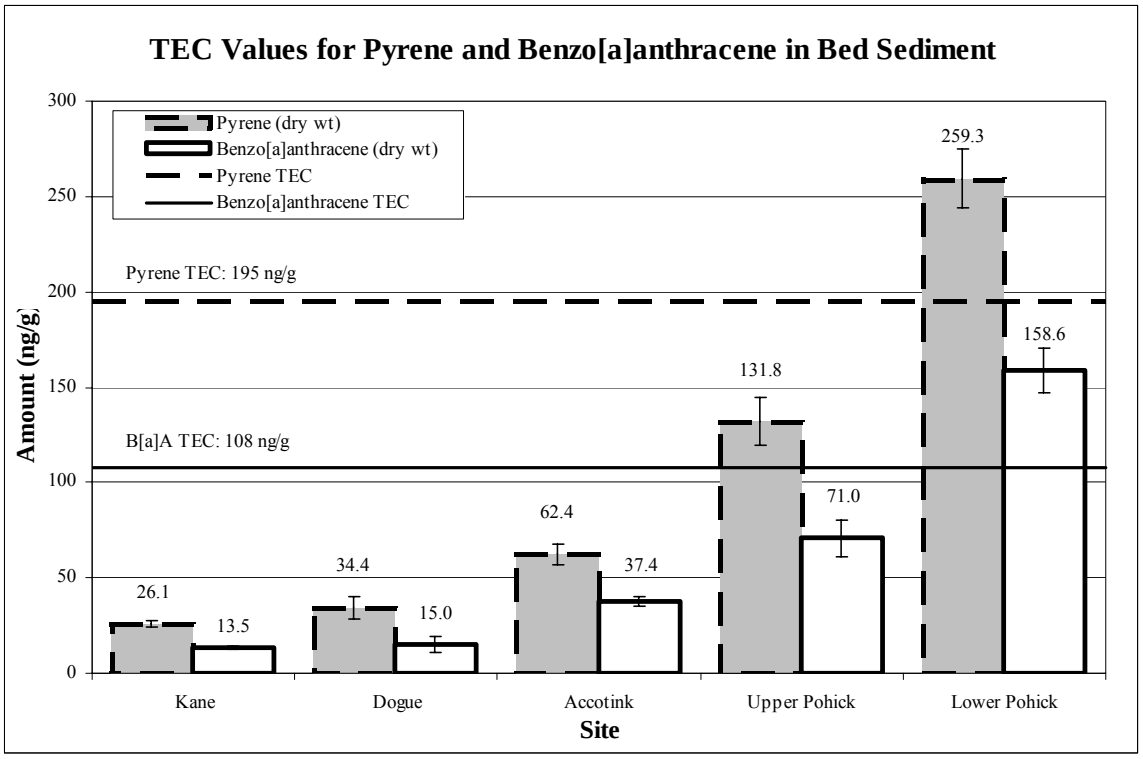


Figure 13: TEC values for pyrene and benzo[a]anthracene in bed sediment

Measured PAH values are also comparable to the measured values by other research groups investigating PAHs in the area (Table 13). The Virginia Department of Environmental Quality (VA DEQ) sampled Pohick Bay approximately four months prior to the current study and determined PAH concentration values in biota only, specifically the Large Mouth Bass (*Micropterus salmoides*) with a concentration of 9.2 ng/g wet weight. This species is in a trophic level above the Spottail Shiner; however, the parent

PAHs are readily metabolized in biota and substantially reduce bioaccumulation[59]. In 2005, the VA DEQ sampled bed sediment in Accotink Creek and found 7,450 ng/g of tPAHs. In December of 2000, Foster et al., found 3380 ng/g of tPAHs in bed sediment in the Potomac River Basin. These two concentration values are the same order of magnitude with each other and with the measured values in this study.

Bed sediment PAH concentration values have also been reported. In 1999 in Baltimore, Maryland, Ashley and Baker found a range of 89 to 30,400 ng/g of PAH residues. Kimbrough and Dickhut (2006) reports concentration values between 1,200 and 22,200 ng/g for 16 PAH congeners. These two locations are known locations of PAH and PCB impairment.

Table 13: Concentrations (ng/g) of PAHs in sediments and fish in the Potomac River region

Potomac River PAH concentrations							
Sampling Locale	**Date**	**# of Compounds**	**Fish Tissue ng/g**	**Bed Sediment ng/g**	**Suspended ng/g**	**Suspended ng/L**	**Reference**
Pohick Bay region of Potomac River (all sites), VA	Dec 8, 2008	30	86-113	285-2352	64-167	nr[a]	Current Study
Pohick Bay, VA	Sept 4, 2008	34	9.22[b]	nr	nr	nr	VA DEQ (2008)
Accotink Creek, VA	June 13, 2005	34	nr	7446	nr	nr	VA DEQ (2005)
Potomac River Basin, VA and MD	May and Dec. 2000	22	nr	3380	nr	nr	Foster *et al.* (2008)
PAH concentrations outside the Potomac River							
Susquehanna River, MD	March to Dec. 1994	13	nr	nr	2,000-11,000	25.0-240	Foster et al. (2000)
Tidal Anacostia River, MD	2002	35	nr	nr	nr	89-457	Hwang, et al (2006)
Elizabeth River, VA	2006	16	nr	1,200-22,200	nr	nr	Kimbrough and Dickhut (2006)
Baltimore Harbor, MD	1999	33	nr	89-30,400	nr	nr	Ashley and Baker (1999)

[a] nr = not reported

[b] Large Mouth Bass (trophic level IV)

Endocrine Disrupting Chemical (EDC) Concentrations

The mean detectable concentrations of the EDC pollutants are presented in Table 14 along with the percent differences between the duplicate measurements ($\ln X_1/X_2 \times 100$, where $X_1>X_2$) next to the EDC concentrations. Statistical analysis was not performed on the above data due to limited replicates of the environmental concentrations. Logistically difficult conditions of sampling events resulted in few sample collection periods.

The EDC found at the largest concentration was triclosan in bed sediment (130 ng/g dry wt) at the Lower Pohick site. At the Upper Pohick Creek site, triclosan in bed sediment (51.2 ng/g dry wt) was the largest EDC. The largest EDC at the Accotink site was EE2 in fish tissue (62.0 ± 0.3 ng/g wet wt). The largest EDC at the Kane Creek site was also EE2 in fish tissue (30.8 ± 2.4 ng/g wet wt). The Dogue Creek site had BPA in fish tissue (29.9 ± 1.8 ng/g wet wt) as the largest concentration of an EDC.

Table 14: Average concentrations (ng/g) of EDCs in suspended sediment, bed sediment and fish tissue

Site	Sample	OP	NP	TRI	BPA	Estrone	EE2
Dogue	Suspended Sediment	0.3 ± 0.3	0.3 ± 0.1	1.5 ± 0.7	0.7 ± 0.2	0.1 ± 0.1	0.4 ± 0.04
	Bed Sediment	5.6 ± 0.5	0.7 ± 0.01	0.6 ± 0.02	13.3 ± 0.04	0.9 ± 0.01	18.1 ± 1.8
	Fish Tissue	2.6 ± 0.6	1.7 ± 1.0	0.6 ± 0.2	29.9 ± 1.8	2.6 ± 0.01	29.4 ± 7.3
Kane	Suspended Sediment	1.5 ± 0.2	2.1 ± 0.1	0.4 ± 0.1	2.0 ± 1.6	ND	0.7 ± 0.3
	Bed Sediment[o]	16.3	14	7.3	17.8	5.5	15.6
	Fish Tissue	2.7 ± 0.2	ND[a]	2.1 ± 0.9	2.5 ± 0.2	15.7 ± 4.0	30.8 ± 2.4
Accotink	Suspended Sediment[o]	1.4	0.8	0.6	0.8	8.1	7.8
	Bed Sediment[o]	0.9	1.3	3.8	2.6	0.4	3.7
	Fish Tissue	6.6 ± 2.2	0.9 ± 0.1	1.3 ± 0.2	45.5 ± 9.8	7.3 ± 0.8	62.0 ± 0.3
Upper Pohick	Suspended Sediment	0.9 ± 0.2	0.3 ± 0.2	0.4 ± 0.2	4.1 ± 0.9	0.5 ± 0.2	0.4 ± 0.5
	Bed Sediment	4.2 ± 0.8	10.8 ± 0.7	51.2 ± 3.8	19.6 ± 1.8	1.9 ± 0.4	11.4 ± 3.1
	Fish Tissue	10.0 ± 1.1	1.9 ± 0.6	3.8 ± 3.2	18.5 ± 0.8	4.9 ± 1.4	20.5 ± 4.8
Lower Pohick	Suspended Sediment	13.7 ± 7.7	2.5 ± 0.8	2.8 ± 1.9	7.8 ± 0.5	2.2 ± 1.4	6.8 ± 0.4
	Bed Sediment[o]	25.3	18.5	130	25.6	8.0	8.7
	Fish Tissue	15.0 ± 2.7	5.6 ± 1.3	11.9 ± 1.5	124 ± 8.4	5.9 ± 0.5	3.9 ± 1.0

