FINAL

Water Quality Analysis of Mercury in Fish Tissue in Liberty Reservoir in Baltimore and Carroll Counties, Maryland

FINAL

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List of Abbreviations

ASG	Atmospheric Studies Group
BCDPW	Baltimore City Department of Public Works
BIBI	Benthic Index of Biotic Integrity
C	Celsius
CBP P5.3.2	Chesapeake Bay Program Phase 5.3.2
Cl^{-1}	Chloride
COMAR	Code of Maryland Regulations
CWA	Clean Water Act
DNR	Maryland Department of Natural Resources
E_h	Oxidation Potential
EGU	Electrical Generating Unit
ft^2	Square feet
ft^3/s	Cubic feet per second
g	Grams
g/day	Grams per day
g/yr	Grams per year
g/cm^3	Grams per centimeter cubed
EPA	US Environmental Protection Agency
FIBI	Fish Index of Biotic Integrity
HAA	Maryland Healthy Air Act
Hg	Mercury
Hg0	Uncharged, elemental mercury
Hg+1	Mercurous ion
Hg+2	Mercuric ion
Hg(OH)2	Mercuric Hydroxide
HgCl2	Mercuric Chloride
HgS	Mercury Sulfide
LMB	Largemouth Bass
MD 8-Digit	Maryland 8-Digit
MATS	Mercury and Air Toxics Standards
MDE	Maryland Department of the Environment
mg/kg	Milligrams per kilogram
mm	Millimeters
mi^2	Square miles
mol/L	Mols per liter
MS4	Municipal Separate Storm Sewer System
NEI	National Emissions Inventory
NPDES	National Pollutant Discharge Elimination System
PPRP	Power Plant Research Program
RfD	Reference Dose
S^{-2}	Sulfide
SCS	Soil Conservation Service

SHA	Maryland State Highway Administration
TMDL	Total Maximum Daily Load
USDA	United States Department of Agriculture
WQA	Water Quality Analysis
WQLS	Water Quality Limited Segment
WWTP	Wastewater Treatment Plant
µg/kg	Micrograms per kilogram
µg/L	Micrograms per liter
µg/kg-day	Micrograms per kilogram per day
YOY	Young of the Year

EXECUTIVE SUMMARY

Section 303(d) of the federal Clean Water Act (CWA) and the US Environmental Protection Agency's (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. For each WQLS listed on the *Integrated Report of Surface Water Quality in Maryland* (Integrated Report), the State is required to either establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating water quality standards, or demonstrate via a Water Quality Analysis (WQA) that water quality standards are being met (CFR 2012a). This document, upon approval by the EPA, presents a WQA of mercury (Hg) in Liberty Reservoir [Maryland 8-Digit (MD 8-Digit) basin number 02130907] (2012 Integrated Report Assessment Unit ID: MD-02130907_Liberty_Reservoir).

The MD 8-Digit Liberty Reservoir watershed consists of:

1) The actual impoundment created behind the Liberty Dam, and
2) The nontidal tributaries within the watershed that drain to the impoundment.

The use of the term "Liberty Reservoir" throughout this report will refer to solely the impoundment created behind Liberty Dam. Use of the term "non-tidal portion of the Liberty Reservoir watershed" will refer to the non-tidal tributaries within the watershed draining to the Reservoir.

Maryland's water quality standards specify that all surface waters of the State shall be protected for water contact recreation, fishing, and the protection of aquatic life (COMAR 2012a). The specific Maryland Surface Water Use Designation in the Code of Maryland Regulations (COMAR) for Liberty Reservoir is Use I-P (*Water Contact Recreation, Protection of Aquatic Life, and Public Water Supply*) (COMAR 2012b,c). The Maryland Department of the Environment (MDE) has identified Liberty Reservoir on the State's 2012 Integrated Report as impaired by mercury in fish tissue (2002), sediments – sedimentation/siltation (1996), nutrients – phosphorus (1996), and metals – chromium and lead (1996). The non-tidal portion of the Liberty Reservoir watershed has been identified by MDE on the State's 2012 Integrated Report as impaired by bacteria (mainstem only; 2002) and impacts to biological communities (2004) (MDE 2012).

The WQA presented herein by MDE will address the 2002 mercury in fish tissue listing for Liberty Reservoir, for which a data solicitation was conducted, and all readily available data from the past five years have been considered. A WQA for chromium and lead in Liberty Reservoir was approved by the EPA in 2003, and a bacteria TMDL for the nontidal portion of the watershed was approved by the EPA in 2009. TMDLs for phosphorus and sediments were submitted to EPA in 2012. In the final 2012 Integrated Report, the biological listing was addressed by the Biological Stressor Identification (BSID) analysis which more specifically identified chloride as a stressor to biological communities within the 1st- through 4th-order streams of the Liberty Reservoir watershed. As a result, in the 2012 Integrated report, the biological impairment listing was replaced with a category 5 chlorides listing.

An analysis of recent fish tissue monitoring data in Liberty Reservoir demonstrates that the "fishing" designated use of the reservoir (COMAR 2012d) is supported to allow for the consumption of fish that is protective of human health, as it relates to mercury levels in fish tissue, thus indicating that the reservoir is not impaired for mercury in fish tissue. The EPA recommended and State adopted a numeric criterion concentration for methylmercury in fish tissue of 300.0 micrograms per kilogram (μg/kg). This numeric criterion is deemed to be protective of human health relative to the consumption of fish. The conclusion that the "fishing" designated use of Liberty Reservoir is being supported is based on two composite tissue samples of trophic-level four fish (in this case, largemouth bass) taken from the Reservoir in April 2012, which indicate that the median fish tissue mercury concentration is less than MDE's numeric criterion concentration for methylmercury in fish tissue, which is deemed to be protective of human health relative to the consumption of fish.

As stated above, the analysis presented in this report supports the conclusion that a TMDL for mercury is not necessary to achieve water quality standards in Liberty Reservoir. Although Liberty Reservoir does not display signs of an impairment due to mercury in fish tissue, the State reserves the right to require future controls if evidence suggests that mercury from the reservoir is contributing to downstream water quality problems. Barring the receipt of contradictory data, this report will be used to support the revision of the 2012 Integrated Report listing for mercury in fish tissue in Liberty Reservoir from Category 5 ("waterbody is impaired, does not attain the water quality standard, and a TMDL is required") to Category 2 ("waterbody is meeting some [in this case mercury in fish tissue related] water quality standards, but with insufficient data to assess all impairments")**.**

1.0 INTRODUCTION

Section 303(d) of the federal Clean Water Act (CWA) and the US Environmental Protection Agency's (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. For each WQLS listed on the *Integrated Report of Surface Water Quality in Maryland* (Integrated Report), the State is required to either establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating water quality standards, or demonstrate via a Water Quality Analysis (WQA) that water quality standards are being met (CFR 2012a). The most common scenarios that would eliminate the need for a TMDL are:

(1) Analysis of more recent data indicating that the impairment no longer exists (i.e., water quality standards are being met);
(2) Results of more recent and updated water quality modeling demonstrate that the segment is attaining water quality standards;
(3) Refinements to water quality standards or to the interpretation of those standards accompanied by analysis demonstrating that the standards are being met;
(4) Identification and correction of errors made in the initial listing.

Based on recent data, this document, upon approval by the EPA, presents a WQA of mercury (Hg) in Liberty Reservoir [Maryland 8-Digit (MD 8-Digit) basin number 02130907] (2012 Integrated Report Assessment Unit ID: MD-02130907_Liberty_Reservoir), which indicates that a mercury impairment no longer exists in the reservoir.

The MD 8-Digit Liberty Reservoir watershed consists of:

1) The actual impoundment created behind the Liberty Dam, and
2) The nontidal tributaries within the watershed that drain to the impoundment.

The use of the term "Liberty Reservoir" throughout this report will refer to solely the impoundment created behind Liberty Dam. Use of the term "non-tidal portion of the Liberty Reservoir watershed" will refer to the non-tidal tributaries within the watershed draining to the Reservoir.

