

The Vertical Profile of PCBs at the Estuarine Turbidity Maximum Zone in a Coastal Plain River
and the Influence of Salinity-Induced Flocculation on PCB Concentrations in Particles

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science at George Mason University

By

Kathleen J. Housman
Bachelor of Science
Mount Saint Mary's University, 2006

Director: Gregory D. Foster, Professor
Department of Chemistry

Fall Semester 2009
George Mason University
Fairfax, VA

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ACKNOWLEDGEMENTS

Without the support of all my friends and family the completion of this project would not have happened. The students in the Foster group offered their time and energy various aspects of this project including:

- Mr. Kevin Dove: Without whom, I really could not have done this. Over the past few years we have gone through this together, all the way from understanding general GC theory to getting results, from sampling to discussing extraction techniques. Most of all, thanks for being a friend! We are almost done!
- Mr. Matt Kershis: Always willing to help no matter how dull the task
- Ms. Tiffany Ha: For helping with salinity-induced flocculation studies
- Ms. Ashley Ripple: For helping with salinity-induced flocculation studies
- Mr. David Lieu: For his input on organic matter analysis
- Mr. Thomas Huff: For general chromatography theory

In addition, I would like to thank my father Chuck Housman who offered the usage of his Carolina Skiff for all three environmental samplings, who drove four hours round trip each time, and who has to deal with me. And my sister Molly Housman who offered a helping hand while sampling.

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ABSTRACT

THE VERTICAL PROFILE OF PCBs AT THE ESTUARINE TURBIDITY MAXIMUM ZONE IN A COASTAL PLAIN RIVER AND THE INFLUENCE OF SALINITY-INDUCED FLOCCULATION ON PCB CONCENTRATIONS IN PARTICLES

Kathleen J. Housman, M.S.

George Mason University, 2009

Thesis Director: Dr. Gregory D. Foster

Polychlorinated biphenyls (PCBs) are ubiquitous, persistent organic pollutants. It is known that this class of chemicals has a high affinity towards suspended particles in the water column based on their hydrophobic properties and relatively high octanol-water partition coefficients (K_{ow}). An estuarine turbidity maximum (ETM) is a known region of enhanced concentrations of sediment in suspension. The dynamics of the ETM are driven by multiple variables including tidal resuspension, estuarine stratification, and electrical double-layer influenced flocculation. Because PCBs bind readily to sediments, the ETM is an important zone to study fate, distribution, and transport of contaminants in coastal rivers. The ETM is especially important in the Potomac River because it is located downstream of two major PCB hotspots, including the Anacostia River and Quantico Bay, VA. This region of the Potomac River has not been previously studied for PCB fate, and remains an important missing piece of the puzzle in understanding the

downstream transport of PCBs from regions of severe contamination to the Chesapeake Bay and Atlantic Ocean.

Environmental sampling of the Potomac River ETM took place on three occasions during the spring of 2008 and 2009. Potomac River water was sampled along a vertical transect at ~2 m intervals through the halocline of the ETM to 30 m depths using a submersible pump. Both suspended sediment and bed sediments were collected, extracted, and analyzed for PCBs. Water geochemistry parameters such as total suspended matter (TSM) and salinity along with sediment organic matter (OM) were also determined. PCB-bound suspended sediments were found at elevated levels as compared to bed sediments (238 ± 126 compared to 28 ± 13 ng/g), indicating that the ETM is not a likely depositional zone for PCBs in the Potomac River. It is likely that PCB-bound suspended materials are transported farther downstream and are widely dispersed in coastal waters.

Because ETM sampling is extremely variable, a controlled laboratory study was performed by flocculating resuspended sediment material that was highly contaminated with PCBs. The goal was to study the influence of salinity-induced flocculation on the concentrations of PCBs in river particles, thus simulating the Potomac River ETM. The salinity-induced flocculation studies were performed on a 20-L scale by first mixing PCB contaminated sediment and water. The large particles in resuspended sediment were allowed to settle, and the salinity of decanted overlying water containing colloid-sized particles was enhanced to promote flocculation. The floc material was filtered, extracted, and analyzed for PCB concentrations. An unexpected trend of decreasing PCB

concentrations in floc with increasing salinity was found for both PCBs and OM, indicating that dilution in particles results during PCB flocculation.

In addition, evidence was found for the natural PCB homologue fractionation of PCBs along the downstream transect of the Potomac River from the Anacostia River hotpot to the ETM. The higher molecular weight, heavily chlorinated PCBs were more abundant in Anacostia River sediments while less chlorinated congeners dominate ETM sediments.

It is clear from the current work that the ETM is a dynamic region and must be more rigorously studied in order to fully understand the dynamics of contaminant transport from highly contaminated regions such as the Anacostia River and Quantico Bay, VA to the Chesapeake.

INTRODUCTION

PCBs as Contaminants

Polychlorinated biphenyls (PCBs) are a class of chemicals that give rise to health concerns because of their environmental persistence (Sinkkonen and Paasivirta, 2000), ability to disperse widely around the earth (Iwata *et al.*, 1993), and high toxicity. Environmentally, PCBs are very stable, where the more heavily chlorinated congeners can have half-lives of up to 38 years based on natural degradation via photolysis, hydrolysis, and biodegradation (Sinkkonen and Paasivirta, 2000). PCBs are considered by the United States Environmental Protection Agency (EPA) to be persistent, bioaccumulative, and toxic substances (i.e. PBTs), whose toxic properties can lead to skin irritation as well as damage to the stomach, liver, and kidneys; and are potential carcinogens and endocrine disruptors (U.S. EPA, 2008). It is well known that PCBs are ubiquitous, even found far from known point sources of pollution because they possess properties permitting long-range transport through atmospheric advection currents, and thus, disperse on a global scale (Nisbet and Sarofim, 1972 and Iwata *et al.*, 1993).

PCBs were manufactured originally for purposes of cooling and insulating as dielectric fluids in the electrical utility industry. Additional applications for PCB usage included hydraulic fluids, plasticizers, resins, waxes, paints and flame retardants (Erickson, 1997 and Edgar *et al.*, 1999). Just within the United States, the primary

manufacturer of PCBs, the Monsanto Company (St. Louis, MO), produced over 640,000 tons during its 47-year production span, contributing to more than 48% of the world's total PCB production (Breivik *et al.*, 2002a). The EPA placed a ban on the production of PCBs within the United States in 1979 (USEPA, 2007), and further regulations for the phasing out of PCBs and twelve other persistent organic pollutants (POPs) were initiated by participating countries in the 2001 Stockholm Convention (Porta and Zumeta, 2002). Despite the U.S. manufacturing ban and further policy regulations, PCBs remain a significant contaminant worldwide because more than 35% of the originally manufactured material is escaped containment and continues to cycle through the global environment (Eisenrich, 1987). The primary PCB emissions to the environment occur through accidental leakage from decommissioned transformers and large capacitors (Nisbet and Sarofim, 1972 and Breivek *et al.*, 2002b), and because PCBs are anthropocentric in origin, having no known natural sources, it should follow that heavily contaminated areas tend to be located in industrial areas.

Structurally, the PCB chemical class contains 209 individual congeners, corresponding to the substitution of up to 10 chlorine atoms around a molecule of biphenyl. All 209 congeners have unique chemical and physical properties. PCBs are highly lipophilic, having octanol-water partition coefficients (K_{ow}) ranging from 10^4 to 10^8 (Hawker and Connell, 1988) and concentrate extensively in biota and in sediments (Miller *et al.*, 1985). Monsanto produced commercial PCB mixtures under the trademark name "Aroclor." Each Aroclor mixture corresponds to various levels of average chlorination, yielding mixtures of varying densities and viscosities, which have been

optimized for various applications (Erickson, 1997). The nomenclature for the 209 PCB congeners has been described in detail by Mills *et al.* (2007). Environmentally, determining the incidence of individual PCB congeners is not only important in a forensic sense, by pinpointing the Aroclor mixture of origin, but also for identifying the environmental compartment in which each congener will ultimately concentrate based on physicochemical properties. Therefore, PCBs are a complex mixture of contaminants analyzed as a subset of the individual 209 congeners that correspond to the predominant constituents in all the Aroclor mixtures. The Monsanto Aroclor mixtures are considered the primary source of PCBs in the environment, and as such ~85 congeners are considered to dominate the total PCB concentration in environmental samples based upon PCB congener abundances in the Aroclors.

PCBs remain a threat to the global environment, and within the Chesapeake Bay PCBs are considered the primary organic chemical on the Toxics of Concern List (CBP, 2006). Understanding the environmental distribution and transport of PCBs is especially important within the Potomac not only because it is the second largest tributary of the Bay (Foster and Cui, 2008), but because it also contains two major PCB hotspots including the Anacostia River, Washington, D.C. (McEachern, 2005, Haywood and Buchanan, 2007) and Quantico, VA (USEPA, 1997). In addition, the Chesapeake Bay Program (CBP) recognizes the Anacostia River as one of the three regions of greatest concern in terms of chemical contamination in the Bay (CBP, 1996).

Coastal Rivers and the Land-to-Sea Transport of PCBs

Coastal rivers are important and unique water bodies because of their ideal geography for commercial transportation juxtaposed with the development of human population centers, as well as their position at the interface of tidal freshwater and saltwater mixing. Estuaries are positioned at the downstream end of coastal rivers, and large coastal rivers are home to some of the most populated cities in the U.S., making them vulnerable to contamination by industrial pollutants. Because estuarine turbidity maxima are located towards the middle of estuaries and experience a relatively high degree of tidal mixing, they represent significant regions for contaminant-bound sediment transport.

The estuarine turbidity maximum (ETM) is the zone of a coastal river that occurs at the limit of saltwater intrusion in an estuary where a natural saltwater density gradient contributes to elevated turbidity, and thereby elevated total suspended matter (TSM) as compared to those found upstream and downstream of the ETM (Schubel, 1968 and Sanford *et al.*, 2001). The primary mechanisms of the formation of large particle aggregates, referred to as floc, at the Chesapeake ETM are not well-defined (Droppo, 2005 and Sanford *et al.*, 2001). The ETM is a highly dynamic region of an estuary influenced by changes in diurnal (high, low and slack tides) and lunar tides (spring versus neap) (Gelfenbaum, 1983, Sanford *et al.*, 2001, and Schubel, 1968). The enhancement in the concentration of suspended sediment at the ETM has been explained through various physical properties such as tidal and current-related resuspension (Althausen and Kjerfve,

1992) and an electrochemical phenomenon known as flocculation (Edzwald *et al.*, 1974 , Drever, 1997, and Verney *et al.*, 2009).

Estuarine flocculation is dependant on salinity and pH (Edzwald *et al.*, 1974 and Santschi *et al.*, 1997). The surface of both inorganic sediments (alumino-silicates) and organic sediments (humic and fulvic acids) is dominated by hydroxyls (Tinsley, 2004). Upon ionization hydroxyls exist as oxygen anions creating a negative electrical charge on the particle which interacts with cations in aqueous suspension surrounding the sediment particle. In waters with low salinity, thereby lesser ionic strength, a diffuse electrical double layer exists and the colloidal particles repel each other allowing conditions for the formation of stable suspensions (Edzwald *et al.*, 1974 and Drever, 1997). An increase in salinity contributes to a constriction of the double layer which previously existed in upstream, freshwater conditions, and van der Waals forces dominate over repulsive forces creating agglomerations known as flocs (Edzwald *et al.*, 1974 and Drever, 1997). A visual representation of the dynamics of flocculation can be seen in Figure 1.

The Potomac River ETM represents an important segment of the tidal river because it is the region of very high suspended sediment concentrations between the Anacostia River and Chesapeake Bay. In addition, estuarine turbidity maxima are thought to act as natural sediment traps (Sanford *et al.*, 2001), and this could have implications for the distribution and transport of PCBs from the upstream margin, through the ETM, and ultimately to the Bay and the Atlantic Ocean. Little work has been done in characterizing PCB concentrations in suspended sediments along the tidal segment of the river from the Anacostia River to the Bay. The literature contains work

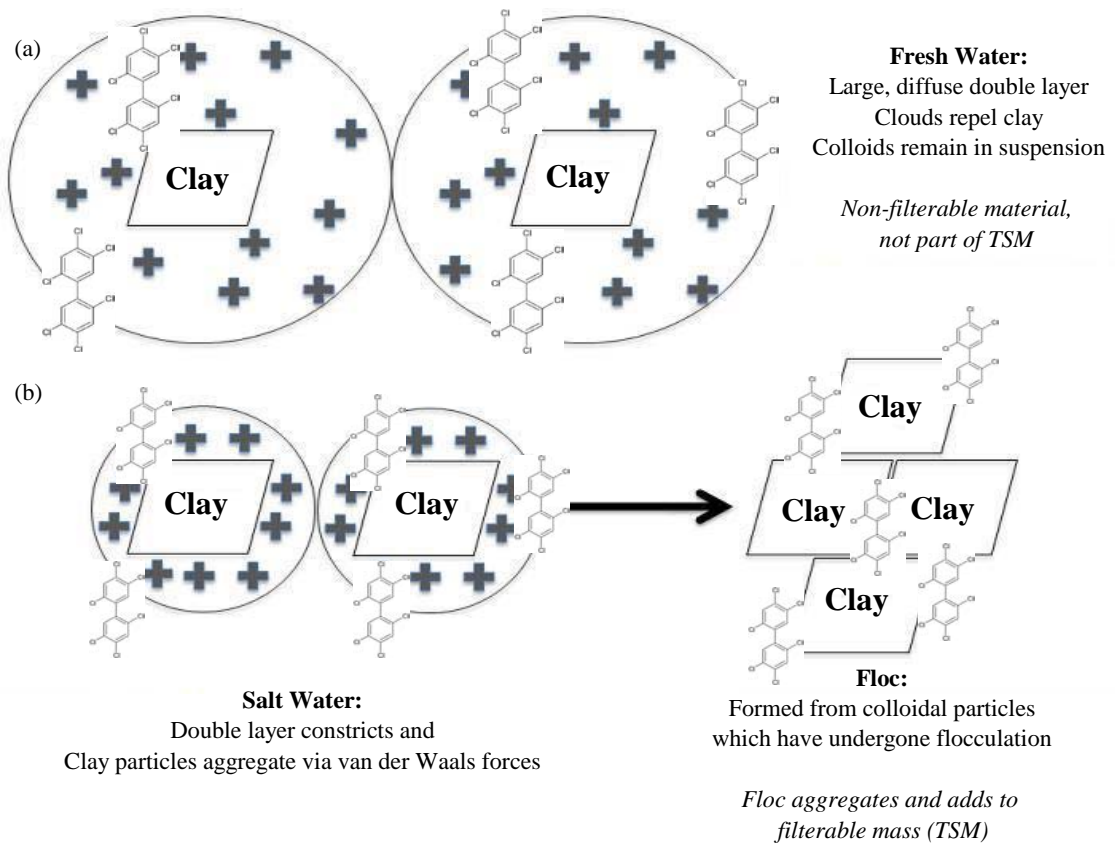


Figure 1: Visual of Flocculation at the ETM

on surficial sediments in the tidal Potomac River (McEachern, 2005, Foster and Cui, 2008, Wade *et al.*, 1994), and a few studies provide information on suspended sediments in the Susquehanna River (Foster *et al.*, 2000a, Foster *et al.*, 2000b) and the Chesapeake Bay (Ko and Baker, 1995). Only one study can be identified in the literature pertaining to PCBs in bed sediments in the tidal Potomac River ETM (McEachern, 2005). Clearly, further research is needed to better understand dynamics in organic contaminant distribution and transport in the tidal regions of coastal rivers.

The central hypothesis of the present study is that the ETM promotes stratified concentrations of PCBs that correlate with suspended sediment concentrations. That is, PCB concentrations should increase through the vertical profile of the ETM in proportion to TSM because PCBs are particle-reactive. The objectives are to investigate TSM and PCB concentration gradients through a vertical transect of the ETM, compare particle-bound PCB concentrations through the depth profile, define the role of flocculation in controlling PCB concentrations at the ETM, and identify the major geochemical processes at the ETM influencing the downstream transport of PCBs in the Potomac River. Such new information will provide fresh insights relating to the mechanisms of river-based transport for PCBs in the tidal region of the Potomac River as well as other coastal rivers.

MATERIALS AND METHODS

Site Description

The Potomac River sub-estuary is a tributary of the Chesapeake Bay, and it contributes to 18% of the total freshwater input into Chesapeake Bay (Pritchard, 1952, Elliott, 1978, and Guo and Valle-Levinson, 2007), making it the second largest tributary of the Bay (Foster and Cui, 2008). It is considered a partially mixed sub-estuary, similar in hydrology and geochemistry to the much larger Chesapeake Bay (Pritchard, 1952 and Elliott, 1978). The tidal region of the Potomac is a 160 km segment from the Bay to Great Falls, just north and upstream of Washington, D.C. (Elliott, 1978), and is tidally classified as semi-diurnal, having two high and two low tides daily with a tidal range of 0.37 – 0.43 m at the ETM (Hicks, 1964).