OP: octylphenol, NP: nonylphenol, TRI: triclosan, BPA: bisphenol A, EE2: 17α-ethinyl estradiol
Suspended Sediment and Bed Sediment are ng/g dry weight, Fish Tissue is ng/g wet weight
[a]ND = not detected or below IDL
[o]One sample analyzed

The largest mean concentrations of octylphenol were observed in Lower Pohick bed sediments (25.3 ng/g dry wt), fish tissue (15.0 ± 2.7 ng/g wet wt) and suspended sediment (13.7 ± 7.7 ng/g dry wt). The Lower Pohick site also had the largest average concentrations of nonylphenol, triclosan and bisphenol A in all sub-compartments.

The highest concentration of estrone in fish tissue was observed at the Lower Pohick site with 8.0 ng/g, however the largest concentration observed in fish tissue and bed sediment were the Accotink (8.2 ng/g) and Kane (15.7 ng/g) sites, respectively. The largest concentrations of 17α-ethinyl estradiol were found in Dogue bed sediment (18.1 ± 1.8 ng/g), and at the Accotink site in suspended sediments (7.8 ng/g) and fish tissue (62.0 ng/g). Surprisingly, the Lower Pohick site did not have the highest concentration of 17α-ethinyl estradiol in any of the sub-compartments.

The Lower Pohick site has the largest average total-EDC (tEDC = sum of all measured EDC concentrations) concentration (418 ng/g) found in any of the studied sites as shown in Figure 14. The bed sediment sub-compartment at the Lower Pohick site had the largest tEDC concentration (216 ± 15 ng/g) followed by the fish tissue (166 ± 29 ng/g wet wt) and suspended sediment (35.9 ± 8.2 ng/g dry wt) sub-compartments.

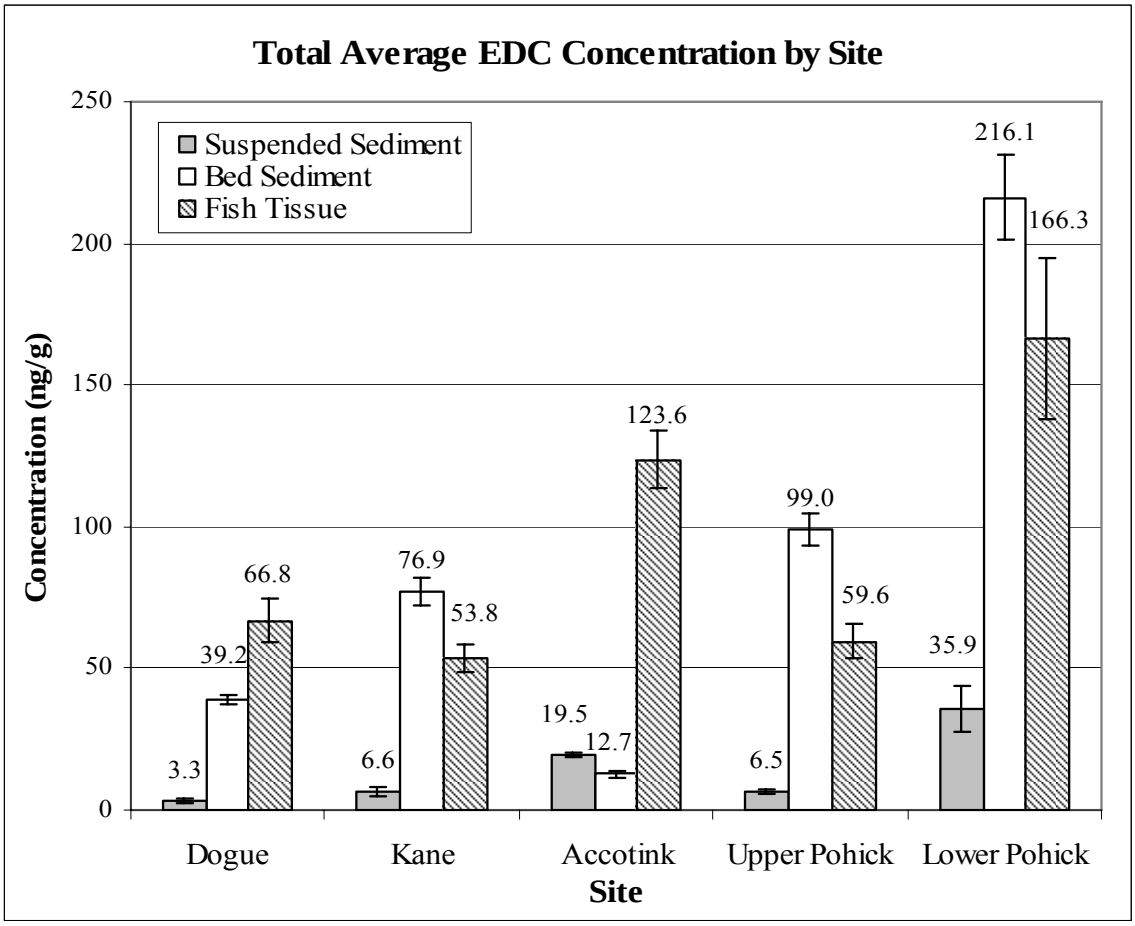


Figure 14: Total Average EDC Concentration (ng/g) by Site

The bed sediment sub-compartment had the largest concentrations of tEDCs in the Upper Pohick and Kane Creek sites (99.0 ± 5.3 ng/g and 76.9 ± 5.0 ng/g, respectively) whereas the fish tissue sub-compartment has the largest portion of the total concentration at the Dogue and Accotink sites (66.8 ± 7.6 ng/g and 124 ± 10 ng/g, respectively). The suspended sediment sub-compartment contributed less than 10% of the tEDC concentration and was, therefore, not compared against the other sub-compartments for concentration differences. However, it should be noted that suspended sediment concentrations will differ with river flow and TSM concentration. Weather, time of year, and average stream flow effect the suspended sediment concentrations more than bed sediment and fish tissue concentrations.

