Total Maximum Daily Loads of Polychlorinated Biphenyls in the Sassafras River, Oligohaline Segment, Cecil and Kent Counties, Maryland

FINAL

MARYLAND

DEPARTMENT OF THE ENVIRONMENT

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List of Abbreviations

Adj-SediBAF	Adjusted Sediment Bioaccumulation Factor
Adj-tBAF	Adjusted Total Bioaccumulation Factor
BAF	Bioaccumulation Factor
BSAF	Biota-sediment accumulation factor
CBP P5	Chesapeake Bay Program Phase 5
CFR	Code of Federal Regulations
COMAR	Code of Maryland Regulations
CV	Coefficient of Variation
DOC	Dissolved Organic Carbon
DRBC	Delaware River Basin Commission
g	Gram
kg	Kilogram
km	Kilometer
Kow	PCB Octanol-Water Partition Coefficient
L	Liters
LA	Load Allocation
m	Meter
MDE	Maryland Department of the Environment
MDL	Maximum Daily Load
MDP	Maryland Department of Planning
mg/kg	Milligrams/kilogram, ppm
MGD	Million gallons per day
MOS	Margin of Safety
MS4	Municipal Separate Storm Sewer System
ng/g	Nanograms per gram, ppb
ng/kg	Nanograms per kilogram, ppt
ng/L	Nanograms per liter, ppt
NPDES	National Pollutant Discharge Elimination System

PCB	Polychlorinated Biphenyl
POC	Particulate Organic Carbon
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
QEA	Quantitative Environmental Analysis
TMDL	Total Maximum Daily Load
tPCB	Total PCB
TSD	Technical Support Document
TSS	Total Suspended Solids
UMCES	University of Maryland Center for Environmental Science
US EPA	U. S. Environmental Protection Agency
USGS	United States Geological Survey
WLA	Waste Load Allocation
WQLS	Water Quality Limited Segment
WQS	Water Quality Standard
WWTP	Waste Water Treatment Plant
yr	Year

EXECUTIVE SUMMARY

Section 303(d) of the federal Clean Water Act and the U.S. Environmental Protection Agency's (US EPA) implementing regulations direct each State to identify and list waters, known as water quality limited segments (WQLSs), in which current required controls of a specified substance are inadequate to achieve water quality standards (WQSs). For each WQLS, the State is to either establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating WQSs, or demonstrate that WQSs are being met (CFR 2007).

The Maryland water quality regulations state that all surface waters of Maryland shall be protected for water contact recreation, fishing, and protection of aquatic life and wildlife (COMAR 2007a). The specific designated use for Sassafras River Oligohaline segments (also referred to as the Sassafras River embayment) is Use II – Support of Estuarine and Marine Aquatic Life and Shellfish Harvesting (COMAR 2007b). The Maryland Department of the Environment (MDE) has identified the waters of the Sassafras River Oligohaline segment (Integrated Report Assessment Unit Identification: MD-SASOH) on the State's Integrated Report as impaired by the following pollutants (listing year in parentheses): nutrients (1996), sediments (1996 – later changed to a total suspended solids (TSS) listing), and polychlorinated biphenyls (PCBs) in fish tissue (2002) (MDE 2008).

A phosphorus TMDL was approved by the US EPA in 2002 to address the 1996 nutrients listing. The TSS listing was moved from Category 5 of the Integrated Report (*waterbody is impaired, does not attain the water quality standard, and a TMDL is required*) to Category 2 (*water body is meeting some* [in this case TSS-related] *water quality standards, but with insufficient data to assess all impairments*) in the 2008 Integrated Report. This document, upon US EPA approval, establishes a total PCB (tPCB) TMDL for the Sassafras River Oligohaline segment. Data solicitation for PCB related information was conducted by MDE, and all readily available data have been considered.

The objective of the tPCB TMDL established in this document is to ensure that the "fishing" designated use in the Sassafras River embayment is supported to allow consumption of fish protective of human health. This objective was achieved with the use of a tidally averaged multi-segment one-dimensional transport model and the tPCB fish tissue listing threshold of 39 nanograms/gram (ng/g, ppb) – wet weight (MDE 2008, 72-74). The model incorporates the long-term influences of fresh water discharge, dispersion, and exchanges between the water column and bottom sediments, thereby representing the dynamic transport within the Sassafras River embayment. The model was used to:

1. Estimate and predict tPCB transport and fate based on the measured tPCB concentrations in the water column and sediment of the Sassafras River embayment.
2. Simulate the long-term tPCB concentrations in the water column and bottom sediments of the Sassafras River embayment.
3. Based on the available literature, the TMDL methodology assumes that on average the tPCB concentrations at the Sassafras River open boundary with the Bay are decreasing at a rate of 6.5% per year (Appendix H). Given the estimated rate of decline, the model estimates that the time needed for the tPCB concentrations to meet the site-specific tPCB

water column and sediment TMDL endpoints of 0.11 nanograms/liter (ng/L) and 2.34 ng/g, respectively is approximately 38 years.

As part of this analysis, point and nonpoint PCB sources have been identified throughout the Sassafras River watershed. Two nonpoint sources (i.e., resuspension and diffusion from the bottom sediments and the Chesapeake Bay tidal influence) were determined to be the major sources of tPCBs to the Sassafras River embayment. The Chesapeake Bay tPCB loads are transported to the embayment during flood tides and tend to accumulate in the bottom sediments. Other nonpoint sources include atmospheric deposition to the embayment and runoff from watershed sources in Maryland and upstream in Delaware. Point sources include two wastewater treatment plants (WWTPs) and National Pollutant Discharge Elimination System (NPDES) regulated stormwater.

The Total Baseline (i.e., 2006) Load of tPCBs to the Sassafras River embayment is 9,777.3 g/year. It can be further subdivided into a Nonpoint Source Baseline Load and Point Source Baseline Load. The tPCB TMDL for the Sassafras River embayment is 1,112.6 g/year with a reduction of 88.6% from the Total Baseline Load (see Table ES- 1). This TMDL when implemented will ensure that the tPCB loads are at a level expected to support the “fishing” designated use in the Sassafras River embayment that is protective of human health.

Table ES- 1: Summary of tPCB Baseline Loads, TMDL Allocations, and Associated Percent Reductions

Source	Baseline (g/year)	Baseline (%)	TMDL (g/year)	Load Reduction (%)
Bottom Sediment (Resuspension and Diffusion)	4,496.1	45.99	463.2	89.7
Chesapeake Bay (Tidal Influence)	5,133.2	52.50	390.1	92.4
Direct Atmospheric Deposition (to the Surface of the Embayment)	117.9	1.21	117.9	0.0
Maryland Watershed Nonpoint Sources*	25.0	0.26	25.0	0.0
Delaware Upstream	2.6	0.03	2.6	0.0
Nonpoint Sources/Load Allocations	***9,774.8***	**99.97**	***998.8***	***89.8***
WWTP*△	2.0	0.02	2.0	0.0
NPDES Regulated Stormwater*	0.5	0.01	0.5	0.0
Point Sources/Waste Load Allocations*	***2.5***	**0.03**	***2.5***	***0.0***
MOS	-	-	***111.3***	-
Total	**9,777.3**	**100**	**1,112.6**	**88.6**

Notes: *These sources were characterized only for the Maryland portion of the watershed.
△WWTP Baseline Loads were considered to be *de minimis.*

All TMDLs need to be presented as a sum of waste load allocations (WLAs) for the identified point sources and load allocations (LAs) for nonpoint source loads generated within the assessment unit, and where applicable LAs for natural background, tributary, and adjacent segment loads. WLAs were assigned to NPDES regulated stormwater sources and WWTPs. The WWTP Baseline Loads were considered to be *de minimis* therefore no appreciable environmental benefit would be gained by reducing this load (see Appendix J for details). There are currently no effluent PCB limits established in the discharge permits for WWTPs. The sensitivity analysis provided in this document (Appendix J) suggests that there is no "reasonable potential" for PCBs to exceed water quality even at 100 times the current WWTP loadings. Inclusion of a WLA in this document does not reflect any determination to impose an effluent limit.

Furthermore, all TMDLs must include a margin of safety (MOS) to account for uncertainty in the relationship between pollutant loads and water quality as well as the scientific and technical understanding and simulation of water quality parameters in natural systems (CFR 2007). An explicit MOS of 10% or 111.3 g/year was incorporated into the analysis to account for such uncertainty. The State reserves the right to revise these allocations provided the revisions are consistent with achieving WQSs.

The TMDL presented in this document is protective of human health at all times and in this way implicitly accounts for seasonal variations as well as critical conditions. Since tPCB levels in fish become elevated due to long-term exposure, rather than temporary spikes in water column tPCB concentration, it has been determined that the selection of the average tPCB concentrations within each model segment as representing the baseline conditions adequately considers the impact of seasonal variations and critical conditions on the “fishing” designated use in the Sassafras River embayment. Furthermore, the site-specific tPCB water column TMDL endpoint used to develop this TMDL is lower than the Maryland fresh and salt water chronic aquatic life tPCB criteria protective of fish and wildlife as well as the Maryland water column human health tPCB criterion protective of human health associated with consumption of PCB contaminated fish.

Resuspension and diffusion from the bottom sediments and the Chesapeake Bay tidal influence have been identified as the two major sources of tPCBs to the Sassafras River embayment. Given that on average the tPCB concentrations in the Upper Chesapeake Bay are decreasing at a rate of 6.5% per year (Appendix H), the tPCB levels in the Sassafras River embayment are expected to decline over time. Discovering and remediating any existing PCB land sources throughout the Upper Chesapeake Bay watershed via future TMDL development and implementation efforts will further help to meet water quality goals in the Sassafras River embayment.

Once US EPA has approved this TMDL, MDE will begin an iterative process of implementation, focusing first on those sources with the largest impact on water quality and giving consideration to the relative cost and ease of implementation. MDE’s Water Quality Standards Section will continue to monitor PCB levels in Maryland fish. This information will be used to evaluate the PCB impairment in the Sassafras River embayment on an ongoing basis.

1.0 INTRODUCTION

Section 303(d) of the federal Clean Water Act and the U.S. Environmental Protection Agency's (US EPA) implementing regulations direct each State to identify and list waters, known as water quality limited segments (WQLSs), in which current required controls of a specified substance are inadequate to achieve water quality standards (WQSs). For each WQLS, the State is to either establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating WQSs, or demonstrate that WQSs are being met (CFR 2007).

TMDLs are established to determine the pollutant load reductions needed to achieve and maintain WQSs. A WQS is the combination of a designated use for a particular body of water and the water quality criteria designed to protect that use. Designated uses include activities such as swimming, drinking water supply, fish and shellfish propagation and harvest, etc. Water quality criteria can be either narrative statements or numeric values designed to protect the designated uses. Criteria may differ among waters with different designated uses.

The Maryland water quality regulations state that all surface waters of Maryland shall be protected for water contact recreation, fishing, and protection of aquatic life and wildlife (COMAR 2007a). The specific designated use for Sassafras River Oligohaline segments (also referred to as the Sassafras River embayment) is Use II – Support of Estuarine and Marine Aquatic Life and Shellfish Harvesting (COMAR 2007b). The Maryland Department of the Environment (MDE) has identified the waters of the Sassafras River Oligohaline segment (Integrated Report Assessment Unit Identification: MD-SASOH) on the State's Integrated Report as impaired by the following pollutants (listing year in parentheses): nutrients (1996), sediments (1996 – later changed to a total suspended solids (TSS) listing), and polychlorinated biphenyls (PCBs) in fish tissue (2002) (MDE 2008).

A phosphorus TMDL was approved by the US EPA in 2002 to address the 1996 nutrients listing. The TSS listing was moved from Category 5 of the Integrated Report (*waterbody is impaired, does not attain the water quality standard, and a TMDL is required*) to Category 2 (*water body is meeting some* [in this case TSS-related] *water quality standards, but with insufficient data to assess all impairments*) in the 2008 Integrated Report. This document, upon US EPA approval, establishes a total PCB (tPCB) TMDL for the Sassafras River Oligohaline segment. Data solicitation for PCB related information was conducted by MDE, and all readily available data have been considered.

PCBs are a class of man-made compounds that were manufactured and used for a variety of industrial applications. They consist of 209 related chemical compounds (congeners) that were manufactured and sold as mixtures under various trade names (QEA 1999). Each of the 209 possible PCB compounds consists of two phenyl groups and one or more chlorine atoms. The congeners differ in the number and position of the chlorine atoms along the phenyl group. From the 1940s to the 1970s, they were extensively used as heat transfer fluids, flame retardants, hydraulic fluids, and dielectric fluids because of their dielectric and flame resistant properties. They have been identified as a pollutant of concern due to the following:

1. They are bioaccumulative and can cause both acute and chronic toxic effects;
2. They have carcinogenic properties;

3. They are persistent organic pollutants that do not readily breakdown in the environment.

In the late 1970s, concerns regarding potential human health effects led the United States government to take action to cease PCB production, restrict PCB use, and regulate the storage and disposal of PCBs. Despite these actions, PCBs are still being released into the environment through fires or leaks from old PCB containing equipment, accidental spills, burning of PCB containing oils, leaks from hazardous waste sites, etc. As PCBs tend to bioaccumulate in aquatic organisms including fish, people who ingest fish may become exposed to PCBs. In fact, elevated levels of PCBs in fish are one of the leading causes of fish consumption advisories in the United States.

The Sassafras River Oligohaline segment is identified as impaired by PCBs on the State's Integrated Report based on fish tissue PCB data from MDE's monitoring program that exceeded the tPCB fish tissue listing threshold of 39 nanograms/gram (ng/g, ppb) - wet weight (MDE 2008, 72-74). Besides identifying impaired waterbodies, MDE also issues statewide and site-specific fish consumption advisories (ranging from 0 to 4 meals per month) and recommendations (ranging from 4 to 8 meals per month). Current fish consumption advisories within the Sassafras River embayment suggest limiting the consumption of the following fish species: channel catfish and white perch.

2.0 SETTING AND WATER QUALITY DESCRIPTION

2.1 General Setting

The Sassafras River watershed is located in Cecil and Kent Counties, with the eastern most portion of the watershed extending through Delaware. It drains to the Chesapeake Bay (see Figure 2). The tidal portion of the watershed extends as far east as its intersection with Route 301. The tidal range is 1.6 feet (0.49 meters (m)) based on the United States National Oceanic and Atmospheric Administration tidal station in Betterton, MD. The depths of the river range from about 6 inches (0.15 m) in the headwaters to greater than 35 feet (11 m) in the middle of the river. The widths vary from 400 feet (122 m) at the headwaters of the tidal embayment to 6,560 feet (2,000 m) at the mouth (MDE 2002).