The drainage area of the Potomac is 37,995 km², encompassing regions of West Virginia, Maryland, Virginia, and Washington DC (Wiley *et al.*, 2007) supporting a population of 5.8 million (ICPRB, 2009). The magnitude of both its drainage area and population size coupled with the fact its tidal zone is primarily downstream of the Anacostia River, a major point-source of PCBs (CBP, 1996 and CBP, 2006), make this study of Potomac River ETM an important piece of the puzzle in the fate and transport of PCBs in coastal rivers. The Potomac River ETM was found (Figure 2) off the Port Tobacco River near Dahlgren, VA north of the Highway 301 Bridge (38° 25' 10.45" N,

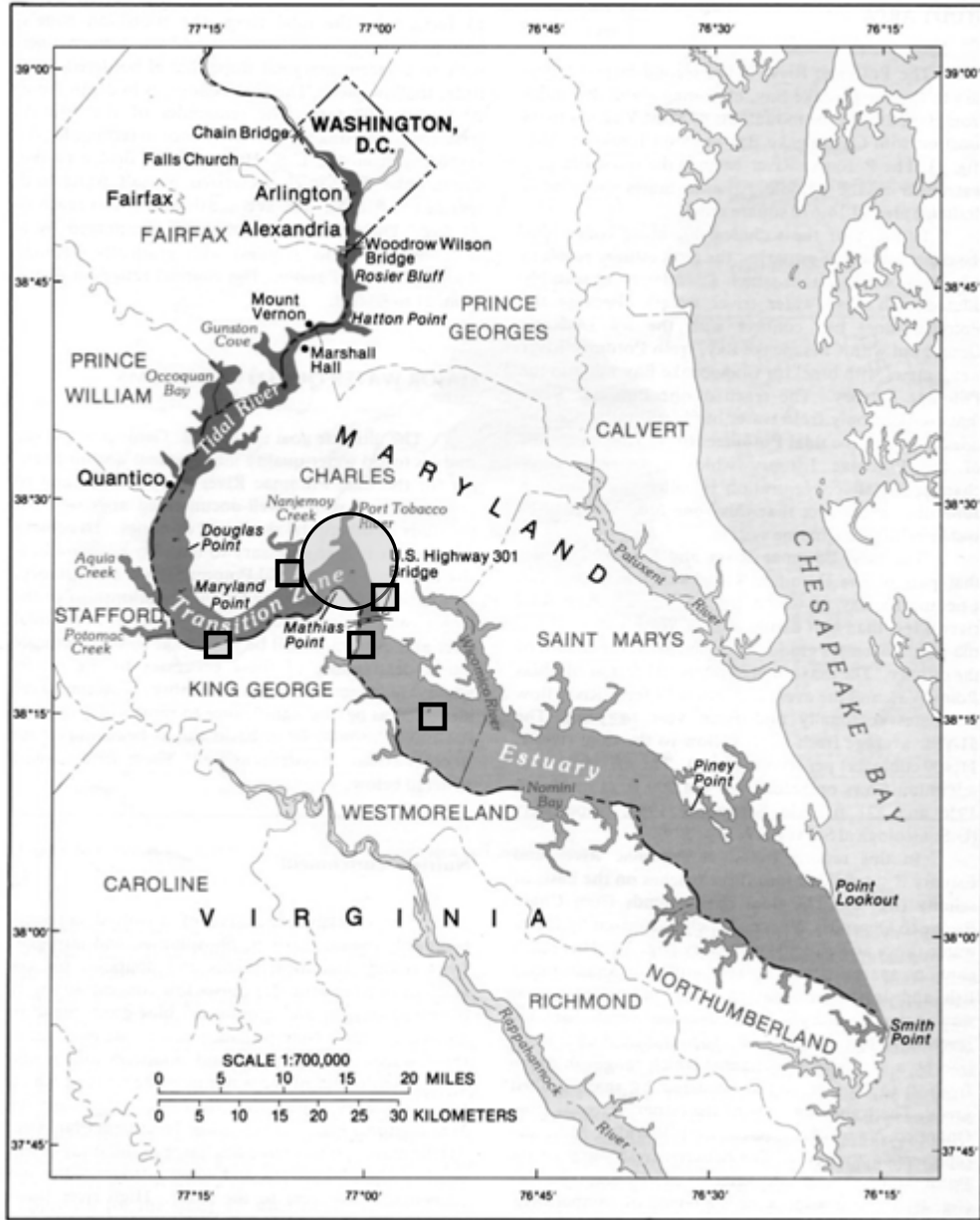


Figure 2: The Potomac River ETM (circled) located just off Port Tobacco River above the 301 Bridge. Boxes represent bed sediment samples taken from a previous study by McEachern (2005) at Nanjemoy Creek, Mathias point, the 301 Bridge, Dahlgren, and Kettle Bottom Shoals, going downstream. Image courtesy of USGS (1984).

77° 2' 35.73" W) (Donato, 1996) at the limit of salt intrusion, which occurs 95 km upstream from the Bay main-stem (Elliott, 1978).

Field Sampling

The ETM was sampled three times in the spring of 2008 (March 30 and May 21) and 2009 (May 8) during one neap and two spring tides, respectively. Samples were collected during the high and low tide crests on March 30 and May 21 (2008) and during the low tide and slack tide on May 8 (2009).

Potomac River water samples were collected through the halocline on a vertical transect at ~2 m intervals from the surface to depths of 10 m or 30 m using a Fultz submersible positive displacement pump (Fultz Inc., Lewistown, PA). The Fultz pump was equipped with a Model SP-300 pump head, and was deployed from a 17-foot (5.18 m) Carolina Skiff. The river bottom at this location consisted of a shallow shoal having a depth of approximately 4 – 6 m, which dropped into the main-stem channel having depths up to 35 m. Samples were taken in the main channel where tidal mixing is greatest. The samples were collected at least 5 m from the river bottom to avoid collecting suspended sediment representative of tidal resuspension alone.



The Fultz pump was fitted with 30 m of Teflon-lined rubber hose. The pump motor also possessed an impeller blade composed of Teflon to prevent PCB sorption to the pump surface. The water sample was allowed contact with only Teflon and stainless steel surfaces. Prior to field sampling, the pump was flushed with warm, soapy (Alconox) water followed with a rinsing of distilled water and a final flush with a 10%

aqueous methanol. At each depth, the pump was flushed for 3 minutes at maximum pump speed before each fresh sample was collected (to completely purge the lines of the previous sample). River water samples were collected in 20 L stainless steel Cornelius kegs, which had been rigorously pre-cleaned with Alconox soap followed by distilled water and methanol rinsing. The kegs were equipped with sealed gaskets and quick-connect fittings to eliminate sample contamination both in the field and in transport, and to avoid a headspace for PCB volatilization. Upon arrival to the environmental chemistry laboratory at George Mason University, the kegs were stored at 4 °C until filtration within 48 h of arrival. Table 1 lists the number of samples taken during each sampling event.

Water chemistry parameters including conductivity, temperature, salinity, and depth were recorded using a YSI Hydrolab (Cole-Parmer, Vernon Hills, IL). The Hydrolab was anchored to the Fultz pump head so as to coincide water chemistry data with river water sampling at each depth. In addition, total suspended sediment (TSM) samples were separately collected in 1-L polyethylene bottles using the Fultz pump. The TSM samples were collected prior to the large volume ETM water samples at the identical depths. The filled bottles were labeled, stored on ice, and transported to the environmental chemistry laboratory for TSM determinations.

Bed sediment samples were also collected during each vertical transect by using a Petite Ponar grab (Wildco, Yulee, FL). Sediment from the Ponar was released in a stainless steel pan (60 x 20 x 5 cm), where surficial sediment (upper 2-3 cm) was subsampled using a stainless steel spatula, and the sediment was stored in wide-mouth amber

Table 1: Complete List of Environmental and Laboratory Samples

		Sampling Date					Salinity-Induced Flocculation Study	
		Mar. 30, 2008		May 21, 2008		May 8, 2009		
Lunar Cycle	Neap Tide  Spring Tide 							na
Daily Tide	Low High	Low High	Low High	Low Slack			na	
No. Filtered Samples	12	6	6	5	5	5	4	4
	2.3	3.0 (<i>dup</i>)	2.1	2.0	3.0	3.0		
	4.3	7.6 (<i>dup</i>)	4.0	3.7	10	10		
Depth from Surface (m)	6.3	12 (<i>dup</i>)	5.3	5.4	18 (<i>dup</i>)	18 (<i>dup</i>)		na
	8.5		7.5	7.1	25	25		
	12 (<i>dup</i>)		9.5	9.8				
			11					
Salinity Range (‰)	6 - 12		1 - 9		0 - 6		0 - 40	
No. Bed Sed Samples	2	2	2	2	2	2	2	2

^a na = not applicable

^b dup = duplicate

jars fitted with Teflon-lined lids. The jars were labeled and stored in an ice chest during transport to the environmental chemistry laboratory. After arrival to the laboratory, the sediments were centrifuged at 1500 rpm (Du Pont Sorval RC-5B, New Town, CT), the extruded pore water was decanted, and the sediments were transferred back to their original jars for storage at -30 °C until analysis.

Salinity, TSM, and Organic Matter Determinations

For the determination of TSM, ~200 mL of water from the plastic 1-L bottle was filtered using a Millipore vacuum filtration apparatus containing a preweighed 47 mm Whatman (Florham Park, NJ) glass fiber filter (GFF; 0.70 µm nominal pore size). The volume of water passing through the filter was measured with a graduated cylinder, and the GFF filters were dried to a constant mass overnight at 50 °C in a drying oven. The mass of TSM was determined gravimetrically, and TSM was then calculated as mass of sediment per volume filtered (mg/L).

Filters used for TSM analysis were then subjected to ignition at 475 °C (48 hrs) in a furnace to measure the combustible organic matter content (OM). The thermal gravimetric technique was used to determine the amount of organic matter (Davies, 1974) in particles and sediments. The remaining material is identified as non-combustible inorganic matter (InOM). Percent organic matter (% OM) is determined by:

$$\left(\frac{mass_{50^{\circ}C} - mass_{475^{\circ}C}}{mass_{50^{\circ}C}} \right) \cdot 100 = \% OM .$$

Organic matter was also quantified as mass per volume of the sample (mg/L):

$$\left(\frac{mass_{50^{\circ}C} - mass_{475^{\circ}C}}{L_{filtered}} \right) = OM \left(\frac{mg}{L} \right).$$

Salinity was calculated based on the American Public Health Association (APHA) conversion from conductivity. The practical salinity scale (PSS) is based on the ratio of the recorded conductivity of the sample to the conductivity of a standard solution of KCl where 32.4356 g KCl in a 1 kg of solution has a PSS of 35 ‰ at 15 °C . The conductivity ratio (R_t) is a function the temperature of the solution where standard salinity is 35 ($S = 35$ ‰) for seawater at 15 °C; the standard conductivity of sea water (C_{35}) must then vary with temperature. Conductivity was recorded for each sample and was converted to salinity on the practical salinity scale (APHA, 2007). Conductivity was measured using a hand-held conductivity meter (Cole-Parmer, Vernon Hills, IL) that was calibrated to 12.88 mS/cm in a solution of 0.1 M KCl at 25 °C prior to data collection.

Standards and Reagents

The PCB calibration consisted of 117 individual PCB congeners (Table 2 and Appendix A), two surrogate standards, 2,2',4,5',6-pentachlorobiphenyl (PCB 103) and 2,2',3,4,4',6'-hexachlorobiphenyl (PCB 140), and two internal-injection quantitation standards, 2,4,6-trichlorobiphenyl (PCB 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204), all of which were purchased in concentrated solutions of preassembled mixtures from Accustandard Inc. (New Haven, CT). All dilutions including working mixes, surrogate standard spiking mixes, internal standard spiking mixes, and calibrations

Table 2: List of PCBs Analyzed in Method

<i>Quality Assurance Congeners</i>		
CI	CAS Structural PCB Number and Structural Name ^a	
3	IS 30 (2,4,6-Trichloro)	
5	SS 103 (2,2',4,5',6-Pentachloro)	
6	SS 140 (2,2',3,4,4',6'-Hexachloro)	
8	IS 204 (2,2',3,4,4',5,6,6'-Octachloro)	
<i>Congeners in Calibration</i>		
CI	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

^b IS = Internal Injection Standard

^c SS = Surrogate Standard

were prepared in *n*-hexane (Fisher Scientific), and stored in amber bottles sealed with Teflon-lined lids wrapped with Teflon tape. All standard stock solutions were stored at -30 °C and were brought to room temperature before the seal was removed at any point during experimental work to ensure the proper volumes were delivered.

Sampling bottles and all glassware used for sample collection and preparation were cleaned by washing with soap, rinsing with distilled water followed by rinse with DDW, and then ashed at 450 °C overnight. All laboratory materials that had any contact with the sample were made of glass or Teflon to avoid sample contamination and surface reaction. Teflon materials were cleaned the same way as glass but without ashing. All materials both made of glass and Teflon were solvent-rinsed with either methanol or *n*-hexane prior to use.

Sample Extraction, Clean-up, and PCB Analysis

The large-volume ETM water samples were filtered within 48 h of arrival to the laboratory. Filtration was performed using 293 mm dia., 0.7 µm pore size Whatman GFF filters housed in a 293 mm Millipore stainless steel filter holder. The filter holder was fitted with a Teflon O-ring to prevent contamination. The GFF filters were precleaned by ashing overnight at 450 °C, cooled to room temperature, and stored in *n*-hexane-rinsed foil prior to filtration. Following filtration of an entire ETM sample, the filter (1 per sample) was wrapped in solvent-rinsed foil and stored at -30 °C for preservation until PCB analysis. Filtered river water was collected in 20-L carboy and was measured in aliquots by 2-L graduated cylinder to determine the exact volume filtered (± 0.1 L) used

for the scale-up determination of total mass of sediment filtered (g) in each sample, which was derived from previously measured TSM values (mg/L).

The GFF filters were thawed to room temperature prior to performing microwave assisted extraction (MAE) using a MARS-X (CEM Corp., Matthews, NC) and 100 mL Teflon GreenChem extraction vessels. All vessels were solvent-rinsed with ~5 mL *n*-hexane prior to extraction. To account for the proper and safe headspace within the extraction vessels, the 293 mm filters were halved and extracted in two separate vessels, and the extracts were combined following each extraction to yield a single filter extract per sample filter. The filters were extracted with 25-30 mL of 3:2 (v/v) acetone:*n*-hexane for 15 minutes at 100 °C and 600 W. The extractions were repeated twice more for a total of three 15 minute extractions per sample. To aid in the removal of residual water from the extracts, ~5 g of KCl per sample (Fisher Scientific, Fair Lawn, NJ) were added to increase the polarity of water, thereby increasing the solubility of acetone in the less polar *n*-hexane phase and promoting phase separation between the water and organic solvent phases. The hexane layer, which contains the PCBs, was pipetted off the lower aqueous layer using a clean disposable glass Pasteur pipet into a clean, solvent-rinsed 50 mL centrifuge tube.

The sample extracts were reduced in volume under a constant stream of nitrogen (N₂) gas using an N-VAP model 112 nitrogen evaporator (Organomation Associates Inc., Berlin, MA) to approximately 10 mL in preparation for column chromatography. The volume-reduced extracts were subjected to column chromatography clean-up using 6 g of 2% (v/m) water-deactivated Florisil (J.T. Baker, Phillipsburg, NJ), sandwiched between

layers of 3 g of sodium sulfate, packed in a stoppered glass chromatography columns. The Florisil column was first rinsed with ~40 mL *n*-hexane, followed by loading the sample on top of the Florisil column. The PCBs were eluted from the column with 60 mL *n*-hexane into two 50 mL glass centrifuge tubes. The eluent was subjected to solvent-volume reduction under N₂ gas where it was combined into one tube and reduced to a final volume of ~1 mL.

The collected PCB fraction from Florisil clean-up was treated with pre-activated copper to aid in the removal of rhombic elemental sulfur (S₈). Copper granules (Fisher Scientific) were activated with 6 M HCl, washed with distilled water, rinsed with acetone to remove residual water, and solvent-rinsed with *n*-hexane with prior to addition to the sample extracts. The sample extracts were allowed to sit overnight or until the copper became discolored, indicating sulfur precipitation. Solvent volume reduction to ~250 μL was continued under a stream of N₂ gas, and samples were vialled with 30 ng each of PCB 30 and 204 added as internal standards. The sample extracts were stored at -20 °C until chromatographic analysis

PCB Analysis

The quantitative analysis of PCBs was conducted using a Hewlett-Packard (HP) Model 5890 Series II gas chromatograph (GC) fitted with a Ni-63 electron capture detector (ECD). The GC-ECD was equipped with an HP Model 6890 autoinjector programmed to introduce 2 μL injections into a splitless injector having the split and purge vent flows adjusted to 30 and 3 mL/min, respectively. The GC column was a

RTX-1 (Restek, Bellefonte, PA) capillary column, 30 m 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: 100 °C (2 min), 100 to 135 °C at 10 °C/min (0.1 min), 135 to 235 °C at 1.3 °C/min (0.1 min), and 235 to 290 °C at 20 °C/min (20 min), making the total run time 105.4 minutes per sample. The oven was set at 290 °C for twenty (20) minutes to ensure proper removal of residual analytes to avoid sample cross contamination. The injector and detector temperatures were maintained at 250 and 325 °C, respectively. The detector used P5 quench gas, a mixture of 5% methane in argon, at a flow rate of 50 mL/min through the detector.