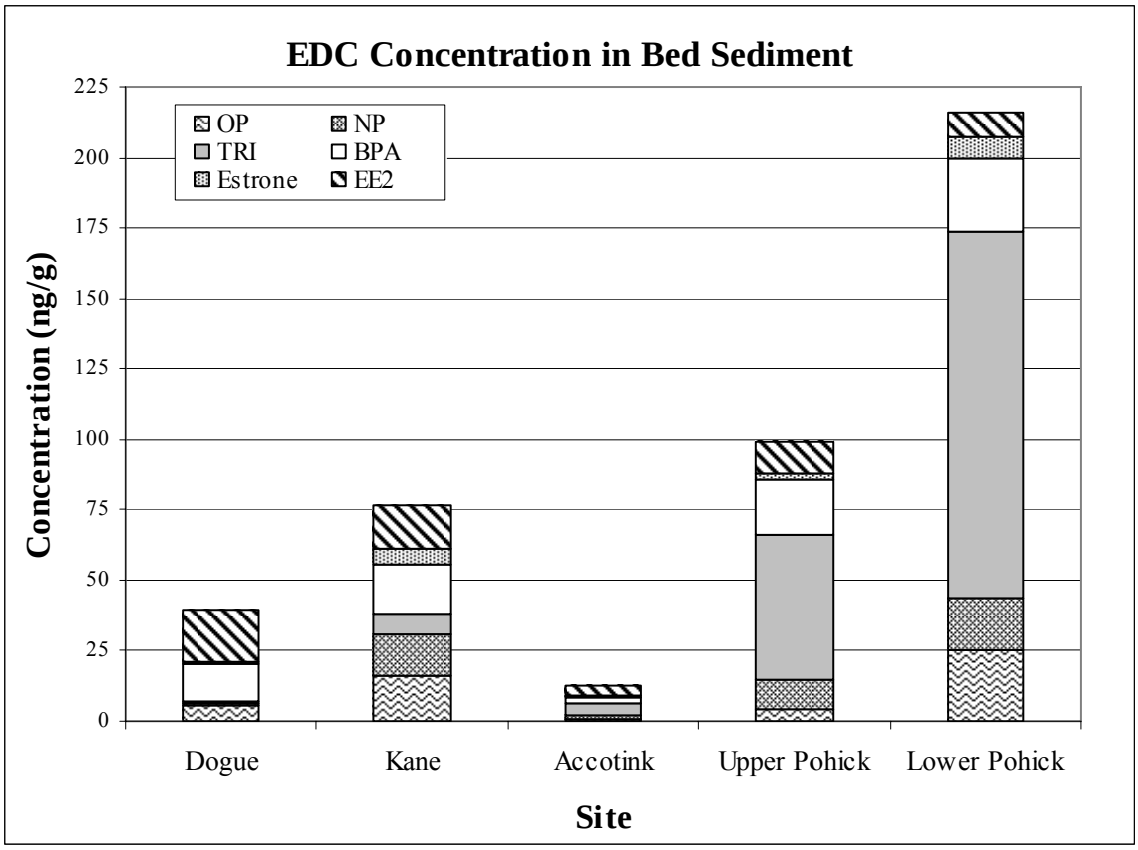


Figure 15: EDC concentrations (ng/g dry wt) in bed sediment

Octylphenol is the dominant chemical found in suspended sediment at the Lower Pohick Creek site (13.7 ± 7.7 ng/g) as compared to the other sites in this sub-compartment as shown in Figure 16. However, the octylphenol concentration at the Lower Pohick site in bed sediment (25.3 ng/g) was larger, which suggests that there is input from the WWTP. Having these concentrations closer in value would suggest that there is resuspension of bed sediments at the site.

Nonylphenol, which is similar in chemical properties and characteristic to octylphenol, shows a different trend in that the concentration in bed sediment is much

larger (18.6 ng/g) than the suspended sediment concentration (2.5 ± 0.8 ng/g). This shows that resuspension of bed sediment is not a factor for the increased octylphenol concentration in suspended sediment.

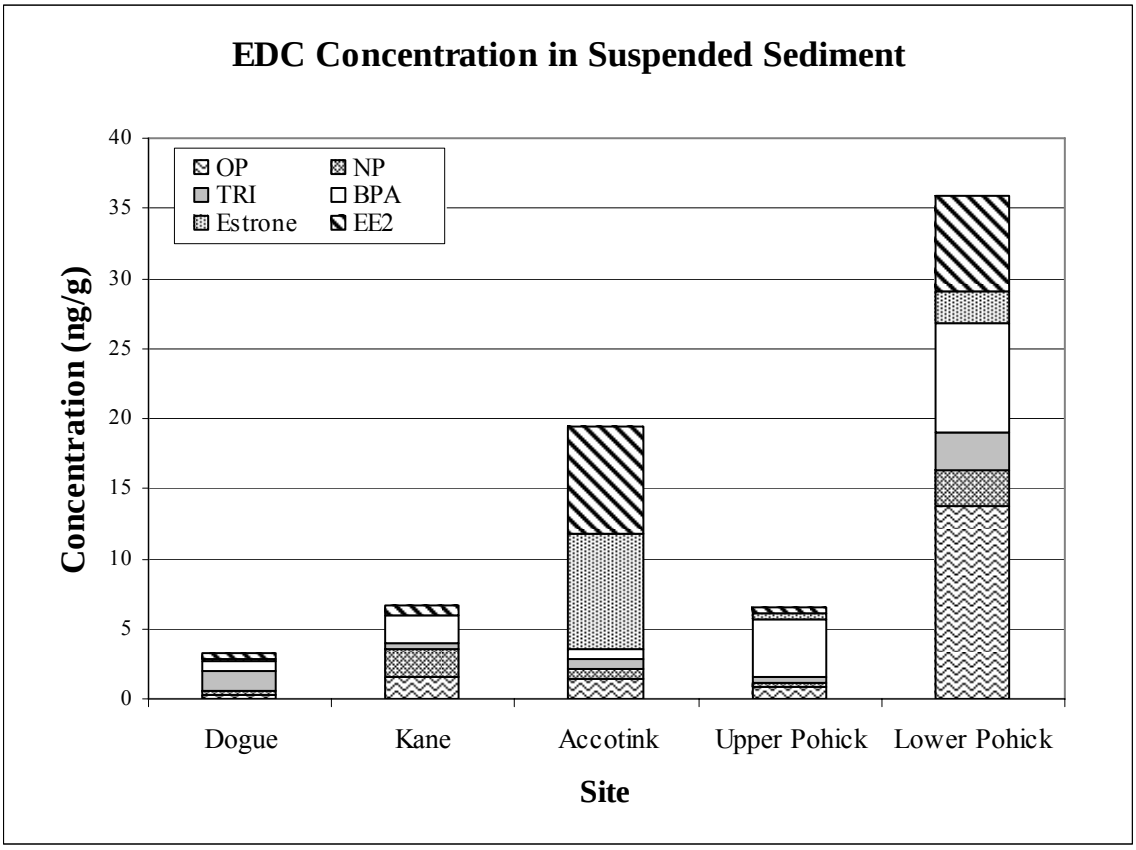


Figure 16: EDC concentrations (ng/g dry wt) in suspended sediments.

17α-ethinyl estradiol was a major EDC present in the fish tissue compartment in all sites except for the Lower Pohick site (Figure 17). Bisphenol A was present in fish tissue at all locations except for the Kane Creek site. Additionally, triclosan was present in all sub-compartments at the Upper and Lower Pohick sites.