There are no Tier II (i.e., high quality) stream segments (Benthic Index of Biotic Integrity/Fish Index of Biotic Integrity aquatic health scores > 4 – scale 1 to 5) located within the watershed requiring the implementation of Maryland's antidegradation policy procedures (COMAR 2007d; MDE 2009c). The total population in the Maryland portion of the Sassafras River watershed is approximately 10,000 (US Census Bureau 2000).

The entire Sassafras River watershed stretches over approximately 97 square miles (252 kilometers (km^2)). The tidal portion of the river is approximately 16 miles (26 km) in length. The watershed is predominately rural in nature consisting of 28.54% forest and 45.92% agricultural land (see Figure 1, Figure 3, and Table 1).

Table 1: Land Use Distribution in the Sassafras River Watershed

Land Use	Area (km^2)	Percent of Total
Water	32.4	12.87
Urban	17.9	7.12
Barren	0.3	0.13
Forest	71.9	28.54
Agriculture	115.7	45.92
Natural grass	0.1	0.05
Wetland	13.5	5.37
Total	**252**	**100**

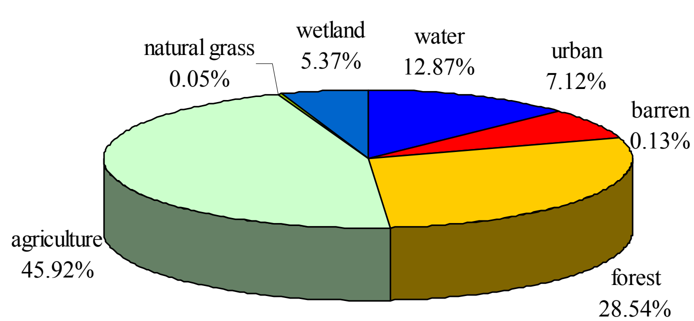

Figure 1: Land Use Distribution in the Sassafras River Watershed

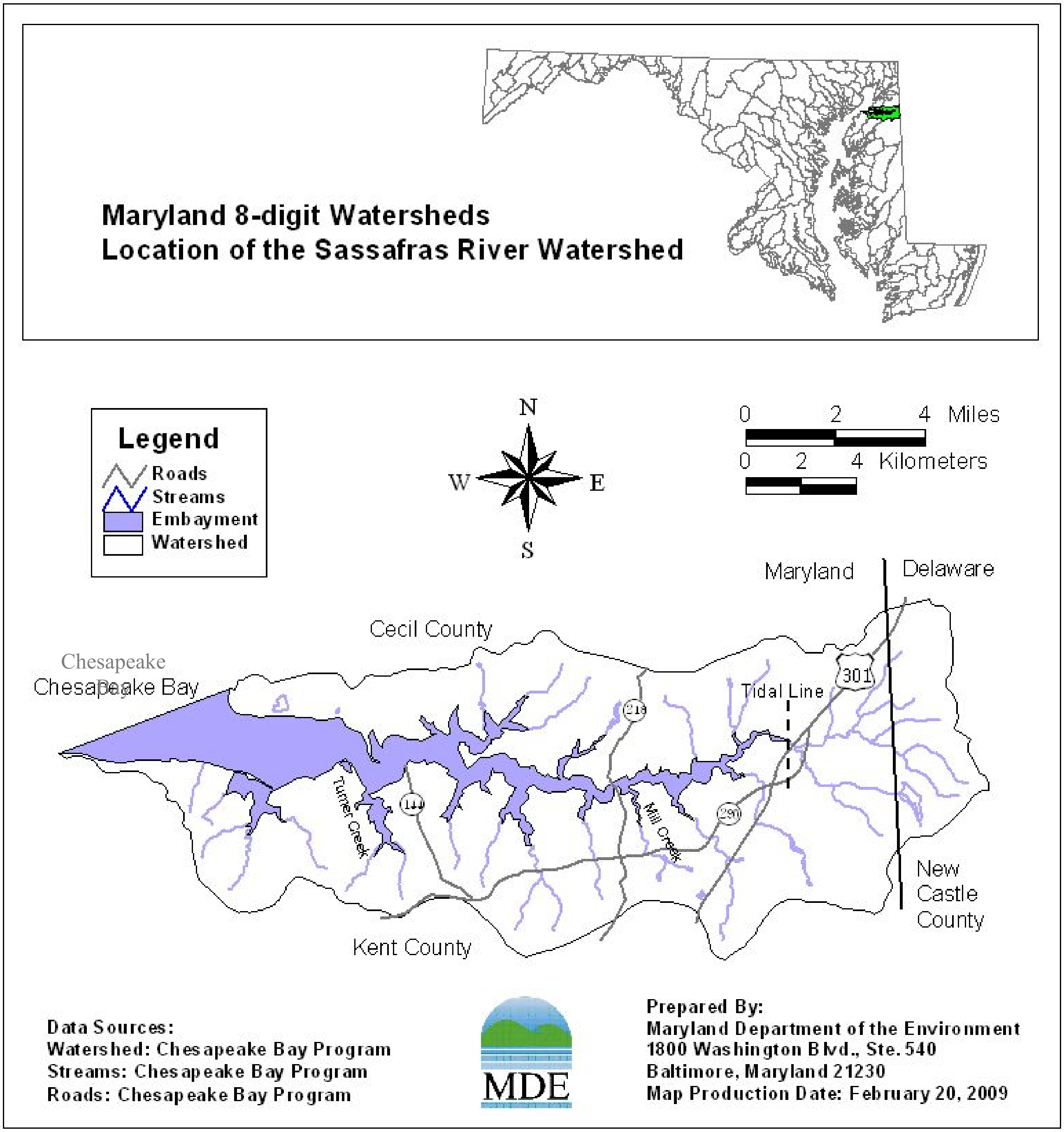

Figure 2: Location Map of the Sassafras River Watershed and Embayment

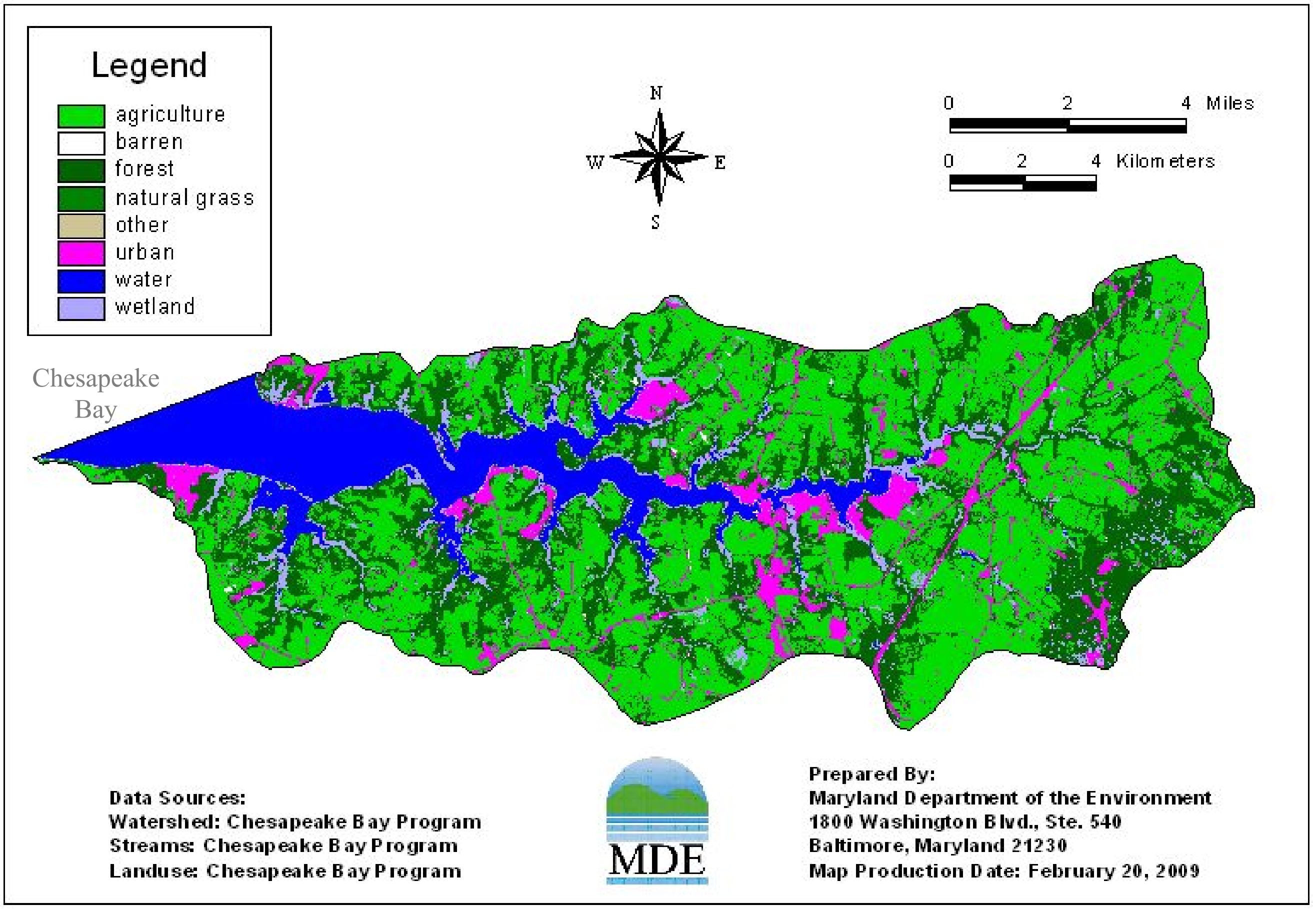

Figure 3: Land Use in the Sassafras River Watershed

2.2 Water Quality Characterization and Impairment

The Maryland water quality regulations state that all surface waters of Maryland shall be protected for water contact recreation, fishing, and protection of aquatic life and wildlife (COMAR 2007a). The specific designated use for Sassafras River Oligohaline segments is Use II – Support of Estuarine and Marine Aquatic Life and Shellfish Harvesting (COMAR 2007b). The State of Maryland adopted three separate water column tPCB criteria: human health criterion for protection of human health associated with consumption of PCB contaminated fish, as well as fresh and salt water chronic tPCB criteria for protection of aquatic life. The Maryland water column human health tPCB criterion is set at 0.64 nanograms/liter (ng/L, ppt) (COMAR 2007c; US EPA 2006). This criterion is based on a cancer slope factor of 2 milligrams/kilogram-day $^{-1}$ (mg/kg-day)$^{-1}$, bioconcentration factor of 31,200 liters/kilogram (L/kg), risk level of 10^{-5}, lifetime risk level and exposure duration of 70 years, and fish intake of 17.5 grams/day (g/day). A cancer risk level provides an estimate of the additional incidence of cancer that may be expected in an exposed population. A risk level of 10^{-5} indicates a probability of one additional case of cancer for every 100,000 people exposed. The Maryland fresh and salt water chronic aquatic life tPCB criteria are set at 14 ng/L and 30 ng/L, respectively (COMAR 2007c; US EPA 2006). A sediment tPCB criterion has not been established within Maryland water quality standards.

In addition to the water column criteria described above, fish tissue monitoring data can serve as an indicator of PCB water quality conditions. The Maryland fish tissue monitoring data is used to issue fish consumption advisories/recommendations and determine whether Maryland waterbodies are meeting the "fishing" designated use. Currently Maryland applies 39 ng/g as the tPCB fish tissue listing threshold (MDE 2008, 72-74). MDE has collected fish tissue samples in the Sassafras River embayment in September 2000 (see Table 2). The average concentration for each of the indicator fish species exceeds the tPCB listing threshold, indicating PCB impairment.

Table 2: Fish Tissue tPCB Concentrations in the Sassafras River Embayment (2000)

Species Name	Mean Lipid Content (%)	tPCBs* (ng/g wet weight)	Number of Individual Fish in a Composite	Exceed Maryland Threshold
Channel Catfish	3	261.4	3	Yes
Channel Catfish	5	608.9	4	Yes
Channel Catfish	5	538.7	5	Yes
White Perch	1	185.1	5	Yes
White Perch	2	162.9	5	Yes

Note: *Actual values (i.e., not lipid normalized).

In 2006, sampling surveys were conducted by MDE to measure sediment and water column tPCB concentrations throughout the embayment. Water column samples were also collected in the Sassafras River nontidal watershed in 2008 and 2009. While none of the total averaged water column tPCB concentrations (particulate + dissolved) in the embayment exceed the 30 ng/L Maryland salt water chronic aquatic life tPCB criterion, all of them exceeded the 0.64 ng/L Maryland water column human health tPCB criterion (see Table 3). Figure 4 displays the locations of the Sassafras River monitoring stations. Detailed tPCB results for each measurement are presented in Appendix A.