HP GC ChemStation (ver. A.07.01) was used to operate the GC-ECD and quantitate the PCBs. Frame *et al.* (1996) was used to determine the elution order and retention times of the 117 individual PCB congeners in the calibration mixture on the RTX-1 column by GC-ECD. A six-point calibration curve was created from stock solutions of the 117 individual congeners provided by Accustandard, Inc. All dilutions were made in *n*-hexane as the solvent. The six calibrations were made precisely at the following concentrations of individual 117 PCBs and surrogate standards, 0.5, 1.0, 5.0, 10, 20, and 30 pg/ μL , while the internal-injection standard concentrations remained constant at 120 pg/ μL . In the GC-ECD sample chromatograms, each of the 117 PCB analyte congeners and internal and surrogate standards were identified and integrated manually to ensure correct peak identifications and accurate quantitation.

All congeners were detected above the detection limit in both bed and suspended sediments. Of the 117 available congeners, the predominate congeners during these

analyses contributed to 30% all PCB amounts and included the following congeners: PCB 7/9, 6, 15/18, 46, 52/69, 48, 84/92, 99, 77/136, 118/149, 153, 137, and 138/164.

Laboratory Flocculation Experiments

To better understand the influence of flocculation at the ETM with the variation of PCB concentrations in particles, a series of laboratory experiments were initiated where the primary variable was increasing salinity, thus simulating the downward vertical profile of the ETM. The overall design of this portion of the study was to generate a sediment suspension in freshwater (simulating the upstream side of river) followed by the addition of various amounts of synthetic sea salt to promote flocculation (simulating the ETM). Flocculated sediments were filtered, extracted, and analyzed for PCB to distinguish trends in PCB abundance with increasing salinity.

Bed sediment was collected from the Washington Ship Channel region of the Anacostia River, Washington, D. C. (Figure 3). It was collected in the same fashion as previously mentioned by using a Petite Ponar grab except it was deployed from a pier rather than by boat. Approximately 3 kg of sediment was homogenized on site by mixing with a pre-cleaned stirring rod and was stored in a large amber bottle at 4 °C until it was used for the laboratory study.

In order to ensure that the trend of increasing floc is directly related to an increase in salt content, two 1-L scale bench-top studies were performed. The only parameters which were investigated in this bench-top study were salinity and TSM; no PCB analysis was performed on the 1-L studies. A stock mixture of suspended sediment was created

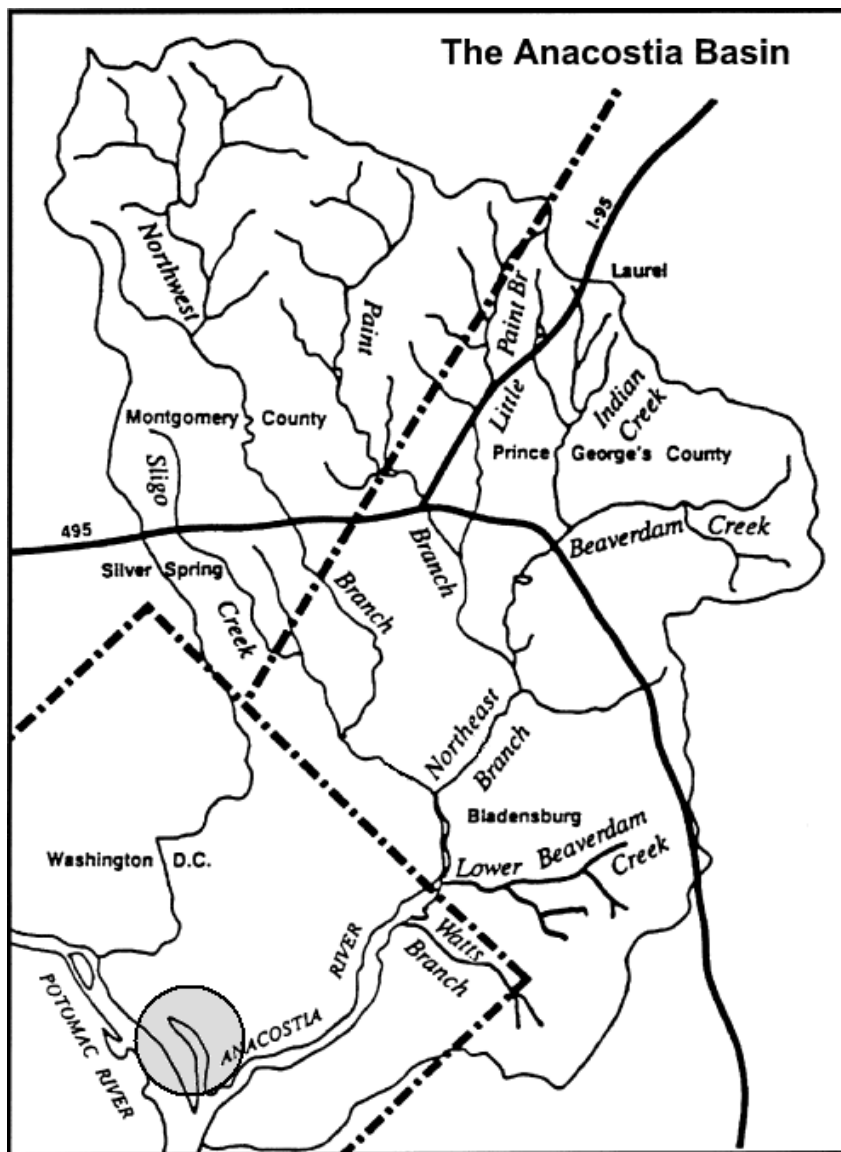


Figure 3: Bed sediments were collected from the Washington Ship Channel (circled) on the Anacostia River for the purposes of a series of laboratory-based flocculation studies. Figure courtesy of Foster *et al.* (2000b).

by adding bed sediment to a 20-L canister of water which was stirred for 1 hour with an electric stirrer, allowed to settle for 1 hour while the large particles were cleared from suspension, and the remaining colloid-sized particles were decanted in several (9-12) 1-L beakers. Each beaker was treated with a different mass of synthetic sea salt to adjust the conductivity to typical estuarine levels, ranging from 0 – 30 ‰. Each beaker was mixed on a stir plate for 1-hour to dissolve salt. Because flocculation is a function of both salinity and pH (Edzwald *et al.*, 1974 and Santschi *et al.*, 1997), the pH of each sample was adjusted to that of the Potomac River ETM which is in the range of 7.0 - 8.0. This is essential in order to achieve a proper relationship between TSM and salinity. Because sea salt contains carbonates, the addition of salt caused an increase in pH, so the adjustment of pH was performed using 1 M HCl. After proper pH adjustment, the 1-L samples were filtered on pre-weighed 47 mm GFFs (0.7 µm nominal pore size), dried overnight in a drying oven at 50 °C, and TSM was gravimetrically determined.

Two laboratory experiments in salinity-induced flocculation studies were performed on a 20-L scale. A stock solution of suspended sediment was generated by mixing copious amounts of bed sediment (95 and 120 g for each respective experiment) with ~80 L of double distilled water (DDW). After the water and sediment solution was mixed for 1 hour with an electric stirrer and allowed to settle for 1 hour, suspended sediment was decanted into 4 clean, methanol-rinsed, 20-L stainless steel Cornelius kegs.

The experiments were designed to mimic freshwater-saltwater mixing and the salinity gradient at the ETM, and this was done by varying the levels of salinity in each of the four 20-L kegs. Salinity was adjusted to approximately 0, 10, 20, and 30 ‰ through

the addition of synthetic sea salt (~0, 200, 350, 550 g sea salt to 20-L, respectively). HCl was added carefully using a buret (~0, 7, 13, 20 mL of 1 M HCl to 20-L, respectively), the 20-L solution was mixed vigorously, and pH was adjusted to 7.5.

After the addition of the appropriate mass of salt and volume of acid, the 20-L kegs were sealed and mixed vigorously to dissolve salt and equally distribute acid through the sample. Final measurements of conductivity, temperature, and pH were recorded. A 1-L aliquot of the homogenized 20-L solution was collected for TSM analysis. Following mixing, each 20-L sample was filtered, extracted, and analyzed for PCBs in the floc sediments using the same methods as were described for the suspended sediment samples collected from the Potomac River ETM.

Quality Assurance

Quality assurance techniques included laboratory blanks, surrogate standard spikes, and detection limit determinations. Laboratory blanks were performed for suspended sediment, bed sediment, and synthetic sea salt. Suspended sediment blanks were performed by adding 20-L DDW which had no previous contact with the Fultz pump, to a clean, hexane-rinsed 20-L keg, filtering it, and extracting it in the same fashion as environmental samples. Bed sediment blanks were performed by extracting 25 mL of 3:2 acetone:*n*-hexane. Because synthetic sea salt could not be ashed, it required a blank which was performed by extracting 5 g salt the same way the bed sediment was extracted. None of the five (5) synthetic sea salt blanks yielded PCB values above the EIDL for any congener, and contamination from sea salt is not considered.

Estimated instrument detection limits (EIDLs) in pg were determined for each congener from the three (3) times the standard deviation of 10 replicate injections of the least concentrated calibration (0.5 pg/ μ L) added to the average of all blanks performed:

$$EIDL = b_{ave} + 3 \cdot s_{cal}.$$

The classical instrument detection limit (IDL) technique as suggested by Harris (2000) employs the usage of the Student's *t* (95% confidence interval, $t_{95\%}$) from 10 replicate injections of the least concentrated calibration multiplied by the standard deviation:

$$IDL = t_{95\%} \cdot s_{cal}.$$

This yielded extremely low and improbable values for the IDL as $t = 2.262$ (when $n-1=9$) and the standard deviation ranged from ± 1.77 to ± 31.7 pg. For this reason an EIDL was generated.

An estimated method detection limit (EMDL) was then calculated from the EIDL for both bed sediment and suspended sediment. The EMDL was calculated by multiplying the EIDL by 1000 to convert to ng and dividing that value by the average mass of bed sediment (ng/g), average mass of suspended sediment (ng/g), and average volume filtered (ng/L), respectively:

$$EMDL = 1000 \cdot \left(\frac{EIDL}{mass} \right) \text{ or } EMDL = 1000 \cdot \left(\frac{EIDL}{volume} \right).$$

All calculated detection limit values can be found in Appendix D.

Surrogate standards (PCB 103 and 140) were introduced to all samples prior to extraction as a performance check. Recoveries of the individual PCB 103 and 140 spiked in suspended sediment samples ranged from 35% to 104% and from 50% to 99% in bed

sediment (Table 3). Recoveries (mean \pm standard deviation) in the suspended sediment samples were $73 \pm 13\%$ and $70 \pm 15\%$ for PCB 103 and 140 respectively, and for bed sediment recoveries were $72 \pm 12\%$ and $79 \pm 13\%$.

Recoveries of both matrices were achieved by averaging suspended and bed sediment recoveries yielding $73 \pm 13\%$ for PCB 103 and $73 \pm 15\%$ for PCB 140. All data was normalized to these averages for consistency.

DDW was produced in the laboratory using a Corning Megapure still with lab-supply distilled water pre-filtered through a high-capacity activated carbon cartridge as the source water.

Table 3: Surrogate Recoveries

Matrix	PCB	EMDL^{a,b} (pg/g)	Range^c (%)	Average^d (%)
Suspended Sediment	103	41	49 - 99	73 ± 13
	140	91	35 - 104	70 ± 15
Bed Sediment	103	8	50 - 95	72 ± 12
	140	18	60 - 99	79 ± 13
All Samples	103	25	49 - 99	73 ± 13
	140	54	35 - 104	73 ± 15

^aEMDL calculated from the average of a series of blanks plus three standard deviations

^bHarris, 2000

^cRange of % recoveries on all bed sediment samples (n=16), all suspended samples (n=41), and the sum of the both (n=57)

^dAverage and standard deviation of % recoveries

RESULTS AND DISCUSSION

ETM Salinity and Suspended Sediment Concentrations

Samples from vertical transects at the ETM were collected to a depth of 12 m below the surface on March 30, 2008 (3 depths at high tide and 5 depths at low tide) and May 21, 2008 (6 depths at low tide and 5 at high tide) and 25 m on May 8, 2009 (4 depths at low and slack tides), as an additional length of Teflon tubing was used during the third sampling to extend the vertical transect to near the river bottom. Sampling switched from duplicates at all depths to more depths with fewer replicates to provide better resolution on the ETM depth profiles (Table 1). On each sampling day, a total of 10 to 12 20-L samples were collected for PCB analysis during two diurnal tidal periods. Measurements of salinity and TSM were made at all depths. River depths along the main channel of the Potomac River at the sampling location were >30 m.

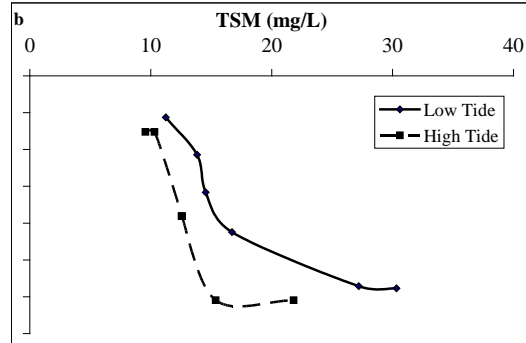
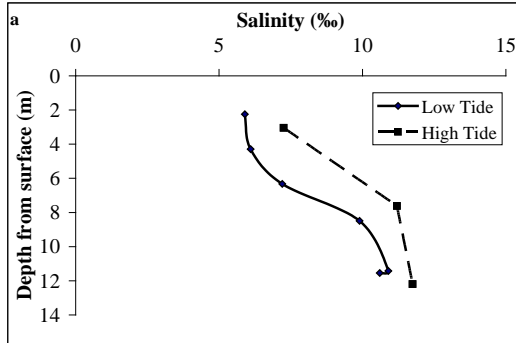
The ETM was clearly evident at the Dahlgren location in the Potomac River because both TSM and salinity increased with depth on all three sampling dates (Figures 4 a-f). The dramatic increase in both parameters can be seen at ~7 m during relatively normal flow (Figures 4 a-d) and ~19 m during high flow collection in May 2009 (Figures 4 e-f). The steep gradients in salinity and TSM with depth validated that sampling through the ETM was successful.

Mar. 30, 2008: Neap Tide

Actual Flow^a: 379 m³/s

Mean Monthly Flow (March)^a: 476 m³/s

Flow Conditions: Normal Flow

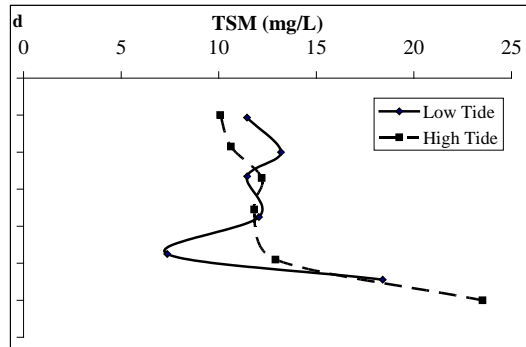
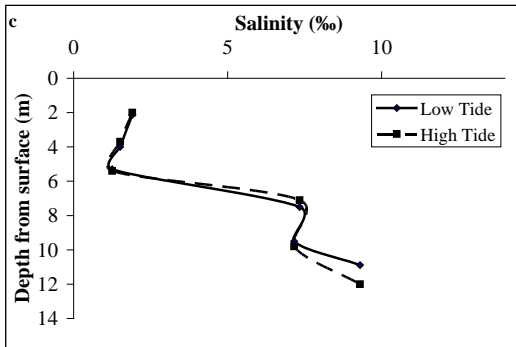


May 21, 2008: Spring Tide

Actual Flow^a: 572 m³/s

Mean Monthly Flow (May)^a: 883 m³/s

Flow Conditions: Normal Flow

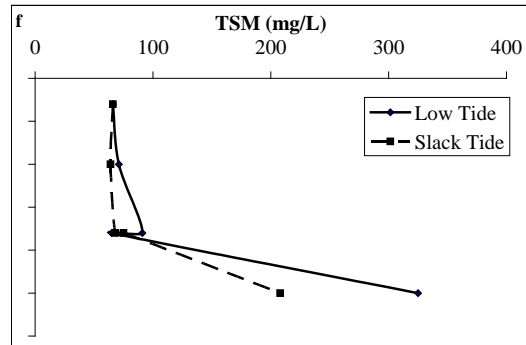
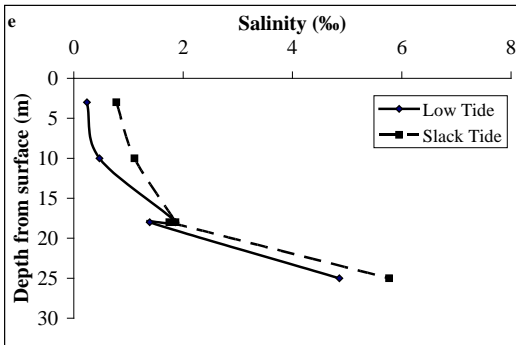


May 8, 2009: Spring Tide

Actual Flow^a: 2250 m³/s

Mean Monthly Flow (May)^a: 883 m³/s

Flow Conditions: High Flow



^a Flows are recorded at the USGS pump station at Little River Falls, Washington, D. C. (USGS, 2009)

Figures 4 a-f: Salinity (‰) and TSM (mg/L) along the vertical sampling transect during the three sampling events, Mar., 2008 (a, b), May 2008 (c,d), and May 2009 (e,f).