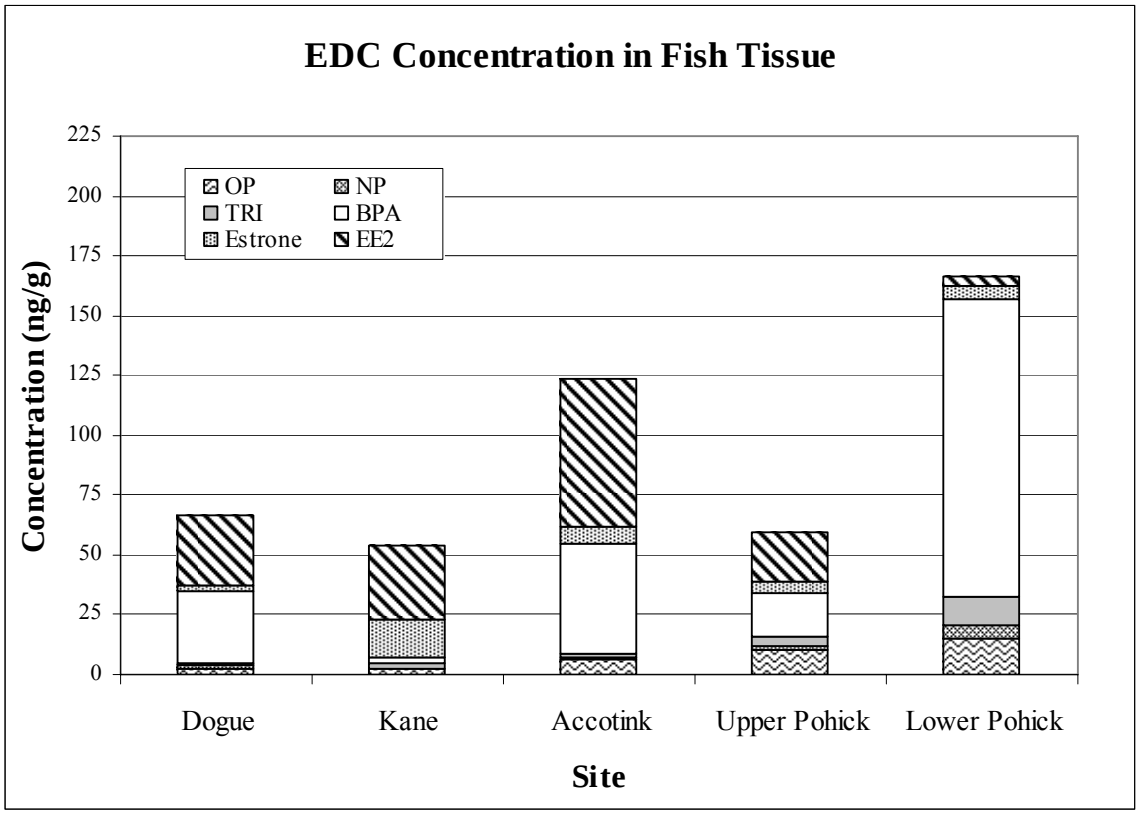


Figure 17: EDC concentrations (ng/g wet wt) in fish tissue

A correlation can be made by subtracting the concentrations of EDCs found at the Lower Pohick site and the Upper Pohick site to possible EDC loading (Figure 18). The EDC concentration values for all six chemicals studied for the Lower Pohick site minus the Upper Pohick site range from 1.7 to 12.8 ng/g for suspended sediment, -2.7 to 78.8 ng/g for bed sediment and -16.5 to 105.5 ng/g for fish tissue. Noticeable results include triclosan in bed sediment (78.8 ± 3.8 ng/g) and bisphenol A in fish tissue (106 ± 28 ng/g) as seen in Table 15.

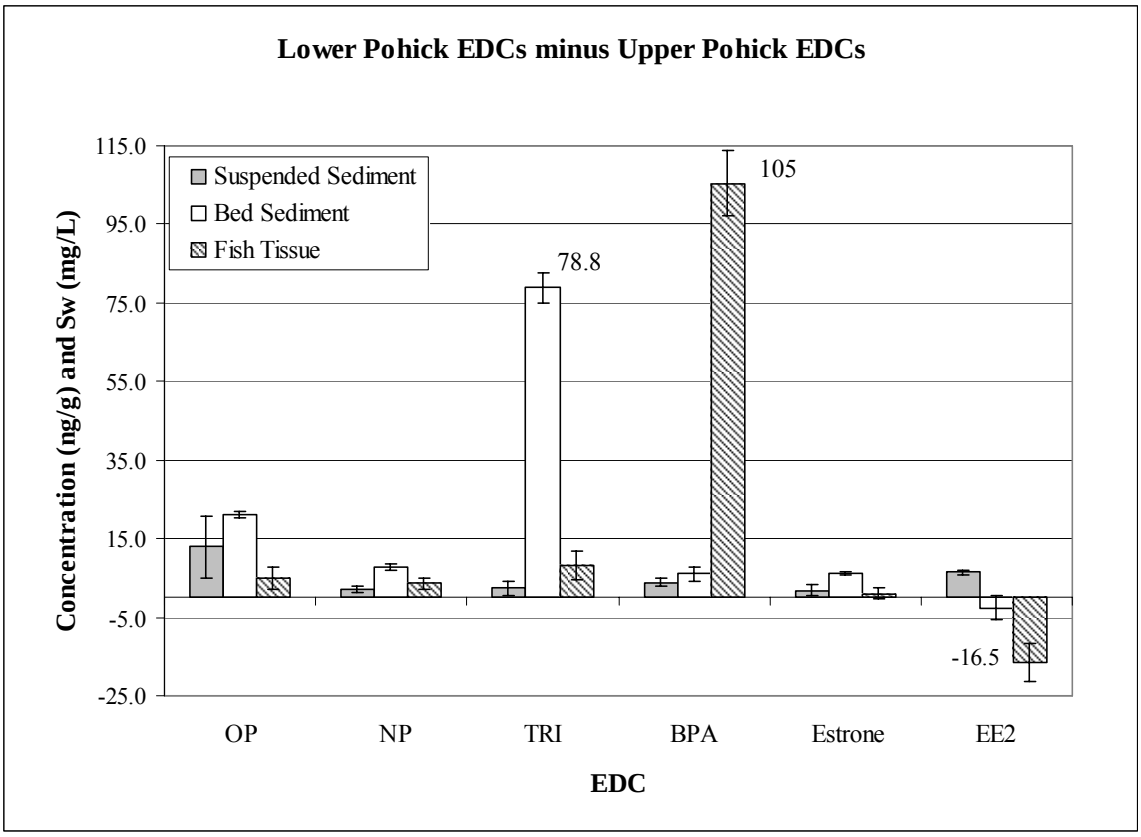


Figure 18: Lower Pohick EDC concentration minus Upper Pohick EDC concentration (ng/g)

Table 15: Lower Pohick EDC concentration minus Upper Pohick EDC concentration

Site	Sample	OP	NP	TRI	BPA	Estrone	EE2
Lower Pohick	Suspended Sediment	12.8 ± 7.7	2.2 ± 0.9	2.4 ± 1.9	3.8 ± 1.0	1.7 ± 1.4	6.4 ± 0.6
minus	Bed Sediment	21.1 ± 0.8	7.7 ± 0.7	78.8 ± 3.8	6.0 ± 1.8	6.0 ± 0.4	-2.7 ± 3.1
Upper Pohick	Fish Tissue	5.0 ± 2.9	3.7 ± 1.5	8.1 ± 3.5	105 ± 8.4	1.1 ± 1.5	-16.5 ± 4.9

It is noted that the concentration of 17α-ethinyl estradiol is lower at the Lower Pohick site than at the Upper Pohick site in fish tissue and bed sediment. This difference is shown in Figure 18 as a negative value on the bar graph. While all other EDC values

for this figure are positive, suggesting a loading from the WWTP, this graph shows a decrease in concentration as compared to the concentration in organisms from upstream. As treated wastewater (approx. 45 million gallons per day) is discharged into the creek the mass available for adsorption from suspended sediment is present as seen by the positive bar. However, the spottail shiner consumes benthic invertebrates that live in the sediment that have already metabolized EE2 [60]. Therefore, it is postulated that the fish do not receive as much EE2 exposure from the suspended sediment but rather from bed sediment. This explanation is reasonable for the Lower Pohick site but not for Accotink Creek. In Accotink Creek, the EE2 concentration is higher in fish tissue than bed sediment. The source of EE2 exposure to fish is likely to be resuspended bed sediment rather than stationary bed sediment. This is due to the mostly rocky, sandy river bottom at this location which mechanically washes any exposed sediment into the Creek.

Triclosan was found in large concentrations in bed sediment relative to fish tissue (Figure 15 and Figure 17). It is postulated that the absence of triclosan in fish tissue is due to metabolism of the compound into the methyl triclosan derivative (5-chloro-2-(2,4 dichlorophenoxy)anisole). Lindström et al. (2002), found little triclosan in fish tissue but instead found much larger concentrations of methyl triclosan. It was unclear in their results whether metabolism was responsible for the low levels of triclosan in fish tissue, however, this would explain the discrepancies [61].

Low levels of triclosan in suspended sediment are possibly the result of photolysis. Dissociated triclosan (slightly basic conditions) will absorb UV light between 300 to 320 nm and undergoes photolysis at several orders of magnitude greater than

undissociated triclosan. Triclosan photolysis under natural sunlight conditions and relation to pH dependencies has been shown [61]. As suspended sediment passes through the water column, any bound residues on the surface of the particles would undergo rapid photolysis and the measured concentration would be significantly lower in that sub-compartment. Suspended sediment that falls to the bottom of the water body and becomes bed sediment is effectively protected from sunlight.

Bisphenol A is shown to be non-persistent in the environment (half life 1-10 days) however its abundance in the environment make it a compound of concern [62-64]. Lindholst *et al*. (2001), found BPA in fish tissue and the glucuronidated degradation product at twice the concentration as the parent chemical when fish were exposed to BPA in a laboratory setting. It was also shown than BPA levels in fish reached a steady state within 12-24 hours and then BPA levels in fish tissue declined as the compound was metabolized and excreted.

Bioconcentration factors were reported by Lindholst et at (2001), to be 3.5 to 5.5 as a measure of BPA in plasma over BPA in water. BPA measurements from fish tissue in this study support that there is bioconcentration of BPA from water. Since concentrations BPA in the water compartment was not studied, biota-sediment accumulation factors were created at the various sites. Continuous addition of BPA to the environment from various sources would explain the high levels of the compound found in fish tissue in this study. Further analysis of EDC metabolites is needed to determine if the compounds are present in fish tissue, suspended sediments and bed sediments.