Table 3: Water Quality Monitoring Stations and Average tPCB Concentrations in the Sassafras River Embayment, Watershed, and Bay Boundary (2006, 2008, 2009)

Station Name	Collection Year	Latitude	Longitude	Average Water Column Concentration (ng/L)			Sediment Concentration (ng/g dry weight)
				Dissolved	Particulate	Total	
XJI1953	2006	39.3650	-75.9115	0.207	0.814	1.021	28.6
XJH2567	2006	39.3749	-76.0546	0.143	0.665	0.808	39.4
XJI2192	2006	39.3677	-75.8466	0.208	0.717	0.925	10.1
XJI2112	2006	39.3686	-75.9799	0.125	0.988	1.113	1.4
XJH3156	2006	39.3863	-76.0738	0.406	0.561	1.078	NA
SA5 0148	2008/2009	39.3780	-75.8075	0.097	0.083	0.179	NA
SA5 0176	2008/2009	39.3777	-75.7665	0.292	0.068	0.360	NA
SWO 0015	2008/2009	39.3481	-75.8413	0.226	0.219	0.445	NA

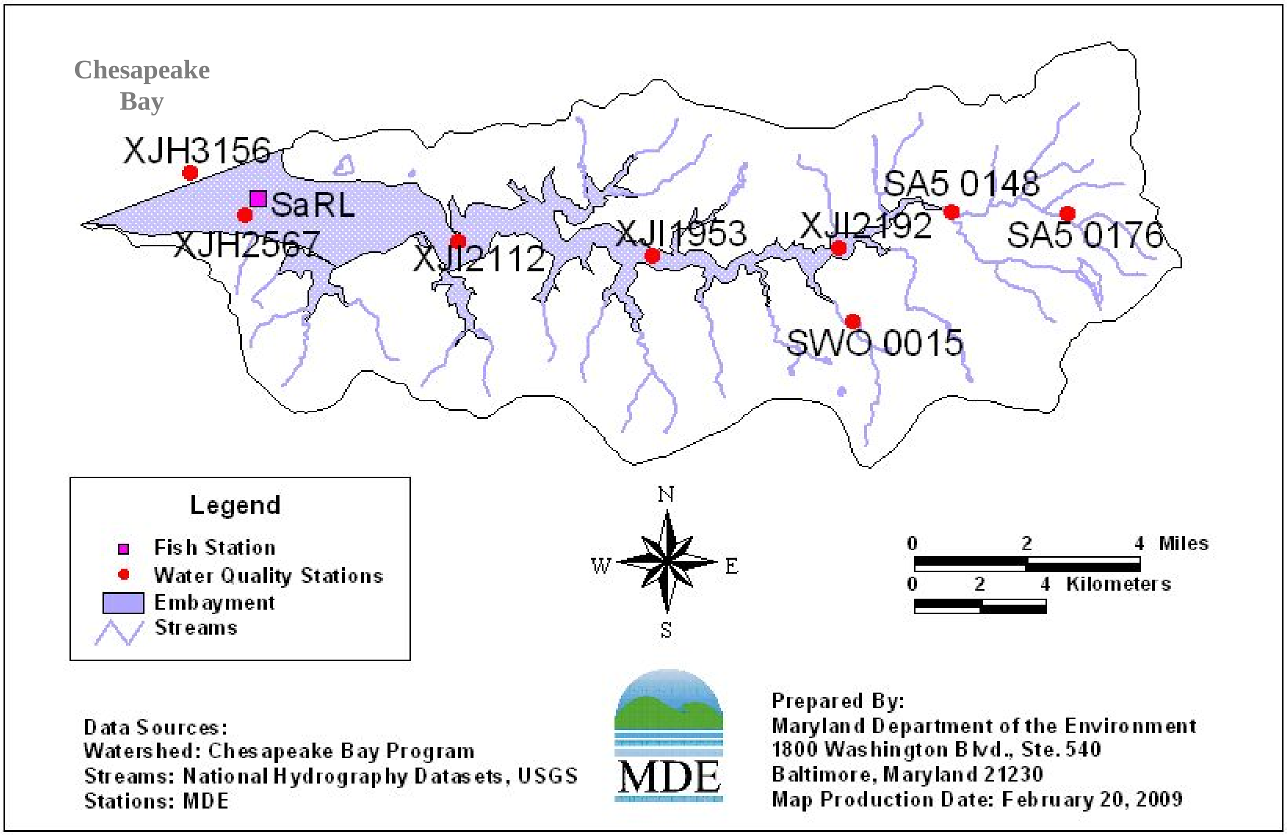

Figure 4: Water Quality Monitoring Stations in Sassafras River

PCB analytical services were provided by the University of Maryland Center for Environmental Science (UMCES). PCB congeners were identified and quantified by high resolution gas chromatography with electron capture detection. UMCES uses a slightly modified version of the PCB congener specific method described in Ashley and Baker (1999), in which the identities and concentrations of each congener in a mixed Aroclor standard (25:18:18 mixture of Aroclors 1232, 1248, and 1262) are determined based on their chromatographic retention times relative to the internal standards (PCB 30 and PCB 204). Based on this method, 86 chromatographic peaks can be quantified (see Appendix I). Some of the peaks contain one PCB congener, while others are comprised of two or more co-eluting congeners. The PCB analysis presented in this document is based on tPCB concentrations that are calculated as the sum of the detected PCB congeners/congener groups representing most common congeners that were historically used in the Aroclor commercial mixtures.

2.3 Source Assessment

PCBs do not occur naturally in the environment. Therefore, unless existing or historical anthropogenic sources are present, their natural background levels are expected to be zero. However, although PCBs are no longer manufactured in the United States, they are still being released to the environment via accidental fires, leaks, or spills from older PCB-containing equipment; potential leaks from hazardous waste sites that contain PCBs; illegal or improper dumping; and disposal of PCB-containing products (e.g., transformers, old fluorescent lighting fixtures, electrical devices or appliances containing PCB capacitors, old microscope oil, and old hydraulic oil) into landfills not designed to handle hazardous waste. Once in the environment, PCBs do not readily break down and tend to cycle between various environmental media such as air, water, and soil. This section provides a detailed description of the existing nonpoint and point sources that have been identified as contributing tPCB loads to the Sassafras River embayment.

2.3.1 Nonpoint Sources

Nonpoint sources do not have a single discharge point, but rather can occur over a part of or the entire length of a waterbody. For the purpose of this TMDL, the following nonpoint sources have been identified: resuspension and diffusion from the bottom sediments, the Chesapeake Bay tidal influence, direct atmospheric deposition to the embayment, and watershed runoff.

Chesapeake Bay (Tidal Influence)

Based on the tPCB concentrations measured at the mouth of Sassafras River and the dispersion coefficient calculated and calibrated from the available salinity data, the Chesapeake Bay tPCB Baseline Load of 5,133.2 g/year is one of the major sources of tPCBs to the Sassafras River embayment (see Table 6, Appendix C, and Appendix D).

The Susquehanna River is the major source of flow and PCBs to the Upper Chesapeake Bay (Ko and Baker 2004). In order to determine the temporal changes in tPCB loads from the Susquehanna River to the Upper Chesapeake Bay, Ko and Baker (2004) measured tPCB concentration downstream of the Susquehanna River and compared their results with those reported by Foster et al. (2000) and Godfrey et al. (1995). According to this analysis, flow normalized tPCB loadings decreased from 37 kg/m^3/year in 1992 to 24 kg/m^3/year in 1998. Based on these results, it is estimated that on average the tPCB concentrations in the Upper Chesapeake Bay are decreasing at a rate of 6.5% per year (Appendix H). This rate was applied in the model to account for the expected temporal changes in tPCB concentrations at the Sassafras River embayment boundary.

Bottom Sediments (Resuspension and Diffusion)

Because PCBs tend to bind to sediments, a large portion of the tPCB loads delivered to the embayment from various sources will quickly end up in the bottom sediments. This accumulation of PCBs can subsequently become a significant source of PCBs to the water column in the embayment. Based on the measured tPCB concentrations in the water column and bottom sediments, the Bottom Sediment tPCB Baseline Load of 4,496.1 g/year is one of the major sources of tPCBs to the Sassafras River embayment (see Table 6, Appendix C, and Appendix D).

Atmospheric Deposition

Based on previous research conducted in the Chesapeake Bay area, a portion of the tPCB load to the Sassafras River embayment can be attributed to atmospheric deposition. That being said, it should be pointed out that overall a net loss of tPCB occurs due to volatilization of the dissolved PCBs in the water column to the atmosphere (Totten et al. 2006). The TMDL analysis accounts for both atmospheric deposition and volatilization. The observed annual atmospheric tPCB loading to the entire surface of the Chesapeake Bay is approximately 38 ± 7 kg/year (Leister and Baker 1994). Based on the Chesapeake Bay surface area of 1.15×10^{10} m^2 and Sassafras River embayment surface area of 3.568×10^7 m^2, the estimated direct tPCB atmospheric deposition to the surface of the Sassafras River embayment is:

$$\frac{38}{(1.15\times10^{10})}\times(3.568\times10^{7})\approx\mathbf{117.9\ g/year}\qquad\text{(Calculation 1)}$$

Using the same method, the atmospheric loading to the entire land surface of the watershed (2.163×10^{8} m^2) is:

$$\frac{38}{(1.15\times10^{10})}\times(2.163\times10^{8})\approx\mathbf{714.7\ g/year}\qquad\text{(Calculation 2)}$$

However, according to Totten et al. (2006) not all of the atmospheric deposition to the terrestrial part of the watershed is expected to be delivered to the embayment. Considering that the PCB pass-through efficiency, estimated by Totten et al. for the Delaware River watershed, is about 1%, the atmospheric tPCB loading to the Sassafras River embayment from the watershed is approximately 7.1 g/year. The watershed runoff calculation below accounts for this load due to atmospheric deposition. Compared to other sources (see Table 6), atmospheric deposition constitutes a relatively small portion of the tPCB load delivered to the Sassafras River embayment.

Watershed Runoff

The Total Watershed tPCB Baseline Load of the Sassafras River was estimated by multiplying the mean ambient water column tPCB concentration (0.33 ng/L) observed at the nontidal watershed stations by the average watershed stream flow.

Using the 20-year monthly mean flows at the United States Geological Survey (USGS) station located at New Castle County, Delaware (USGS 01483200) and Kent County, Maryland (USGS 01493500) (see Figure 5), and the ratio of the Sassafras River watershed area to the USGS station drainage area, the Sassafras River watershed average stream flow was estimated to be equal to 2.7 m^3/s (95 cfs). The average stream flow was then distributed between Delaware (0.25 m^3/s) and Maryland (2.45 m^3/s), according to their respective areas, and used to calculate the watershed tPCB baseline loads (Calculation 3).

Delaware Load = 0.25 m^3/s × 0.33 ng/L × 1,000 L/m^3 × 10^{-9} g/ng × 60 minutes/hour × 60 seconds/minute × 24 hours/day × 365 days/year = **2.6 g/year**

(Calculation 3)

Maryland Load = 2.45 m^3/s × 0.33 ng/L × 1,000 L/m^3 × 10^{-9} g/ng × 60 minutes/hour × 60 seconds/minute × 24 hours/day × 365 days/year = **25.5 g/year**

While the Upstream Delaware Baseline Load is presented as a single upstream load, the Maryland Watershed Baseline Load is further subdivided into:

- *Point Source Loads*: National Pollutant Discharge Elimination System (NPDES) Regulated Stormwater Baseline Load and
- *Nonpoint Source Loads*: Maryland Watershed Nonpoint Source Baseline Load (see Table 4 and Table 6).

Table 4: Breakdown of the Total Watershed tPCB Baseline Load

Source	Baseline (g/year)
Maryland Watershed Nonpoint Sources	25.0
NPDES Regulated Stormwater	0.5
Maryland Watershed Baseline Loads	*25.5*
Delaware Upstream Baseline Loads	*2.6*
Total Watershed Baseline Load	**28.1**

About 7.1 g/year of the Sassafras River Total Watershed tPCB Baseline Load is attributed to atmospheric deposition to the entire land surface of the watershed. The watershed runoff calculation accounts for this load due to atmospheric deposition. The remaining load is due to unidentified sources of PCB contamination from historical uses and releases. However, when compared with the Chesapeake Bay and Bottom Sediment Baseline Loads, the Total Watershed tPCB Baseline Load is insignificant and even its complete elimination would not result in noticeable decrease in the tPCB concentrations in the Sassafras River embayment. Based on the information gathered from the US EPA's Superfund Database (US EPA 2007a) and MDE's Environmental Restoration and Redevelopment Program (MDE 2007a), no known contaminated sites have been identified throughout the watershed.

2.3.2 Point Sources

The Department applies US EPA's requirement that "stormwater discharges that are regulated under Phase I or Phase II of the NPDES storm water program are point sources that must be included in the WLA portion of a TMDL" (US EPA 2002). Other point sources in the Sassafras River watershed include loads from wastewater treatment plants (WWTPs). While, for the purpose of this TMDL, the WWTP Baseline Loads have been estimated, they have been considered *de minimis* (see Appendix J). This section provides detailed explanation about how the point source baseline loads have been estimated.

Waste Water Treatment Plants

There are two WWTPs located in the watershed: Betterton WWTP (MD0020575), which discharges directly to the Sassafras River embayment, and Galena WWTP (MD0020605), which discharges to the watershed (see Figure 5). The Betterton WWTP was monitored for the discharge of tPCBs for the purposes of this analysis. As no PCB data for Galena WWTP have been identified, the tPCB concentration for this facility was estimated as the median tPCB concentration of 31 samples from 13 WWTPs monitored by MDE in the Chesapeake Bay watershed. The baseline tPCB loads were based on the permit design flow for the Betterton WWTP and Galena WWTP and the appropriate tPCB concentrations of 7.081 ng/L and 0.906 ng/L, respectively. Thus, the estimated tPCB baseline loads for the Betterton WWTP and Galena WWTP are 1.96 and 0.08 g/year, respectively (see Table 5), which for the purpose of this analysis are treated as separate model inputs.

Table 5: WWTP tPCB Baseline Loads

WWTP	tPCB Concentration (ng/L)	Design Flow (MGD)	Baseline Load (g/year)
Betterton WWTP	7.081	0.2	1.96
Galena WWTP*	0.906	0.06	0.08

Note: * It should be noted that the Galena WWTP is due for an expansion. However, since the permit has not been yet approved, the current design flow has been used in the TMDL analysis. As demonstrated in Appendix J, a possible future increase in both of the WWTP loads (e.g., due to potential future development or expansion of plant capacity) is not expected to have any significant impact on meeting the tPCB water quality TMDL endpoints; a 10-fold increase in WWTP load (up to 1.8% of the TMDL) is expected to increase the time it takes to reach the TMDL endpoints by 0.86% or 120 days.