Maryland's water quality standards specify that all surface waters of the State shall be protected for water contact recreation, fishing, and the protection of aquatic life (COMAR 2012a). The specific Maryland Surface Water Use Designation in the Code of Maryland Regulations (COMAR) for Liberty Reservoir is Use I-P (*Water Contact Recreation, Protection of Nontidal Warm Water Aquatic Life and Public Water Supply*) (COMAR 2012b,c). The Maryland Department of the Environment (MDE) has identified Liberty Reservoir on the State's 2012 Integrated Report as impaired by mercury in fish tissue (2002), sediments – sedimentation/siltation (1996), nutrients – phosphorus (1996) and metals – chromium and lead (1996). The non-tidal portion of the Liberty Reservoir watershed has been identified by MDE on the State's 2012 Integrated Report as impaired by bacteria (mainstem only; 2002) and impacts to biological communities (2004) (MDE 2012).

The WQA presented herein by MDE will address the 2002 mercury in fish tissue listing for Liberty Reservoir, for which a data solicitation was conducted, and all readily available data from the past five years have been considered. A WQA for chromium and lead in Liberty Reservoir was approved by the EPA in 2003, and a bacteria TMDL for the nontidal portion of the watershed was approved by the EPA in 2009. TMDLs for phosphorus and sediments are currently under development and are scheduled for submittal to EPA in 2012. In the final 2012 Integrated Report, the listing for impacts to biological communities within the 1st- through 4th-order streams of the nontidal portion of the Liberty Reservoir watershed includes the results of a stressor identification analysis.

MDE had previously developed a TMDL to address the 2002 Integrated Report mercury in fish tissue impairment listing for Liberty Reservoir. The *Total Maximum Daily Load of Mercury for Liberty Reservoir Baltimore and Carroll Counties, Maryland* was submitted by MDE to EPA in 2002 (MDE 2002a). Approval of the TMDL was withheld by EPA until the air deposition model, applied within the analysis to estimate the atmospheric deposition of mercury to the reservoir and its surrounding watershed, could be improved to provide more detail in terms of source assessment and deposition rates, in order to bolster the TMDL's assurance of implementation. Advances in modeling atmospheric mercury transport now enable atmospherically deposited mercury loads to be attributed to specific emission sources, both in Maryland and other states, as well as those originating from global/background sources, including natural sources. However, the analysis of fish tissue samples collected in April of 2012 in Liberty Reservoir indicate that the reservoir is no longer impaired by mercury in fish tissue. Therefore, a TMDL is not required.

This report provides an analysis of recent fish tissue monitoring data that supports the removal of the mercury in fish tissue impairment listing for Liberty Reservoir, when MDE proposes the revision of the State's Integrated Report. The remainder of this report lays out the general setting of the Liberty Reservoir watershed, presents a discussion of the reservoir's water quality characteristics relative to established water quality standards related to mercury and the applicable designated uses of the reservoir, and provides conclusions with regard to the characterization.

2.0 GENERAL SETTING

Location

The Liberty Reservoir watershed is located within the Patapsco River sub-basin of the Chesapeake Bay watershed, within Maryland. The reservoir's watershed drains 104,800 acres of western Baltimore County and eastern Carroll County (see Figure 1) (majority of watershed is located in Carroll County). A dam was completed on the North Branch Patapsco River in 1953, creating the Liberty Reservoir, which is owned by the City of Baltimore and managed by the Baltimore City Department of Public Works (BCDPW). Water supply intakes in the reservoir feed the BCDPW's Ashburton Water Filtration Plant, which provides drinking water to Baltimore City, Carroll County, and Baltimore County. The reservoir is primarily fed by the North Branch Patapsco River; other tributaries include Beaver Run, Keyer's Run, Prugh Run, Morgan Run, Middle Run, Locust Run, and Cooks Branch. There are several "high quality," or Tier II, stream segments (Benthic Index of Biotic Integrity (BIBI) and Fish Index of Biotic Integrity (FIBI) aquatic life assessment scores > 4 (scale 1-5)) located within the watershed requiring the implementation of Maryland's anti-degradation policy (COMAR 2012e). These include Keyser Run, Cooks Branch, an unnamed tributary to Morgan Run, an unnamed tributary to Little Morgan Run, and portions of Morgan Run, Joe Branch, Little Morgan Run, Middle Run, Beaver Run, the North Branch Patapsco River mainstem, and an unnamed tributary to the North Branch Patapsco River mainstem (MDE 2011a). Approximately 1.9% percent of the watershed area is covered by water (i.e., streams, ponds, etc). The total population in the MD 8-digit Liberty Reservoir watershed is approximately 115,288 (US Census Bureau 2010).

Reservoir Characteristics

Table 1 lists the Liberty Reservoir's physical characteristics.

Table 1: Current Physical Characteristics of Liberty Reservoir[1]

Location:	Baltimore and Carroll Counties, Maryland
Latitude - At Dam:	39° 22' 36" N
Longitude - At Dam:	76° 53' 30" W
Surface Area:	3,106 acres (107.3×10^6 ft^2)[2]
Normal Reservoir Depth:	133 feet
Designated Use:	I-P (Water Supply/Recreation) (COMAR 2012b)
Average Volume:	132,000 acre-feet
Drainage Area to Reservoir:	164 mi^2 (104,800 acres)[3]
Average Discharge:[4]	20 ft^3/s

Notes: [1] Sources: Weisberg et al. 1985 and James, Saffer, and Tallman 2001.
[2] ft^2: square feet.
[3] mi^2: square miles.
[4] ft^3/s: feet cubed per second.

Geology/Soils

The Liberty Reservoir watershed lies within the north-central Piedmont Plateau physiographic province of Maryland, which is characterized by a gentle to steep rolling topography. The surficial geology of the watershed is composed of hard, crystalline igneous and metamorphic

rocks of probable volcanic origin, which consist mainly of schist and gneiss, with smaller amounts of marble (Edwards 1981). The watershed drains in a northwest to southeasterly direction, following the dip of the underlying crystalline bedrock in the Piedmont physiographic province. Ground water is found primarily in the fractures and bedding-plane partings of rocks, but it may also be found in the solutional cavities of limestone and marble deposits (McCoy and Summers 1992).

The soils in the Liberty Reservoir watershed belong primarily to the Baile soil series (59%) and the Chester soil series (40%) (USDA 2013). The Baile soil series consists of soils that are very deep and poorly drained. These soils can be found on upland depressions and foot slopes and were formed in mica schist and granitized schist and gneiss. The Chester soil series consists of deep, well drained soils that are located on upland divides and upper slopes and were formed in materials weathered from micaceous schist (USDA 1976).

Soil type for the Liberty Reservoir watershed is also characterized by the United States Department of Agriculture (USDA) Soil Conservation Service (SCS) into four hydrologic soil groups: Group A soils have high infiltration rates and are typically deep well drained/excessively drained sands or gravels; Group B soils have moderate infiltration rates and consist of moderately deep-to-deep and moderately well-to-well drained soils, with moderately fine/coarse textures; Group C soils have slow infiltration rates with a layer that impedes downward water movement, and they primarily have moderately fine-to-fine textures; Group D soils have very slow infiltration rates consisting of clay soils with a permanently high water table that are often shallow over nearly impervious material. The Liberty Reservoir watershed is comprised primarily of Group B soils (81%) with smaller portions of Group C and Group D soils (13% and 6% respectively) (USDA 2013).

Land-Use

Based on the Chesapeake Bay Program Phase 5.3.2 (CBP P5.3.2) watershed model 2009 Progress Scenario, the land-use distribution in the watershed is 35.3% forested, 31.0% urban, 1.9% water, and 31.8% agricultural. The land-use distribution is displayed and summarized in Figures 2 and 3.