Biota Sediment Accumulation Factors

Biota Sediment Accumulation Factors (BSAFs) are presented in Table 16 for tPCBs, tPAHs and tEDCs. Also presented are compounds from each class of chemical as the BSAF values often differ from the total BSAF of the class. Theoretical BSAF levels, as calculated from the LFERs, for the respective compound class range from 1.5 to 6.5 for PCBs, 1.9 to 8.0 for PAHs, and 1.9 to 8.1 for EDCs. Measured BSAF values that fall outside of the expected theoretical range of BSAF values are underlined in the table. BSAFs for PCB 153 in Dogue Creek, Accotink Creek and Kane Creek as well as PCB 180 in Kane Creek were unable to be obtained. Also, nonylphenol in Kane Creek were unobtainable. The undeterminable BSAF values are due to the analyte concentration in either the bed sediment or fish tissue sub-compartment being below the detection limit.

Table 16: Theoretical and Measured BSAF values for studied compounds

	$BSAF_{theoretical}$	$BSAF_{measured}$ [a,b]				
Chemical	**Expected Range**	**Dogue**	**Accotink**	**Kane**	**Lower Pohick**	**Upper Pohick**
tPCBs	1.5--6.5	2.71	0.89	2.57	2.29	1.06
PCB 110	1.5--6.5	0.41	0.19	0.19	0.40	0.04
PCB 153	1.5--6.5	UD	UD	UD	1.23	0.09
PCB 180	1.5--6.5	0.39	0.38	UD	0.58	0.06
PCB 209	1.5--6.5	0.32	0.05	0.63	0.21	0.02
tPAHs	2.0--8.0	1.00	0.39	2.80	0.25	0.23
Phenanthrene	2.0--7.9	1.49	0.70	8.83	0.52	0.46
Benzo[a]pyrene	1.9--7.7	1.65	0.10	0.39	0.08	0.10
tEDCs	2.0--8.0	2.51	11.36	2.99	2.30	1.01
Octylphenol	2.0--7.8	0.68	8.30	2.77	1.82	4.05
Nonylphenol	1.9--7.7	3.77	0.80	UD	0.93	0.30
Triclosan	2.0--7.9	1.59	0.40	0.54	0.27	0.13
Bisphenol A	2.0--8.0	3.31	20.63	0.94	14.86	1.59
Estrone	2.0--8.1	4.12	20.68	12.13	2.26	4.22
17α-Ethinyl Estradiol	2.0--8.0	2.39	19.51	8.03	1.39	3.04

[a]Underlined values fall outside expected range

[b]Unable to determine

Values that fall within the expected range for the measured BSAF value are considered to be in equilibrium with respect to bed sediment and fish tissue. This equilibrium facilitates a predictive ability with regard to environmental concentrations. With a bed sediment concentration at a given area, the fish tissue concentration can be determined as long as a measured BSAF falls in the range of the theoretical BSAF. The same is true given a fish tissue concentration that a bed sediment concentration can be interpolated.

Several factors influence the BSAF to be above or below the theoretical range. Factors that influence the BSAF to be small are an increased organic carbon concentration (C_{oc}) that is over estimated due to low fraction organic carbon usually less than 0.5%. However, none of the measured BSAFs in this study were below the theoretical range because of low organic carbon content. Additionally, a decreased lipid normalized concentration (C_{lipid}) will result in a low BSAF because of metabolism or the inability of the compound to bioaccumulate.

Many of the BSAF values for individual PCBs fall below the expected theoretical range (18 out of 21). This is due to a difference among the number of detectable concentrations in bed sediment versus fish tissue concentrations. PCB homologue profiles suggest that the main sources of PCBs are different in that the suspended sediment has a greater concentration of lower molecular weight PCBs and the bed sediments and fish tissues have a larger concentration of higher molecular weight PCBs. Total-PCB BSAF measurements have low values in Accotink Creek and Upper Pohick

Creek. Dogue Creek, Kane Creek and Lower Pohick Creek have a BSAF value for PCBs that will allow partitioning prediction.

PAHs are rapidly enzymatically metabolized by organisms that are exposed to them. Therefore the BSAF values will be artificially low due to depressed fish tissue concentrations. The only value that is within the expected BSAF range is the tPAH BSAF in the Kane Creek watershed. Additionally, phenanthrene is above the expected theoretical BSAF. The ratio of fluoranthene to perylene at the Kane Creek site is below one whereas all other sites are above one. This reinforces that the Kane Creek watershed has a different source of PAH influence than the other sites as perylene is found mainly from plant material [65, 66].

Only thirteen BSAF values for individual EDCs are below the theoretical value. However, eight BSAF values are above the theoretical value for EDCs and five of those are in the Accotink Creek site. Large BSAF values are due the fish tissue and organic carbon concentrations are not in equilibrium. The fish are moving to another contaminated area and the organic carbon concentration does not reflect the same concentration. The large lipid normalized concentration (C_{lipid}), likely due to food uptake, comes from fish mobility.

Watershed Evaluation

The total concentrations of measured PCBs, PAHs and tEDCs are the largest at the Lower Pohick site. This site is influenced by a large wastewater treatment plant that likely discharges UOPs into the Potomac River. However this is not the only source of

UOPs into the region. Roadway runoff, accidental sewage discharge and storm water erosion also release UOPs into the Potomac River.

Homologue profiles for PCBs in suspended sediment show lower molecular weight congeners in greater abundance for the Lower Pohick site versus the other sites in most sub-compartments. Higher molecular weight PCB homologue profiles are evident in the fish tissue and bed sediment sub-compartments. This is also evident in the BSAF values for individual congeners being very low. This suggests that the source of PCBs influencing the various compartment are different but it is unlikely that a source can be identified.

PCB concentrations are prominent around locations of electrical utilities or large electrical usage centers such as train stations and military bases. PCB homologue profiles show that the Lower Pohick site has a different profile for homologue groups than the other sites. This suggests that the source of contamination is different for the different sites.

As stated in the *PCB Homologue Comparisons* section, it is likely that the Upper and Lower Pohick site source of PCBs are different from the other sites. The same homologue shift that is evident in the Lower Pohick site fish tissue and bed sediment is also evident between sites. The Accotink Creek, Kane Creek and Dogue Creek sites show a greater abundance of lower molecular weight PCBs in fish tissue and bed sediment while the Upper and Lower Pohick sites show a greater abundance of the higher molecular weight PCBs. Contrasting this, however, is a greater concentration of lower molecular weight PCBs in suspended sediment at the Upper and Lower Pohick site as

compared to greater concentration of higher molecular weight PCBs at the Accotink Creek, Kane Creek and Dogue Creek. This shift in homologue profiles suggest that fish obtain PCBs from bed sediment and not from suspended sediment.

Since many anthropogenic pollutants find their way into water bodies through storm water runoff, a comparison of watershed impervious surface versus concentration of pollutant is necessary to determine if this is a source of contamination. This study found that there is little mathematical relation between total PCB concentration and the square mileage of impervious surface in the respective watershed. Similar to PCBs, the PAHs that were measured in this study do not correlate with the percentage of impervious surface throughout their respective watersheds. However, roadway runoff is likely the largest source of PAHs to the Pohick Region. Total PAH concentration increases in bed sediment as square mileage increases but a regression cannot be established from the few numbers of samples analyzed. Other groups have shown that storm water and roadway runoff is a positive source for PCBs and PAHs into surrounding water bodies [4, 7, 67].

The fish tissue and suspended sediment sub-compartments are similar at each location. The major noticeable difference among the locations studied is the concentration values in the bed sediment sub-compartment. The Lower Pohick site and Upper Pohick site contain much higher mean tPAHs than the other sites in bed sediment. The Upper Pohick site shows a large tPAH concentration as compared to Dogue Creek, Accotink Creek and Kane Creek sites. The Accotink Creek site is higher than the Dogue Creek and Kane Creek sites and is the largest watershed. It also has the largest percentage impervious surface and a US Army Base. The Upper Pohick site is the closest

site to Interstate Highway 95, a large nine lane roadway with significant traffic volume and the Lorton Amtrak Train Station. These two sources can release PAHs into the watershed most during rain events and are significant sources for anthropogenic PAHs because of the presence of asphalt (petroleum derived) and fossil fuel combustion by-products. The WWTP along with the Lorton Train Station and Interstate 95 are also likely to increase the levels of tPAHs in the Pohick Bay sub-watershed.