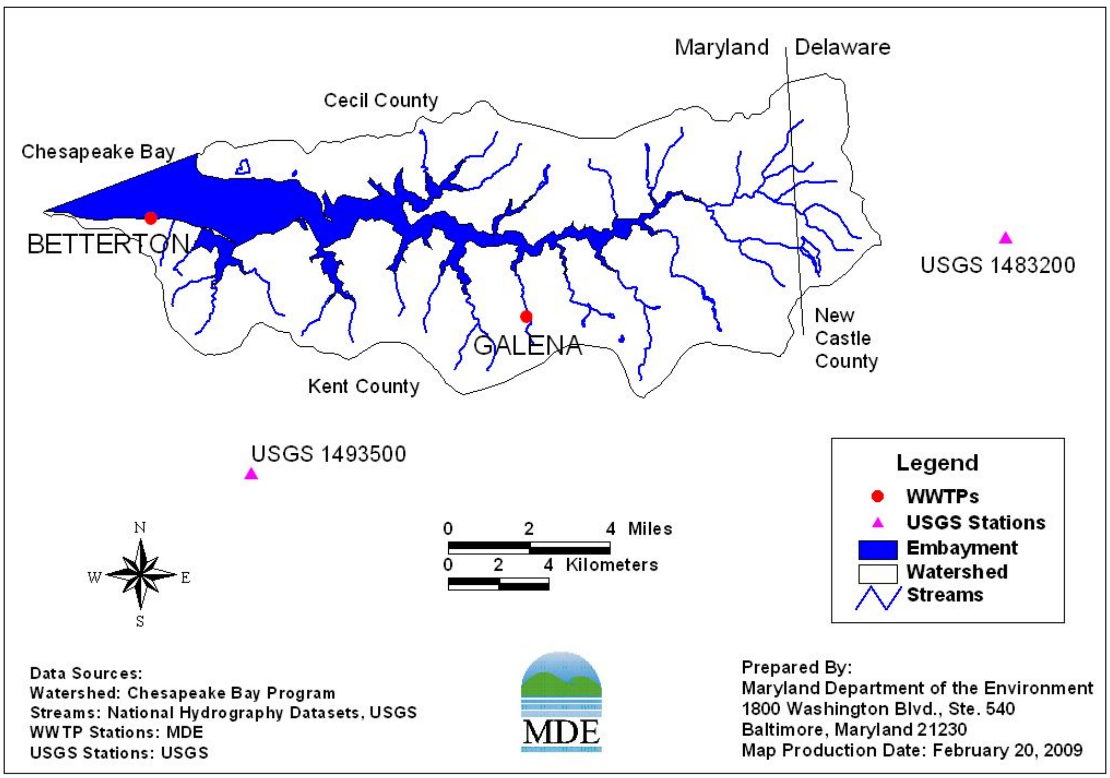

Figure 5: Locations of the WWTPs in the Sassafras River Watershed and the USGS Stations Used for Flow Estimation

NPDES Regulated Stormwater

MDE estimates pollutant loadings from NPDES regulated stormwater areas based on urban land use classification within a watershed. This methodology assumes certain relationships between specific

Maryland Department of Planning (MDP) urban land use classification (as modified by MDE; for further details please see MDE 2009b) and various categories of NPDES regulated stormwater permits, whereby the identification of the existing permits determines what portion of the urban land use is considered regulated. Based on this information, the Chesapeake Bay Program Phase 5 (CBP P5) land use applied in this TMDL analysis can be refined into more detailed classifications associated with specific categories of NPDES regulated stormwater permits, which can subsequently be used to estimate the NPDES Regulated Stormwater Baseline Load.

The Maryland portion of the Sassafras River watershed is located in both Cecil and Kent counties. The NPDES stormwater permits within the Sassafras watershed include: (i) the area covered under Cecil County's Phase II jurisdictional Municipal Separate Storm Sewer System (MS4) permit, and (ii) state and federal general MS4s, industrial, and construction permits in both counties, collectively termed "Other NPDES Regulated Stormwater."

Applying MDE's methodology, the areas regulated by the NPDES stormwater permits are represented by the CBP P5 urban land use associated with (i) MDP residential, commercial, and open urban land use classifications within Cecil County as well as (ii) MDP industrial and institutional land use classifications within both Counties. However, since the MDP industrial and institutional land use areas within Kent County comprise a relatively small percentage of the total Kent County watershed area (i.e., 25 acres or 0.08%), it was determined that the characterization of the associated tPCB loads was not practical. Consequently, the MDP industrial and institutional land use loadings within Kent County have not been considered as part of the regulated stormwater load, and instead are included as part of the overall watershed nonpoint source load. Therefore, for the purposes of this TMDL analysis, the proportion of the CBP P5 urban land use area that is considered to be regulated includes: MDP residential, commercial, open urban, industrial, and institutional land use classifications within Cecil County (MDE 2009b). The resulting NPDES Regulated Stormwater tPCB Baseline Load of 0.5 g/year (see Table 6) was estimated by multiplying (i) the proportion of the CBP P5 urban land use area that is considered regulated out of the total watershed land use area (1.8%) by (ii) the Total Maryland Watershed Baseline Load (25.5 g/year). A list of all the NPDES regulated stormwater permits within the Cecil County portion of the Sassafras River watershed that could potentially convey tPCB loads to the Sassafras River embayment has been compiled within Appendix G.

2.3.3 Summary

In summary, resuspension and diffusion from the bottom sediments and the Chesapeake Bay tidal influence are the two major tPCB sources to the Sassafras River embayment. The remaining nonpoint sources (i.e., watershed runoff and atmospheric deposition to the embayment) and point sources (i.e., WWTPs and NPDES regulated stormwater) comprise a relatively small portion of the Total Baseline Load. Table 6 summarizes the estimated Total tPCB Baseline Load from all identified sources.

Table 6: Summary of the Total tPCB Baseline Load

Source	Baseline (g/year)	Baseline (%)
Bottom Sediment (Resuspension and Diffusion)	4,496.1	45.99
Chesapeake Bay (Tidal Influence)	5,133.2	52.50
Direct Atmospheric Deposition (to the Surface of the Embayment)	117.9	1.21
Maryland Watershed Nonpoint Sources*	25.0	0.26
Delaware Upstream	2.6	0.03
Nonpoint Sources	***9,774.8***	**99.97**
WWTPs*	2.0	0.02
NPDES Regulated Stormwater*	0.5	0.01
Point Sources*	***2.5***	**0.03**
Total	**9,777.3**	**100**

Note: * These sources were characterized only for the Maryland portion of the watershed.

3.0 TARGETED WATER COLUMN AND SEDIMENT GOALS

The overall objective of the tPCB TMDL established in this document is to ensure that the "fishing" designated use in the Sassafras River embayment is protected. As described in Section 2.2, MDE evaluates PCB water quality conditions with the use of either the tPCB fish tissue listing threshold (39 ng/g) or the Maryland water column human health tPCB criterion (0.64 ng/L). In order to determine which one of these targets is more environmentally protective, the tPCB fish tissue listing threshold was converted to a corresponding tPCB water column concentration (see Equation 1 and Calculation 4). This was done with the use of a site-specific Adjusted Total Bioaccumulation Factor (Adj-tBAF) of 343,114 L/kg following the method of the Tidal Potomac River PCB TMDLs (see Appendix B for the derivation of the Adj-tBAF) (MDE 2007b).

$$\text{Water Column Target} = \text{Fish Tissue Concentration} \div \text{Adj-tBAF} \times \text{Unit} \qquad \text{(Equation 1)}$$

$$\text{Water Column Target} = 39\ \text{ng/g} \div 343{,}114\ \text{L/kg} \times \frac{1{,}000\ \text{g}}{1\ \text{kg}} = 0.11\ \text{ng/L} < 0.64\ \text{ng/L} \qquad \text{(Calculation 4)}$$

Based on this analysis, the water column tPCB target of 0.11 ng/L derived from the tPCB fish tissue listing threshold is more environmentally protective than the Maryland water column human health tPCB criterion of 0.64 ng/L, and therefore will be applied in this analysis as the site-specific tPCB water column TMDL endpoint.

Similarly, in order to establish whether levels of PCBs in the sediment are protective of the "fishing" designated use, a site-specific tPCB sediment target for the Sassafras River embayment was derived based on the tPCB fish tissue listing threshold (see Equation 2 and Calculation 5). This was done with the use of a site-specific adjusted sediment bioaccumulation factor (Adj-SediBAF) of 16.7 (unitless) following the method of the Tidal Potomac River PCB TMDLs (see Appendix B for the derivation of the Adj-SediBAF) (MDE 2007b).

$$\text{Sediment Target} = \frac{\text{Fish Tissue Threshold}}{\text{Adj SediBAF}} \qquad \text{(Equation 2)}$$

$$\text{Sediment Target} = \frac{39\ \text{ng/g}}{16.7} = 2.34\ \text{ng/g} \qquad \text{(Calculation 5)}$$

Both the site-specific tPCB water column and sediment targets will be used as TMDL endpoints and the more restrictive one will determine the actual TMDL (Section 4.2).

4.0 TOTAL MAXIMUM DAILY LOADS AND LOAD ALLOCATION

4.1 Overview

A TMDL is the total amount of impairing substance that a waterbody can receive and still meet WQSs. The TMDL may be expressed as a mass per unit time, toxicity, or other appropriate measure and should be presented in terms of wasteload allocations (WLAs), load allocations (LAs), and either implicitly or explicitly margin of safety (MOS) (CFR 2007):

$$TMDL = WLAs + LAs + MOS \qquad \text{(Equation 3)}$$

This section describes how the tPCB TMDL and the corresponding LAs and WLAs have been developed for the Sassafras River embayment. The analysis framework for simulating tPCB concentrations is described in Section 4.2, Section 4.3 addresses critical conditions and seasonality, and Section 4.4 presents the allocation of loads between point and nonpoint sources. The MOS is discussed in Section 4.5. Finally, the TMDL is summarized in Section 4.6.

4.2 Analysis Framework

A tidally averaged multi-segment one-dimensional transport model was applied to simulate the tPCB dynamic interactions between the water column and bottom sediments within the Sassafras River embayment and the Chesapeake Bay. The embayment was divided into 8 segments and the watershed into 14 subwatersheds (see Figure 6). In general, tidal waters are exchanged through their connecting boundaries. Within the Sassafras River embayment the dominant processes affecting the transport of PCBs throughout the water column include: the dispersion induced by tide and concentration gradient between the Bay and the embayment, fresh water discharge, the atmospheric exchange due to volatilization and deposition, and the exchange with the bottom sediments (through diffusion, resuspension, and settling). Burial to the deeper inactive layers and the exchange with the water column (through diffusion, resuspension, and settling) are the dominant processes affecting the transport of PCBs in the bottom sediments. Technical description of the model is presented in Appendix C and Appendix D.

The average observed tPCB concentrations in each segment were used as the model inputs representing baseline (2006) conditions. In instances where PCB data were not available for a specific segment, the average concentration from the adjacent segments was used. Based on the available literature, the TMDL methodology assumes that on average the tPCB concentrations at the Sassafras open boundary with the Bay are decreasing at a rate of 6.5% per year (see Section 2.3.1 and Appendix H). All other inputs (i.e., fresh water inputs, dispersion coefficients, sediment and water column exchange rates, atmosphere exchange rates, and burial rates) were kept constant.

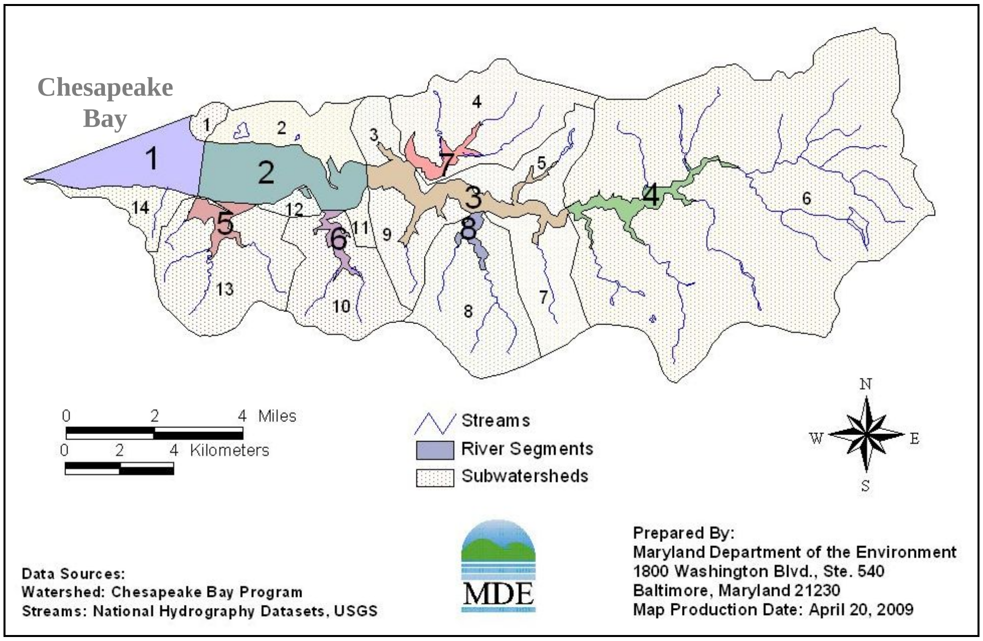

Figure 6: Subwatersheds and River Segments of the Sassafras River Watershed

The model was run for 40,000 days to predict the time needed for the water column tPCB concentration to meet the site-specific tPCB water column TMDL endpoint. The results indicated that when the site-specific water column TMDL endpoint (0.11 ng/L) was met, the site-specific sediment TMDL endpoint (2.34 ng/g) was met as well. Figure 7 and Figure 8 show the simulated results: after 13,996 days (about 38 years) the tPCB water column concentration reached 0.11 ng/L (see Figure 7), at which time the sediment tPCB concentration was equal to 2.29 ng/g (see Figure 8).

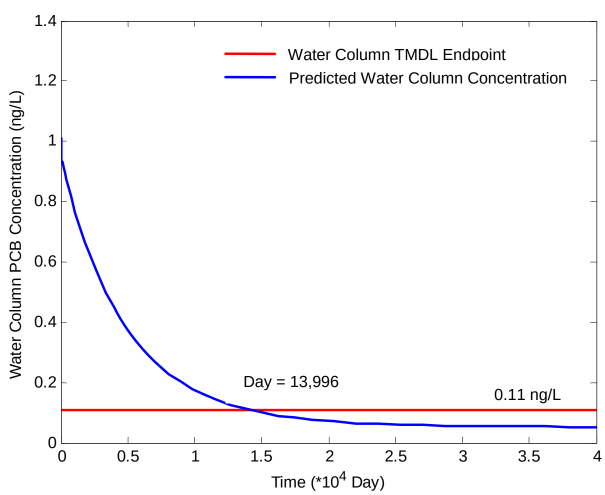

Figure 7: Changes in Water Column tPCB Concentration with Time

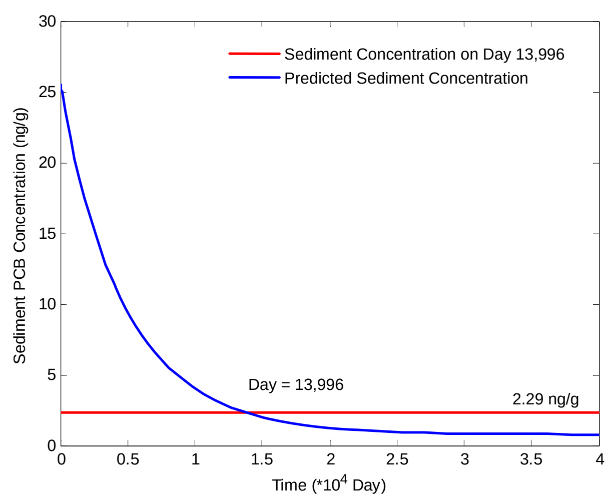

Figure 8: Changes in Sediment tPCB Concentration with Time

As presented in Table 6, resuspension and diffusion from the bottom sediments as well as the Chesapeake Bay tidal influence are the two primary sources of tPCB baseline loads resulting in the PCB impairment in the Sassafras River embayment. Attainment of the site-specific tPCB water quality TMDL endpoints will only be possible with significant reduction in these primary loadings (see Table 7), which is expected to take place over time as the Upper Chesapeake Bay concentrations continue to decline resulting also in natural attenuation of tPCB levels in the legacy sediments (i.e., the covering of contaminated sediments with newer, less contaminated materials, flushing of sediments during periods of high stream flow, and biodegradation). Assuming that the tPCB concentrations in the Upper Chesapeake Bay will continue to decline, at or above the current rate (see Section 2.3.1 and Appendix H), no additional tPCB reductions will be necessary to meet the “fishing” designated use in the Sassafras River embayment.