TSM and salinity values in this study were comparable to those in similar, partially mixed estuaries experiencing semi-diurnal tides (Table 4). In the Chesapeake Bay estuary, TSM has been reported in the range of 10-480 mg/L (Schubel, 1968, Sanford *et al.*, 2001, Lin and Kuo, 2001). The elevated TSM observed on May 8, 2009 in the range of 66-325 mg/L was likely due to the fact that the ETM was sampled following three days of heavy rain. River discharge in the Potomac River at Little River Falls, Washington D.C. on this date was 2250 m³/s, which is four times greater than the average flow at this location for the month of May 2009 (572 m³/s) (USGS, 2009). The 2008 samples were more representative of mean monthly flows where the actual flow was 379 and 883 m³/s March 30 and May 21, 2008, compared to average monthly flows of 476 and 572 m³/s, respectively. Lower TSM in the ranges of 9-30 mg/L and 10-24 mg/L were recorded during the normal flow samplings. The weakest ETM was observed on March 30, 2008 as the salinity varied the least with depth on the range of 5.9 – 11 ‰. Higher Potomac River discharge promoted enhanced gradients in both TSM and salinity when compared to normal flow conditions, resulting in the most intense ETM in May 2009.

Replicates of ETM samples indicated that there was relatively high variability among TSM measurements where the percent difference between all duplicates ranged from 0 – 35 % (Table 5). Percent differences between duplicate measurements were estimated as:

$$\frac{|X_2 - X_1|}{(X_2 + X_1)/2} \cdot 100.$$

Table 4: Salinity and TSM in Comparable Turbidity Maxima

Sampling Locale	Estuary Classification	Tidal Classification	Sampling Date (s)	Mean Depth (m)	Salinity (‰)	TSM (mg/L)	Notes	Reference
<i>Chesapeake Turbidity Maxima</i>								
Potomac River Estuary, MD	partially mixed	semi-diurnal	Springs 2008-2009	30	6-12 1-9 0.3-6	9-30 10-24 66-325	Mar. 30, 2008 May 21, 2008 May 8, 2009	Current study
Chesapeake Bay, MD	partially mixed	semi-diurnal	1966-1967	9.5	nr	14±4 15-280 14-93 10-36	ETM _{ave} at 9m at 8m at 6m	Schubel, 1968
Chesapeake Bay, MD	partially mixed	semi-diurnal	1996	12	2-14 2-14 2-8 2-8	20-30 10-30 10-30 10-60 30-200	February 1 July 21 July 25-26 October 22 October 27	Sanford <i>et al.</i> , 2001
York River Estuary, VA	partially mixed	semi-diurnal	1996-1998	9 12	1-15 9-25	90-250 40-480	1° ETM (up estuary) 2° ETM (down estuary)	Lin and Kuo, 2001
<i>Turbidity Maxima Outside of the Chesapeake</i>								
Charleston Harbor Estuary, SC	partially mixed	semi-diurnal	1989	14	5-15	40-100		Althausen and Kjerfve, 1992
Hudson River Estuary, NY	partially mixed	semi-diurnal	May 1993	7	6-16	200-1000		Geyer <i>et al.</i> , 2001

^a nr = not reported

Table 4: A literature comparison of salinity and TSM in other turbidity maxima comparable to the Potomac ETM based on estuary and tidal classification.

**Table 5: Replicate Sample Variability for
TSM, Σ PCB (ng/g) and Σ PCB (ng/L)**

Sample Depth (m)	Tide	Duplicate Percent Differences		
		TSM	Σ PCB (ng/g)	Σ PCB (ng/L)
<i>March 30, 2008</i>				
3.0	H	7.65	48.7	49.2
12	H	34.6	31.0	13.3
7.6	L	0.32	103	94.6
11	L	10.8	48.0	14.4
18	L	33.3	69.5	92.8
<i>May 8, 2009</i>				
18	L	33.3	69.5	92.8
18	S	9.79	25.7	16.8

^a H = high tide, L = low tide, S = slack tide

Environmental TSM, especially at the Potomac River ETM is highly heterogeneous as the formation and dynamics of the ETM are based on multiple variables including tidal currents, turbulent flows, resuspension (Althausen and Kjerfve, 1992), estuarine circulation caused by salinity gradients (Sanford *et al.*, 2001), and flocculation (Edzwald *et al.*, 1974 , Drever, 1997, and Verney *et al.*, 2009).

The ETM variability is demonstrated in the vertical profile plots of salinity and TSM at the time of ETM sampling (Figures 4 a-f). The ETM is a dynamic boundary that moves upstream and downstream in the Potomac River in relation to upland river flow. Sampling in this study was conducted at a fixed point in the river, so each sampling event occurred during a unique ETM boundary condition.

TSM and salinity are important variables that influence PCB concentrations in natural water bodies. Because PCBs readily bind to sediment any TSM enhancement through natural flocculation or through other means should be followed by an enhancement of the occurrence of PCBs bound to sediment. Based on the initial geochemistry parameters and sediment organic matter properties through the ETM and along the vertical transect, it can be seen that the ETM is highly dynamic. This characteristic carries over into the results for PCBs at the ETM. Due to the variability of both salinity and TSM at the ETM, it should be expected that a similar degree of variability will be found for trends in PCB through the same vertical transect.

The organic matter (OM) content in all of the Potomac River particles remained relatively consistent with depth (26.7 ± 6.3 , 20.7 ± 4.5 , and $9.59 \pm 2.0\%$ for each respective date). No statistically significant correlation could be identified for OM with

increasing TSM, salinity, or depth based on the Pearson's r at the 95% confidence interval for any of the ETM samples (Table 6).

ETM Σ PCB Concentrations

No significant differences could be determined between daily tides (high, low, and slack tides) and Σ PCB concentrations (sum of 117 congeners), and, therefore, all data points were pooled for a given sampling date to increase sample size along a vertical transect. The limited sampling design in this study was insufficient to detect differences in PCB concentrations among diurnal and seasonal tidal cycles, but the pooled results did provide a more detailed perspective of the vertical profile of PCB concentrations through the ETM.

The mass-based Σ PCB concentrations (ng Σ PCBs/g TSM) in Potomac River particles did not show consistent trends with water depth. Conflicting correlations (Table 6) showed that Σ PCB in particles increased, decreased or showed no significant correlation. Significant linear regressions (R^2) were determined by two-tailed Pearson's r correlations at the 95% confidence interval (Table 6).

Although variability existed for volume-based Σ PCB concentrations (ng Σ PCB in particles /L water) with depth (Figures 5 a-c), a trend of increasing Σ PCB concentrations with depth was evident on two of the three sampling dates. The trend existed on the days where the ETM was the most intense. The ETM intensity can be expressed by the ratio of salinities at the shallowest and deepest depths. The ratios were found to be 2 and 9 for March 30 and May 21, 2008, respectively, and 20 for May 8, 2009. A greater ratio

Table 6: Depth and Percent Organic Matter Correlations

	Sampling Date			Salinity-Induced Flocculation Study	
	Mar. 30, 2008	May 21, 2008	May 8, 2009	Exp. 1	Exp. 2
<i>Depth Correlations^a</i>					
ΣPCB (ng/g) and depth	R ² = 0.30 r = -0.62	R ² = 0.36 r = 0.55	ns	na	na
ΣPCB (ng/L) and depth	ns	R ² = 0.57 r = 0.67	R ² = 0.29 r = 0.73	na	na
ΣPCB (ng/g) range	21 - 530	83 - 471	21 - 66	49 - 199	407 - 144
ΣPCB (ng/L) range	1.6 - 5.6	1.6 - 7.2	1.3 - 14	11 - 16	26 - 40
<i>OM Correlations^a</i>					
Depth and OM	ns	ns	ns	na	na
TSM and OM	ns	ns	ns	R ² = 0.68 r = 1.0	R ² = 0.98 r = 1.0
Salinity and OM	ns	ns	ns	R ² = 0.84 r = 1.0	R ² = 0.95 r = 1.0
ΣPCB (ng/g) and OM	ns	ns	R ² = 0.57 r = 0.75	R ² = 0.99 r = 1.0	R ² = 0.96 r = 1.0
ΣPCB (ng/L) and OM	ns	ns	ns	ns	R ² = 0.93 r = 1.0
OM Range (%)	13.3 - 36.7	13.6 - 27.5	6.52 - 12.7	18.6 - 29.0	12.3 - 24.5
OM Average (%)	26.7 ± 6.3	20.7 ± 4.5	9.59 ± 1.99	25.6 ± 4.8	19.7 ± 5.6

^a Two-tailed Pearson's r correlation at the 95% confidence interval

^b R² = linear regression

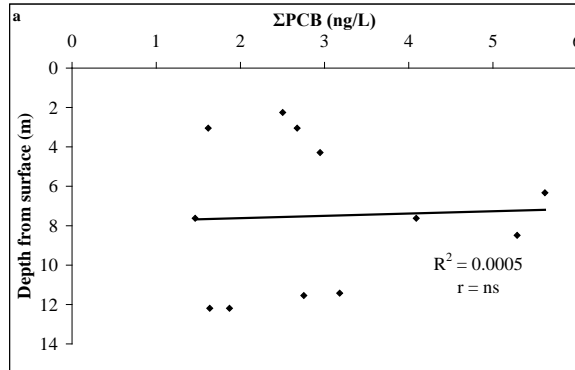
^c r = Pearson's r

^d ns = not statistically significant

^e na = not applicable

Mar. 30, 2008: Neap Tide

Actual Flow^a: ;
379 m³/s
Mean Monthly Flow (Mar.)^a:
476 m³/s
NORMAL FLOW

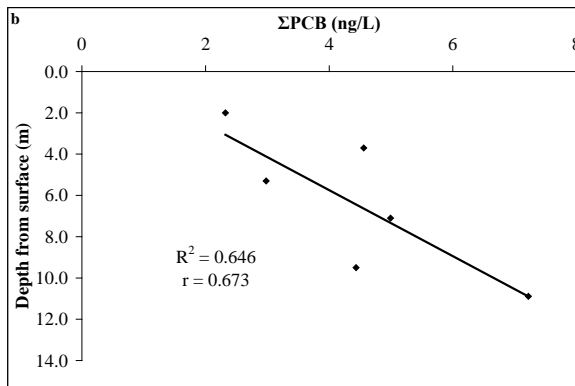


Weakest
ETM

$$\text{Salinity Ratio : } \frac{\text{Deepest}}{\text{Shallowest}} = 2$$

May 21, 2008: Spring Tide

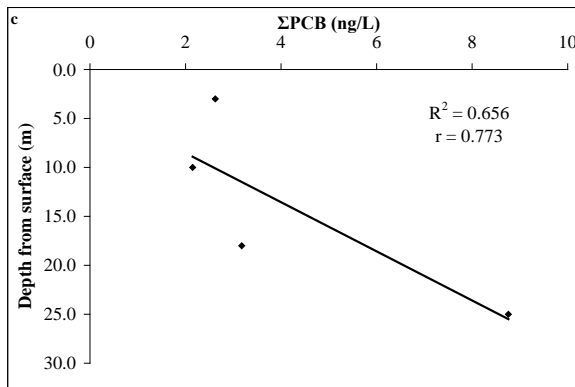
Actual Flow^a: ;
572 m³/s
Mean Monthly Flow (May)^a:
883 m³/s
NORMAL FLOW



$$\text{Salinity Ratio : } \frac{\text{Deepest}}{\text{Shallowest}} = 9$$

May 8, 2009: Spring Tide

Actual Flow^a: ;
2250 m³/s
Mean Monthly Flow (May)^a:
883 m³/s
HIGH FLOW



$$\text{Salinity Ratio : } \frac{\text{Deepest}}{\text{Shallowest}} = 20$$

Strongest
ETM

^a Flows are recorded at the USGS pump station at Little River Falls, Washington, D. C. (USGS, 2009)

Figures 5 a-c: ΣPCB (ng/L) along the vertical sampling transect during the three sampling events, Mar., 2008 (a), May 2008 (b), and May 2009 (c).

indicates that the ETM salinity, and corresponding TSM, gradients were the steepest. The first sampling (March 30, 2008) yielded no significant depth trend with Σ PCB concentrations (ng/L), but a significant positive correlation was found on both May 21, 2008 ($R^2 = 0.646$, $r = 0.673$, Figure 5 b) and May 8, 2009 ($R^2 = 0.656$, $r = 0.773$, Table 6).

The depth trend between TSM and Σ PCB concentration (ng/L) indicated in Figures 5 a-c is expected based on theoretical considerations, which can be represented as $C_p = C_s \cdot [\text{TSM}]$ (Tinsley, 2004). In this expression, C_p represents the Σ PCB concentration (ng/L) in particles based on sample volume and C_s is the Σ PCB concentration (ng/g) based on particle mass. As TSM increases through the ETM (Figures 4 b,d, and f) C_p is expected to increase proportionately. This trend was, in fact, observed while the ETM had its greatest intensities (i.e., steepest geochemical gradients) during May 21, 2008 and May 8, 2009 (Figures 5 b-c).

Modeled profiles of Σ PCB (ng/L; C_p) are illustrated in Figure 6 relative to measured concentrations. The modeled relations (dotted lines) assume Σ PCB (ng/g; C_s) remains constant, by using the measured Σ PCB (ng/g) values at the most shallow depth (~2m below the surface) for each sampling date. These measured C_s values were multiplied by the increasing TSM observed with depth through the ETM and the resulting value was than the theoretical C_p or the theoretical volume-based PCB concentration. In looking at the slopes of both the theoretical and observed trends for Σ PCB (ng/L) several observations can be made. Because the observed trend for March 30, 2008 (Figures 5 a) is not significant, it will not be included in the following analysis. The theoretical slope

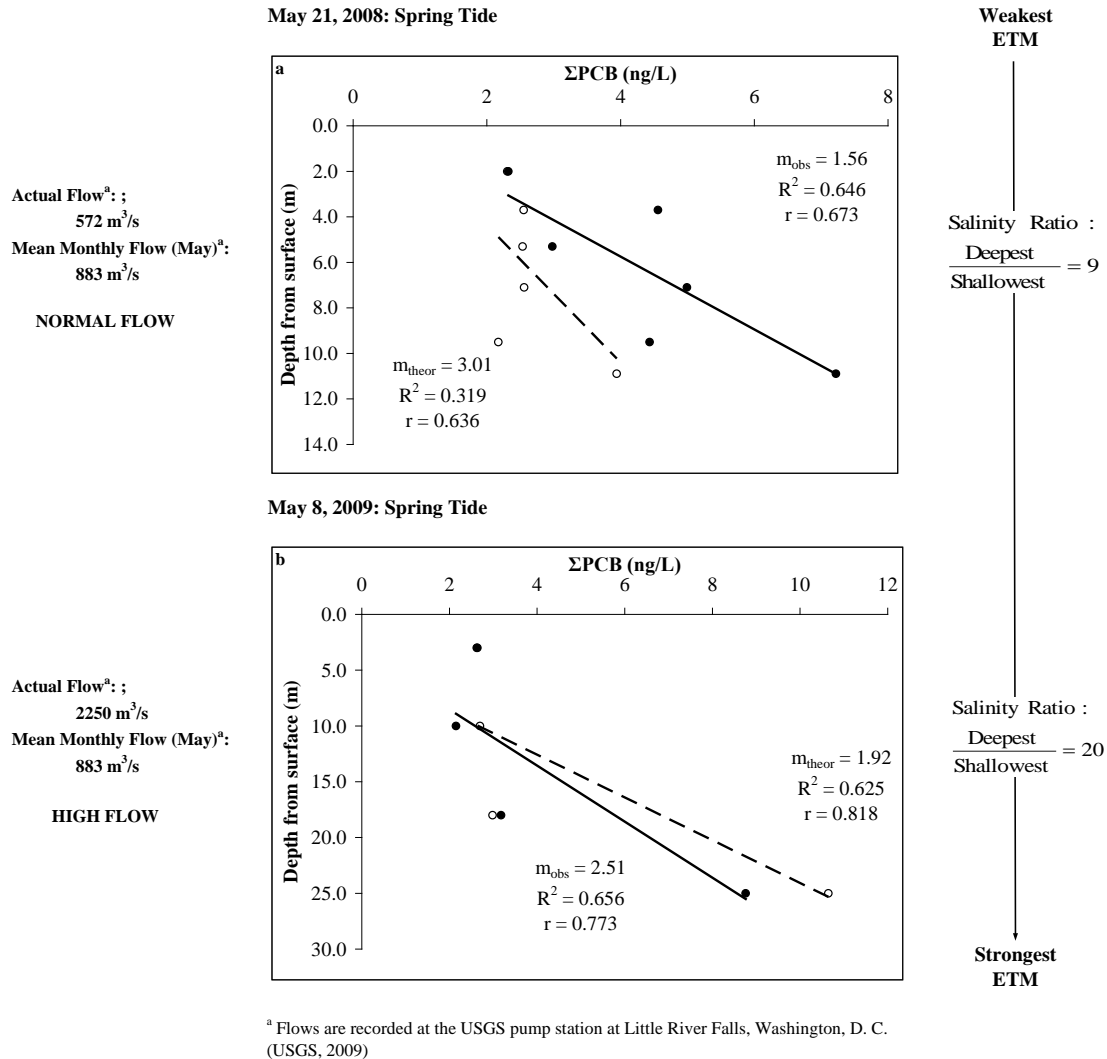


Figure 6: The dotted lines represent the theoretical trend for ΣPCB (ng/L), also referred to as “ C_p ”, with depth if ΣPCB (ng/g) remained constant with depth, varying only TSM. (Mar. 30, 2009 data not presented in the above figure, as the trend for ΣPCB (ng/L) with depth was deemed non-significant).

for May 21, 2008 (Figure 6 a) is greater than the observed slope ($m_{\text{theor}} = 3.01$; $m_{\text{obs}} = 1.56$) indicating that while there is an increase in ΣPCB (ng/L) with depth, it is not to the degree that is expected. On the other hand, May 8, 2009 the opposite occurred, where ΣPCB (ng/L) increased at a greater rate than predicted ($m_{\text{theor}} = 1.92$; $m_{\text{obs}} = 2.51$; Figure 6 b). Likely this is because of the extreme increase in TSM due to high flow on this date. Unfortunately, the limited sampling design cannot resolve the difference in trends of ΣPCB (ng/L) with depth as a result of increased river flow and TSM.