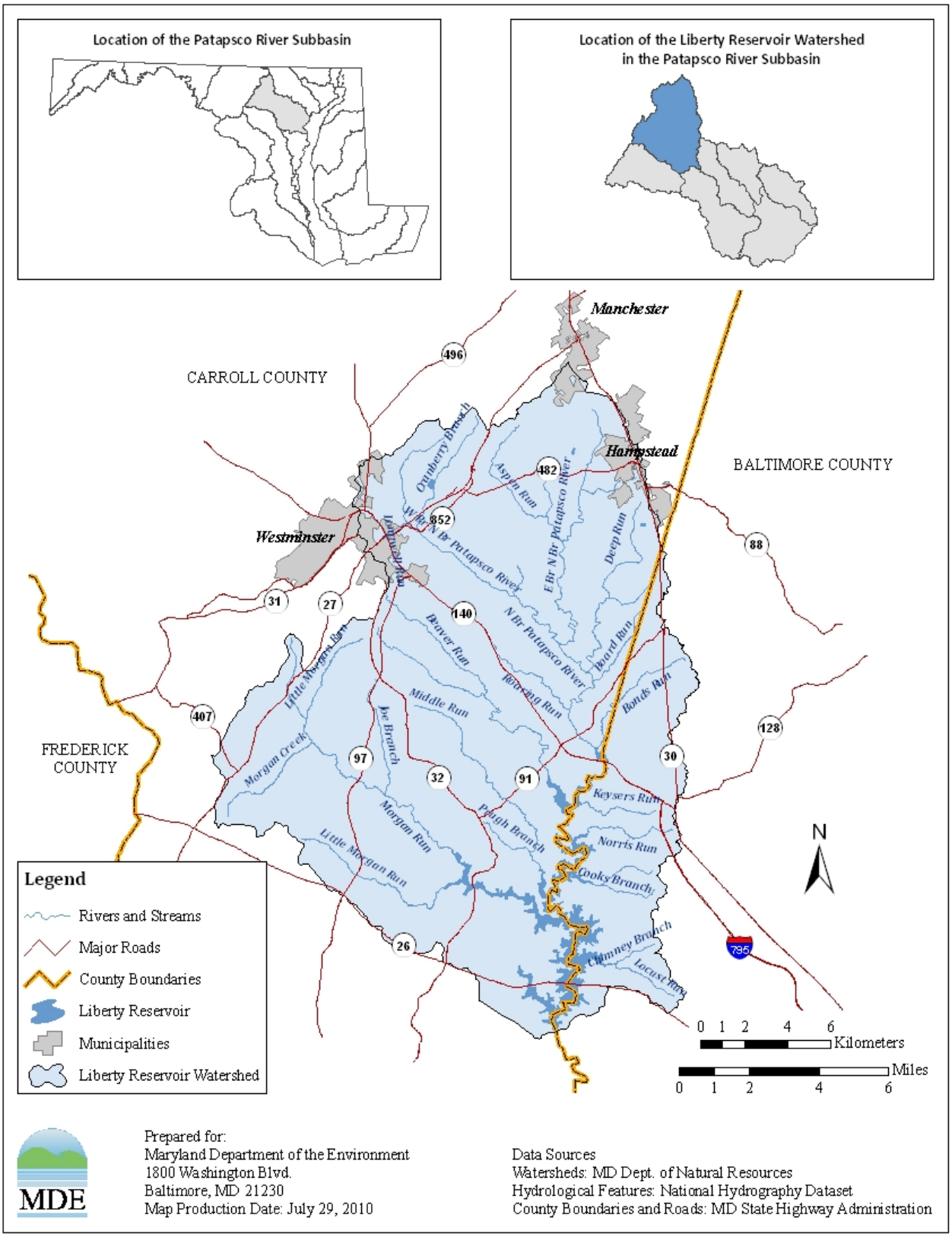

Figure 1: Location Map of the Liberty Reservoir Watershed

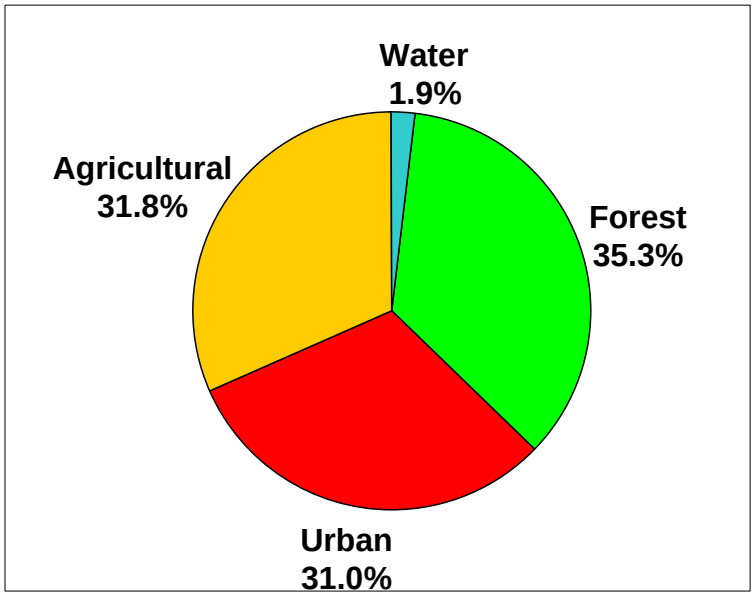

Figure 2: Land-Use Distribution in the Liberty Reservoir Watershed

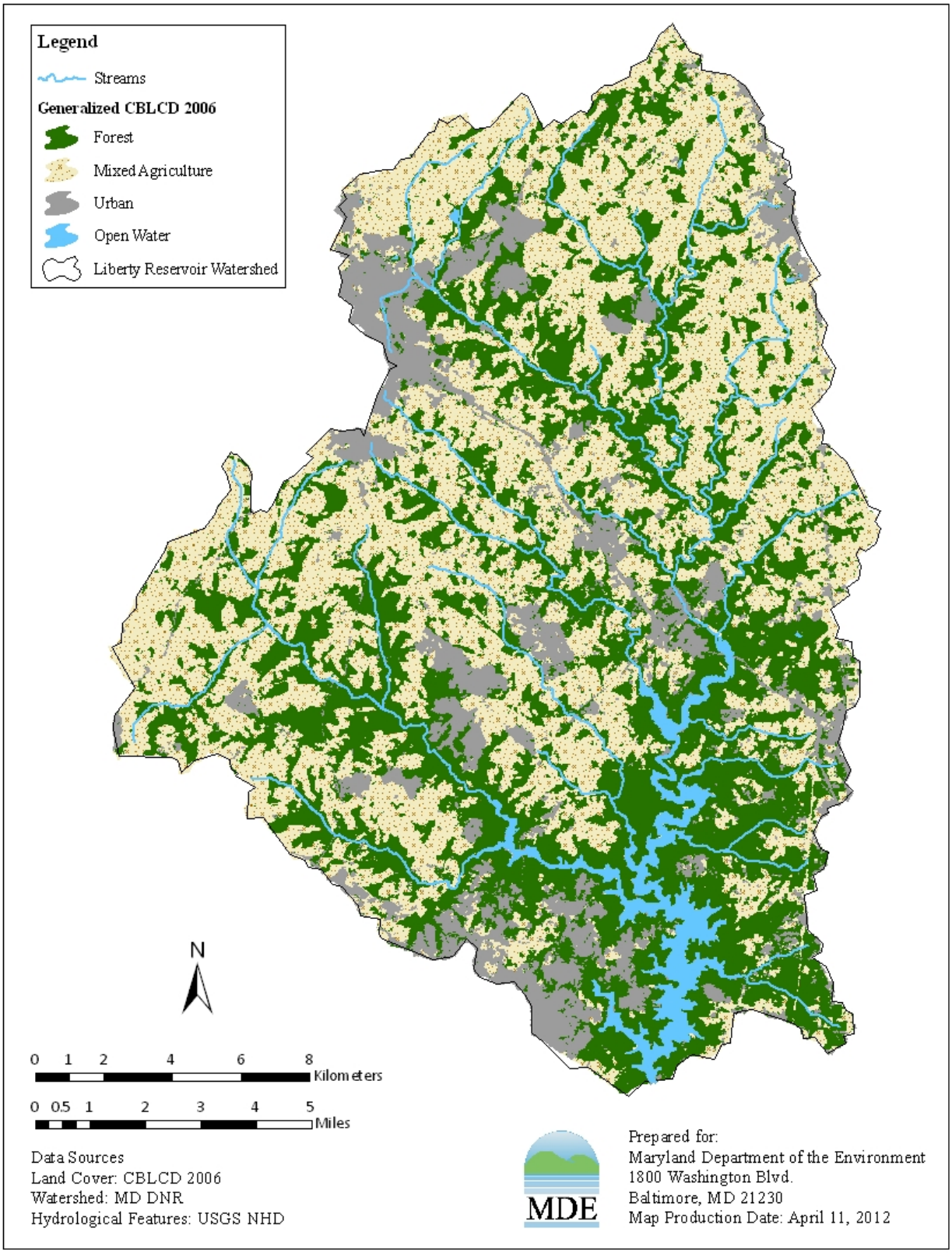

Figure 3: Land-Use Map for the Liberty Reservoir Watershed

3.0 WATER QUALITY CHARACTERIZATION

A water quality standard 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 support of aquatic life, primary or secondary contact recreation, drinking water supply, and shellfish propagation and harvest. Water quality criteria consist of narrative statements and numeric values designed to protect the designated uses. Criteria may differ among waters with different designated uses.