4.3 Critical Conditions and Seasonality

Federal regulations require TMDL determinations to take into account the impact of critical conditions and seasonality on water quality (CFR 2007). The intent of this requirement is to ensure that the water quality is protected during the most vulnerable times.

Because all the water column tPCB samples were collected within the same month (Appendix A), no temporal trends could be established. However, since tPCB levels in fish become elevated due to long-term exposure, rather than temporary spikes in water column tPCB concentration, it has been determined that the selection of the average tPCB concentrations within each model segments as representing the baseline conditions adequately considers the impact of seasonal variations and critical conditions on the “fishing” designated use in the Sassafras River embayment. Furthermore, the site-specific tPCB water column TMDL endpoint used to develop this TMDL is lower than the Maryland fresh and salt water chronic aquatic life tPCB criteria protective of fish and wildlife as well as the Maryland water column human health tPCB criterion protective of human health associated with consumption of PCB contaminated fish.

Selection of the average tPCB concentrations to represent the baseline model conditions will not affect the TMDL, which was established to meet the site-specific tPCB water column and sediment TMDL endpoints at all times. However, the length of time required to reach the TMDL endpoints will depend on the selection of the baseline conditions. Although it is not feasible to conduct uncertainty analysis for the multi-segment model used to develop this TMDL, based on the similar TMDL studies for the Northeast River, Bohemia River, and Corsica River, the time durations required to reach the tPCB TMDL endpoints is expected to increase no more than 15% when the upper 95% confidence interval (vs. the mean) is used as the baseline condition (MDE 2009a).

4.4 TMDL Allocations

All TMDLs need to be presented in terms of WLAs for point sources and LAs for nonpoint source loads generated within the assessment unit, and if applicable LAs for the natural background, tributary, and adjacent segment loads (CFR 2007). The State reserves the right to revise these allocations provided the revisions are consistent with achieving WQSs. This section summarizes the tPCB TMDL allocations established to meet the “fishing” designated use in the Sassafras River embayment.

4.4.1 Point Sources

<u>**Waste Water Treatment Plants**</u>

Two WWTPs were identified in the Sassafras River watershed: Betterton WWTP (MD0020575) and Galena WWTP (MD0020605). The estimated WWTP tPCB Baseline Loads are 1.96 and 0.08 g/year, respectively (see Table 6). For more information on methods used to calculate these loads, see Section 2.3.2. At 0.18% of the TMDL, the Sassafras River cumulative WWTP Baseline Loads were considered *de minimis*, therefore no appreciable environmental benefit would be gained by reducing this load (see Appendix J). The elevated tPCB concentrations in wastewater are believed to be primarily due to external sources (e.g., source water, atmospheric deposition, and stormwater runoff) infiltrating the waste water collection system through broken sewer lines and connections. There are currently no effluent PCB limits established in the discharge permits for WWTPs. The sensitivity analysis provided in this document (Appendix J) suggests that there is no "reasonable potential" for PCBs to exceed water quality even at 100 times the current WWTP loadings. Inclusion of a WLA in this document does not reflect any determination to impose an effluent limit.

<u>**NPDES Regulated Stormwater**</u>

Per US EPA requirements, "stormwater discharges that are regulated under Phase I or Phase II of the NPDES stormwater program are point sources that must be included in the WLA portion of a TMDL" (US EPA 2002). Phase I and II permits can include the following types of discharges:

- Small, medium, and large MS4s – these can be owned by local jurisdictions, municipalities, and state and federal entities (e.g., departments of transportation, hospitals, military bases),
- Industrial facilities permitted for stormwater discharges, and
- Small and large construction sites.

US EPA recognizes that available data and information are usually not detailed enough to determine WLAs for NPDES regulated stormwater discharges on an outfall-specific basis (US EPA 2002). Therefore, NPDES regulated stormwater allocations to the Sassafras River embayment will be expressed as a single WLA. Upon approval of the TMDL, "NPDES-regulated municipal stormwater and small construction storm water discharges effluent limits should be expressed as BMPs or other similar requirements, rather than as numeric effluent limits" (US EPA 2002).

The NPDES Regulated Stormwater WLA constitutes a proportional allocation of the Watershed tPCB Baseline Load to the regulated portion of the CBP P5 urban land use within Cecil County (see Section 2.3.2). This NPDES Regulated Stormwater WLA may include any or all of the NPDES stormwater discharges listed above within the Cecil County portion of the watershed (see Appendix G for a specific list of stormwater permits within the Cecil County portion of the Sassafras River watershed). A WLA for NPDES regulated stormwater within the Kent County portion of the watershed has not been characterized as part of this analysis since the majority of the urban land use within the Kent County portion of the watershed constitutes unregulated stormwater runoff, and the tPCB loadings from the portion of the CBP P5 urban land use area that is considered regulated (0.08%) is relatively insignificant (see Section 2.3.2). Therefore, any tPCB loads associated with the regulated portion of the CBP P5 urban land use within the Kent County portion of the watershed are included as part of the Watershed Nonpoint Source LA. As stormwater assessment and/or other program monitoring efforts result in a more refined source assessment, MDE reserves the right to revise the current NPDES Regulated Stormwater WLA provided the revisions are consistent with achieving WQSs.

The NPDES Regulated Stormwater tPCB Baseline Load to the Sassafras River embayment was considered to be insignificant relative to the resuspension and diffusion from the bottom sediments and Chesapeake Bay tidal influence. Therefore, no reductions were applied to this source category and the NPDES Regulated Stormwater tPCB WLA was set as equivalent to the Baseline Load (see Table 7). For more information on methods used to calculate the NPDES Regulated Stormwater tPCB Baseline Loads, please see Section 2.3.2.

4.4.2 Nonpoint Sources

Load allocations have been assigned to the following nonpoint sources: bottom sediment, the Chesapeake Bay tidal influence, direct atmospheric deposition to the surface of the embayment, Maryland watershed nonpoint sources, and Delaware upstream sources. PCB loadings from the bottom sediments and the Chesapeake Bay tidal influence are the most significant sources of PCBs to the Sassafras River embayment and as such are the only ones requiring reductions in order to meet the "fishing" designated use in the Sassafras River embayment. These reductions are expected to take place over time as the Upper Chesapeake Bay concentrations continue to decline resulting also in natural attenuation of tPCB levels in the legacy sediments. Assuming that the tPCB concentrations in the Upper Chesapeake Bay will continue to decline at or above the current rate, no additional tPCB load reductions should be required for the remaining nonpoint sources. The remaining LAs were set as equivalent to the corresponding baseline loads (see Table 7).

4.5 Margin of Safety

All TMDLs must include a MOS to account for the lack of knowledge and the many uncertainties in the understanding and simulation of water quality parameters in natural systems. The MOS is intended to account for such uncertainties in a manner that is conservative from the standpoint of environmental protection. Considering the uncertainty surrounding the estimated rate at which tPCB concentrations are decreasing in the Upper Bay region, MDE decided to apply a 10% MOS in order to provide an adequate and environmentally protective TMDL (see Table 7).

4.6 Summary of Total Maximum Daily Load Allocations

Table 7 summarizes the tPCB TMDL allocations for the Sassafras River embayment as well as the corresponding baseline loads, the maximum daily load (MDL) (Appendix F), and the associated load reductions.

**Table 7: Summary of tPCB Baseline Loads,
TMDL Allocations, MDL, and Associated Percent Reductions**

Source	Baseline Load (g/year)	TMDL (g/year)	Load Reduction (%)	MDL[a] (g/day)
Bottom Sediment (Resuspension and Diffusion)	4,496.1	463.2	89.7	1.738
Chesapeake Bay (Tidal Influence)	5,133.2	390.1	92.4	1.464
Direct Atmospheric Deposition (to the Surface of the Embayment)	117.9	117.9	0.0	0.442
Maryland Watershed Nonpoint Sources*	25.0	25.0	0.0	0.094
Delaware Upstream	2.6	2.6	0.0	0.010
Nonpoint Sources/Load Allocations	***9,774.8***	***998.8***	***89.8***	***3.748***
WWTP*△	2.0	2.0	0.0	0.017
NPDES Regulated Stormwater*	0.5	0.5	0.0	0.002
Point Sources/Waste Load Allocations*	***2.5***	***2.5***	***0.0***	***0.019***
MOS	**-**	***111.3***	**-**	***0.419***
Total	**9,777.3**	**1,112.6**	**88.6**	**4.19**

Notes: *These sources were characterized only for the Maryland portion of the watershed.

△WWTP Baseline Loads were considered to be *de minimis.*

[a] For details see Appendix F.

5.0 ASSURANCE OF IMPLEMENTATION

As discussed in the previous sections, resuspension and diffusion from the bottom sediments and the Chesapeake Bay tidal influence have been identified as the two major sources of tPCBs to the Sassafras River embayment. As described in Section 2.3.1, it has been estimated that on average the tPCB concentrations in the Upper Chesapeake Bay are decreasing at a rate of 6.5% per year (see Section 2.3.1 and Appendix H). Given this rate of decline, the tPCB levels in the Sassafras River embayment are expected to decline over time due to natural attenuation, such as the burial of contaminated sediments with newer, less contaminated materials, flushing of sediments during periods of high stream flow, and biodegradation.

Aside from the processes of natural attenuation, there are two alternatives that can assist in reducing the tPCB concentrations in the water column so as to meet WQSs. First, the physical removal of the PCB-contaminated sediments (i.e., dredging) would minimize one of the primary sources of tPCB to the water column. Second, a reduction in the Chesapeake Bay tPCB loads would greatly accelerate the process of attenuation.

In this particular situation, dredging is the least desirable alternative because of its potential biological destruction. It damages the habitat of benthic macroinvertebrates and may directly kill some organisms. The process of stirring up suspended sediments during dredging may damage the gills and/or sensory organs of benthic macroinvertebrates and fish. Suspended sediments can also affect the prey gathering ability of sight-feeding fish. In addition, the resuspension of contaminated sediments provides organisms with additional exposure to PCBs.

In the case of the Sassafras River Oligohaline segment natural attenuation is a better implementation method because it involves less habitat disturbance/destruction and is less costly. Discovering and remediating any existing PCB land sources throughout the Upper Chesapeake Bay watershed via future TMDL development and implementation efforts will further help to meet water quality goals in the Sassafras River embayment. MDE's Water Quality Standards Section will continue to monitor PCB levels in Maryland fish. This information will be used to evaluate the PCB impairment in the Sassafras River embayment on an ongoing basis.

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Appendix A. List of Individual tPCB Measurements

The Sassafras River polychlorinated biphenyl (PCB) data were collected in 2000, 2006, 2008, and 2009. The observed total PCB (tPCB) concentrations in fish tissue, sediment, and water column are listed in Table A-1, Table A-2, and Table A-3.

Table A-1: Fish Tissue tPCB Concentrations

Station	Fish Species	Date	tPCB* (ng/g – wet weight)
SaRL	Channel Catfish	9/12/2000	261.4
SaRL	Channel Catfish	9/12/2000	608.9
SaRL	Channel Catfish	9/12/2000	538.7
SaRL	White Perch	9/12/2000	185.1
SaRL	White Perch	9/12/2000	162.9

Note: *Actual values (i.e., not lipid normalized).

Table A-2: Sediment tPCB Concentrations

Station	Date	tPCB (ng/g –wet weight)
XJI1953	11/28/2006	28.6
XJH2567	11/28/2006	39.4
XJI2192	11/28/2006	10.1
XJI2112	11/28/2006	1.4

Table A-3: Water Column tPCB Concentrations

Station	Date	Particulate (ng/L)	Dissolved (ng/L)	Total (ng/L)
XJI1953	11/28/2006	0.470	0.364	0.834
XJI1953	12/05/2006	1.157	0.051	1.208
XJH2567	11/29/2006	0.936	0.200	1.137
XJH2567	12/12/2006	0.393	0.085	0.479
XJI2192	11/28/2006	0.647	0.504	1.151
XJI2192	12/05/2006	1.185	0.066	1.251
XJI2192	12/12/2006	0.319	0.053	0.372
XJI2112	11/28/2006	0.717	0.323	1.040
XJI2112	12/05/2006	1.908	0.002	1.910
XJI2112	12/12/2006	0.339	0.051	0.390
XJH3156	11/28/2006	0.339	0.076	0.414
XJH3156	12/05/2006	1.465	1.357	2.822
XJH3156	12/05/2006	0.447	0.000	0.447
XJH3156	12/12/2006	0.439	0.192	0.630
SA5 0148	12/2008	0.070	0.083	0.153
SA5 0148	3/2009	0.096	0.110	0.206
SW0 0015	12/2008	0.295	0.186	0.481
SW0 0015	3/2009	0.143	0.266	0.409
SA5 0176	12/2008	0.050	0.040	0.090
SA5 0176	3/2009	0.085	0.545	0.630

Appendix B. Derivation of Adj-tBAFs and Adj-SediBAFs

This appendix describes how the site-specific Adjusted Total Bioaccumulation Factor (Adj-tBAF) and Adjusted Sediment Bioaccumulation Factor (Adj-SediBAF) were derived. These values are then used to convert the total Polychlorinated Biphenyl (tPCB) fish tissue listing threshold to the corresponding site-specific tPCB water column and sediment concentrations protective of the "fishing" designated use in the Sassafras River embayment. These methods are based on the approach used in the development of the Tidal Potomac River PCB TMDLs (MDE 2007b).