Replicate measurements for ΣPCB concentrations also yielded a significant degree of variability evidenced by percent differences between duplicate measurements (Table 5). The average percent differences for duplicate measurements on all samples for both mass-based ΣPCB (ng/g) and volume-based ΣPCB (ng/L) concentrations were 56.6% and 53.4%, ranging from 25.7 – 103% and 13.3 – 96.4%, respectively. The average differences in concentrations among duplicate samples can be broadly applied to the PCB concentrations as a measure of uncertainties.

There is no significant trend between OM and ΣPCB concentrations (Table 6), except for the May 8, 2009 sampling where a positive correlation ($R^2 = 0.571$, $r = 0.745$) was observed for ΣPCB (ng/g) and OM (Figure 7). This however, does not explain the lack of correlation between ΣPCB concentrations (ng/g) and depth. This coupled with the fact that there is no statistical correlation between OM and ΣPCB (neither ng/g nor ng/L) indicates that OM content is not a significant variable for PCB sorption at the Potomac River ETM which is contradictory to the expected trend. PCBs are known to

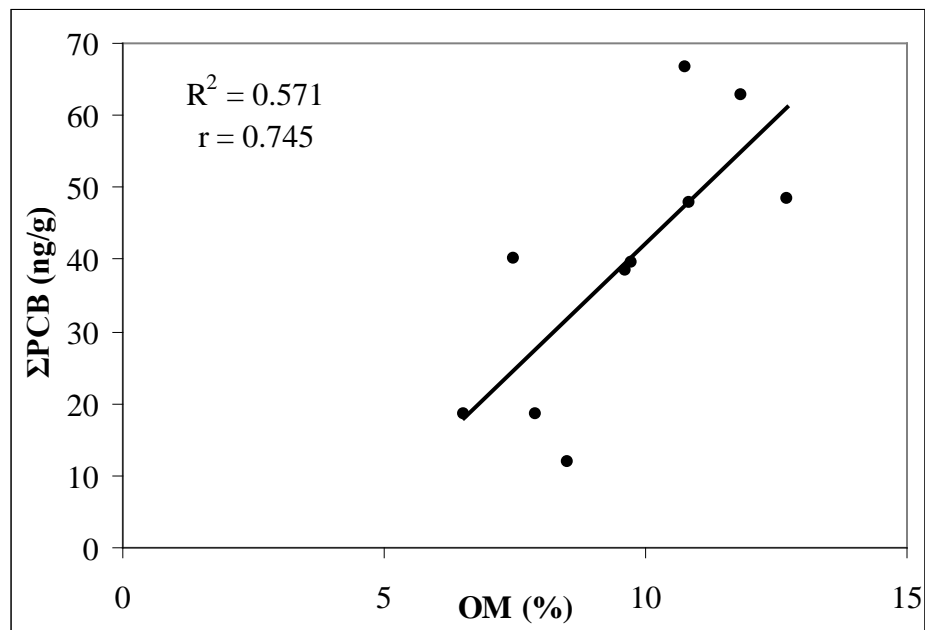


Figure 7: A positive correlation at the 95% confidence interval between ΣPCB (ng/g) and OM can be seen for only the May 8, 2009 sampling at the ETM.

have a high affinity towards OM in sediment. This relationship between OM can be seen in the following expression for the K_D (the distribution constant for sediment and water):

$$K_D = \frac{C_s}{C_w} = 0.41K_{ow}f_{oc} \text{ and } f_{oc} \propto f_{om} \text{ where:}$$

- K_{ow} = octanol-water partition coefficient,
- f_{oc} = fraction organic carbon,
- C_s = concentration of PCB in sediment,
- C_w = concentration of water, and
- f_{om} = fraction organic matter (Tinsley, 2004).

From the above it can be seen that the fraction of OM is directly proportional to the expected concentrations of PCBs in sediments (C_s). Clearly there must be additional variables contributing to the concentrations of PCB in sediment at the ETM where the increase in OM does not increase Σ PCB concentrations as was observed in the current study. The lack of a positive correlation for Σ PCB with OM is exhibited in the controlled laboratory experiments, and is discussed further in the following sections.

The concentrations of Σ PCB in suspended sediment ranged from 21 – 530 ng/g and 1.3 – 14 ng/L at the Potomac River ETM. Under normal flow conditions (Mar. 30 and May 21, 2008) Σ PCB concentrations were found to be much higher than those found during high flow (May 8, 2009): 21 – 530 ng/g compared to 21 – 66 ng/g. During periods of high flow the sediment source is much different than during normal flow. Runoff from the less contaminated landward margin is enhanced during periods of increased rainfall. When the Potomac experiences increased runoff, a net dilution effect occurs as contaminated sediments from upstream PCB hotspots (the Anacostia River and Quantico Bay, VA) are diluted by less-contaminated sediment from the landward margin.

Similar trends were found in other studies where PCB concentrations are diluted with increased river flow. On the Aire River, UK PCB levels decreased by two orders of magnitude during periods of high flow (TSM \approx 100 – 1000 mg/L) from 0.1 to 10 ng/L, and periods of low flow resulted in the highest PCB concentrations in suspended sediment (Meharg *et al.*, 2003). The dependence of river flow on PCB concentrations in which an increase in flow yields a decrease in suspended sediment concentrations have also been discussed by Bremle and Larsson (1997) in the Emån River, Sweden. A decrease in concentration indicates that the contaminant source tends to be within the river itself (Bremle and Larsson, 1997) or, in this case, upstream of the Potomac ETM at the Anacostia and Quantico. On the other hand, a net increase in particulate PCB concentrations with increased river flow have been found in the Seine River, France by Chevreuil and Granier (1991) and the Susquehanna River, MD by Foster *et al.* (2000a). The influence of rainfall, and thereby increased river flow on particulate PCB levels is dependant on the location of PCB point sources in relation to the sampling site.

PCB concentrations in bed sediments remained consistent throughout all three samplings, ranging from 16 – 54 ng/g (28.1 ± 12.7 ng/g), and for this reason all bed sediment PCB measurements were pulled. Anacostia River bed sediment samples were taken for the salinity-induced flocculation study and ranged in concentrations of 222 – 256 ng/g (238 ± 126 ng/g), and Foster and Cui (2008) reported PCB in bed sediment in the Anacostia at 104 ng/g. Because bed sediment Σ PCB concentrations at the ETM are much lower than the concentrations found in ETM suspended sediment during periods of normal flow, it is clear that resuspension cannot be the sole source for PCB loadings in

suspended sediment at the ETM indicating that the source of particulate PCB must be from an upstream location.

PCB concentrations in both bed sediments and TSM (ng/g and ng/L) comparable to this study have been reported in previous studies (Table 7). Anacostia River bed sediments were sampled by Foster and Cui (2008) and McEachern (2005) and were found to be elevated (104 and 141 ng/g, respectively) as compared to concentrations in other Potomac River Basin samples (12 ng/g, Foster and Cui, 2005). McEachern (2005) found PCB in bed sediment in the Potomac River ETM region at Nanjemoy Creek, MD, Mathias Point, VA, the 301 Bridge, MD, and Dahlgren, VA (Figure 2) at 158, 63.4, 40.4 ng/g, and 55.8 ng/g respectively. It should be expected that as sediment undergoes downstream transport, PCB concentrations will be diluted by the accumulation of less contaminated sediment entering the river from the landward margin.

Mass-based PCB concentrations in suspended sediment in the Chesapeake Bay region has been found in the ranges of 29-107 ng/g (Foster *et al.*, 2000a), 1-124 ng/g (Foster *et al.*, 2003), and 30-140 ng/g (Ko and Baker, 1995). These ranges are typical for suspended sediment in other regions, where Oliver and Niimi (1998) found an average concentration of 140 ± 140 ng/g in Lake Ontario waters, and Owens *et al.* (2001) found PCB in the range of 2-260 ng/g in several United Kingdom rivers. Typical volume-based PCB concentrations range from 0.24-27 ng/L (Anacostia River; Foster *et al.*, 2003), 0.4-4.5 ng/L (Sweden; Breme and Larsson, 1997), and 0.1 – 9 ng/L (Meharg *et al.*, 2003).

As for the relationship between bed sediments and suspended sediments, Meharg *et al.* (2003) found a similar relationship in the Aire and Calder Rivers, UK as was found

Table 7: Reported PCB Values in Chesapeake Suspended and Bed Sediments

Sampling Locale	Sample Type	TSM (mg/L)	Bed Sediment ng/g	Suspended Sediment ng/g	Suspended Sediment ng/L	# congeners	Reference
<i>Chesapeake Bay PCB concentrations</i>							
Potomac River ETM	SW, BW, BS	9.6-30.3	26-41	21-530	1.6-5.6	117	Current study
		10.1-23.5	16-54	83-471	1.6-7.2		
		66-325	22-35	21-66	1.3-14		
Anacostia River Washington Ship Channel	BS	nr	222-256	nr	nr	117	Current study
Potomac River Basin VA and MD	BS	nr	12 (0.2-104) 104 ^a	nr	nr	75	Foster and Cui (2008)
Nanjemoy Creek, MD	BS	nr	158	nr	nr	90	McEachern (2005)
Mathias Point, VA			63.4				
301 Bridge, MD			40.4				
Dahlgren, VA			55.8				
<i>Oligohaline Potomac River</i>							
Susquehanna River Fall Line	SW	7 - 132	nr	62 (107-29)	nr	85	Foster <i>et al.</i> (2000a)
Conowingo, MD	SW	4.0 - 740 (NE) 3.2 - 780 (NW)	nr	nr	5.8 (0.24-27)	85	Foster <i>et al.</i> (2000b)
NE and NW Branches Anacostia River							
Bladensburg, MD							
Chesterville Branch and Nanticoke River, MD	SW	15 (6-239)	nr	10 (1-124)	nr	85	Foster <i>et al.</i> (2003)
Chesapeake Bay	SW, BW	4.1 ± 1.5 (SW)	nr	32-82	nr	70	Ko and Baker (1995)
		24.5 (max from BW)		30-140			
<i>PCB concentrations outside of the Chesapeake Bay</i>							
Detriot River	SS	nr	nr	nr	10 ± 5.3	110	Froese <i>et al.</i> (1997)
Trenton Channel, MI					22-47 ^b		
Lake Ontario	BS, SS	nr	570 ± 240	440 ± 140	nr	209	Oliver and Niimi (1988)
Emån River, Sweden	SS	nr	nr	nr	0.4-4.5	53	Bremle and Larsson (1997)
Swale River, Aire River, and Calder River, UK	BS, SS	50 - 600 (high flow)	nr	2 - 52	nr	23	Owens <i>et al.</i> (2001)
Aire River, and Calder River, UK			nr	2-260			
Aire River, and Calder River, UK			90	120			
Aire River, and Calder River, UK	BS, SS	13.2 and 15.0 12.2 and 22.2	4.0	53.8	0.1 - 8 0.1 - 9	11	Meharg <i>et al.</i> (2003)

^a Sample from the Anacostia River Washington Ship Channel

^b Point source PCB concentrations

^c nr = not reported

^d BW = bottom waters, BS = bed sediment, SW = surface water, SS = suspended sediment along entire water column

in the current study where there was an enhancement in PCB in suspended sediment from 4.0 ng/g in bed sediment to 53.8 ng/g in particulates. On the other hand, a study by Oliver and Niimi (1998) at Lake Ontario yielded similar concentrations in bed and suspended sediments, 570 ± 240 and 440 ± 140 ng/g, respectively. Likely this has to do with the nature of the bodies of water where the Aire and Calder Rivers experience more downstream transport of contaminated sediments, indicating that bed sediment is not necessarily the source for contaminated particulates.

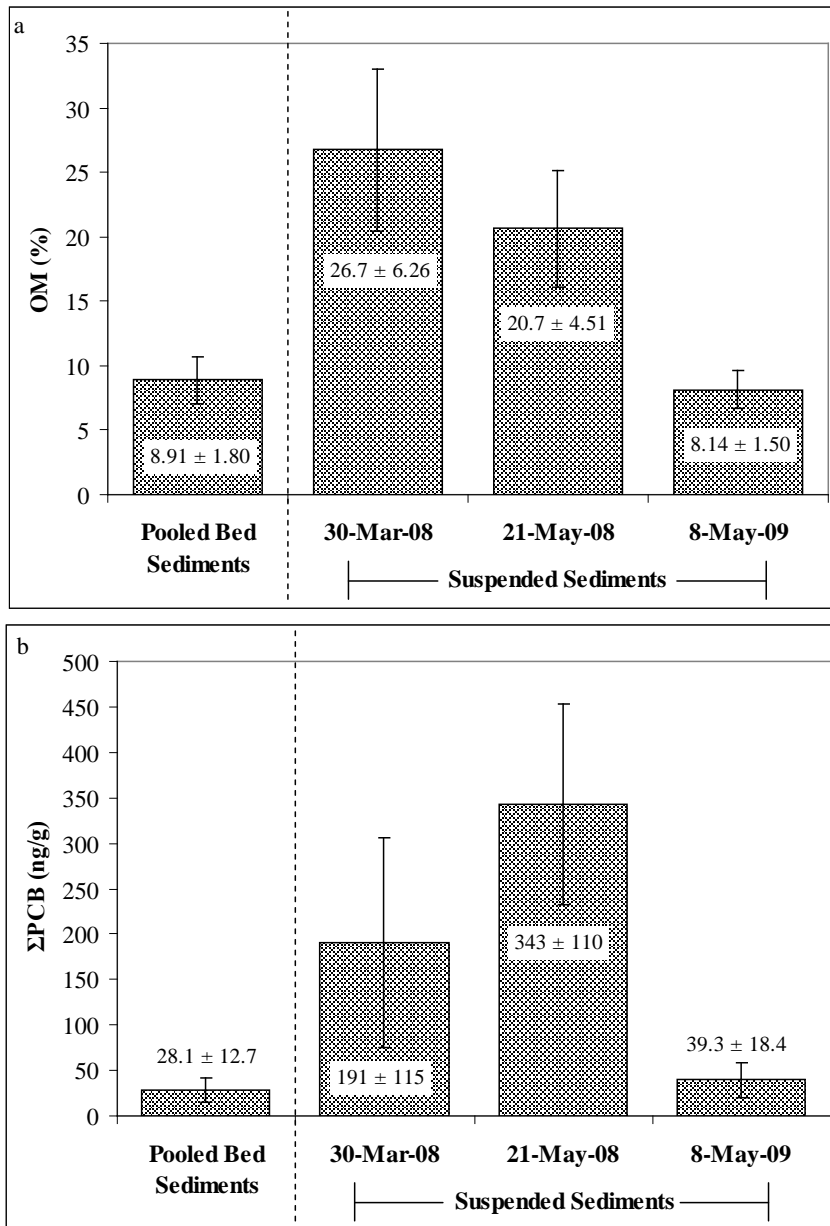
The ETM does not appear to be a high deposition zone for Σ PCBs from the water column to bed sediments as bed sediment concentrations indicate no elevation of Σ PCBs at the ETM. Suspended sediment concentrations during normal flow conditions at the ETM appear at concentrations much higher than those in the bed sediment. Average Σ PCB particle concentrations of 284 ± 135 ng/g differ significantly based on the Student's t at the 95% confidence interval from bed sediment concentrations (28 ± 13 ng/g).

The work done by McEachern (2005) indicated that the bed sediment from the ETM region (Figure 2) was slightly higher than was found in this study on the range of 40.4-458 ng/g), and results from his work along the entire transect of the Potomac River indicate a slight overall increase in PCB concentrations in bottom sediments (McEachern, 2005). Just downstream of the location of the ETM, McEachern (2005) found another elevation of PCB in bed sediments at Kettle Bottom Shoals (Figure 2), indicating that the deposition of high concentration suspended sediments may occur downstream rather than

within the ETM itself. Further work is needed to investigate where the enhanced PCB concentrations in particles found in this study are depositing to bottom sediments.