Maryland's water quality standards specify that all surface waters of the State shall be protected for water contact recreation, fishing, and the protection of aquatic life (COMAR 2012a). The specific Maryland Surface Water Use Designation in COMAR for Liberty Reservoir is Use I-P (*Water Contact Recreation, Protection of Nontidal Warm Water Aquatic Life and Public Water Supply*) (COMAR 2012b,c).

MDE interprets the "fishable" designated use under section 101(a) of the CWA to mean the protection of human health, as it relates to the consumption of fish and shellfish. Thus, "fishable" implies that when fish and shellfish are harvested, they can be safely consumed by humans (COMAR 2010d). The 2012 Integrated Report states that the Liberty Reservoir does not support its "fishing" designated use, due to elevated mercury levels in fish tissue, which does not allow for the consumption of fish that is protective of human health.

Mercury chemistry in the environment is complex and not fully understood. Mercury exhibits the properties of a metal, specifically its persistence in the environment, and it does not chemically break down beyond its elemental, uncharged form (Hg^0) or its ionic mercurous (Hg^+) and mercuric (Hg^{+2}) forms. However, it also has properties similar to a hydrophobic organic chemical, due to its ability to methylate via a bacterial process. Methylation of mercury can occur in water, sediment, and soil matrices under anaerobic conditions and, to a lesser extent, under aerobic conditions. In water, methylation occurs mainly at the water-sediment interface and at the oxic-anoxic boundary within the water column. Methylmercury is readily taken up by organisms and subsequently bioaccumulates, as it has a strong affinity for muscle tissue. It is effectively transferred through the food web, with tissue concentrations magnifying at each trophic-level. This process can result in elevated levels of methylmercury in organisms high on the food chain, despite nearly immeasurable mercury/methylmercury concentrations in the water column. Appendix B discusses mercury chemistry, including methylation, in greater detail.

In fish tissue, mercury is not usually found in concentrations high enough to cause fish to exhibit signs of toxicity, but the mercury in sport (trophic-level four) fish can present a potential health risk to humans. The health risk to humans posed by the mercury content in consumed fish tissue is due to methylmercury. Typically, almost all of the mercury found in fish tissue (90 to 95%) is in the form of methylmercury.

For public health purposes, MDE has the responsibility to monitor and evaluate the contaminant levels in Maryland's fish, shellfish and crabs, to determine if contaminant levels are within the limits established as safe for human consumption. In fulfillment of this public health responsibility, MDE issued a statewide fish consumption advisory for mercury in fish in 2001. This original 2001 advisory was established statewide as a precautionary measure, because the

primary source of mercury is understood to be atmospheric deposition, which is widely dispersed (MDE 2001). This advisory has subsequently been revised, and is updated on a regular basis, using actual monitoring data of fish tissue mercury concentrations. The updated advisory provides guidelines on fish consumption (allowable meals per month) for recreational anglers and their families (not including commercially harvested fish) and includes fish species in publicly accessible lakes, impoundments, rivers, etc. (MDE 2011b). The fish consumption guidelines were developed, in part, to protect against the possible neurobehavioral damages that could occur during human fetal development and early childhood.

To determine if the "fishing" designated use of a waterbody is impaired for a particular contaminant, the contaminant fish tissue concentration from a composite sample of fish fillets of any single common species of recreational fish is compared to the criterion concentration or established fish consumption advisory threshold concentration (for contaminants that do not have an existing criterion as per Maryland's water quality standards) for that contaminant. Appendix C describes in further detail MDE's methodology for fish tissue sampling and subsequent assessment of impairment relative to the "fishing" designated use of waterbodies throughout the state. Maryland collects composite samples of trophic-level four fish, such as largemouth bass, of legally harvestable size on a regular basis to determine whether or not the fish are safe for human consumption. If the numeric criterion or fish consumption advisory threshold concentration for a given contaminant is exceeded, the waterbody's "fishable", or "fishing", designated use is not being attained, and the waterbody is considered to be impaired for the presence of that contaminant in fish tissue.

As a state water quality standard (i.e., numeric criterion for a specific designated use), MDE has adopted the EPA recommended concentration of 300 micrograms per kilogram (µg/kg) as the mercury (methyl, not total) fish tissue concentration considered to be the highest possible concentration, or threshold concentration, that still supports the "fishable" designated use of a waterbody (US EPA 2001; COMAR 2012f). This numeric criterion represents the maximum allowable methylmercury concentration in the tissues of both freshwater and estuarine fish, as it relates to the protection of human health due to fish consumption amongst the general population. A waterbody with mercury fish tissue concentrations greater than 300 µg/kg is therefore not in attainment of its "fishing" designated use and is thus impaired for mercury in fish tissue.

Both the fish consumption guidelines and numeric criterion were developed based on methylmercury concentrations; however, the analysis presented in this document, and in general, MDE's analysis of fish tissue monitoring data and resultant fish consumption advisories, are conducted using total mercury. Therefore, they incorporate a conservative assumption.

Based on fish tissue data collected in 2000 and 2002, Maryland identified the Liberty Reservoir as impaired due to elevated levels of mercury in fish tissue on the 2002 Integrated Report (MDE 2002b). The 2002 Liberty Reservoir mercury TMDL (see Introduction for details) was based on the fish tissue sampling data collected in 2000 and 2002. The geometric mean methylmercury concentration for the sixteen fish tissue samples was 261 µg/kg. In 2002, the State's Integrated Report impairment listing threshold for methylmercury in fish tissue was a geometric mean of 235 µg/kg. In 2004, MDE adopted a 300 µg/kg arithmetic mean methylmercury in fish tissue

concentration as a new threshold for identifying waters impaired for mercury in fish tissue (MDE 2004). Then, in 2010, MDE changed the assessment methodology yet again so as to calculate the median, total mercury concentration in fish tissue for comparison to the 300 µg/kg threshold concentration. The change to a 300 µg/kg concentration made MDE's Integrated Report impairment listing threshold consistent with the State adopted, numeric criterion (i.e., water quality standard), as recommended by EPA, for mercury in fish tissue. The new impairment listing threshold was based on findings from a statewide survey of fish consumption by licensed recreational fishermen.

Subsequent fish tissue sampling in the reservoir was performed in 2003, 2007 and 2010. These samples will not be included in this WQA, however, since they do not meet MDE's data requirements (See Appendix C for further details on data requirements). The samples from 2003 and 2007 are not considered to be representative of current water quality conditions in the reservoir (i.e., they are considered to be out-dated). Three of five fish tissue composite samples collected in 2010 were not included in this analysis since the sampled fish species, blue gill (two samples) and yellow perch (one sample), are not uniquely trophic-level four consumers. The two other composite samples collected in 2010 were from largemouth bass, but they will not be included in this analysis because the average length of the sampled bass was 246 millimeters (mm), or about 10.7 inches, which is below the legal, "keepable", length of 12 inches. Therefore, these fish tissue samples would not be representative of mercury concentrations in consumable fish in the reservoir (See Appendix D for further details)**.**

Scientists have linked methylmercury concentrations in fish tissue with atmospheric mercury deposition, and it is estimated that two-thirds of this atmospheric deposition is derived from anthropogenic sources (Hammerschmidt and Fitzgerald 2006). Furthermore, EPA considers coal-fired electric power generating plants to be the largest anthropogenic source of mercury emissions in the nation. Thus, while a portion of the total mercury loading to Liberty Reservoir may be transported by National Pollutant Discharge Elimination System (NPDES) regulated urban stormwater conveyance systems, it can be assumed that the origin of any urban stormwater mercury loadings is from atmospheric deposition, since there are very few land sources of mercury. The same rationale also applies to both non-NPDES regulated urban stormwater mercury loadings and other nonpoint watershed mercury loadings. Whatever small contribution of mercury loadings that is derived from on-land sources can be attributed to the improper management of mercury-containing products.

The contribution of mercury to the reservoir from NPDES process water point sources is assumed to be minimal, as well. In 2008, MDE sampled the effluent of a large number of municipal wastewater treatment plants (WWTPs) in Maryland to determine the representative mercury concentrations in municipal WWTP discharges. This analysis was specifically conducted to aid in the development of mercury TMDLs in Maryland. Based on this study, in the majority of watersheds in Maryland, the total mercury contribution from process water point source loads is be considered insignificant (MDE 2010). Therefore, all NPDES regulated sources are considered to be insignificant contributors of mercury to the Liberty Reservoir. For informational purposes, Appendix A presents a summary of discharge permits in the watershed.