I. Data Description

The site-specific observation-based Adj-tBAFs and Adj-SediBAFs were calculated based on the available tPCB concentrations for the various fish species and accompanying water column and sediment samples collected in the Sassafras River embayment. Each fish species was assigned a trophic level and home range (Table B-1). The Adj-tBAFs and Adj-SediBAFs were calculated based on the geometric mean tPCB concentrations of all the water quality samples within each species' home range.

Table B-1: Trophic Levels and Home Ranges of Sampled Fish Species

Common Name	Scientific Name	Trophic Level	Home Range (Mile)
Channel Catfish	*Ictalurus punctatus*	Benthivore-generalist	5
White Perch	*Morone americana*	Predator	10

II. Total BAFs

The Total Bioaccumulation Factors (BAFs) for each fish sample (individual or composited) was calculated using Equation B1 (US EPA 2003):

$$\text{Total BAF} = \frac{[\text{tPCB}]_{\text{fish}}}{[\text{tPCB}]_{\text{Water}}} \quad \text{(B1)}$$

Where: $[\text{tPCB}]_{\text{fish}}$ = fish tissue tPCB concentration (ng/kg – wet weight)
$[\text{tPCB}]_{\text{water}}$ = geometric mean of water column tPCB concentrations within fish species' home range (ng/L).

Next, for fish species with more than one sample, a single Total BAF was calculated as the median of the applicable total BAFs.

III. Baseline BAFs

As the Total BAFs vary depending on the food habits and lipid concentration of each fish species and on the freely-dissolved tPCB concentrations in ambient water, it was determined that for the purpose of the TMDL analysis, Adj-tBAFs should be used. To calculate the site-specific Adj-tBAFs, first Baseline BAFs were calculated as recommended by US EPA (2000):

$$\text{Baseline BAF} = \frac{[\text{tPCB}]_{\text{fish}} \div \%\text{Lipid}}{[\text{tPCB}]_{\text{water}} \times \% fd} \quad \text{(B2)}$$

Where: $[\text{tPCB}]_{\text{fish}}$ = fish tissue tPCB concentration (ng/kg – wet weight)

$[tPCB]_{water}$ = geometric mean of water column tPCB concentrations within fish species' home range (ng/L)
%lipid = fraction of fish tissue that is lipid
%fd = fraction of tPCB concentration in ambient water that is freely-dissolved.

Again, the above calculation was done for each fish sample (individual or composited). Next, for fish species with more than one sample, a single Baseline BAF was calculated as the median of the applicable Baseline BAFs.

The freely-dissolved tPCBs are those not associated with dissolved organic carbon (DOC) or particulate organic carbon (POC). The %fd can be calculated as (US EPA 2003):

$$\%fd = \frac{1}{1 + POC \times K_{ow} + DOC \times 0.08 \times K_{ow}} \tag{B3}$$

Where: K_{ow} = PCB octanol-water partition coefficient
POC = particulate organic carbon concentrations in the water column
DOC = dissolved organic carbon concentrations in the water column.

The K_{ow} of different PCB congeners vary widely. Therefore, the %fd value was first calculated for each PCB homolog (Homolog %fd) using the midpoint of the homolog's K_{ow} range (Table B-2; MDE 2007b page D-10).

Table B-2: K_{ow} Values of PCB Homologs

Homolog	Midpoint K_{ow}
Mono+Di	47,315
Tri	266,073
Tetra	1,011,579
Penta	3,349,654
Hexa	5,370,318
Hepta	17,179,084
Octa	39,810,717
Nona	82,224,265
Deca	151,356,125

The tPCB freely dissolved fraction (tPCB %fd) for each water sample within fish species' home range was derived as described in Equation B4 and multiplied by the appropriate water column tPCB concentration. The geometric mean of all of the results within fish species' home range was then used in Equation B2 (in place of $[tPCB]_{water} \times$ %fd) to calculate the Baseline BAFs for each fish sample.

$$tPCB\ \%fd = \frac{\sum (Homolog\ \%fd \times Homolog\ Concentration)}{[tPCB]_{water}} \tag{B4}$$

The freely dissolved tPCB, POC, and DOC concentrations for each water sample are listed in Table B-3.

Table B-3: Freely Dissolved tPCB, POC, and DOC Concentrations

Station	Sample Date	Freely-Dissolved tPCB (ng/L)	POC (kg/L)*	DOC (kg/L)*
XJH2567	28-Nov-06	2.1E-01	1.28E-06	3.40E-06
XJH3156	28-Nov-06	1.4E-01	1.28E-06	3.40E-06
XJI2112	05-Dec-06	2.2E-01	1.28E-06	3.40E-06
XJI2112	12-Dec-06	1.1E-01	1.28E-06	3.40E-06
XJI2112	28-Nov-06	9.1E-02	1.28E-06	3.40E-06
CB1	08-Mar-93	1.2E+00	2.05E-06	1.81E-06
CB1	12-Apr-93	1.5E+00	1.29E-06	2.34E-06
CB1	01-Jun-93	7.7E-01	1.87E-06	2.19E-06
CB1	20-Sep-93	1.4E+00	1.02E-06	3.20E-06
CBTOX1	24-Feb-03	2.0E-01	4.04E-07	2.11E-06
CBTOX1	01-Apr-03	5.4E-01	6.31E-07	2.52E-06
CBTOX1	25-Jun-03	1.5E+00	1.06E-06	3.99E-06
XJI1953	28-Nov-06	8.7E-02	1.28E-06	3.40E-06
XJI1953	05-Dec-06	1.2E-01	1.28E-06	3.40E-06
XJI1953	12-Dec-06	6.4E-02	1.28E-06	3.40E-06
ELR12	13-Mar-03	1.2E+00	7.26E-07	3.43E-06
ELR12	17-Apr-03	7.8E-02	1.68E-06	4.86E-06
ELR4	13-Mar-03	9.9E-01	7.87E-07	3.34E-06
ELR4	17-Apr-03	8.4E-01	1.34E-06	4.39E-06
BOR4	13-Mar-03	2.7E-01	1.05E-06	3.18E-06
BOR4	17-Apr-03	7.7E-01	2.46E-06	4.68E-06
BOR4	17-Jul-03	1.7E+00	2.05E-06	4.21E-06
BOR4	16-Sep-03	1.9E+00	7.18E-07	4.39E-06
BOR4	01-Oct-03	1.8E+00	1.34E-06	3.82E-06

Note: *When the POC or DOC data were not available, the averaged value within the range was used.

IV. Adjusted Total BAFs

Next, the Baseline BAFs was normalized by the species median lipid content and a median freely-dissolved water column tPCB concentration within species' home range, thus minimizing variability associated with the differences in fish lipid content or freely-dissolved water column tPCB concentrations:

$$\text{Adj - tBAF} = (\text{Baseline BAF} \times \text{Median \% Lipid} + 1) \times \text{Median \%fd} \qquad \text{(B5)}$$

Table B-4: Site-Specific Total BAF, Baseline BAF, Adj-tBAF, and Water Column Target, as well as Median %fd and Median Lipid Content for Each Fish Species

Species Name	tBAF (L/kg)	bBAF (L/kg)	Adj-tBAF (L/kg)	Water Column Target (ng/L)	Median %fd	Median Lipid Content
Channel Catfish	342,067	25,848,619	343,114	**0.11**	0.27	0.050
White Perch	111,282	31,203,134	130,856	0.30	0.28	0.015

Finally, the tPCB fish tissue listing threshold of 39 ng/g was divided by the site-specific Adj-tBAF calculated for each fish species (Table B-4). To be environmentally protective, the lowest value (i.e., 0.11 ng/L – channel catfish) was used as the site-specific tPCB water column TMDL endpoint protective of the "fishing" designated use in the Sassafras River embayment.

V. BSAFs and Adj-SedBAFs

Similarly as in the case of the Baseline BAF calculation, the biota-sediment accumulation factors (BSAFs) for each fish sample (individual or composited) were derived using the following equation:

$$BSAF = \frac{tPCB_{tissue} / \%\ Lipid}{tPCB_{sediment} / \%\ Oraganic\ Carbon} \quad (B6)$$

Where: $[tPCB]_{fish}$ = fish tissue tPCB concentration (ng/kg – wet weight)
$[tPCB]_{sediment}$ = geometric mean of sediment tPCB concentrations within fish species' home range (ng/L)
%lipid = fraction of fish tissue that is lipid
%Organic Carbon = sediment organic carbon fraction within fish species' home range.

As the %Organic Carbon data were not available for the Sassafras River embayment, a default value of 1% was used (US EPA 2004).

For fish species with more than one result, a single BSAF was calculated as the median of the applicable total BSAFs. Each species' BSAF was then normalized with the use of the median lipid content (Table B-4) and the sediment organic carbon fraction:

$$Adj\text{-}SedBAF = BSAF \times \frac{Median\ \%\ Lipid}{Median\ \%\ Oraganic\ Carbon} \quad (B7)$$

The tPCB fish tissue listing threshold of 39 ng/g was then divided by the Adj-SedBAF calculated for each species (Table B-5). To be environmentally protective, the lowest value (i.e, 2.34 ng/g – channel catfish) was used as the site-specific tPCB sediment TMDL endpoint protective of the "fishing" designated use in the Sassafras River embayment.

Table B-5: Site-Specific BSAF, Adj-SedBAF, and Sediment Target for Each Fish Species

Species Name	BSAF	Adj-SedBAF	Sediment Target (ng/g)
Channel Catfish	3.34	16.70	**2.34**
White Perch	3.96	5.94	6.57

Appendix C. Multi-Segment Tidally-Averaged One-Dimensional Transport Model

A tidally averaged multi-segment one-dimensional transport model was applied to simulate the total polychlorinated biphenyl (tPCB) dynamic interactions between the water column and bottom sediments within the Sassafras River embayment and the Chesapeake Bay. The model is based one-dimensional tidally averaged model (Thomann and Mueller 1987) and adopts the basic assumptions and methodology of the Water Quality Analysis Simulation Program (WASP) (Di Toro et al. 1983, Chapra, S.C. 1997). It is assumed that the pollutant is well mixed in each segment and there is no decay of PCBs.

In each segment, PCBs can enter the water column via loadings from adjacent watershed and atmosphere (W_n), loadings from upstream and the adjacent branch through flow ($Q_{n+1}Cw_{n+1}$ and $Q_{nb}Cw_{nb}$), loadings from upstream and the adjacent branch through dispersion ($D_{n+1}(Cw_{n+1}-Cw_n)CA_{n+1}/L_{n+1}$ and $D_{nb}(Cw_{nb}-Cw_n)CA_{nb}/L_{nb}$), resuspension from the sediment ($Vr_nSA_nCs_n$), and diffusion between sediment-water column interface ($VdSA_n(Fds_nCs_n - Fdw_nCw_n)$). PCBs leave the water column via loadings to downstream segments through flow and dispersion (Q_nCw_n and $D_n(Cw_n-Cw_{n-1})CA_n/L_n$), volatilization ($VvSA_nFdw_nCw_n$), and settling ($VsetSA_nFpw_nCw_n$).

In the sediment, the PCBs enter the system via settling ($VsetSA_nFpw_nCw_n$), and leave the system via diffusion ($VdSA_n(Fds_nCs_n - Fdw_nCw_n)$), resuspension ($Vr_nSA_nCs_n$) and burial to a deeper layer ($VbSA_nCs_n$).

Specifically, the mass balance for the tPCBs in the water column of segment *n* can be written as:

$$\begin{aligned}\frac{dVw_nCw_n}{dt} &= W_n + Q_{n+1}Cw_{n+1} + Q_{nb}Cw_{nb} + D_{n+1}(Cw_{n+1} - Cw_n)CA_{n+1}/L_{n+1} \\ &+ D_{nb}(Cw_{nb} - Cw_n)CA_{nb}/L_{nb} + Vr_nSA_nCs_n + VdSA_n(Fds_nCs_n - Fdw_nCw_n) \\ &- Q_nCw_n - D_n(Cw_n - Cw_{n-1})CA_n/L_n - VvSA_nFdw_nCw_n - VsetSA_nFpw_nCw_n\end{aligned} \qquad \text{(C1)}$$

and that in the sediment of segment *n* can be written as:

$$\frac{dVs_nCs_n}{dt} = VsetSA_nFpw_nCw_n - VdSA_n(Fds_nCs_n - Fdw_nCw_n) - Vr_nSA_nCs_n - VbSA_nCs_n \qquad \text{(C2)}$$

Where:

n = the nth river segment;

Vw_n and Vs_n = volume of the water and sediment (m^3);

Cw_n *and* Cs_n = tPCB concentration in water and sediment (ng/L);

t = time (day);

W_n = tPCB loading from adjacent watershed (point and nonpoint sources) and atmosphere (ug/day);

Q_n = quantity of water that flows from segment *n* to *n-1* (m^3/day);

Q_{nb} = quantity of water that flows from adjacent branch to segment *n* (m^3/day);

D_n and D_{nb} = dispersion coefficients (tidal averaged diffusivity) at the upstream and downstream sides of segment *n* (m^2/day);

CA_n and CA_{nb} = cross sectional area between segment *n* and *n-1* and between its branch and segment *n* (m^2);
L_n and L_{nb} = distance between center of segment *n* to *n-1* and between center of its branch to segment *n* (m);
SA_n = surface area of segment *n* (m^2);
Vr_n = rate of resuspension (m/day);
Vd = diffusive mixing velocity (m/day), which is same for all the segments;
Vv = volatilization coefficient (m/day), which is same for all the segments;
Vset = rate of settling (m/day);
Vb = burial rate (m/day), which is same for all the segments;
Fdw_n = fraction of truly dissolved and dissolved organic carbon (DOC) associated PCBs in the water column;
Fds_n = fraction of truly dissolved and DOC associated PCBs in the sediment;
Fpw_n = fraction of particular associated PCBs in the water column.