As with tPCBs, a large difference in concentration between the Upper Pohick and Lower Pohick tPAH concentration exists suggesting a loading from an unknown source. Not far down stream from the Lower Pohick site (approximately 1000 yards) there is a busy public boat launch as well as the permanent docking site for a large fire and rescue boat. A large portion of most boat exhaust is diverted under the surface of the water effectively muffling exhaust noise. It has been shown that this discharge of exhaust under the surface of the water adds to overall tPAH concentration in bed sediments due to deposition [68]. High temperature combustion creates pyrolytic PAHs with a high molecular weight such as pyrene. This reliably gives a clue to the source of PAH contamination from combustion [69, 70].

The Kane site shows the lowest concentration of bed sediment PAHs. The location and land use as well as the BSAF value of the Kane site suggest that the source of PAHs is different from the other sites. The land use for most other sites is highly developed while the Kane site maintains a high percentage of forested and undeveloped land.

Interesting though is the low levels of tPAHs in suspended sediment in all the sites. The PAHs in bed sediment must arrive from somewhere and suspended sediment deposition onto the bottom of the stream is a likely source. The addition of suspended sediment over time allows the tPAH concentration to increase.

The concentrations of octylphenol and nonylphenol were similar in the Lower Pohick Creek and Kane Creek in bed sediments. This suggests that there is little influence of the WWTP loadings of these compounds into the river as the Kane Creek site has different watershed characteristics including more forested land than an urbanized landscape.

At the Accotink Creek site there is a high incidence of 17α-ethinyl estradiol in fish tissue with 62.0 ± 0.3 ng/g and suspended sediment with 7.8 ng/g, relative to the other sites. The source of this synthetic hormone is unknown however residential septic systems in the area may contribute to elevated levels.

17α-ethinyl estradiol is also present in similar concentrations at all sites in bed sediment (except Accotink Creek) which suggests that the WWTP is not influencing the observed concentrations directly and that there is another unknown source influencing these watersheds.

Triclosan was the dominant chemical found in bed sediment at the Lower Pohick site as well as the Upper Pohick site as seen in Figure 15. The Dogue, Kane and Accotink Creek sites have little observed triclosan in bed sediments. This suggests that there is an unknown source of triclosan that is being loaded into the Upper Pohick Creek above the WWTP. Triclosan is anthropogenic and therefore it is interesting to compare

its concentration at the more rural Kane Creek site to that of a largely urban site such as the Accotink watershed [11].

Since bisphenol A was found in suspended sediment and bed sediment it would be expected that it would be present in fish tissue as well. However, this was not the case. It has been shown that bisphenol is easily metabolized in fish tissue yet under anaerobic conditions BPA has been shown to be stable for extended periods of time in bed sediment [63, 64]. It this study however, large concentration values were found for BPA in fish tissue. Different fish have different metabolic rates of BPA metabolism however since the spottail shiner is benthivorous and consumes mainly benthic invertebrates the uptake of BPA from food might keep BPA levels elevated in fish tissue.

CONCLUSIONS

Concentrations of Urban Organic Pollutants in the Lower Pohick watershed reveal that the upstream wastewater treatment plant is a possible point source of certain chemicals including triclosan and bisphenol A, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. As with any environmental sampling effort, more samples to give more discrete data points will assist in a more accurate determination of the concentrations and trends present in an area. Loading of creeks and streams that feed into larger water bodies will add to the complexity of modeling a tidal water body such as the Potomac River. A bigger concern however is the probability of contaminates binding to treated bio-solids and then being redistributed on farm lands therefore reintroducing them to the environment.

Water, sediment, and biota quality guidelines need to be established for the EDC class of compounds as have been done for PCBs and PAHs. These values will allow investigators to compare concentration values and raise awareness within their communities.

Human health effects should also be considered for frequently detected organic contaminants in urban regions because of the large scale consumption of fish by the public. Recreational usage of the waterways for boating and swimming also represent a route of human exposure to organic contaminants. This research will aid water quality

managers in determining the potential impact of the studied pollutants on human health. Sediment Quality Guidelines (SQGs) have been determined for many compounds in bed sediment for determining overall sediment contamination. Several consensus-based Threshold Effect Concentrations (TECs) developed by MacDonald (2000b) have also been examined for PCBs and PAHs [58]. Concentrations below these values are "not likely to show harmful effects" [46, 58] . However, even though concentrations are below the TEC values today, over time the bioavailability of these pollutants could increase.

APPENDIX A

Complete List of Congeners in Calibration in Order of Retention Time

CAS Structural PCB Number[a]		CAS Structural Name[b]	CAS Registry Number[b]
	1	2-Chlorobiphenyl	2051-60-7
	2	3-Chlorobiphenyl	2051-61-8
	3	4-Chlorobiphenyl	2051-62-9
Coelute {	4	2,2'-Dichlorobiphenyl	13029-08-8
	10	2,6-Dichlorobiphenyl	33146-45-1
Coelute {	7	2,4-Dichlorobiphenyl	33284-50-3
	9	2,5-Dichlorobiphenyl	34883-39-1
	6	2,3'-Dichlorobiphenyl	25569-80-6
Coelute {	5	2,3-Dichlorobiphenyl	16605-91-7
	8	2,4'-Dichlorobiphenyl	34883-43-7
	19	2,2',6-Trichlorobiphenyl	38444-73-4
IS	**30**	**2,4,6-Trichlorobiphenyl**	**35693-92-6**
	12	3,4-Dichlorobiphenyl	2974-92-7
	15	4,4'-Dichlorobiphenyl	2050-68-2
	18	2,2',5-Trichlorobiphenyl	37680-65-2
	17	2,2',4-Trichlorobiphenyl	37680-66-3
Coelute {	24	2,3,6-Trichlorobiphenyl	55702-45-9
	27	2,3',6-Trichlorobiphenyl	38444-76-7
	16	2,2',3-Trichlorobiphenyl	38444-78-9
	32	2,4',6-Trichlorobiphenyl	38444-77-8
	34	2',3,5-Trichlorobiphenyl	37680-68-5
	29	2,4,5-Trichlorobiphenyl	15862-07-4
	26	2,3',5-Trichlorobiphenyl	38444-81-4
	25	2,3',4-Trichlorobiphenyl	55712-37-3
	31	2,4',5-Trichlorobiphenyl	16606-02-3
	28	2,4,4'-Trichlorobiphenyl	7012-37-5
Coelute {	20	2,3,3'-Trichlorobiphenyl	38444-84-7
	33	2',3,4-Trichlorobiphenyl	38444-86-9
	22	2,3,4'-Trichlorobiphenyl	38444-85-8
	45	2,2',3,6-Tetrachlorobiphenyl	70362-45-7
	46	2,2',3,6'-Tetrachlorobiphenyl	41464-47-5