3.1 WATER QUALITY EVALUATION

A data solicitation for information pertaining to the mercury in fish tissue impairment in Liberty Reservoir, as identified in the 2010 Integrated Report, was conducted by MDE in 2012, and all readily available data from the past five years has been considered.

3.1.1 FISH TISSUE ANALYSIS

For this WQA, fish tissue concentrations of total mercury – instead of methylmercury – will be compared to the 300 µg/kg numeric criterion.

Two, five-fish composite samples of trophic-level four fish – largemouth bass – were collected from Liberty Reservoir and analyzed for total mercury fish tissue concentrations. The physical characteristics of the fish that were collected (see Appendix D) confirm that all of the fish were of legal, "keepable" size (*i.e.*, greater than 12 inches long)**.** By only including fish that were larger than 12 inches in length, the median fish tissue mercury concentration of the sampling data is indicative of long-term mercury accumulation in fish that are several years old. Thus, the fish tissue sampling data reflects any and all seasonal variations and critical conditions in water quality that have occurred over the life of the fish in the reservoir. The results of this analysis are shown below in Table 2.

Table 2: Summary of Fish Tissue Mercury Concentrations in Liberty Reservoir

Species	Trophic Level	Composite Sample Count	Number of Fish per Composite	Total Mercury Median Concentration (µg/kg)	MDE Human Health Criterion for Mercury in Fish Tissue (µg/kg)
Largemouth Bass	4	1	5	269.7	300
Largemouth Bass	4	2	5	128.9	300

The median mercury concentration in the composite fish tissue samples is 199.3 µg/kg. Thus, MDE's 300 µg/kg fish tissue mercury concentration, numeric criterion for the protection of human health via fish consumption is not being exceeded in Liberty Reservoir. Therefore, based on this fish tissue sampling data, the "fishable" designated use of the Liberty Reservoir is not impaired due to mercury in fish tissue.

3.1.2 ATMOSPHERIC DEPOSITION MODELING

As discussed previously in Section 3.0, the atmospheric deposition of mercury has been identified as the only significant source of mercury to the Liberty Reservoir watershed. Therefore, it is the primary source of mercury found in the tissues of the reservoir's fish populations. Most of this atmospherically deposited mercury is believed to have originated from stationary combustion sources, and of the mercury loading to the reservoir watershed from these stationary combustion sources, a large portion comes from electric generating units (EGUs). The Maryland Healthy Air Act (HAA) was put into effect in July of 2007 and was expected to reduce mercury loadings to watersheds throughout the State by requiring EGUs covered under the act to reduce their mercury emissions. An 80% reduction in mercury emissions, from 2002 levels, was required from these EGUs by 2010, and a 90% reduction, from 2002 levels, was required by 2013 (COMAR 2012g).

To estimate the effectiveness of the HAA, the atmospheric deposition of mercury to several MD 8-Digit watersheds was modeled for two different years: the baseline year, 2007, before implementation of the HAA; and 2013, when the HAA caps will be fully implemented. The estimates were performed using the California PUFF Model, an advanced, non-steady-state, time variable, Gaussian meteorological and air quality model, approved by EPA for many atmospheric pollutant modeling purposes. The model scenario runs and output were made available to MDE via the Maryland Department of Natural Resources' (DNR's) Power Plant Research Program (PPRP). Sherwell et al. (2006) provides a detailed description of the CALPUFF model, and the model itself is made available to the general public for download by the Atmospheric Studies Group (ASG) (ASG 2012).

The sources of the mercury loadings in the model were divided into five categories: EGUs and non-EGUs, both within and outside of Maryland; and global background (including natural) sources of mercury. Appendix E presents a discussion of the assumptions used in developing the model. The model output for the Liberty Reservoir watershed is summarized in Table 3 below.

Table 3: Modeled Atmospheric Mercury Loads to the Liberty Reservoir Watershed Using CALPUFF

Source Category	Baseline (2007)		Full HAA Implementation (2013)	
	Load (g/yr)[1]	**Percent of Total** (%)	**Load** (g/yr)	**Percent of Total** (%)
Maryland Non-EGU Total	508.5	5.4	508.5	6.6
Maryland EGU Total	1,927.0	20.4	176.2	2.3
Non-Maryland Non-EGU	1,577.3	16.7	1,577.3	20.5
Non-Maryland EGU	2,993.9	31.7	2,993.9	38.9
Global Background	2,431.7	25.8	2,431.7	31.6
TOTAL	**9,438.0**	**100**	**7,688.0**	**100**

Note: [1] g/yr: grams per year.

The model shows a large decrease (19.0%) in total mercury loadings to the reservoir watershed from 2007 to 2013. This entire reduction in loadings is due to reductions in mercury emissions from Maryland EGUs, as required by the HAA, and the subsequent decrease in atmospherically deposited mercury to the reservoir's watershed from these EGUs (90.9%). Because the HAA mandated EGUs reduce mercury emissions 80% by 2010, significant decreases in mercury emissions have already been achieved. It follows that the deposition of mercury to various watersheds across the State should have decreased as well. Thus, the decrease in fish tissue mercury concentrations that was observed between 2002 and 2012 is consistent with the decrease in mercury emissions and corresponding deposition to the watershed during the HAA implementation period. However, there is a lag-time between: (a) the reduction of mercury emissions, (b) the reduction of mercury loadings to the reservoir watershed, and (c) the corresponding uptake, bioaccumulation, and biomagnification of mercury through the food web in the reservoir. Therefore, the full benefits of the HAA may continue to become apparent as time progresses. Further reductions to mercury loadings, particularly due to a reduction in mercury emissions from non-Maryland EGUs, could occur with the eventual implementation of the federal Mercury and Air Toxics Standards (MATS) (U.S. EPA 2012).

4.0 CONCLUSION

Based on the analysis presented in this report, it is concluded that the State water quality standards (*i.e.*, numeric criterion) for mercury in fish tissue are being met within the Liberty Reservoir. Thus, the "fishing" designated use of the reservoir, which allows for the consumption of fish that is protective of human health, is being supported. This conclusion is based on two composite fish tissue samples collected from Liberty Reservoir in April 2012. The composite samples had a median mercury concentration (199.3 µg/kg) that was substantially less than MDE's numeric criterion for the protection of human health via fish consumption (300 µg/kg). Therefore, it is concluded that the impoundment is not impaired for mercury in fish tissue.

MDE maintains the authority to re-list the Liberty Reservoir as impaired for mercury in fish tissue in the future if new data indicate that the "fishing" designated use of the reservoir is no longer being met. Monitoring of the reservoir will continue through MDE's Fish and Shellfish Monitoring Program. This program will sample fish tissue from the Liberty Reservoir at least once every five years to determine whether various species of fish are safe for human consumption. If the results of this sampling indicate that fish from the reservoir are unsafe to eat because of mercury concentrations in their tissue, the reservoir would be re-listed as impaired for mercury in fish tissue on the Integrated Report.

Also, beginning in 2008, MDE in conjunction with DNR began commissioning yearly "young-of-the-year" (YOY) fish surveys. For the State's freshwater impoundments, largemouth bass were selected as the indicator species. Since the fish sampled in this study are yearlings and have therefore only had half a year of exposure to methylmercury, they are not representative of consumable fish and could not be used as data for a new listing. They should, however, show medium- and long-term mercury trends in fish tissue far sooner than would adult fish. Therefore, this sampling should be useful in determining the effectiveness of state and federal programs, such as the HAA and MATS, in reducing the atmospheric deposition of mercury. However, because YOY sampling began in 2008, at this point, there is not sufficient data to support any meaningful conclusions.

Barring the receipt of contradictory data, this report will be used to support the revision of the Integrated Report listing for mercury in fish tissue for Liberty Reservoir from Category 5 ("waterbody is impaired, does not attain the water quality standards, and a TMDL is required") to Category 2 ("waterbody is meeting some [in this case mercury in fish tissue related] water quality standards, but with insufficient data to assess all impairments") when MDE proposes the revision of Maryland's Integrated Report.

5.0 REFERENCES

ASG (Atmospheric Studies Group). 2012. The CALPUFF Modeling System. http://www.src.com/calpuff/calpuff1.htm (Accessed July, 2012).