It also is possible that diagenesis plays a role in reducing Σ PCB concentrations through organic matter alterations. While no depth trend for OM could be ascertained through the vertical transect in the water column at the ETM, the average percent organic matter in suspended sediment differed significantly from the bed sediment organic matter content based on the Student's *t* at the 95% confidence interval during periods of normal flow (March 30 and May 21, 2008.) Both organic matter content and Σ PCB (ng/g) in suspended sediments differed by a factor of two from bed sediments during these dates (Figures 8 a-b). The enhanced organic matter content in suspended sediments explains the elevated levels of Σ PCB in particulates versus surficial sediments on these dates. During the high flow sampling on May 8, 2009, where the strongest ETM was observed, neither organic matter content nor Σ PCB (ng/g) in suspended sediments were found to be significantly different than those found in bed sediments.

From the profiles of the vertical transects of Σ PCB concentrations with depth, it can be seen that the ETM yields highly variable results, which also includes geochemical variables like TSM. The only viable depth trend that can be identified is that the volume-based concentration of Σ PCBs increases with depth, as expected (Figures 5 b-c). Variability carried over into the results for duplicate samples where a significant range of percent differences were observed (Table 5). Additionally, no significant correlation was found for the Σ PCBs with OM, where the expected trends for the increase of Σ PCB concentrations with OM were not observed. It can also be concluded that the depth trend



Figures 8 a-b: Both (a) percent organic matter content and (b) Σ PCB (ng/g) found in bed sediments differed significantly at the 95% confidence interval from suspended sediments on March 30 and May 21, 2008. These significant differences were not observed on May 8, 2009, offering insight into the role of organic matter diagenesis in PCB binding at the ETM.

in Σ PCB concentrations (ng/L) can be related to the ETM intensity, as steeper gradients in salinity and TSM yield a more pronounced increase in Σ PCB concentrations with depth. However, no clear trend in mass-based Σ PCB concentrations related to ETM intensity could be found, but it was observed that the higher ETM intensity lead to a dilution of Σ PCBs in particles while a less steep gradient in ETM intensity lead to an increase in mass-based Σ PCB concentrations in particles. The latter process is much more variable.

What could be resolved from the current study was that the ETM does not appear to be a depositional zone for Σ PCB because Σ PCB concentrations in particulate matter exceed concentrations found in bottom sediments. Likely, due to the downstream transport of sediment and the lack of correlation between suspended and bed sediments within the region of the ETM, an enhancement in PCB deposition occurs farther downstream. Another important implication from our results relates to Σ PCB sampling in the Potomac River. Clearly, sampling in the tidal Potomac River must take into consideration the salinity of water being sampled, as the ETM influences particle PCB concentrations.

Salinity-Induced Flocculation Study

The field data supports the dependence of PCB concentrations in water (i.e., C_p) or concentrations of total suspended matter in river water for two of the sampling dates. Geochemical measurements indicated that TSM increased proportionately with salinity through the ETM. This dependence is supported by the mass distribution theory, as was

described above. As the concentrations of particles increase it logically follows that PCB concentrations should increase proportionately per unit volume of water, especially since PCB particle/water distribution constants (K_D 's) are exceptionally large. What is less clear is any ETM influence on PCB concentrations in particles (i.e., C_s). The field data was completely contradictory on this matter. Since the ETM is such a complex phenomenon, controlled experiments were developed to shed light on any influence salinity has on concentrations of PCBs in the particles themselves. The two predominant processes that influence the fate, transport, and water column concentrations of organic pollutants in coastal rivers are (i) salinity-induced flocculation (Edzwald *et al.*, 1974, Drever, 1997, and Verney *et al.*, 2009) and (ii) the resuspension of bed sediments (Althausen and Kjerfve, 1992). Experiments were conducted using heavily PCB contaminated sediments from the Anacostia River (a large source to the tidal Potomac River) that were artificially resuspended and treated with synthetic sea salts to simulate flocculation processes at the ETM. The properties of the floc material were investigated with respect to TSM, OM, and Σ PCB concentration relations.

One liter (1-L) scale experiments were initially performed to determine whether or not salinity-induced flocculation could be simulated in the laboratory from resuspended sediments. The premise of salinity-induced flocculation is that natural colloidal-sized particles (not retained on GFF filters) in suspension aggregate as salinity is increased, forming more filterable particles thereby mimicking the boundary mixing of freshwater and saltwater in the Potomac River ETM. These basic experiments resulted in a significant linear regression ($R^2 = 0.989$ and 0.998 , Figure 9) indicating that TSM is

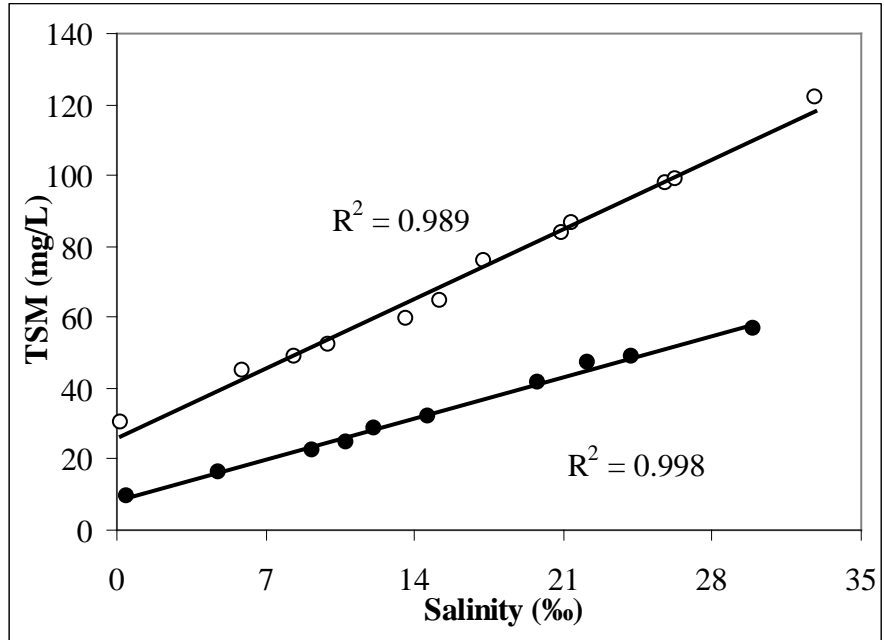


Figure 9: The results of the 1L bench-top study indicate that TSM directly related to salinity and is indicative of flocculation.

directly related to salinity. Bench-top experiments were performed in 1-L beakers from two separate stock suspended sediment mixtures, each of which had different initial TSM (9.76 mg/L and 30.1 mg/L, respectively). For this reason, each of the two lines in Figure 9 vary in slope, but both are highly correlated with similar slope values. Because creating two separate stock resuspension-settling mixtures of equal TSM is quite difficult, it is important to maximize the number of samples generated from each stock. Because TSM was highly correlated with salinity at the 1-L scale, it was possible to continue to scale up to 20-L where PCB analysis could be included.

Two sets of experiments at the 20-L scale were performed and yielded a similar relationship between TSM and salinity as was observed in the 1-L scale experiments (Figure 10). Because the samples from the 20-L experiments were going to be extracted and analyzed for PCBs, the initial TSM in the stock resuspension mixture was increased to 81 and 188 mg/L to obtain sufficient mass (>1 g in suspension is required) of TSM to detect PCBs.

Organic matter content for the laboratory experiments yielded a perfect positive correlation with both salinity and TSM as %OM is a direct function of both parameters (Table 6, Figures 11 a-b). Given this information, it is expected that with the increase in both TSM and salinity, there should be an increase in Σ PCB concentrations in particles (ng/g) in this controlled environment because PCBs have a higher affinity towards organic material (Tinsley, 2004).

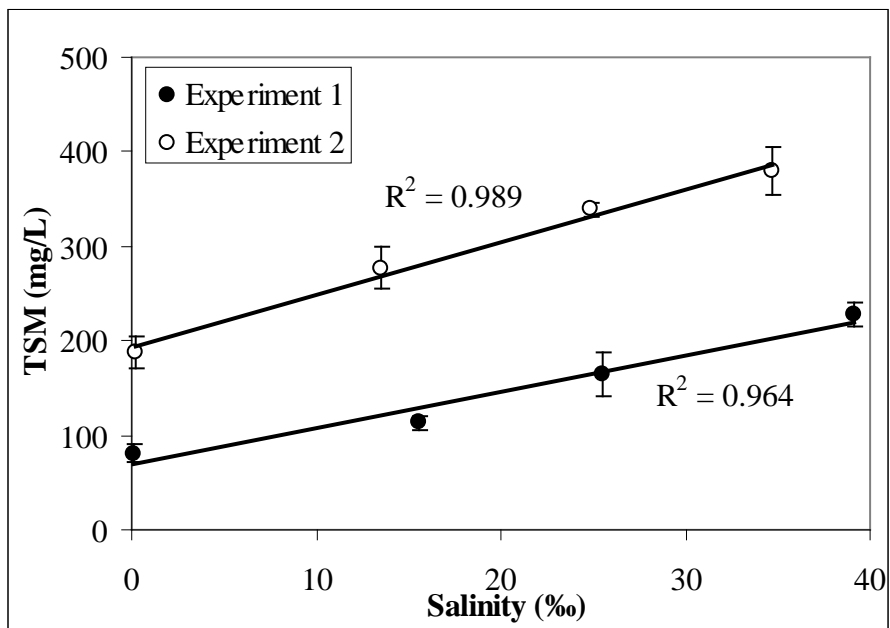
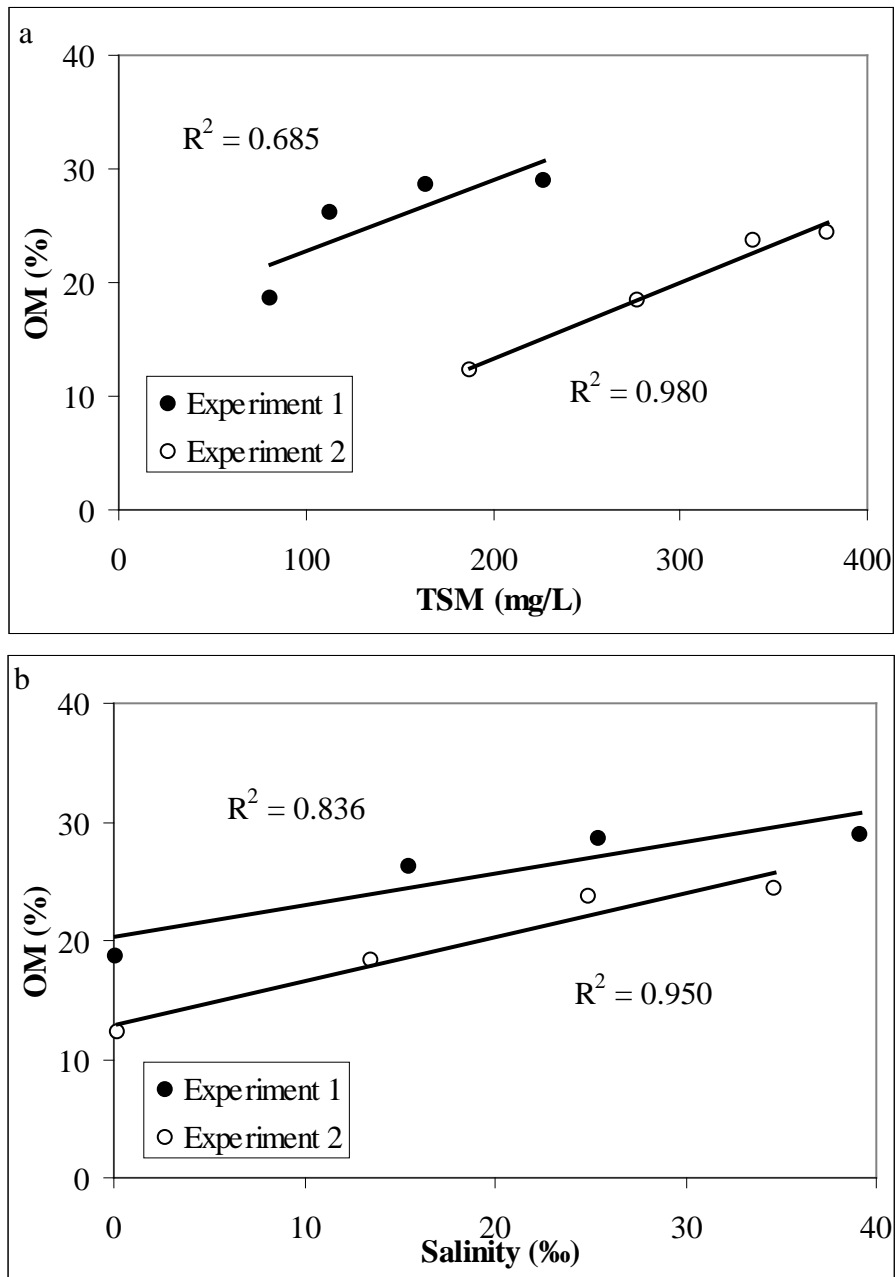


Figure 10: Linear trend observed in the 20-L scale up laboratory experiments, where TSM increases with salinity.



Figures 11 a-b: OM increases linearly with increasing salinity and TSM, as observed in both laboratory experiments.

ΣPCB Floc Mass-Balance Model

A more complete understanding of the influence of flocculation on PCB sorption is found through the usage of a mass-balance model. The model employs two main variables including ΣPCB-bound sediment at zero salinity, designated “ΣPCB_o” (Figure 2 a) and additional ΣPCB-bound sediment formed after colloidal particles have undergone flocculation; this parameter is designated “ΣPCB_{floc}” (Figure 2 b). The sum of the two variables is the empirically derived value for mass based ΣPCB concentrations found through the salinity-induced flocculation study, or simply ΣPCB concentrations (ng/g) as “ΣPCB_T.” Also, ΣPCB_T represents the analytical concentration, which is measured PCB concentration. The mass-balance model is as follows:

$$\Sigma\text{PCB}_T = \Sigma\text{PCB}_o + \Sigma\text{PCB}_{\text{floc}}.$$

The anticipated trend of increasing ΣPCB (ng/g) with OM, described above in Figures 11 a-b, was not observed in the current study. In fact, both experiments yielded a negative correlation for ΣPCB (ng/g) and OM (Figure 12).

This atypical negative correlation indicates that less organic matter than expected is found in colloidal, suspended material. This can be investigated further through the manipulation of the mass-balance model. A ΣPCB dilution model is presented in Figure 13 where the dotted line ($\Sigma\text{PCB}_T = \Sigma\text{PCB}_o$) represents the theoretical trend if dilution occurred as a result of an increase in TSM without additional PCB concentrations in floc material (i.e., $\text{PCB}_{\text{floc}} = 0$). The solid line ($\Sigma\text{PCB}_T = \Sigma\text{PCB}_o + \Sigma\text{PCB}_{\text{floc}}$) is the observed, empirically determined mass-based ΣPCB concentration. The difference in the two is the

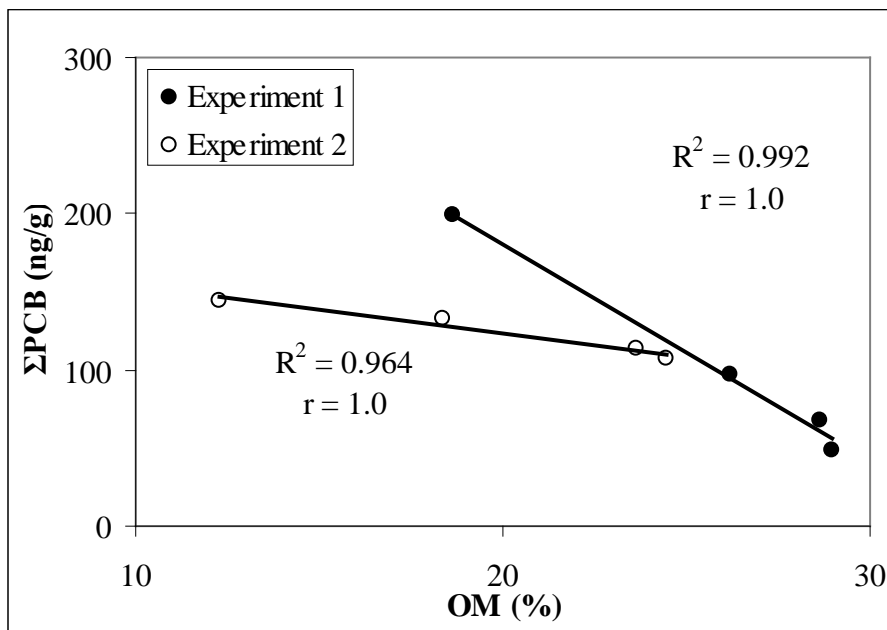


Figure 12: Salinity-induced flocculation study results for mass-based PCB concentrations (ng/g) versus %OM.