Appendix D. Model Calculation for Sassafras River

For Sassafras River, the model domain includes the whole oligohaline embayment, which is divided into 8 segments (Figure 6 of the main report). The parameter values and methods for deriving some of the parameters are as follows:

n = 8. It was delineated in consideration of the locations of the water quality monitoring stations and the bathymetry of the Sassafras River;

Vw_n = mean water depth of segment n × surface area of segment n. The mean water depth was obtained from the bathymetry data of the Sassafras River;

Vs_n = surface area of segment n × active sediment layer thickness (0.1 m);

Cw_n = measured tPCB water column concentration of segment n. If the measurement was not available, the averaged concentration of the adjacent segments was used;

Cs_n = Measured tPCB concentration on a dry sediment base × Sediment density × (1-porosity) ÷ Fraction of particulate associated PCBs in the sediment, and the porosity (water content on a volume base) of 0.85 is selected based on observations and reference (Thomann and Mueller 1987);

W_n = tPCB loading from the adjacent watershed of segment n and atmosphere. As showed in Figure 6 of the main report, the whole watershed was divided into 14 subwatersheds using the GIS topography layer. The total tPCB watershed runoff loading (Section 2.3.1) was partitioned to each subwatershed proportional to their respective areas. If a segment has any direct or indirect WWTP loading, it was added into the model as well. The atmosphere loading was partitioned into each segment with similar method;

Q_n = total flow from all the upstream subwatersheds of segment $n-1$. The flow was calculated using the 20-year monthly mean flows at the United States Geological Survey (USGS) station located at New Castle County, Delaware (USGS 01483200) and Kent County, Maryland (USGS 01493500). The unit area flows of the two stations were averaged and multiplied by the area of a subwatershed to get its flow;

Q_{nb} = total flow from the branch subwatershed of segment n;

D_n and D_{nb} = dispersion coefficient of each segment. They are calibrated based on the salinity data of the Sassafras River (MDE 2002). Salinity is a conservative constituent. It has no loss due to reaction, volatilization, or settling in the water and no source from the watershed. The deposition from the atmosphere is minimal and can be ignored. Therefore, the only source of salinity in the system is from the Chesapeake Bay water at the mouth. Consequently, in Equation (C1), all the terms W_n, $Vr_nSA_nCs_n$, $VdSA_n(Fds_nCs_n – Fdw_nCw_n)$, $VvSA_nFdw_nCw_n$, and $VsetSA_nFpw_nCw_n$ become zero. Dispersion coefficient can be obtained by solving the steady state, Equation (C1) providing know parameters of flow and measured salinity. D_n can be estimated for the boundary segments first (Segments 4, 5, 6, 7, and 8). Then the D_ns of Segments 3, 2, and 1 can be estimated in sequence;

CA_n and CA_{nb} = mean depth × length of the cross section;

L_n and L_{nb} = distance between segments directly measured using ArcView GIS.

SA_n = surface area calculated from ArcView GIS;

Vd = 69.35 × Porosity × (Molecular weight of PCBs)$^{-2/3}$ ÷ 365 = 69.35 × 0.85 × (305.6)$^{-2/3}$ ÷ 365 = 0.00356 (m/day, Thomann and Mueller 1987).

Vv = 0.246 m/day, which was derived from empirical method of Chapra (1997);

Vset = 1 (m/d), a default value of settling rate used in literature (DRBC 2003);
Vb = 2.137×10^{-6} (m/day, average of the measured sedimentation rates through ^{210}Pb technology).
Vr_n can be calculated via mass balance of the sediment in the active sediment layer at steady state:

$$\frac{d\rho(1-\varphi)}{dt} = V_s \times TSS - V_r \times \rho \times (1-\varphi) - V_b \times \rho \times (1-\varphi) = 0 \qquad \text{(D1)}$$

Where *TSS* is the total suspended solid concentration (g/m^3; measured), ρ is the sediment density (g/m^3; Thomann and Mueller 1987), and φ is the porosity. Rearrange Equation D1:

$$V_r = \frac{V_s \times TSS}{\rho \times (1-\varphi)} - V_b = 3.47 \times 10^{-5}\,\text{(m/d)} \qquad \text{(D2)}$$

The V_r value was then calibrated assuming the initial equilibrium has been reached in the water column and sediment.

Some physical parameters of each segment can be found in Table D-1. For Fdw_n, Fds_n, and Fpw_n see Table D-2 for values and Appendix E for derivation.

Table D-1: Physical Parameters of the Model for Each Segment

n	*SA* (m^2)	*Vw* (m^3)	*Vs*	*CA* (between *n* and *n-1*)	*L* (between *n* and *n-1*)
1	9,249,471	39,921,306	924,947	43,359	10,500
2	11,042,933	36,265,180	1,104,293	6,600	3,862
3	6,679,944	17,509,389	667,994	3,750	6,900
4	3,017,302	3,421,473	301,730	889	6,500
5	1,959,160	1,213,584	195,916	2,528	2,200
6	1,179,957	1,149,393	117,996	1,176	2,300
7	1,660,065	1,257,774	166,007	815	1,700
8	939,920	527,516	93,992	588	2,500

Table D-2: Fdw, Fds, and Fpw Values for Each Segment

n	*Fdw*	*Fds*	*Fpw*
1	0.5827	0.0024	0.4173
2	0.6761	0.0024	0.3239
3	0.7186	0.0024	0.2814
4	0.7186	0.0024	0.2814
5	0.6761	0.0024	0.3239
6	0.6761	0.0024	0.3239
7	0.7186	0.0024	0.2814
8	0.7186	0.0024	0.2814

Appendix E. Calculation of Fraction of Different PCB Forms

The fractions in equations (C1) and (C2) can be calculated as follows:

$$F_{p1} = \frac{TSS \times 10^{-6} K_{oc} \times f_{oc1}}{1 + (K_{oc} \times 10^{-6})(TSS \times f_{oc1} + DOC_1)} \tag{E1}$$

$$F_{do1} = \frac{1 + (K_{oc} \times 10^{-6}) DOC_1}{1 + (K_{oc} \times 10^{-6})(TSS \times f_{oc1} + DOC_1)} \tag{E2}$$

$$F_{do2} = \frac{\phi + \phi (K_{oc} \times 10^{-6}) DOC_2}{\phi + (K_{oc} \times 10^{-6})(f_{oc2} \times \rho \times (1-\phi) + \phi DOC_2)} \tag{E3}$$

Where:

K_{oc} is the PCB organic carbon/water partition coefficient (L/kg). It describes the ratio of a compound adsorbed to solids and in solution, normalized for organic carbon content. It can be calculated via the relationship of $\log_{10} K_{oc} = 0.00028 + 0.983 \times \log_{10} K_{ow}$ (Hoke et al. 1994), where K_{ow} is the octanol-water partition coefficient with $\log_{10} K_{ow}$ equal to 6.261 (de Bruijn et al. 1989).

f_{oc1} and f_{oc2} are the fractions of organic carbon in suspended solids in the water column and the sediment solids, respectively (US EPA 2004).

DOC_1 and DOC_2 are the dissolved organic carbon concentrations in water column and pore water, respectively.

φ is the porosity of the sediment.

Appendix F. Technical Approach Used to Generate Maximum Daily Loads

Summary

This appendix documents the technical approach used to define the maximum daily load (MDL) of total polychlorinated biphenyls (tPCBs) consistent with the average annual Total Maximum Daily Load (TMDL), which is protective of the "fishing" designated use in the Sassafras River embayment. The approach builds upon the modeling analysis that was conducted to determine the average annual tPCB TMDL and can be summarized as follows:

- The approach defines an MDL for each of the source categories;
- The approach builds upon the TMDL modeling analysis that was conducted to ensure that the average annual TMDL results in compliance with water quality standards;
- The approach considers a daily load level of a resolution based on the specific data that exists for each source category.

Introduction

This appendix documents the development and application of the approach used to present the average annual tPCB TMDL allocations in terms of daily loads. It is divided into sections discussing:

- Basis for approach;
- Options considered;
- Selected approach;
- Results of approach.

Basis for Approach

The overall approach for the development of daily loads was based upon the following factors:

- **Average Annual TMDL:** The basis of the average annual tPCB TMDL is that the Baseline Load to the Sassafras River embayment results in fish tissue concentrations that exceed the tPCB fish tissue listing threshold. Thus, the average annual tPCB TMDL was calculated to be protective of the "fishing" designated use.
- **Draft U.S. Environmental Protection Agency (US EPA) guidance document entitled *Options for the Expression of Daily Loads in TMDLs* (US EPA 2007b).**

The rationale for developing TMDL expressed as daily loads was to accept the existing average annual TMDL, but then develop a method for converting this number to an MDL – in a manner consistent with US EPA guidance and available information.

Options Considered

The draft US EPA guidance document for developing daily loads does not specify a single approach that must be adhered to, but rather it contains a range of acceptable options (US EPA 2007b). The selection of a specific method for translating a time-series of allowable loads into the expression of an MDL requires decisions regarding both the level of resolution (e.g., single daily load for all conditions vs. loads that vary with environmental conditions) and level of probability associated with the exceedance of the TMDL.

This section describes the options that were considered when developing methods to calculate the Sassafras River embayment MDL.

Level of Resolution

The level of resolution pertains to the amount of detail used in specifying the MDL. The draft US EPA guidance on daily loads (US EPA 2007b) provides three categories of options for level of resolution, all of which are potentially applicable to the Sassafras River:

1. **Representative daily load:** In this option, a single daily load (or multiple representative daily loads) is specified that covers all time periods and environmental conditions.
2. **Flow-variable daily load:** This option allows the MDL to vary based upon the observed flow conditions.
3. **Temporally-variable daily load:** This option allows the MDL to vary based upon seasons or times of varying source or water body behavior (US EPA 2007b).

Probability Level

All TMDLs have some probability of being exceeded, with the specific probability being explicitly specified or implicitly assumed. This level of probability directly or indirectly reflects two separate phenomena:

1. Water quality criteria consist of components describing acceptable magnitude, duration, and frequency. The frequency component addresses how often conditions can allowably surpass the combined magnitude and duration components.
2. Pollutant loads, especially from wet weather sources, typically exhibit a large degree of variability over time. It is rarely practical to specify a "never to be exceeded value" for a daily load, as essentially any loading value has some finite probability of being exceeded.

The draft daily load guidance document states that the probability component of the MDL should be "based on a representative statistical measure" that is dependent upon the specific TMDL and best professional judgment of the developers (US EPA 2007b). This statistical measure represents how often the MDL is expected/allowed to be exceeded. The primary options for selecting this level of protection would be:

1. **The MDL reflects some central tendency:** In this option, the MDL is based upon the mean or median value of the range of loads expected to occur. The variability in the actual loads is not addressed.

2. **The MDL reflects a level of protection implicitly provided by the selection of some "critical" period**: In this option, the MDL is based upon the allowable load that is predicted to occur during some critical period examined during the analysis. The developer does not explicitly specify the probability of occurrence.

3. **The MDL is a value that will be exceeded with a pre-defined probability:** In this option, a "reasonable" upper bound percentile is selected for the MDL based upon a

characterization of the variability of daily loads. For example, selection of the 95th percentile value would result in an MDL that would be exceeded 5% of the time.

Selected Approach

The level of resolution selected for the Sassafras River embayment MDL was a representative daily load, expressed as a single daily load for each loading source. This approach was chosen due to the nature of PCBs and the focus of this study on a TMDL endpoint that is protective of the "fishing" designated use. Daily flow and temporal variability do not affect the rate of PCB bioaccumulation in fish over the long-term thus establishing no influence on achievement of the TMDL endpoint. An MDL at these levels of resolution is unwarranted.

The approach selected for defining a Sassafras River embayment MDL was based upon the specific data that exists for each source category. The approach consists of unique methods for each of the following categories of sources:

- Approach for Nonpoint Sources and National Pollutant Discharge Elimination System (NPDES) Regulated Stormwater Point Sources within the Sassafras River;
- Approach for NPDES Permitted Waste Water Treatment Plant (WWTP) Point Sources within the Sassafras River; and
- Approach for Upstream Sources.

<u>Approach for Nonpoint Sources and NPDES Regulated Stormwater Point Sources within the Sassafras River</u>

The Nonpoint Source and NPDES Regulated Stormwater Point Source MDLs were estimated based on three factors: a specified probability level, the average annual tPCB TMDL allocations, and the coefficient of variation (CV) of the baseline condition for ambient water column concentrations in the Sassafras River. The probability level (or exceedance frequency) is based upon guidance from US EPA (1991) where examples suggest that when converting from a long-term average to a daily value, the z-score corresponding to the 99th percentile of the log-normal probability distribution should be used.

The CV of 0.14 was calculated using the arithmetic mean and standard deviation of the baseline ambient water column concentrations in the Sassafras River (see Equation G1).

$$CV = \frac{\beta}{\alpha} \qquad \text{(F1)}$$

Where:
CV = coefficient of variation
α = mean (arithmetic)
β = standard deviation (arithmetic)

The MDL for each contributing source is estimated as the appropriate average annual load allocation multiplied by a conversion factor that accounts for expected variability of daily loading values. The equation is as follows:

$$MDL = LTA * e^{(z\sigma - 0.5\sigma^2)} \qquad \text{(G2)}$$

Where:
MDL = Maximum daily load
LTA = Long-term average (average annual load allocation)
Z = z-score associated with target probability level
$\sigma^2 = \ln(CV^2+1)$
CV = Coefficient of variation based on arithmetic mean and standard deviation

Using a z-score associated with the 99th percent probability (z value of 2.326), a CV of 0.14, and an appropriate unit conversion (i.e., from long-term average load (g/yr) to an MDL (g/day)) results in a conversion factor of 0.0038.

Approach for WWTP Point Sources within the Sassafras River Watershed

The TMDL also considers contributions from NPDES permitted WWTP point sources that discharge quantifiable concentrations of tPCBs in the Sassafras River watershed. The MDLs were calculated based on the guidance provided in the Technical Support Document (TSD) for Water Quality-based Toxics Control (US EPA 1991). The average annual TMDL allocations were converted to maximum daily limits using Table 5-2 of the TSD assuming a coefficient of variation of 0.6, a 99th percentile probability (z value of 2.326), and an appropriate unit conversion (i.e., from long-term average load (g/yr) to an MDL (g/day)). This results in a conversion factor of 0.0085. It should be noted, however, that the WWTP Baseline Loads were considered to be *de minimis*, therefore no appreciable environmental benefit would be gained by reducing this load (see Appendix J for details).