CFR (Code of Federal Regulations). 2012a. *40 CFR 130.7*. http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&tpl=%2Findex.tpl (Accessed July, 2012).

COMAR (Code of Maryland Regulations). 2012a. *26.08.02.07 A*. http://www.dsd.state.md.us/comar/getfile.aspx?file=26.08.02.07.htm (Accessed July, 2012).

_____. 2012b. *26.08.02.02 B(2)*. http://www.dsd.state.md.us/comar/getfile.aspx?file=26.08.02.02.htm (Accessed July, 2012).

_____. 2012c. *26.08.02.08-K(1)*. http://www.dsd.state.md.us/comar/getfile.aspx?file=26.08.02.08.htm (Accessed July, 2012).

_____. 2012d. *26.08.02.02 B(1)(c)*. http://www.dsd.state.md.us/comar/getfile.aspx?file=26.08.02.02.htm (Accessed July, 2012).

_____. 2012e. *26.08.02.04*. http://www.dsd.state.md.us/comar/getfile.aspx?file=26.08.02.04.htm (Accessed July, 2012).

_____. 2012f. *26.08.02.03-2 G(1)*. http://www.dsd.state.md.us/comar/getfile.aspx?file=26.08.02.03-2.htm (Accessed July, 2012).

_____. 2012g. *26.11.27*. http://www.dsd.state.md.us/comar/SubtitleSearch.aspx?search=26.11.27.* (Accessed July, 2012).

Dean, J. A. 1992. *Lange's Handbook of Chemistry and Physics* 14th Ed. New York, NY: McGraw Hill.

Edwards, J. 1981. *A Brief Description of the Geology of Maryland.* Baltimore, MD: Maryland Geological Survey. Also Available at: http://www.mgs.md.gov/esic/brochures/mdgeology.html.

Gavis, J., and J. F. Ferguson. 1972. The Cycling of Mercury Throughout the Environment. *Water Research* 6: 986 – 1008.

Gilmour, C. C., and E. A. Henry. 1991. Mercury Methylation in Aquatic Systems Affected by Acid Deposition. *Environmental Pollution* 71: 131–169.

Hammerschmidt, C. R., and W. F. Fitzgerald. 2006. Methylmercury in Freshwater Fish Linked to Atmospheric Mercury Deposition. *Environmental Science & Technology* 40: 7764 – 7770.

James, R. W., R. W. Saffer, and A. J. Tallman. 2001. *Resources Data - Maryland and Delaware, Water Year 2000 Volume 1: Surface-Water Data WDR-MD-DE-00-1*. Baltimore, MD: U.S. Geological Survey. Also Available at: http://pubs.usgs.gov/wdr/wdr-md-de-dc-00-1/WDR-MD-DE-DC-2000v1.pdf.

McCoy, J. L., and R. L. Summers. 1992. *Maryland Double Pipe Creek (RCWP8)*. Raleigh, NC: North Carolina State University College of Agricultural and Life Sciences. Also Available at: http://www.bae.ncsu.edu/programs/extension/wqg/info/rcwp/mdprof.html.

MDE. 2001. *Press Release: MDE Issues New Fish Consumption Advisories*. Baltimore, MD: Maryland Department of the Environment. Also Available at: http://www.mde.state.md.us/programs/PressRoom/Pages/100.aspx.

_____. 2002a. *Total Maximum Daily Load of Mercury for Liberty Reservoir Baltimore and Carroll Counties, Maryland.* Baltimore, MD: Maryland Department of the Environment.

_____. 2002b. *2002 List of Impaired Surface Waters [303(d) List] and Integrated Assessment of Water Quality in Maryland*. Baltimore, MD: Maryland Department of the Environment. Also Available at: http://www.mde.state.md.us/programs/Water/TMDL/Integrated303dReports/Pages/Programs/WaterPrograms/TMDL/maryland%20303%20dlist/2002_303d_list.aspx.

_____. 2004. *2004 List of Impaired Surface Waters [303(d) List] and Integrated Assessment of Water Quality in Maryland*. Baltimore, MD: Maryland Department of the Environment. Also Available at: http://www.mde.state.md.us/programs/Water/TMDL/TMDLHome/Documents/www.mde.state.md.us/assets/document/Cover_TableofContents_2004-303d_Final.pdf.

_____. 2010. *Summary of Total Mercury Measured in Selected Municipal Wastewater Treatment Plants in Maryland*. Baltimore, MD: Maryland Department of the Environment.

_____. 2011a. *Maryland Tier II Dataset.* Baltimore, MD: Maryland Department of the Environment.

_____. 2011b. *Maryland Fish Consumption Advisories: Statewide Freshwater, Estuarine, and Marine Waters*. Baltimore, MD: Maryland Department of the Environment. Also Available at: http://www.mde.state.md.us/programs/marylander/citizensinfocenterhome/pages/citizensinfocenter/fishandshellfish/index.aspx.

_____. 2012. *The 2012 Integrated Report of Surface Water Quality in Maryland*. Baltimore, MD: Maryland Department of the Environment. Also available at: http://www.mde.maryland.gov/programs/water/tmdl/integrated303dreports/pages/2012_ir.aspx

NEI (National Emissions Inventory). 2012. *National Emissions Inventory Air Pollutant Trends Data*. http://www.epa.gov/ttnchie1/trends/ (Accessed July, 2012).

PPRP (Maryland's Power Plant Research Program). 1994. *Power Plant Contributions to Environmental Mercury in Maryland*. Annapolis MD: Maryland Department of Natural Resources, Power Plant Research Program.

Sherwell, J., M. Garrison, A. Yegnan, A. Baines. 2006. Application of the CALPUFF Modeling System for Mercury Assessments in Maryland. In *Proceedings 99th Annual Meeting of the Air and Waste Management Association* 429. Pittsburgh, PA: Air and Waste Management Association.

Shimomura, S. 1989. Analytical Behavior and Some Physical Properties of Mercury: A Review. *Analytical. Sciences* 5: 633 – 639.

US Census Bureau. 2010. *2010 Census*. Washington, DC: US Census Bureau.

USDA. 1976. *Soil Survey Baltimore County Maryland*. Washington, DC: United States Department of Agriculture. Also Available at: http://www.sawgal.umd.edu/nrcsweb/Baltconvert/index.htm.

_____. 2013. *U.S. General Soil Map (STATSGO2)*. Washington, DC: United States Department of Agriculture, Natural Resources Conservation Service. Also available online at http://soildatamart.nrcs.usda.gov. Accessed (July, 2013).

US EPA (US Environmental protection Agency). 1997. *Mercury Study Report to Congress* (*The Mercury Study*). Washington, DC: U.S. Environmental Protection Agency.

_____. 2000. *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories; Third Edition*. Washington, DC: U.S. Environmental Protection Agency. Also Available at: http://water.epa.gov/scitech/swguidance/fishshellfish/techguidance/.

_____. 2001. *Water Quality Criterion for the Protection of Human Health: Methylmercury*. Washington, DC: U.S. Environmental Protection Agency. Also Available at: http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/pollutants/methylmercury/document.cfm.

_____. 2012. *Mercury and Air Toxics Standards (MATS).* http://www.epa.gov/mats/ *(*Accessed July 2012).

Weisberg, S. B., K. A. Rose, B. S. Clevenger, and J. O. Smith. 1985. *Inventory of Maryland Dams and Assessment of Hydropower Resources*. Columbia, MD: Martin Marietta Environmental Systems.

