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**Total Maximum Daily Load of Mercury
for Big Piney Run Reservoir (a.k.a. Frostburg Reservoir)
Garrett County, Maryland**

FINAL

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List of Abbreviations

AAWCC	Allowable Ambient Water Column Concentration
BAF	Bioaccumulation Factor
BMP	Best Management Practice
CAA	Clean Air Act
CWA	Clean Water Act
COMAR	Code Of Maryland Regulations
DE	Delaware
DNR	Maryland Department of Natural Resources
Eh	Oxidation Potential
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic Precipitator
FA	Future Allocation
ft ³ /s	Cubic feet per second
g	gram
Hg	Mercury
kg	kilogram
km ²	Square kilometers
LA	Load Allocation
L	liter
µg/L	micrograms per liter = ppm (parts per billion)
µg/kg	micrograms per kilogram = ppm (parts per billion)
MDE	Maryland Department of the Environment
MD	Maryland
MeHg	Methylmercury
MGD	Millions of gallons per day
mm	millimeter
m ³	Cubic meters
mi ²	Square miles
MOS	Margin of Safety
MRL	Mercury Load Reduction
m ³ /s	Cubic meters per second
ng/L	nanograms per liter = ppt (parts per trillion)
NADP-MDN	National Atmospheric Deposition Program – Mercury Deposition Network
NPDES	National Pollutant Discharge Elimination System
NPS	Nonpoint Source
PCS	Permit Compliance System (An EPA database – <i>Envirofacts Warehouse</i> on the EPA website)
pH	The inverse logarithm of the hydrogen ion concentration
ppb	Parts per billion
ppm	Parts per million
PS	Point Source
RGM	Reactive Gaseous Mercury

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TMDL	Total Maximum Daily Load
UMCES	University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory
USGS	United States Geological Survey
WLA	Waste Load Allocation
WQS	Water Quality Standard
WQLS	Water Quality Limited Segments
WTP	Water Treatment Plant
WWTP	Waste Water Treatment Plant
yr	Year

EXECUTIVE SUMMARY

Big Piney Reservoir is an impoundment in the Youghiogheny River Watershed (basin code 05-02-02-04) in Garrett County, Maryland. Big Piney Reservoir was identified on the State of Maryland's draft 2002 list of Water Quality Limited Segments [303(d) list] as impaired by mercury contamination, based on data for mercury concentrations in fish tissue. Concentrations in the water are well below the threshold for concern in regard to drinking water. The Maryland water quality standards Surface Water Use Designation [Code of Maryland Regulations (COMAR 26.08.02.07)] for Big Piney Reservoir is Use III-P –*Natural Trout Waters and Public Water Supply*. The Maryland Department of the Environment's (MDE) current public fish consumption advisory to eat limited amounts of fish from Big Piney Reservoir is not supportive of the recreational fishing use. Therefore, this document proposes to establish a Total Maximum Daily Load (TMDL) for mercury in Big Piney Reservoir.

The methodology used to compute this mercury TMDL consists of two broad steps. The first step is to determine a maximum Allowable Ambient Water Column Concentration (AAWCC) of mercury in the water column that ensures the bioaccumulation of the total mercury by fish will remain below a maximum fish tissue concentration. The second step is to determine a maximum allowable load that is consistent with the maximum water column concentration. The resultant TMDL includes a Load Allocation (LA), a Waste Load Allocation, a margin of safety (MOS), and a Future Allocation (FA). The TMDL methodology considers all sources, including direct atmospheric deposition to the surface of the lake, nonpoint source contributions from the watershed, and point source contributions.

The calculated TMDL for mercury to Big Piney Reservoir is an average annual load of 15.34 grams per year (0.0420 grams per day). This is the total amount of mercury that can be assimilated by Big Piney Reservoir without significantly increasing the risk from mercury in fish tissue. This TMDL includes a 3% Future Allocation (FA) and a 97% allocation to nonpoint sources (LA). For nonpoint sources, an estimate is provided of suballocations between direct atmospheric deposition to the surface of the lake and terrestrial nonpoint point sources from the watershed. The TMDL implementation through reduced atmospheric contributions is expected to be accomplished over time through existing and proposed regulatory controls (e.g., Clean Air Act), which will be applied to current sources of atmospheric mercury emissions. These controls are expected to be implemented in phases.

1.0 INTRODUCTION

The federal Clean Water Act (CWA) and Maryland regulations require the State to maintain water quality that supports fish and aquatic life, and fishing as a recreational activity. The U.S. Environmental Protection Agency (EPA) interprets the “fishable” use under section 101(a) of the Clean Water Act to include, at a minimum, the protection of aquatic communities and human health related to the consumption of fish and shellfish. In other words, “fishable” means that not only can fish and shellfish survive in a waterbody, but when harvested, can also be safely eaten by humans and terrestrial wildlife (OWOW Memorandum # WQSP-00-03, October 2000).