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CAS Structural PCB Number[a]		CAS Structural Name[b]	CAS Registry Number[b]
Coelute {	52	2,2’,5,5’-Tetrachlorobiphenyl	35693-99-3
	69	2,3’,4,6-Tetrachlorobiphenyl	60233-24-1
	49	2,2’,4,5’-Tetrachlorobiphenyl	41464-40-8
	47	2,2’,4,4’-Tetrachlorobiphenyl	2437-79-8
	48	2,2’,4,5-Tetrachlorobiphenyl	70362-47-9
	104	2,2’,4,6,6’-Pentachlorobiphenyl	56558-16-8
	44	2,2’,3,5’-Tetrachlorobiphenyl	41464-39-5
	37	3,4,4’-Trichlorobiphenyl	38444-90-5
Coelute {	42	2,2’,3,4’-Tetrachlorobiphenyl	36559-22-5
	59	2,3,3’,6-Tetrachlorobiphenyl	74472-33-6
Coelute {	41	2,2’,3,4-Tetrachlorobiphenyl	52663-59-9
	64	2,3,4’,6-Tetrachlorobiphenyl	52663-58-8
	71	2,3’,4’,6-Tetrachlorobiphenyl	41464-46-4
	40	2,2’,3,3’-Tetrachlorobiphenyl	38444-93-8
SS	**103**	**2,2’,4,5’,6-Pentachlorobiphenyl**	**60145-21-3**
	67	2,3’,4,5-Tetrachlorobiphenyl	73557-53-8
	63	2,3,4’,5-Tetrachlorobiphenyl	74472-34-7
	74	2,4,4’,5-Tetrachlorobiphenyl	32690-93-0
	70	2,3’,4’,5-Tetrachlorobiphenyl	32598-11-1
	66	2,3’,4,4’-Tetrachlorobiphenyl	32598-10-0
Coelute {	93	2,2’,3,5,6-Pentachlorobiphenyl	73575-56-1
	95	2,2’,3,5’,6-Pentachlorobiphenyl	38379-99-6
	91	2,2’,3,4’,6-Pentachlorobiphenyl	68194-05-8
Coelute {	56	2,3,3’,4’-Tetrachlorobiphenyl	41464-43-1
	60	2,3,4,4’-Tetrachlorobiphenyl	33025-41-1
Coelute {	84	2,2’,3,3’,6-Pentachlorobiphenyl	52663-60-2
	92	2,2’,3,5,5’-Pentachlorobiphenyl	52663-61-3
	101	2,2’,4,5,5’-Pentachlorobiphenyl	37680-73-2
	99	2,2’,4,4’,5-Pentachlorobiphenyl	38380-01-7
	119	2,3’,4,4’,6-Pentachlorobiphenyl	56558-17-9
	83	2,2’,3,3’,5-Pentachlorobiphenyl	60145-20-2
	97	2,2’,3’,4,5-Pentachlorobiphenyl	41464-51-1
	87	2,2’,3,4,5’-Pentachlorobiphenyl	38380-02-8
	115	2,3,4,4’,6-Pentachlorobiphenyl	74472-38-1

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CAS Structural PCB Number[a]		CAS Structural Name[b]	CAS Registry Number[b]
	85	2,2’,3,4,4’-Pentachlorobiphenyl	65510-45-4
	77	3,3’,4,4’-Tetrachlorobiphenyl	32598-13-3
	136	2,2’,3,3’,6,6’-Hexachlorobiphenyl	38411-22-2
	110	2,3,3’,4’,6-Pentachlorobiphenyl	38380-03-9
	82	2,2’,3,3’,4-Pentachlorobiphenyl	52663-62-4
	151	2,2’,3,5,5’,6-Hexachlorobiphenyl	52663-63-5
	135	2,2’,3,3’,5,6’-Hexachlorobiphenyl	52744-13-5
	144	2,2’,3,4,5’,6-Hexachlorobiphenyl	68194-14-9
	107	2,3,3’,4’,5-Pentachlorobiphenyl	70424-68-9
	147	2,2’,3,4’,5,6-Hexachlorobiphenyl	68194-13-8
	123	2’,3,4,4’,5-Pentachlorobiphenyl	65510-44-3
	118	2,3’,4,4’,5-Pentachlorobiphenyl	31508-00-6
	149	2,2’,3,4’,5’,6-Hexachlorobiphenyl	38380-04-0
SS	**140**	**2,2',3,4,4',6'-Hexachlorobiphenyl**	**59291-64-4**
	114	2,3,4,4’,5-Pentachlorobiphenyl	74472-37-0
	134	2,2’,3,3’,5,6-Hexachlorobiphenyl	52704-70-8
	131	2,2’,3,3’,4,6-Hexachlorobiphenyl	61798-70-7
	146	2,2’,3,4’,5,5’-Hexachlorobiphenyl	51908-16-8
	105	2,3,3’,4,4’-Pentachlorobiphenyl	32598-14-4
	132	2,2’,3,3’,4,6’-Hexachlorobiphenyl	38380-05-1
	153	2,2’,4,4’,5,5’-Hexachlorobiphenyl	35065-27-1
	141	2,2’,3,4,5,5’-Hexachlorobiphenyl	52712-04-6
	179	2,2’,3,3’,5,6,6’-Heptachlorobiphenyl	52663-64-6
	137	2,2’,3,4,4’,5-Hexachlorobiphenyl	35694-06-5
	176	2,2’,3,3’,4,6,6’-Heptachlorobiphenyl	52663-65-7
Coelute {	138	2,2’,3,4,4’,5’-Hexachlorobiphenyl	35065-28-2
	164	2,3,3’,4’,5’,6-Hexachlorobiphenyl	74472-45-0
	158	2,3,3’,4,4’,6-Hexachlorobiphenyl	74472-42-7
	129	2,2’,3,3’,4,5-Hexachlorobiphenyl	55215-18-4
	178	2,2’,3,3’,5,5’,6-Heptachlorobiphenyl	52663-67-9
	187	2,2’,3,4’,5,5’,6-Heptachlorobiphenyl	52663-68-0
	128	2,2’,3,3’,4,4’-Hexachlorobiphenyl	38380-07-3
	183	2,2’,3,4,4’,5’,6-Heptachlorobiphenyl	52663-69-1
	167	2,3’,4,4’,5,5’-Hexachlorobiphenyl	52663-72-6
	185	2,2’,3,4,5,5’,6-Heptachlorobiphenyl	52712-05-7

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CAS Structural PCB Number[a]		CAS Structural Name[b]	CAS Registry Number[b]
	174	2,2’,3,3’,4,5,6’-Heptachlorobiphenyl	38411-25-5
	177	2,2’,3,3’,4’,5,6-Heptachlorobiphenyl	52663-70-4
	156	2,3,3’,4,4’,5-Hexachlorobiphenyl	38380-08-4
	171	2,2’,3,3’,4,4’,6-Heptachlorobiphenyl	52663-71-5
	157	2,3,3’,4,4’,5’-Hexachlorobiphenyl	69782-90-7
	173	2,2’,3,3’,4,5,6-Heptachlorobiphenyl	68194-16-1
	172	2,2’,3,3’,4,5,5’-Heptachlorobiphenyl	52663-74-8
IS	**204**	**2,2',3,4,4',5,6,6'-Octachlorobiphenyl**	**74472-52-9**
	197	2,2’,3,3’,4,4’,6,6’-Octachlorobiphenyl	33091-17-7
	180	2,2’,3,4,4’,5,5’-Heptachlorobiphenyl	35065-29-3
	193	2,3,3’,4’,5,5’,6-Heptachlorobiphenyl	69782-91-8
	191	2,3,3’,4,4’,5’,6-Heptachlorobiphenyl	74472-50-7
	170	2,2’,3,3’,4,4’,5-Heptachlorobiphenyl	35065-30-6
	190	2,3,3’,4,4’,5,6-Heptachlorobiphenyl	41411-64-7
	199	2,2’,3,3’,4,5,5’,6’-Octachlorobiphenyl	52663-75-9
Coelute {	196	2,2',3,3',4,4',5,6'-Octachlorobiphenyl	42740-50-1
	203	2,2’,3,4,4’,5,5’,6-Octachlorobiphenyl	52663-76-0
	189	2,3,3’,4,4’,5,5’-Heptachlorobiphenyl	39635-31-9
	195	2,2’,3,3’,4,4’,5,6-Octachlorobiphenyl	52663-78-2
	208	2,2’,3,3’,4,5,5’,6,6’-Nonachlorobiphenyl	52663-77-1
	207	2,2’,3,3’,4,4’,5,6,6’-Nonachlorobiphenyl	52663-79-3
	194	2,2’,3,3’,4,4’,5,5’-Octachlorobiphenyl	35694-08-7
	205	2,3,3’,4,4’,5,5’,6-Octachlorobiphenyl	74472-53-0
	206	2,2’,3,3’,4,4’,5,5’,6-Nonachlorobiphenyl	40186-72-9
	209	2,2’,3,3’,4,4’,5,5’,6,6’-Decachlorobipheny	2051-24-3