APPENDIX A – MDE Permit Information

Table A-1: Liberty Reservoir Watershed Process Water Point Source Permit Information

NPDES #	Facility Name	Permit Type	
MD0067644	CRANBERRY WATER TREATMENT PLANT	MUNICIPAL	INDIVIDUAL
MD0067652	FREEDOM DISTRICT WATER TREATMENT PLANT	MUNICIPAL	INDIVIDUAL
MD0001384	CONGOLEUM CORPORATION	INDUSTRIAL	INDIVIDUAL
MD0001881	BTR HAMPSTEAD, LLC	INDUSTRIAL	INDIVIDUAL
MD0058556	CITY OF WESTMINSTER KOONTZ WELL	INDUSTRIAL	INDIVIDUAL
MDG492472	S & G CONCRETE - FINKSBURG PLANT	INDUSTRIAL	GENERAL
MDG766057	CARROLL COUNTY FAMILY YMCA[1]	INDUSTRIAL	GENERAL
MDG766199	THE BOSTON INN, INC.[1]	INDUSTRIAL	GENERAL
MDG766199	GLYNDON TRACE CONDOMINIUMS[1]	INDUSTRIAL	GENERAL
MDG766210	FOUR SEASONS SPORTS COMPLEX[1]	INDUSTRIAL	GENERAL
MDG766371	FREEDOM SWIM CLUB[1]	INDUSTRIAL	GENERAL
MDG766379	GREEN VALLEY SWIM CLUB[1]	INDUSTRIAL	GENERAL
MDG766048	MCDANIEL COLLEGE[1]	INDUSTRIAL	GENERAL
MDG675043	MARYLAND MILITARY FACILITY – CAMP FRETTERD[2]	INDUSTRIAL	GENERAL
MDG675029	PEARLSTONE FAMILY CAMP[2]	INDUSTRIAL	GENERAL

Notes: [1] Swimming pool discharge permits.
[2] Hydrostatic testing facility discharge permits.

Table A-2: Liberty Reservoir Watershed NPDES Stormwater Permit Information

NPDES Permit #[1,2,3]	Facility Name[4]	NPDES Regulated Stormwater Permit Type[2,3]
MD0068314	BALTIMORE COUNTY MS4	BALTIMORE COUNTY PHASE I MS4
MD0068331	CARROLL COUNTY MS4	CARROLL COUNTY PHASE I MS4
MD0055501	STATE HIGHWAY ADMINISTRATION MS4 (PHASE I)	SHA PHASE I MS4
MDR05550	CITY OF WESTMINSTER MS4	MUNICIPAL PHASE II MS4
MDR05550	CITY OF HAMPSTEAD MS4	MUNICIPAL PHASE II MS4
MDR05550	CITY OF MANCHESTER MS4	MUNICIPAL PHASE II MS4
N/A - 02SW1965	BALTIMORE COUNTY BUREAU OF HIGHWAYS - SHOP 3	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1219	BFI WASTE SERVICES, LLC - FINKSBURG	OTHER NPDES REGULATED STORMWATER
N/A - 02SW3001	BULLOCK'S MEATS, INC.	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1824	C AND C MULCH PROCESSING, LLC	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1755	CARROLL COUNTY REGIONAL AIRPORT	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1452	CONDON'S AUTO PARTS, INC.	OTHER NPDES REGULATED STORMWATER
N/A - 02SW2006	GENERAL DYNAMICS ROBOTIC SYSTEMS	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0664	HODGES LANDFILL	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0954	JONES AUTO & SALVAGE	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1144	M & M TRUCK & EQUIPMENT CO., INC.	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0660	NORTHERN MUNICIPAL LANDFILL	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1345	SHA - WESTMINSTER SHOP	OTHER NPDES REGULATED STORMWATER
N/A - 02SW1908	SMITH BROTHERS AUTO PARTS	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0078	THOMAS, BENNETT & HUNTER, INC. - SHOP FACILITY	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0794	TOBACCO TECHNOLOGY, INC.	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0115	CJ MILLER. LLC	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0719	MARYLAND PAVING - FINKSBURG	OTHER NPDES REGULATED STORMWATER
N/A - 02SW0029	MARANDA INDUSTRIES	OTHER NPDES REGULATED STORMWATER
N/A	MDE GENERAL PERMIT TO CONSTRUCT	OTHER NPDES REGULATED STORMWATER

Notes: [1] N/A: Permit does not have an NPDES number. For the industrial stormwater permits, the permit number listed is the MDE permit application number.

[2] Although not listed in this table, some individual permits from Table A-1 incorporate stormwater requirements, and there are additional, general, permitted Phase II MS4s, such as military bases, hospitals, etc., within the watershed.

[3] MS4: Municipal Separate Storm Sewer System

[4] SHA: State Highway Administration

APPENDIX B – Mercury Chemistry

Mercury is a Group IIB (Periodic Table) element, as are zinc and cadmium. Elemental metallic mercury exists as a high luster silver-colored liquid at room temperature. Some key physical properties of metallic mercury are listed in Table B-1. Varied industrial and consumer uses of mercury include electrical apparatuses, such as fluorescent light tubes, and control instruments - including thermometers and barometers. It is also used in the manufacture of pharmaceuticals, antifouling paints, mercury fulminate, electrolytic cells, and dental amalgams. Mercury is also a constituent of a number of antiseptics such as *mercurochrome, merthiolate and mercressin*.

Mercury and all its compounds are toxic. Mercury fulminate, $Hg(CNO)_2$, is used as a detonator for initiating the explosion of smokeless powder and various high explosives (i.e., TNT, dynamite, etc.). Mercury fulminate is very unstable and can be exploded by shock; its explosion causes the main explosive to be detonated. Mercury electrolytic cells are used in a manufacturing process for chlorine/alkali production. Liquid mercury dissolves many metals, especially the softer ones such as copper, silver, gold, and the alkali elements. The resulting alloys, which may be solids or liquids, are called amalgams. Dental amalgam is an alloy of mercury and silver.

Table B-1: Physical Properties of Metallic Mercury[1]

Atomic Number	80
Atomic Weight	200.59
Density[2,3]	13.5 g/cm^3 @ 25°C
Melting Point	-39°C
Boiling Point	357°C
Water Solubility (molarity)[4]	3.0 x 10^{-7} (mol/L) @25°C
Water Solubility (mass basis)[5]	60 µg/L @ 25°C

Notes: [1] Source: (Dean 1992)
[2] g/cm^3 = grams per centimeters cubed
[3] C = Celcius
[4] Mol/L = mols per liter
[5] µg/L = micrograms per liter

Mercury chemistry in the environment is complex and not fully understood. Mercury exhibits the properties of a metal, specifically its persistence in the environment, and it does not chemically break down beyond its elemental, uncharged form or its ionic forms. Mercury exists in three oxidation states: the metallic, uncharged (elemental) state (Hg^0); the mercurous (ionic) state (Hg^{+1}); and the mercuric (ionic) state (Hg^{+2}). These states are separated by only a small oxidation potential (E_h), and the metal readily participates in redox chemical reactions. In particular, Hg^{+1} salts disproportionate under many conditions to yield the Hg^{+2} salt and metallic mercury. Reduction of both the mercurous and the mercuric salts normally yields the metal state (PPRP 1994).

Mercury in natural waters may appear in the form of any of its three oxidation states. The predominate state is determined by the hydrogen ion concentration (described as pH) and the reduction potential of the water. Since chloride and sulfide complex Hg^{+1} and Hg^{+2} ions, concentrations of these compounds also affect the relative species distribution (Gilmour and

Henry 1991; Shimomura 1989). Ammonium, carbonate, bicarbonate, and phosphate concentrations do not affect speciation (PPRP 1994).

In natural systems, pH is generally in the range of 5 to 8 and the reduction potential is typically less than 0.5 Volts. For these systems, mercury sulfide (HgS) and metallic mercury are the most likely solids to be found in equilibrium with saturated solutions of mercury salts at moderate chloride (Cl^{-1}) and sulfide (S^{-2}) concentrations. The predominant species in the corresponding solutions will be mercuric hydroxide ($Hg(OH)_2$) and mercuric chloride ($HgCl_2$) in well oxygenated waters and Hg metal in poorly oxygenated waters (Gavis and Ferguson 1972). In reducing sediments, HgS will predominate the solid phase (PPRP 1994).

Mercury also has properties similar to a hydrophobic organic chemical due to its ability to be methylated through a bacterial process. Methylation of mercury can occur in water, sediment, and soil matrices under anaerobic conditions, and to a lesser extent, under aerobic conditions. In water, methylation occurs mainly at the water-sediment interface and at the oxic-anoxic boundary within the water column. Methylated mercury is thought to be thermodynamically unstable in water; thus, organic mercury found in surface waters is probably preserved through reaction barriers that prevent degradation.

Methylation does not occur in the presence of moderate to high sulfide concentrations, which immobilize Hg^{+2} ions (PPRP 1994). In fish tissue, mercury is not usually found in concentrations high enough to cause fish to exhibit signs of toxicity, but the mercury in sport (trophic-level four) fish can present a potential health risk to humans. This health risk to humans posed by the mercury content in fish tissue, if consumed, is due to methylmercury. Typically, almost all of the mercury found in fish tissue (90 to 95%) is in the form of methylmercury.