Based on mercury data in fish tissue from a subset of lakes across the State, the Maryland Department of Environment (MDE) announced a statewide fish consumption advisory for lakes this year. This advisory has been established statewide as a precautionary measure because the primary source of mercury is understood to be atmospheric deposition, which is widely dispersed. Based on additional fish tissue data, Maryland has verified that Big Piney Reservoir is impaired due to mercury in fish tissue.

Section 303(d) of the federal CWA and EPA’s implementing regulations direct each state to identify and list waters, known as water quality limited segments (WQLS’s), in which current required controls of a specific substance are inadequate to achieve water quality standards. The CWA requires the development of a Total Maximum Daily Load (TMDL) for all impaired waters on their Section 303(d) list. A TMDL reflects the maximum pollutant loading of an impairing substance a waterbody can receive and still meet water quality standards. A TMDL can be expressed in mass per time, toxicity or any other appropriate measure (40CFR 130.2(i)). A TMDL must take into account seasonal variations, critical conditions and a margin of safety (MOS), to allow for uncertainty. Maryland’s 2002 proposed 303(d) list prepared by MDE lists Big Piney Reservoir (watershed code 05-02-02-04) as impaired for mercury in fish tissue.

Immediate public health benefits will be derived from the enhanced public awareness that will be generated through this TMDL process. The timely development of this TMDL will increase public awareness of the need for upgrading controls on the atmospheric emissions of mercury, which are anticipated to result in water quality improvements.

2.0 SETTING AND WATER QUALITY DESCRIPTION

2.1 General Setting and Source Assessment

Big Piney Reservoir is an impoundment located in northeastern Garrett County, Maryland (Figure 1). The impoundment, which is owned by the City of Frostburg, lies on Big Piney Run. The dam was constructed in 1990.

Inflow to the Lake is primarily via Big Piney Run. The watershed map (Figure 2) shows that land use in the area draining to Big Piney Reservoir is predominately forest/herbaceous. Land use distribution in this watershed is approximately 57% forest/herbaceous, 37% mixed agriculture, 5% developed and 1% water (Figure 3) (Maryland Department of Planning, 2000 Land Use Data).

Table 1: Physical Characteristics for Big Piney Reservoir

Location:	Garrett County, Maryland Latitude 39.70 Longitude 79.01 (At the dam)
Surface Area:	0.4452 km ²
Normal Depth:	9.75 meters
Normal Volume	1.74 x 10 ⁶ m ³
Drainage Area to Lake:	30.83 km ²
Average Annual Flow	0.645 m ³ /s