[a] Congeners in order of retention time based on Frame *et al* ., 1996

[b] Mills *et al* ., 2007

[c] "IS" = internal standard

[d] "SS" = surrogate standard

APPENDIX B

Method Detection Limits for Compounds in Method

PAH	Instrument Detection	Estimated Method Detection Limit		
	IDL (ng)	Fish (ng/g)	Bed Sediment (ng/g)	Suspended Sediment (ng/g)
Naphthalene-d8 SS	0.31	0.16	0.06	0.10
Naphthalene	0.35	0.18	0.07	0.12
1-Methylnaphthalene	0.43	0.22	0.09	0.14
2-Methylnaphthalene	0.69	0.35	0.14	0.23
Biphenyl	0.12	0.06	0.02	0.04
Acenaphthylene	0.32	0.16	0.06	0.11
Acenaphthene-d10 SS	0.13	0.06	0.03	0.04
Acenaphthene	0.06	0.03	0.01	0.02
Fluorene	0.06	0.03	0.01	0.02
1-Methylfluorene	0.07	0.03	0.01	0.02
Anthracene	0.04	0.02	0.01	0.01
Phenanthrene-d10 SS	0.32	0.16	0.06	0.11
Phenanthrene	0.27	0.14	0.05	0.09
o-Terphenyl	0.49	0.24	0.10	0.16
2-Methylphenanthrene	0.36	0.18	0.07	0.12
2-Methylanthracene	0.16	0.08	0.03	0.05
4,5-Methylenephenanthrene	0.28	0.14	0.06	0.09
1-Methylanthracene	0.23	0.12	0.05	0.08
1-Methylphenanthrene	0.28	0.14	0.06	0.09
9-Methylanthracene	0.21	0.10	0.04	0.07
Fluoranthene	0.05	0.02	0.01	0.02
Pyrene	0.14	0.07	0.03	0.05
9,10-Dimethylanthracene	0.22	0.11	0.04	0.07
Benz[a]anthracene	0.28	0.14	0.06	0.09
Chrysene-d12 SS	0.10	0.05	0.02	0.03
Chrysene-Triphenylene	0.08	0.04	0.02	0.03
Benzo[b]fluoranthene	0.12	0.06	0.02	0.04
Benzo[k]fluoranthene	0.17	0.08	0.03	0.06
Benzo[e]pyrene	2.82	1.41	0.56	0.94
Benzo[a]pyrene	0.18	0.09	0.04	0.06
Perylene-d12 SS	0.28	0.14	0.06	0.09
Perylene	0.38	0.19	0.08	0.13
Indeno[1,2,3-cd]pyrene	0.26	0.13	0.05	0.09
Dibenz[a,h]anthracene	0.24	0.12	0.05	0.08
Benzo[g,h,i]perylene	0.14	0.07	0.03	0.05
Average	**0.30**	**0.15**	**0.06**	**0.10**

PCB	Instrument Detection Limit	Estimated Method Detection Limit		
	IDL (ng)	Fish (ng/g)	Bed Sediment (ng/g)	Suspended Sediment (ng/g)
1	0.087	0.043	0.009	0.003
2	0.060	0.030	0.006	0.002
3	0.053	0.026	0.005	0.002
4/10	0.157	0.079	0.016	0.005
7/9	0.032	0.016	0.003	0.001
6	0.063	0.031	0.006	0.002
5/8	0.090	0.045	0.009	0.003
19	0.037	0.018	0.004	0.001
12	0.202	0.101	0.020	0.007
18	0.090	0.045	0.009	0.003
15	0.332	0.166	0.033	0.011
17	0.067	0.034	0.007	0.002
24/27	0.137	0.069	0.014	0.005
16	0.176	0.088	0.018	0.006
32	0.154	0.077	0.015	0.005
34	0.141	0.071	0.014	0.005
29	0.218	0.109	0.022	0.007
26	0.202	0.101	0.020	0.007
25	0.204	0.102	0.020	0.007
31	0.284	0.142	0.028	0.009
28	0.254	0.127	0.025	0.008
20/33	0.518	0.259	0.052	0.017
22	0.248	0.124	0.025	0.008
45	0.135	0.067	0.013	0.004
46	0.171	0.085	0.017	0.006
52/69	0.342	0.171	0.034	0.011
49	0.198	0.099	0.020	0.007
47	0.167	0.084	0.017	0.006
48	0.155	0.077	0.015	0.005
104	0.144	0.072	0.014	0.005
44	0.259	0.129	0.026	0.009
37	0.841	0.421	0.084	0.028
59/42	0.518	0.259	0.052	0.017
41/64/71	0.773	0.387	0.077	0.026
40	0.288	0.144	0.029	0.010
103 SS	0.214	0.107	0.021	0.007
67	0.456	0.228	0.046	0.015

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PCB	Instrument Detection Limit	Estimated Method Detection Limit		
	IDL (ng)	Fish (ng/g)	Bed Sediment (ng/g)	Suspended Sediment (ng/g)
74	0.607	0.303	0.061	0.020
70	0.557	0.278	0.056	0.019
66	0.570	0.285	0.057	0.019
93/95	0.745	0.372	0.074	0.025
91	0.272	0.136	0.027	0.009
56/60	1.161	0.581	0.116	0.039
92/84	0.185	0.092	0.018	0.006
101	0.266	0.133	0.027	0.009
99	0.201	0.100	0.020	0.007
119	0.141	0.070	0.014	0.005
83	0.344	0.172	0.034	0.011
97	0.203	0.102	0.020	0.007
87	0.231	0.116	0.023	0.008
115	0.379	0.189	0.038	0.013
85	0.239	0.119	0.024	0.008
136	0.143	0.071	0.014	0.005
77	0.423	0.211	0.042	0.014
110	0.308	0.154	0.031	0.010
82	0.167	0.083	0.017	0.006
151	0.123	0.061	0.012	0.004
135	0.184	0.092	0.018	0.006
144	0.195	0.098	0.020	0.007
107	0.461	0.230	0.046	0.015
147	0.072	0.036	0.007	0.002
123	0.333	0.167	0.033	0.011
149	0.123	0.062	0.012	0.004
118	0.549	0.275	0.055	0.018
140 SS	0.204	0.102	0.020	0.007
134	0.122	0.061	0.012	0.004
114	0.488	0.244	0.049	0.016
131	0.148	0.074	0.015	0.005
146	0.201	0.101	0.020	0.007
105	0.662	0.331	0.066	0.022
132	0.132	0.066	0.013	0.004
153	0.196	0.098	0.020	0.007
141	0.265	0.132	0.026	0.009
137	0.479	0.239	0.096	0.160
176	0.095	0.048	0.019	0.032
138/164	0.382	0.191	0.076	0.127
158	0.382	0.191	0.076	0.127
129	0.299	0.150	0.060	0.100
178	0.141	0.071	0.028	0.047
187	0.139	0.069	0.028	0.046
128	0.411	0.205	0.082	0.137

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PCB	Instrument Detection Limit	Estimated Method Detection Limit		
	IDL (ng)	Fish (ng/g)	Bed Sediment (ng/g)	Suspended Sediment (ng/g)
183	0.273	0.137	0.055	0.091
167	0.468	0.234	0.094	0.156
185	0.206	0.103	0.041	0.069
174	0.458	0.229	0.092	0.153
177	0.382	0.191	0.076	0.127
156	0.549	0.275	0.110	0.183
171	0.512	0.256	0.102	0.171
157	0.625	0.313	0.125	0.208
173	0.221	0.111	0.044	0.074
172	0.257	0.128	0.051	0.086
180	0.738	0.369	0.148	0.246
193	0.284	0.142	0.057	0.095
191	0.521	0.261	0.104	0.174
170	0.494	0.247	0.099	0.165
190	0.278	0.139	0.056	0.093
199	0.172	0.086	0.034	0.057
203/196	0.270	0.135	0.054	0.090
189	1.068	0.534	0.214	0.356
208	0.392	0.196	0.078	0.131
207	0.115	0.058	0.023	0.038
194	0.379	0.189	0.076	0.126
205	0.496	0.248	0.099	0.165
206	0.513	0.257	0.103	0.171
209	0.131	0.066	0.026	0.044
Average	0.31	0.15	0.04	0.04

[a]"SS" Surrogate Standard

EDC	Instrument Detection Limit	Estimated Method Detection Limit		
	IDL (ng)	Fish (ng/g)	Bed Sediment (ng/g)	Suspended Sediment (ng/g)
Octylphenol	0.37	0.18	0.07	0.12
Nonylphenol	0.32	0.16	0.06	0.11
Triclosan	0.33	0.17	0.07	0.11
Bisphenol A	0.34	0.17	0.07	0.11
Estrone	0.32	0.16	0.06	0.11
17a- Ethynyl Estradiol	0.36	0.18	0.07	0.12
Bisphenol A-d6	0.32	0.16	0.06	0.11
Average	**0.34**	**0.17**	**0.07**	**0.11**

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