Methylmercury is readily taken up by organisms and subsequently bioaccumulates, as it has a high affinity for muscle tissue. It is effectively transferred through the food web, with tissue concentrations magnifying at each trophic-level. This process can result in elevated levels of methylmercury in organisms high on the food chain, despite nearly immeasurable mercury/methylmercury concentrations in the water column.

APPENDIX C – Integrated Report Methodology for Determining Toxic Impairments to the "Fishing" Designated Use of Waterbodies in Maryland

Fish Tissue

Section 101(a)(2) of the CWA established as a national goal the attainment of "water quality which provides for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water." This is commonly referred to as the "fishable/swimmable" goal of the Act. Additionally, Section 303(c)(2)(A) of the CWA requires water quality standards to protect public health and welfare, enhance the quality of water, and serve the purposes of the Act. The EPA, along with MDE, interprets these regulations to mean that not only should waters of the State support thriving and diverse fish and shellfish populations, but they should also support fish and shellfish which, when caught, are safe to consume by humans.

Some of the toxic contaminants that are present in various waterbodies throughout Maryland tend to bioaccumulate (primarily mercury and PCBs) in the tissues of gamefish (e.g., largemouth bass) and bottom-feeders (e.g. catfish), often at elevated levels. When the concentration levels of any one specific contaminant in fish tissue are elevated to such a degree that it increases the risk of chronic health effects in humans, if consumed regularly, the State has the responsibility to issue a fish consumption advisory for that particular contaminant in the specific species of fish, in which the contaminant concentrations were found to be elevated. Fish consumption advisories are designed to protect the general public as well as sensitive populations (i.e., young children and women who are or may become pregnant). In addition to such advisories, which stop at four meals per month, the Department also provides fish consumption recommendations, which stop at 8 meals per month. These additional recommendations are issued in order to protect the more frequent fish consumers.

When a fish consumption advisory (not a recommendation) is issued for a waterbody, the designated use of that waterbody (i.e., the "fishing" designated use) is usually not being supported. This may result in the identification of a waterbody as impaired on the Integrated Report for the specific contaminant that is found at elevated levels in fish tissue. To determine if a waterbody is impaired, the median contaminant concentration in the edible portion of the common recreational fish species is compared to the established fish consumption advisory threshold or numeric criterion concentration, when applicable. If the threshold/criterion concentration is exceeded, the waterbody's designated use is not being met, and the waterbody is identified as impaired. The existing fish tissue numeric criteria are used as the impairment identification thresholds (i.e., determines if the "fishing" designated use is supported), where applicable (e.g., the methylmercury numeric fish tissue criterion is 300 μg/kg). For contaminants that do not have an existing criterion (e.g., PCBs), MDE has defined "fishable" as the ability to consume at least four meals per month (i.e., the threshold number of allowable meals per month for a fish consumption advisory) of common recreational fish species by an individual that has a mass of 76 kilograms (kg) (see Contaminant Thresholds Section below).

Data Requirements

The data requirements for identifying a waterbody as impaired are very similar to the data requirements for issuing a fish consumption advisory, with only slight variations. The data requirements for identifying a waterbody as impaired are as follows:

1. All available data should be reviewed when making decisions regarding waterbody impairments.
2. Only contaminant concentrations that are measured in the part of the fish or shellfish that are typically consumed will be used for assessment purposes. Maryland publishes fish consumption advisories based on contaminant concentrations found in fillets only; therefore, only data collected from fillets are to be considered when making decisions regarding waterbody impairments. For shellfish, only data collected from the soft tissue portions of the organisms will be considered.
3. The fish tissue data needs to be collected from the specific waterbody in question.
4. The size of the fish sampled should be within the legal slot limit. If no slot limit exists for a specific species, best professional judgment for a minimum size of a given species will be applied.
5. Minimum data requirement: five fish (individual or composite of the same resident species) for a given waterbody. At times, in order to protect more sensitive populations, MDE might issue a fish consumption advisory that is based on an incomplete dataset (less than five fish of the same species). However, the publication of such an advisory does not automatically result in the identification of a waterbody as impaired. Thus, the minimum data requirement needs to be met in order to identify a waterbody as impaired.
6. All fish that comprise a composite sample must be within the same size class (i.e., the smallest fish must be within seventy-five percent of the total length of the largest fish).
7. Species used to determine impairment should be representative of the waterbody. Migratory and transient species may be used if they are the dominant recreational species, but they should only be used in conjunction with resident species, especially in the case of the tidal rivers of the Chesapeake Bay.
8. To ensure that the impairment is temporally relevant, impairments based on the minimum required samples should be re-sampled prior to TMDL development.

Contaminant Thresholds

The contaminant threshold and criterion concentrations are based on a risk assessment calculation that incorporates numerous risk parameters such as contaminant concentration, reference dose/cancer slope factor, exposure duration, lifetime span, and for some contaminants, cooking loss.

Table C-1: Threshold/Criterion Concentrations for Toxic Contaminants of Concern

Contaminant	Threshold/Criterion	Basis	Group
Mercury	300 µg/kg – wet weight	EPA/MDE Human Health Fish Tissue Consumption Criteria	General Public[1]
PCBs	39.0 µg/kg – wet weight	4 meals/month concentration level	General Public[1]

Note: [1] General Public: Individual with a mass of 76 kg.

Over time, advances in science may require changes in risk assessment parameters that may increase or decrease the currently used contaminant thresholds/criterion, and consequently the concentrations used to make decisions regarding impairments. If this occurs, waterbodies that were previously identified as impaired may no longer be considered impaired, or new waterbodies may need to be identified as impaired.

APPENDIX D – Composite Fish Tissue Sampling Data and Analysis

This appendix presents all of the fish tissue sampling data applied in the analysis.

Table D-1: Liberty Reservoir Composite Fish Tissue Sampling Data

Sample ID	Trophic-Level	Species[1]	Collection Date	Composite #	Length (mm)	Weight (g)[2]	Total Mercury Tissue Concentration (µg/kg)
04_2012_LIBE_01	4	LMB	4/9/12	1	400	935	-
04_2012_LIBE_02	4	LMB	4/9/12	1	426	1,066	-
04_2012_LIBE_03	4	LMB	4/9/12	1	374	802	-
04_2012_LIBE_04	4	LMB	4/9/12	1	370	651	-
04_2012_LIBE_08	4	LMB	4/9/12	1	353	546	-
Composite #1[4]					**385**	**800**	**269.7**
04_2012_LIBE_05	4	LMB	4/9/12	2	348	539	-
04_2012_LIBE_06	4	LMB	4/9/12	2	332	491	-
04_2012_LIBE_07	4	LMB	4/9/12	2	337	516	-
04_2012_LIBE_09	4	LMB	4/9/12	2	314	410	-
04_2012_LIBE_10	4	LMB	4/9/12	2	310	367	-
Composite #2 [4]					**328**	**465**	**128.9**
MEDIAN [5]					**356**	**632**	**199.3**

Notes: 1 LMB = Largemouth Bass
[2] g = grams
[4] Composite length and weight are averages from the individual fillets.
[5] The total length, weight, and mercury tissue concentration are medians of the two composites.

An analysis of the length and weight of these fish indicates that they were of legal, "keepable" size.

APPENDIX E– Mercury Air Deposition

Mercury air deposition loads to the Liberty Reservoir watershed representative of several different scenarios were estimated using the CALPUFF model, which is an advanced, non-steady-state Gaussian meteorological and air quality model that has been approved by EPA for many atmospheric pollutant modeling purposes. The CALPUFF model scenario runs and output were made available to MDE via Maryland DNR's PPRP. The scenarios were conducted and analyzed in the following manner (Sherwell et al. 2006):

- Baseline loads were calculated based on the 2007 stack test for sources in Maryland and the 2002 National Emissions Inventory (NEI) for other sources (NEI 2012). This calculation was representative of typical conditions over the last decade, assuming no reductions from Maryland's HAA;
- Loads reflecting reduced emissions resulting from full implementation of the HAA in 2013 as specified in COMAR were calculated (COMAR 2012g);
- Analysis to separate loads originating from the following sources were performed:
    - Within the state of Maryland:
        - EGUs vs. non-EGUs;
    - Outside of Maryland, but within the model domain (roughly the eastern third of the United States):
        - EGUs vs. non-EGUs;
    - Global background loads, including natural loads (Sherwell et al. 2006).