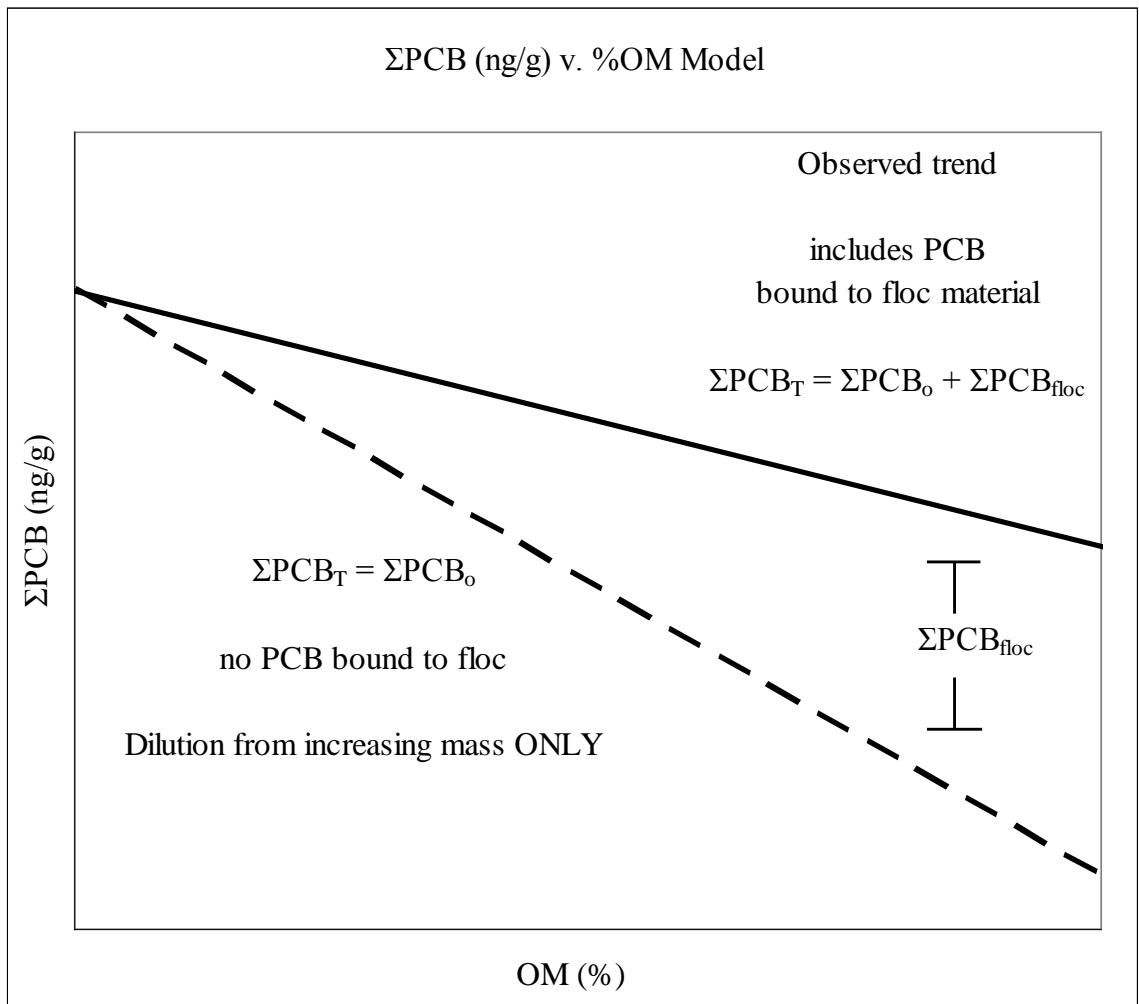


Figure 13: The flocculation dilution model provides a theoretical trend for mass-based PCB concentrations if there were no PCB bound to floc (dotted line). The solid line represents the observed trend from empirical results in the salinity-induced flocculation study. The difference then represents the concentration of PCB in floc formed after colloidal particles have undergone flocculation.

residual amount of Σ PCB bound to floc formed after colloidal particles have aggregated to form floc (PCB_{floc}).

Applied to the results of the salinity-induced flocculation study (Figure 12), the dilution model can be seen in Figure 14. The concentration of Σ PCB bound to floc ($\Sigma\text{PCB}_{\text{floc}}$) was determined to be 0.0, 27.3, 34.4, and 31.5 ng/g for experiment 1, and in experiment 2, floc contains 0, 42.5, 50.6, and 54.0 ng/g Σ PCB (Table 8). Despite the fact that floc contained a significant fraction of the total Σ PCB in the sample (0, 28, 51, and 64% for experiment 1; 0, 32.1, 44.5, and 50.4% for experiment 2), the observed trends for Σ PCB and OM still carry a negative correlation. In order for the trend of Σ PCB versus OM to overcome this negative slope and carry a positive slope as expected theoretically, a greater concentration of Σ PCB must be found in floc (0, 130, 166, 182 ng/g for experiment 1; 0, 54.6, 81.5, 91.4 ng/g for experiment 2). With this in mind, it can be deduced that the concentration of Σ PCB in colloidal OM which undergoes flocculation is much less than expected. It is likely that colloidal OM, which is more heavily concentrated with Σ PCB, has a lesser tendency to undergo electrochemical flocculation. Because less-contaminated OM tends to floc more readily, the accumulation of increasing masses of this OM creates a dilution effect.

On the other hand, volume-based Σ PCB concentrations (ng/L) increase with OM (Figure 15) where the results of experiment 1 are discarded because the correlation is not significant at the 95% confidence interval. Experiment 2 is the only one which holds true because it has a perfect positive correlation ($R^2 = 0.930$).

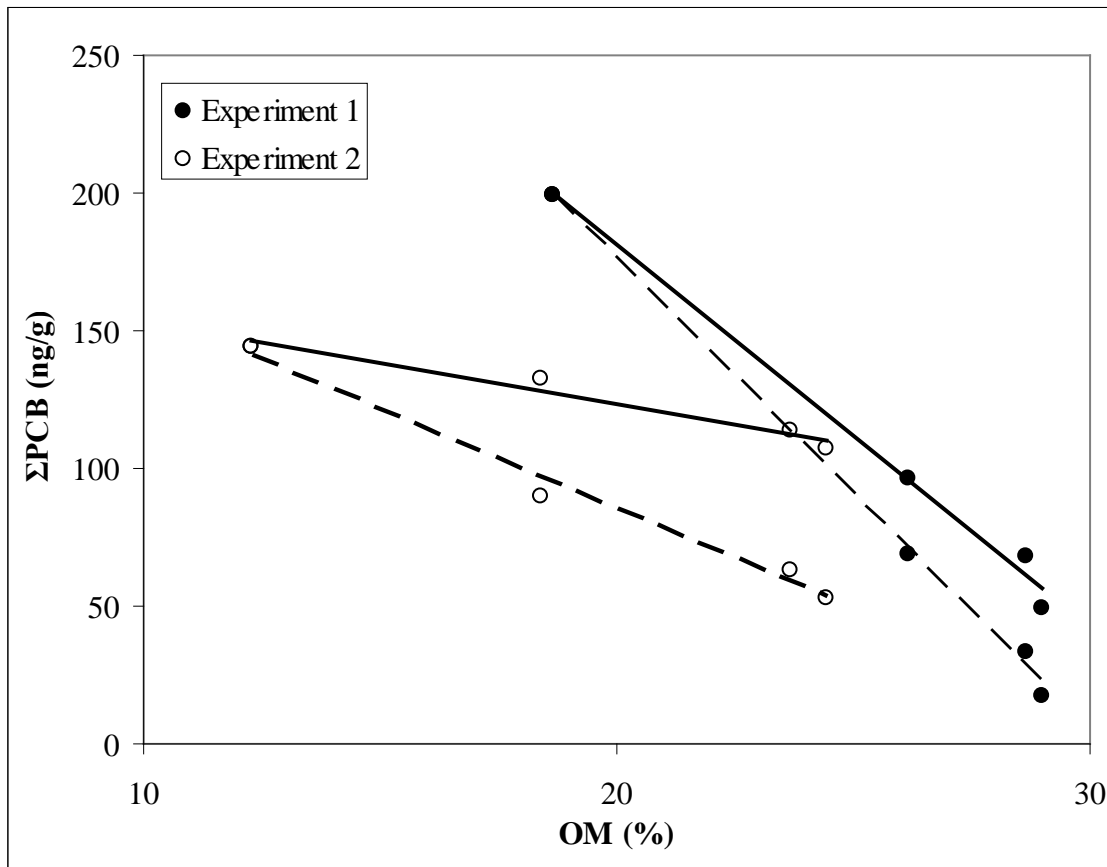


Figure 14: Applied flocculation dilution model with empirical results from laboratory study. The theoretical trend for PCB (ng/g) with OM assuming no PCBs bound to floc is represented by the dotted lines, and the solid line is the observed trend.

Table 8: PCB Dilution Model Determination of PCB in Floc

	<i>Experiment 1</i>					<i>Experiment 2</i>				
OM%	18.6	26.2	28.6	29.0		12.3	18.4	23.7	24.5	
$\Sigma\text{PCB} = \text{PCB}_0 + \text{PCB}_{\text{floc}}$ (ng/g)^a	199	96	68	49		144	132	114	107	
$\Sigma\text{PCB} = \text{PCB}_0$ (ng/g)^b	199	69.1	33.6	17.5		144	89.9	63.0	53.1	
Calculated PCB_{floc} (ng/g)^c	0	27.3	34.4	31.5		0	42.5	50.6	54.0	
% PCB in floc	0	28.3	50.6	64.3		0	32.1	44.5	50.4	
Minimum PCB_{floc} needed for positive slope (ng/g)	0	130	166	182		0	54.6	81.5	91.4	

^aEmpirically observed

^bTheor if no PCB in Floc

^cPCB in Floc

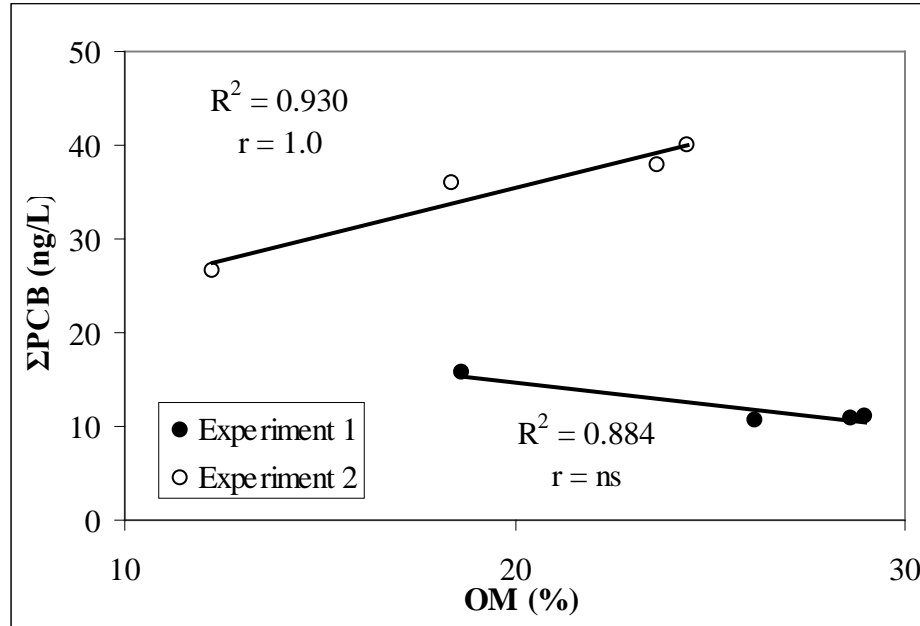


Figure 15: ΣPCB (ng/L) versus OM. Experiment 2 has a perfect positive correlation while experiment 2 has no significant correlation. Only experiment 2 holds true and the trend for ΣPCB (ng/L) increases with increasing OM.

The results of the controlled laboratory study proved to be quite reliable as compared to field work. Positive correlations could be made with TSM and salinity, OM and TSM, and OM and salinity (Figures 10 and 11 a-b), all of which indicate that Σ PCB (ng/g) should also increase with each successive treatment of salt. This, however, was not the case as Σ PCB (ng/g) decreased quite readily with the increase of OM (Figure 12). Likely this is because the colloidal OM which undergoes electrochemical flocculation, contains less Σ PCB than expected, thereby contributing to a net dilution. A similar trend was found during the March 30, 2008 sampling as Σ PCB (ng/g) decreased with depth but was contradictory to that found during May 21, 2008 (Figures 5 a-b).

As for trends with Σ PCB (ng/L) no relationship between the salinity-induced flocculation study and the ETM work can be made as only one experiment from the laboratory studies resulted in a significant correlation (Figure 15) and no significant trends could be deduced from ETM work (Table 6). The lack of a correlation for volume-based Σ PCB concentrations (ng/L) and OM in laboratory and field work indicates that flocculation alone does not drive the formation of the ETM.

Homologue Analysis

Because there are 209 different possible arrangements for chlorine substitution in PCBs, many possible congener combinations may be present in the environment. However, it is normally assumed that the originally manufactured Aroclor mixtures by Monsanto represent the primary sources. There are approximately six prominent Aroclor mixtures, whose ultimate use depended on the various industrial applications, which

differ in the overall weight percent of chlorine. In understanding the source and fate of these contaminants in the environment, it is important to consider the distribution of PCB homologues in environmental samples. PCB sources are most often compared by evaluating the homologue patterns (i.e., Σ dichloro + Σ trichloro + ...).

The homologue profiles for the three ETM sampling dates as well for the laboratory experiments are illustrated in Figures 16 and 17. The homologue profiles differ between the ETM samples and the laboratory experiments where the PCBs at the ETM tend to be more abundant in the tetra and pentachlorinated congeners while the laboratory work yielded a higher abundance of penta, hexa, and heptachlorinated species. ETM samples have more lightweight congeners relative to the Anacostia River source. This is evidence for a natural fractionation process as contaminant-bound sediment transports downstream.

This fractionation occurs as more water soluble congeners (less chlorinated species, having lower K_{ow} values) are more likely to desorb from sediment and are transported downstream while more chlorinated species (having higher K_{ow} values) are more attracted to sediment and, therefore, have a greater tendency to dominate bed sediments. The relative affinities of congeners with varying levels of chlorination, coupled with the natural movement of water, yield a separation of PCB homologues along the downstream transect of the Potomac as heavier congeners tend to dominate bed sediments farther upstream and more water soluble congeners are readily transported downstream.

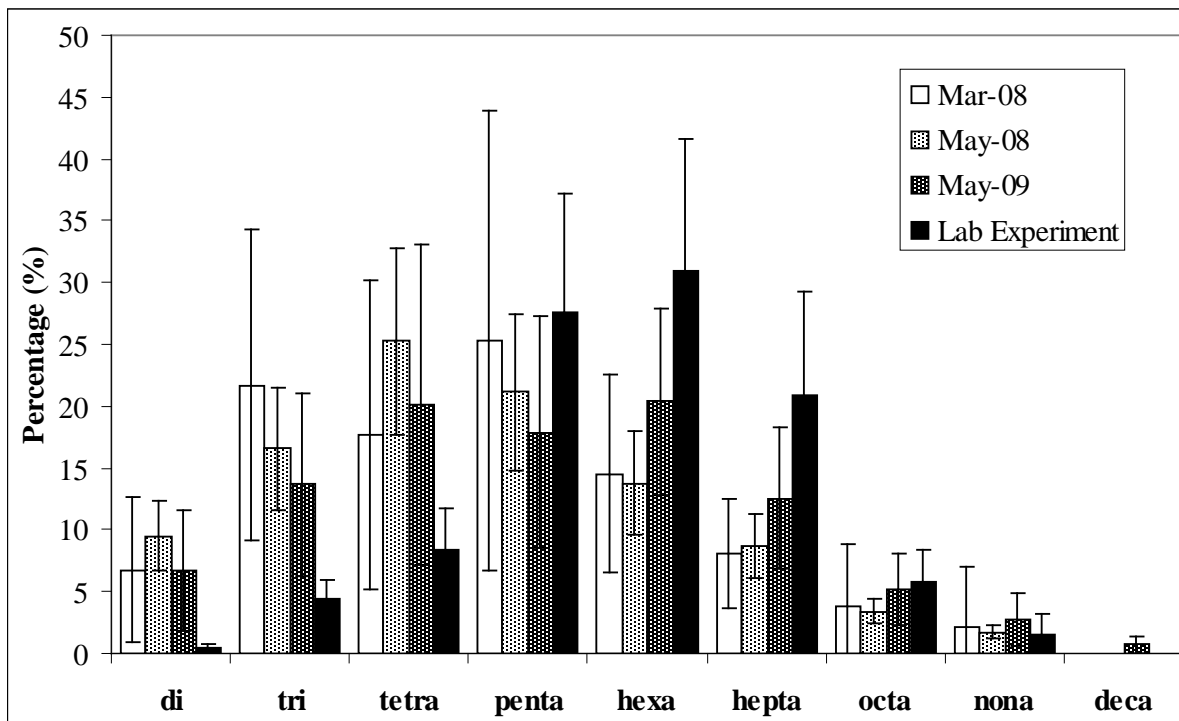


Figure 16: Homologue profile for three ETM particulate samplings (Mar-08, May-08, and May-09) as well as for the laboratory experiment.