Approach for Upstream Sources

For the purpose of this analysis only one upstream watershed has been identified: the Delaware portion of the Sassafras River watershed. Delaware MDL was calculated based on the same approach as was used for nonpoint sources and NPDES regulated stormwater point sources within the Sassafras River watershed (see above).

Results of Approach

This section lists the results of the selected approaches to define the Sassafras River embayment MDL.

- Calculation Approach for Nonpoint Sources (Chesapeake Bay, Bottom Sediment, Direct Atmospheric Deposition, and Maryland Watershed Nonpoint Sources) and NPDES Regulated Stormwater Point Sources within the Sassafras River:

  Nonpoint Source MDL (g/day) = Average Annual Nonpoint Source LA (g/yr) × 0.0038

  NPDES Regulated Stormwater MDL (g/day) = Average Annual NPDES Regulated Stormwater WLA (g/yr) × 0.0038

- Calculation Approach for WWTP Point Sources within the Sassafras River:

  WWTP MDL (g/day)$^{\triangle}$ = Average Annual WWTP WLA (g/yr) × 0.0085

- Calculation Approach for Upstream Sources:

  Delaware Upstream MDL (g/day) = Average Annual Delaware Upstream LA (g/yr) × 0.0038

Table F-1: Summary of tPCB Maximum Daily Load

Source	MDL (g/day)
Bottom Sediment (Resuspension and Diffusion)	1.738
Chesapeake Bay (Tidal Influence)	1.464
Direct Atmospheric Deposition (to the Surface of the Embayment)	0.442
Maryland Watershed Nonpoint Sources*	0.094
Delaware Upstream	0.010
Total Nonpoint Sources	***3.748***
WWTP*, △	0.017
NPDES Regulated Stormwater*	0.002
Total Point Sources*	***0.019***
MOS	***0.419***
Total	**4.19**

Notes: * These sources were characterized only for the Maryland portion of the watershed.
△ WWTP Baseline Loads were considered to be *de minimis*.

Appendix G. MDE Permit Information

Table G-1: NPDES Regulated Stormwater Permit Summary for Sassafras River Watershed[1]

Facility	City	County	Type	TMDL
Cecil County MS4	ALL	Cecil	-	Stormwater WLA
MDE General Permit To Construct	ALL	Cecil[2]	-	Stormwater WLA

Notes: [1] Although not listed in this table, some individual process water permits for municipal and industrial discharges may also incorporate stormwater requirements. Loads from such facilities as well as from general Phase II state and federal MS4s (i.e., military bases, hospitals, etc.) within the Cecil County portion of the watershed (see Section 2.3.2) are inherently included as part of the NPDES stormwater WLA presented in this document.

[2] This permit is applicable within all counties, but for the purposes of this analysis, the SW-WLA only applies to Cecil County permitted areas.

Appendix H. Derivation of the Boundary tPCB Concentration

Sassafras River exchanges waters with the Chesapeake Bay. The Susquehanna River is the major source of flow and polychlorinated biphenyls (PCBs) to the Upper Chesapeake Bay (Ko and Baker 2004). According to Ko and Baker (2004), the tPCB loads of Susquehanna River from 1992 to 1998 are as follows:

Table H-1: The Flow Normalized tPCB loads of Susquehanna River (kg/m^3/year)

Year	Years Since 1992	Load (kg/m^3/year)	Log ($Load_{Current}/Load_{1992}$)
1992	0	37	0
1993	1	37	0
1994	2	35	-0.02413
1995	3	35	-0.02413
1997	5	24	-0.18799
1998	6	24	-0.18799

A linear regression was developed for *Years Since 1992* vs. *Log ($Load_{Current}/Load_{1992}$)*, the slope of -0.0292 stands for log of current year's load as a percentage of the previous year's load. The current year's load as a percentage of the previous year's load is $10^{-0.0292} = 0.935$. Thus, on average the tPCB concentrations in the Upper Chesapeake Bay are decreasing at a rate of 1 - 0.935 = 6.5% per year (Figure H-1). This value was used in the model simulation to account for the expected temporal changes in tPCB concentration at the Bay boundary.

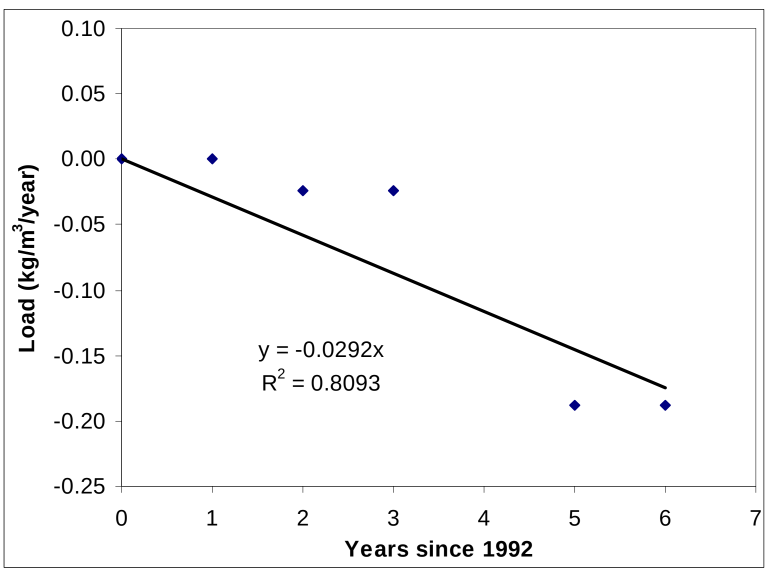

Figure H-1: The Regression Line of the Ko and Baker tPCB Loading Data

Appendix I. List of Analyzed PCB Congeners

Polychlorinated biphenyl (PCB) analytical services were provided by the University of Maryland Center for Environmental Science (UMCES). PCB congeners were identified and quantified by high resolution gas chromatography with electron capture detection. UMCES uses a slightly modified version of the PCB congener specific method described in Ashley and Baker (1999), in which the identities and concentrations of each congener in a mixed Aroclor standard (25:18:18 mixture of Aroclors 1232, 1248, and 1262) are determined based on their chromatographic retention times relative to the internal standards (PCB 30 and PCB 204). Based on this method, 86 chromatographic peaks can be quantified (see Table I-1). Some of the peaks contain one PCB congener, while many are comprised of two or more co-eluting congeners. The PCB analysis presented in this document is based on total PCB concentrations that are calculated as the sum of the detected PCB congeners/congener groups representing the most common congeners that were historically used in the Aroclor commercial mixtures.

Table I-1: List of Analyzed PCB Congeners

1	45	110, 77	177
3	46	114	180
4, 10	47, 48	118	183
6	49	119	185
7, 9	51	123, 149	187, 182
8, 5	52	128	189
12, 13	56, 60	129, 178	191
16, 32	63	132, 153, 105	193
17	66, 95	134	194
18	70, 76	135, 144	197
19	74	136	198
22	81, 87	137, 130	199
24	82, 151	141	201
25	83	146	202, 171, 156
26	84, 92	157, 200	203, 196
29	89	158	205
31, 28	91	163, 138	206
33, 21, 53	97	167	207
37, 42	99	170, 190	208, 195
40	100	172	209
41, 64, 71	101	174	
44	107	176	

Appendix J. WWTP Load Evaluation

This appendix evaluates the significance of the Waste Water Treatment Plant (WWTP) Total Polychlorinated Biphenyl (tPCB) Baseline Load and whether a reduction is necessary in order to meet the TMDL resulting in the attainment of water quality standards. Assigning reductions to loads that are considered *de minimis* (i.e., insignificant or negligible) would produce no appreciable environmental benefit and would require regulated facilities to implement burdensome regulatory requirements.

At 0.18% of the TMDL (Table J-1), the Sassafras River WWTP Baseline Loads are considered *de minimis* because even their complete elimination would not result in any discernible improvement in water quality (Table J-2). Moreover, a possible future increase in these loads (e.g., due to potential future development or expansion of plant capacity) is also not expected to have any significant impact on meeting the site-specific tPCB water quality TMDL endpoints; even a 10-fold increase in WWTP load (up to 1.8% of the TMDL) is expected to increase the time it takes to reach the TMDL endpoints by only 0.86% or 120 days (Table J-3, Figures J-1 and J-2). Therefore, given that even a possible future increase in this load would not have any impact on meeting TMDL endpoints, no appreciable environmental benefit would be gained by reducing this load.

Table J-1: WWTP tPCB Loads as Percent of TMDL

Sources	Allowable Load(g/year)	Percent of TMDL
WWTP	2.0	0.18%
Other	1,110.6	99.82%
Total	**1,112.6**	**100%**

Table J-2: Effect of Eliminating WWTP Baseline Loads on Time Needed to Reach the TMDL Endpoints

Allowable Load	Nr. of Days Needed to Reach the TMDL Endpoints
Including WWTP Baseline Loads	13,996
Reducing WWTP Baseline Loads by 100%	13,982

Loadings from the Chesapeake Bay as well as resuspension and diffusion from the bottom sediments are the primary sources of the tPCB loads resulting in the PCB impairment in the Sassafras River embayment (see Section 2.3). Attainment of the tPCB water quality TMDL endpoints will only be possible with the decline of these primary loadings, which is expected to take place over time as the Upper Chesapeake Bay concentrations continue to decline resulting also in natural attenuation of tPCB levels in the legacy sediments. In the future, if WWTPs are discovered to discharge PCBs at levels that threaten water quality, the assessment of the appropriate WLAs will be revisited.

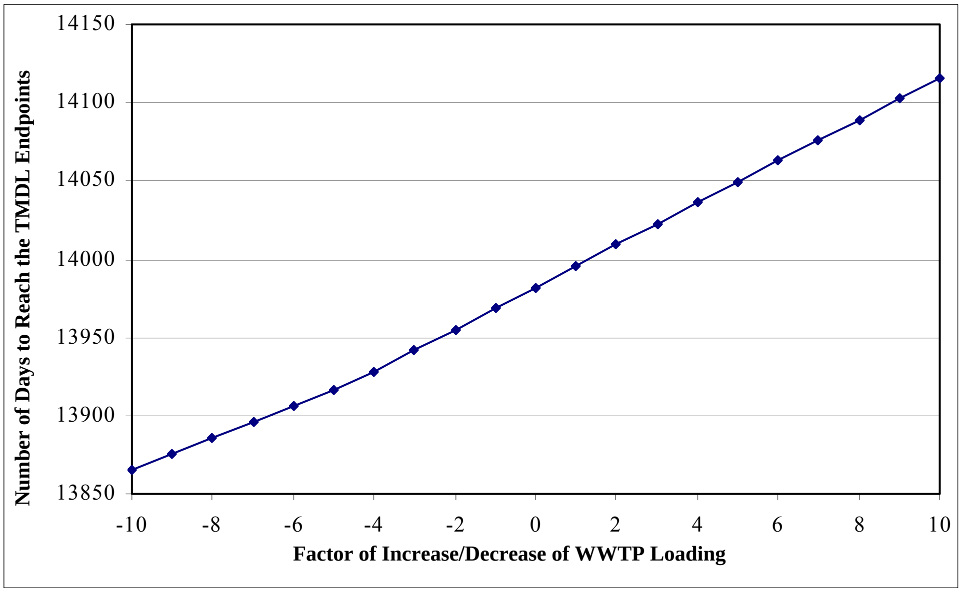

Figure J-1: Effect of Increasing/Decreasing Loads as Factor of WWTP Baseline Loads on Time Needed to Reach the TMDL Endpoints (days)

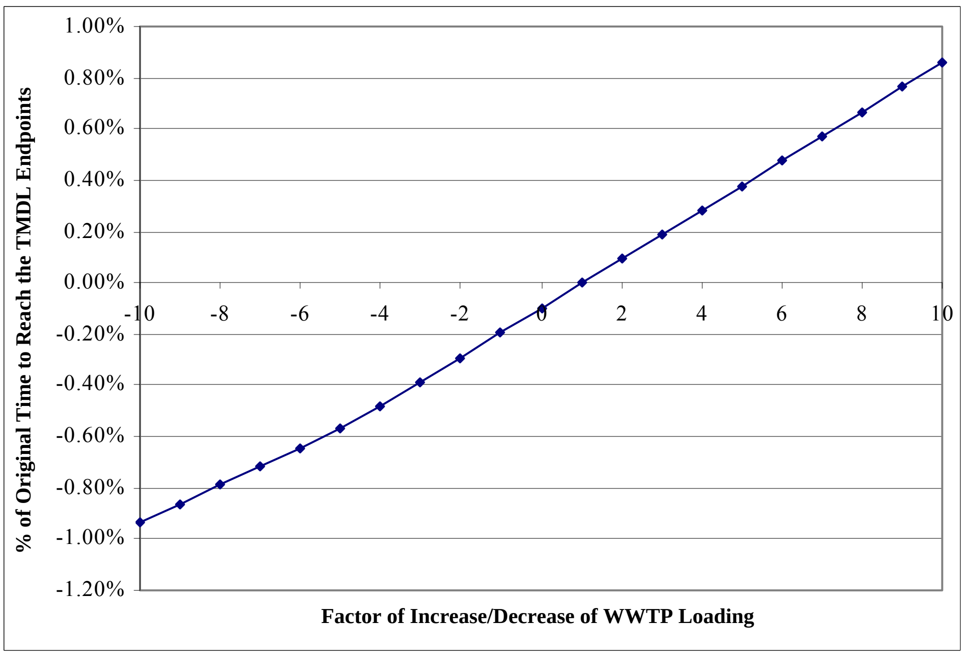

Figure J-2: Effect of Increasing/Decreasing Loads as Factor of WWTP Baseline Loads on Time Needed to Reach the TMDL Endpoints (% of time)

Table J-3: Effect of Increasing/Decreasing Loads as Factor of WWTP Baseline Loads on Time Needed to Reach the TMDL Endpoints

Factor of Increase/ Decrease of WWTP Loading	Nr. of Days Needed to Reach the TMDL Endpoints	Percent Change
10	14,116	0.86%
9	14,103	0.76%
8	14,089	0.66%
7	14,076	0.57%
6	14,063	0.48%
5	14,049	0.38%
4	14,036	0.29%
3	14,022	0.19%
2	14,009	0.09%
1	13,996	0.00%
-2	13,955	-0.29%
-3	13,942	-0.39%
-4	13,928	-0.49%
-5	13,917	-0.56%
-6	13,906	-0.64%
-7	13,896	-0.71%
-8	13,886	-0.79%
-9	13,875	-0.86%
-10	13,865	-0.94%