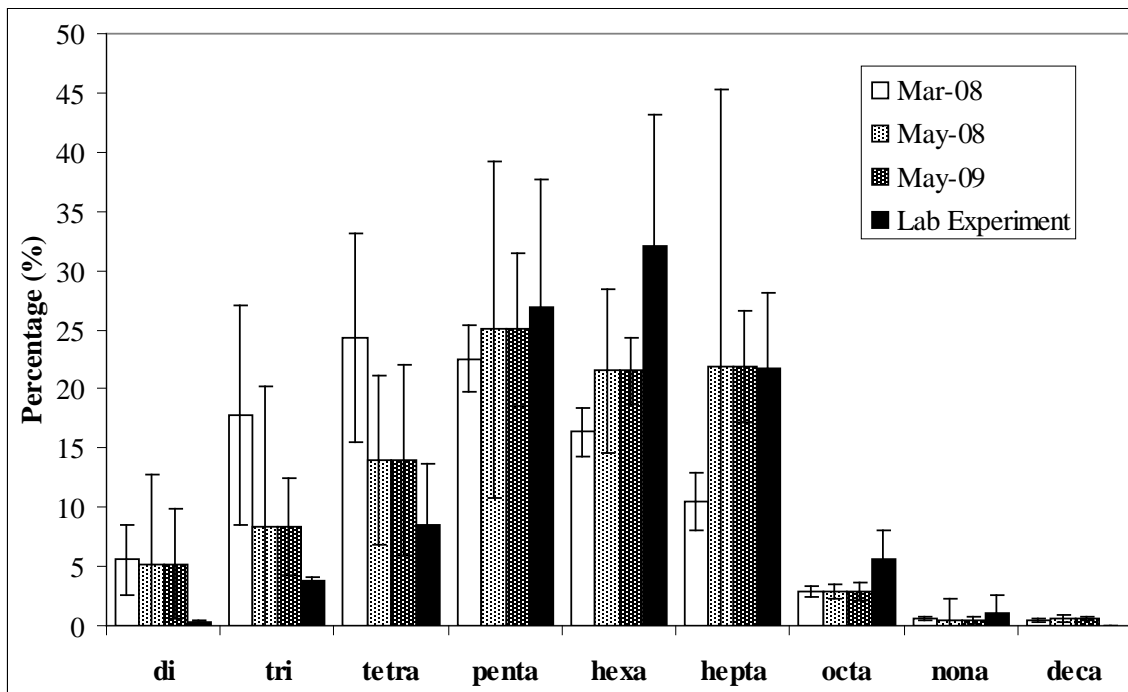


Figure 17: Homologue profile for three ETM bed sediment samplings (Mar-08, May-08, and May-09) as well as for the laboratory experiment.

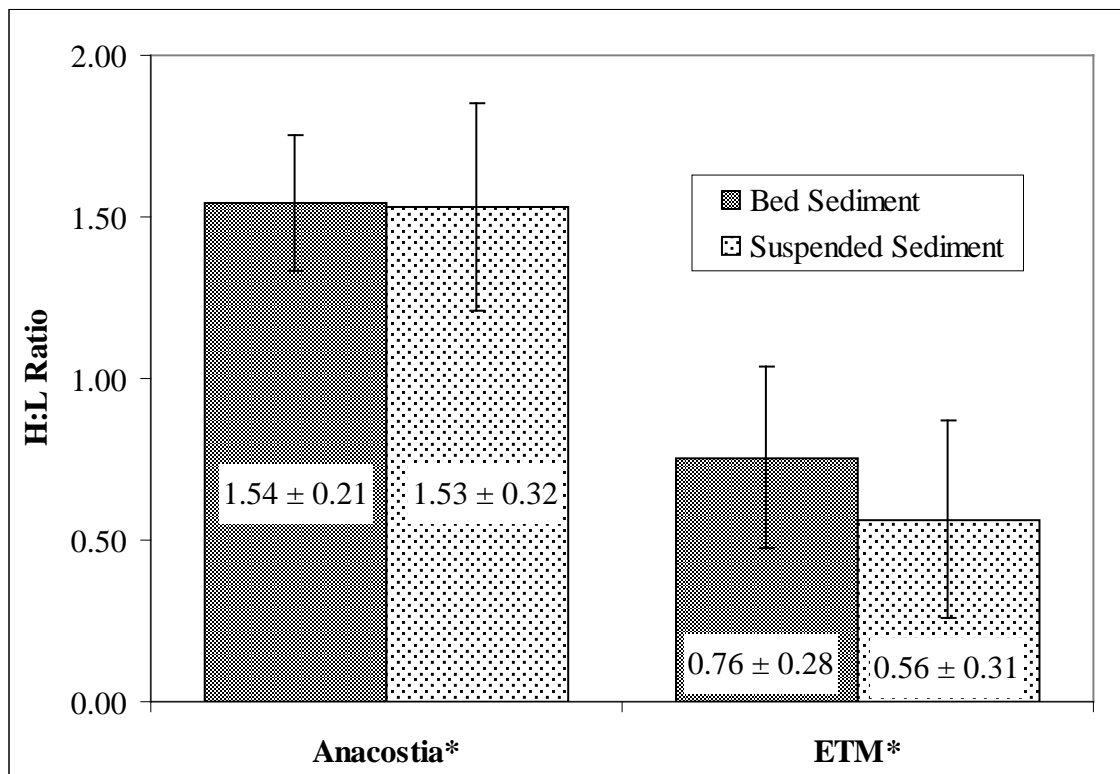
Another way to analyze homologue abundancies is through a high to low molecular weight ratio, or simply a high to low ratio (H:L). H:L ratios are calculated through the following equation:

$$\frac{\sum \text{hexachloro} + \sum \text{heptachloro} + \sum \text{octachloro} + \sum \text{nonachloro} + \sum \text{decachloro}}{\sum \text{dichloro} + \sum \text{trichloro} + \sum \text{tetrachloro} + \sum \text{pentachloro}} = \text{H} : \text{L}$$

All field samples from the ETM have a similar H:L ratio 0.76 ± 0.28 for bed sediment and 0.56 ± 0.31 for particles. ETM H:L ratios differ significantly from the H:L ratio observed in the salinity-induced flocculation study for both bed sediments and particulates (Figure 18). Bed sediment at the ETM has a H:L ratio of 0.76 ± 0.28 compared to 1.54 ± 0.21 for Anacostia sediments. Particulates yielded the same result where the ETM suspended sediment H:L was 0.56 ± 0.31 compared to 1.53 ± 0.32 from the Anacostia source. A significant difference between the two locations was seen at the 95% confidence interval. No evidence was found for a difference in homologue patterns between bed and suspended sediment at the same sampling locale.

As natural sedimentation occurs along the downstream margin of the Potomac, PCB-bound suspended sediments undergo deposition, concentrating in bed sediment. Any remaining suspended sediment continues to move downstream and continues to undergo deposition. Because higher molecular weight congeners have higher K_{ow} values (Hawker and Connell, 1988), they have a higher affinity towards sediment and are more likely to concentrate in bed sediments along the downstream margin than lighter PCBs. Chemical partitioning from environmental compartments like sediment and water, for example, influences the relative rate of fractionation of PCB homologues, and lighter

weight species have a greater tendency to migrate in and out of the aqueous phase than do heavier PCBs. The Potomac River sediments act as a medium for PCB fractionation as particles transport downstream where heavier congeners separate and concentrate in bottom sediments more readily.



**Significantly different at the 95% confidence interval*

Figure 18: High to low ratios indicate partitioning as high molecular weight congeners are found less readily at the ETM than at the Anacostia River source.

Conclusions

While the ETM was found to be extremely dynamic, examination of suspended sediment at the Potomac River ETM has revealed an increasing trend of volume-based concentrations of Σ PCB (ng/L) with depth. This trend can be directly related to the increase in TSM through the vertical transect. A trend for mass-based Σ PCB (ng/g) with depth could not be resolved.

The results from the laboratory study proved to be a useful glimpse into further understanding the influence of flocculation on controlling PCB concentrations at the ETM. In a controlled environment, flocculation could be singled out from all other environmental variables including resuspension which is the other main variable influencing the formation of the ETM.

One of the most interesting findings of the salinity-induced flocculation study is the relation between organic matter and Σ PCB (ng/g). Because PCBs are organic molecules it should be expected that an increase in organic matter should be followed by an increase in Σ PCB (ng/g). Laboratory work yielded a contrary result where an increase in OM was followed by a decrease in Σ PCB (ng/g). With this in mind it can be concluded that colloidal suspended sediment which has undergone flocculation is less enriched with PCBs than the colloidal matter which does not succumb to this electrochemical phenomena.

Unfortunately, due to the heterogeneity of the ETM, no trend for OM along the vertical transect could be ascertained for field work, which corresponds to the previously mentioned lack of trend for Σ PCB (ng/g) with depth.

Samples taken at the ETM indicate that the ETM is not a high depositional zone for PCBs. Suspended and bed sediments differ in not only their OM content but also in the concentrations of Σ PCB (ng/g). ETM bed sediments contain less Σ PCB (28.1 ± 12.7 ng/g) than suspended sediments during the normal flow events in March and May 2008 (191 ± 115 and 343 ± 110 ng/g, respectively). This observation was preceded by an enrichment of OM in suspended versus bed sediments (26.7 ± 6.26 and $20.7 \pm 4.51\%$ compared to $8.91 \pm 1.80\%$), as well. Particulates from May 2009, during high flow, indicate a similarity in OM content and Σ PCB as was found in bed sediments ($8.14 \pm 1.50\%$, 39.3 ± 18.4 ng/g).

Finally, a significant difference was observed in the homologue abundancies of samples at the ETM compared to samples taken from the Anacostia River PCB hotspot, where high molecular weight congeners dominate the upstream margin. A natural fractionation of PCB species occurs as the contaminant is transported through the Potomac River. Lower molecular weight congeners have relatively low octanol-water partition coefficients and are more likely to desorb from the surface of sediment into the aqueous, water phase. More chlorinated species, on the other hand have a much greater affinity towards the surface of sediment and a correspondingly greater tendency to concentrate in bed sediment through the sedimentation and thereby dominate the upstream margin.

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
Coelute {	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
Coelute {	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
Coelute {	52	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3
	69	2,3',4,6-Tetrachlorobiphenyl	60233-24-1

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CAS Structural PCB Number ^a	CAS Structural Name ^b	CAS Registry Number ^b	
	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
Coelute {	37	3,4,4'-Trichlorobiphenyl	38444-90-5
	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
	85	2,2',3,4,4'-Pentachlorobiphenyl	65510-45-4
Coelute {	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

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CAS Structural PCB Number ^a	CAS Structural Name ^b	CAS Registry Number ^b	
	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
Coelute {	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
Coelute {	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	
Coelute {	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
	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

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CAS Structural PCB Number ^a	CAS Structural Name ^b	CAS Registry Number ^b	
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'-Decachlorobiphenyl	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 Congeners in Method

Congener ^a	EIDL (pg)	EMDL		
		Bed Sediment (ng/g)	Suspended Sediment (ng/g)	Suspended Sediment (ng/L)
4, 10	113	4.74E-02	3.93E-02	6.47E-03
7, 9	118	4.95E-02	4.11E-02	6.76E-03
6	9	3.87E-03	3.21E-03	5.29E-04
5, 8	59	2.46E-02	2.04E-02	3.36E-03
19	97	4.05E-02	3.36E-02	5.53E-03
IS 30	na	na	na	na
12	112	4.71E-02	3.91E-02	6.43E-03
15, 18	12	5.20E-03	4.32E-03	7.10E-04
17	12	5.23E-03	4.34E-03	7.14E-04
24, 27	31	1.29E-02	1.07E-02	1.77E-03
16, 32	29	1.22E-02	1.01E-02	1.66E-03
34	15	6.07E-03	5.04E-03	8.30E-04
29	5	2.25E-03	1.87E-03	3.07E-04
26	6	2.69E-03	2.24E-03	3.68E-04
25	43	1.80E-02	1.50E-02	2.46E-03
31	48	1.99E-02	1.65E-02	2.72E-03
28	80	3.36E-02	2.79E-02	4.59E-03
20, 33	81	3.41E-02	2.83E-02	4.66E-03
22	70	2.93E-02	2.43E-02	4.01E-03
45	49	2.04E-02	1.69E-02	2.79E-03
46	38	1.60E-02	1.33E-02	2.19E-03
52, 69	78	3.27E-02	2.72E-02	4.47E-03
49	28	1.18E-02	9.82E-03	1.62E-03
47	23	9.70E-03	8.05E-03	1.32E-03
48	725	3.04E-01	2.52E-01	4.15E-02
104	195	8.15E-02	6.76E-02	1.11E-02
44	48	2.03E-02	1.68E-02	2.77E-03
37, 42, 59	158	6.61E-02	5.49E-02	9.04E-03
41, 64, 71	50	2.09E-02	1.73E-02	2.85E-03
40	73	3.04E-02	2.52E-02	4.15E-03
SS 103	19	8.15E-03	6.76E-03	1.11E-03
67	28	1.18E-02	9.78E-03	1.61E-03

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Congener ^a	EIDL (pg)	EMDL		
		Bed Sediment (ng/g)	Suspended Sediment (ng/g)	Suspended Sediment (ng/L)
63	17	7.31E-03	6.06E-03	9.98E-04
74	43	1.81E-02	1.50E-02	2.47E-03
70	107	4.49E-02	3.73E-02	6.14E-03
66	22	9.01E-03	7.48E-03	1.23E-03
93, 95	132	5.52E-02	4.59E-02	7.55E-03
91	21	8.84E-03	7.34E-03	1.21E-03
56, 60	39	1.61E-02	1.34E-02	2.20E-03
84, 92	61	2.56E-02	2.12E-02	3.49E-03
101	109	4.55E-02	3.78E-02	6.22E-03
99	47	1.98E-02	1.65E-02	2.71E-03
119	27	1.11E-02	9.24E-03	1.52E-03
83	66	2.74E-02	2.28E-02	3.75E-03
97	54	2.25E-02	1.86E-02	3.07E-03
87	55	2.32E-02	1.93E-02	3.17E-03
115	91	3.82E-02	3.17E-02	5.22E-03
85	40	1.69E-02	1.40E-02	2.31E-03
77, 136	154	6.44E-02	5.35E-02	8.80E-03
110	155	6.48E-02	5.38E-02	8.85E-03
82	46	1.92E-02	1.60E-02	2.63E-03
151	15	6.15E-03	5.10E-03	8.40E-04
135	25	1.04E-02	8.61E-03	1.42E-03
144	52	2.16E-02	1.79E-02	2.95E-03
107, 147	99	4.13E-02	3.43E-02	5.64E-03
123	95	3.97E-02	3.30E-02	5.43E-03
118, 149	291	1.22E-01	1.01E-01	1.66E-02
SS 140	43	1.79E-02	1.49E-02	2.45E-03
114, 134	78	3.25E-02	2.70E-02	4.44E-03
131	40	1.68E-02	1.39E-02	2.29E-03
146	35	1.47E-02	1.22E-02	2.01E-03
105, 132	129	5.38E-02	4.47E-02	7.35E-03
153	152	6.34E-02	5.27E-02	8.67E-03
141, 179	68	2.87E-02	2.38E-02	3.91E-03
137	1842	7.71E-01	6.40E-01	1.05E-01
176	36	1.51E-02	1.25E-02	2.06E-03
138, 164	98	4.11E-02	3.41E-02	5.62E-03

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Congener ^a	EIDL (pg)	EMDL		
		Bed Sediment (ng/g)	Suspended Sediment (ng/g)	Suspended Sediment (ng/L)
158	32	1.34E-02	1.12E-02	1.84E-03
129	21	8.77E-03	7.28E-03	1.20E-03
178	79	3.31E-02	2.75E-02	4.52E-03
187	112	4.69E-02	3.89E-02	6.41E-03
128	69	2.90E-02	2.41E-02	3.97E-03
183	43	1.81E-02	1.50E-02	2.47E-03
167	46	1.91E-02	1.58E-02	2.61E-03
185	7	2.76E-03	2.30E-03	3.78E-04
174	60	2.51E-02	2.08E-02	3.43E-03
177	38	1.61E-02	1.34E-02	2.20E-03
156, 171	59	2.49E-02	2.06E-02	3.40E-03
157	36	1.50E-02	1.25E-02	2.05E-03
173	28	1.18E-02	9.80E-03	1.61E-03
172	37	5.59E-02	4.64E-02	7.63E-03
IS 204	na	na	na	na
197	30	1.24E-02	1.03E-02	1.69E-03
180	109	4.55E-02	3.77E-02	6.21E-03
193	38	1.59E-02	1.32E-02	2.17E-03
191	54	2.27E-02	1.88E-02	3.10E-03
170	1251	5.24E-01	4.35E-01	7.16E-02
190	15	6.10E-03	5.06E-03	8.33E-04
199	51	2.12E-02	1.76E-02	2.90E-03
203, 196	88	3.69E-02	3.06E-02	5.04E-03
189	97	4.07E-02	3.38E-02	5.55E-03
195	55	2.31E-02	1.92E-02	3.16E-03
208	33	1.37E-02	1.14E-02	1.88E-03
207	25	1.05E-02	8.71E-03	1.43E-03
194	50	2.11E-02	1.75E-02	2.88E-03
205	30	1.27E-02	1.05E-02	1.73E-03
206	50	2.11E-02	1.75E-02	2.88E-03
209	79	3.31E-02	2.75E-02	4.52E-03

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

^b IS = internal standard

^c SS = surrogate standard

^d na = not applicable

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CURRICULUM VITAE

Kathleen J. Housman graduated from John Carroll High School, Bel Air, Maryland, 2002. She received her Bachelor of Science in Chemistry from Mount Saint Mary's University in 2006.