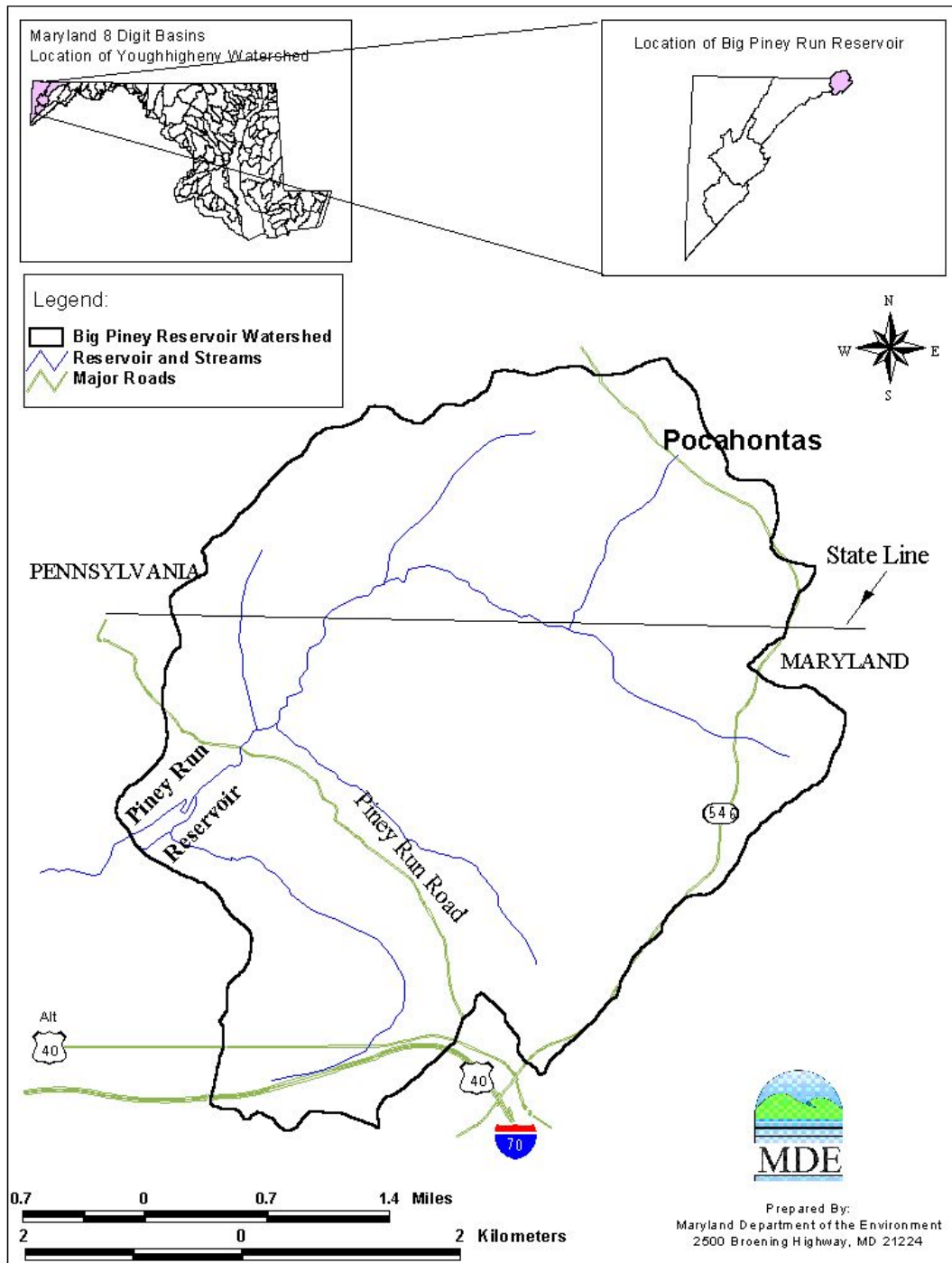


Figure 1: Location Map of Big Piney Reservoir in Garrett County, Maryland

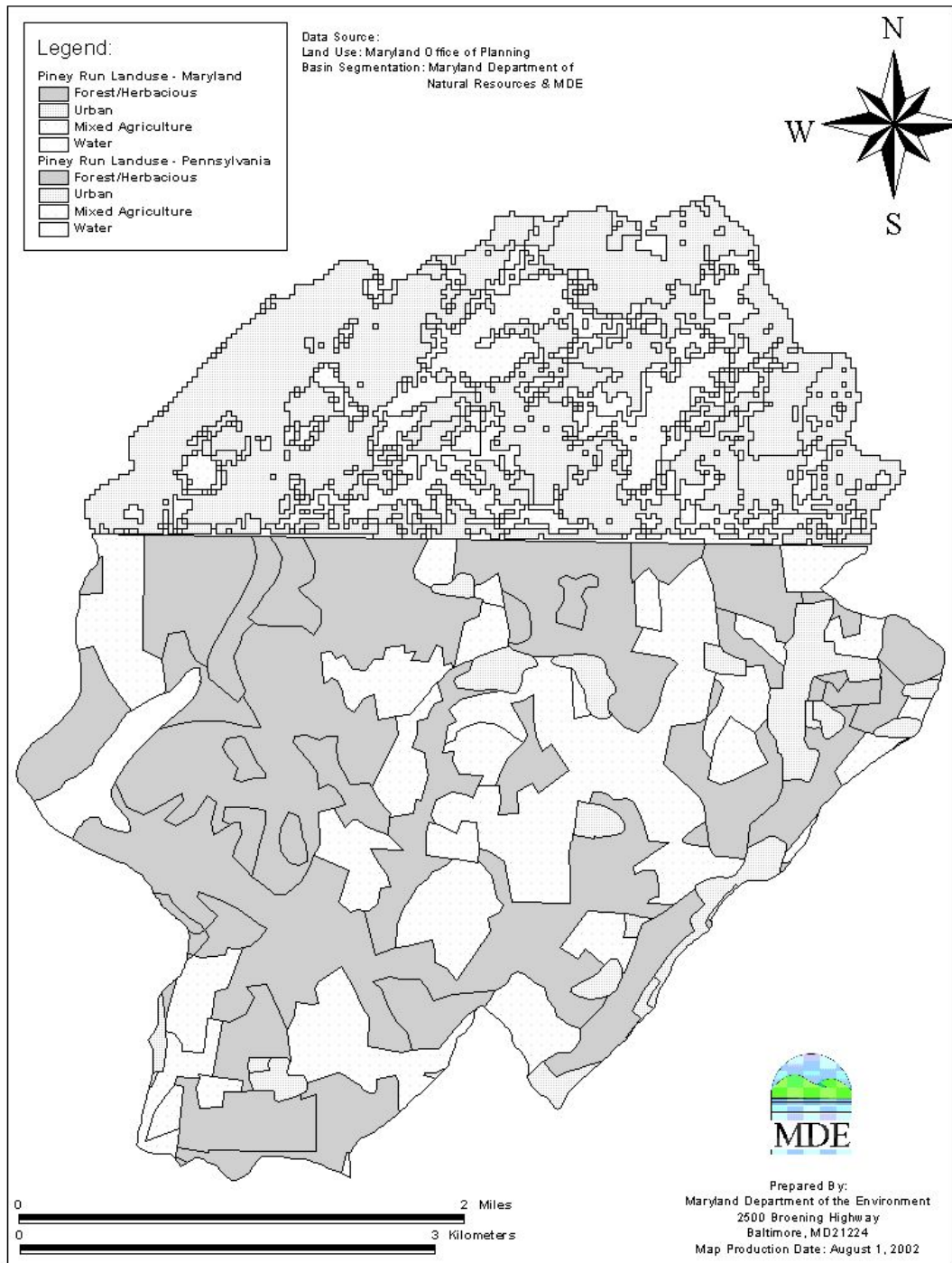


Figure 2: Predominant Land Use in the Big Piney Reservoir Subwatershed

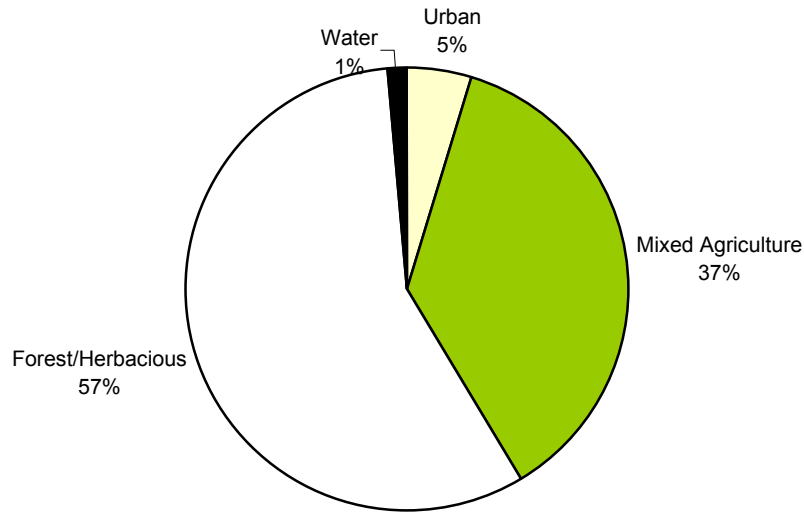


Figure 3: Land Use Distribution in the Big Piney Reservoir Subwatershed

Big Piney Reservoir is located in a watershed in which the mercury impairment is dominated by nonpoint source mercury contributions (via atmospheric deposition). The EPA considers coal-fired electric power generating plants to be the largest anthropogenic source of mercury emissions in the nation (EPA, 2000). Therefore an essentially one-to-one relationship between the Allowable Ambient Water Column Concentration (AAWCC) and atmospheric deposition of mercury is assumed.

The National Atmospheric Deposition Program – Mercury Deposition (NADP-MDN) was instituted in 1995 by federal, state, non-governmental research organizations and state agricultural experimental stations in order to monitor the amount of mercury deposited regionally in precipitation. Five sites of this network were used to estimate mercury air deposition rates in Maryland: Maryland (Wye), Delaware (Lewes), and Pennsylvania (Valley Forge, Arendtsville, Holbrook). Data obtained from this network was analyzed to estimate annual deposition rates (Appendix A). Estimates of current loads are included in Section 4.3.3.

In Maryland, the major sources of mercury air emissions are as follows: 43% attributed to power plants, 31% municipal waste combustors, 19% medical waste incinerators, 6% Portland Cement plants, and 1% other (e.g., landfills, oil-fired power plants, other industries).¹

US industrial demand for mercury dropped 75% from 1988 to 1997. This drop can be attributed to actions including:

¹ www.mde.state.md.us/programs/landprogrms/hazardous_waste/mercury/mercuryinfo.asp

- Federal bans on mercury additives in paint and pesticides;
- Industry efforts to reduce mercury in batteries;
- Increasing state regulation of mercury emissions and mercury in products;
- State-mandated recycling programs; and
- Voluntary actions by industry.²

There are no point sources for Big Piney Reservoir.

2.2 Water Quality Characterization

To characterize the water quality of Big Piney Reservoir, two site-specific elements are addressed below: mercury residue in fish tissue data and mercury concentrations in the water column.

2.2.1 General Discussion

Trophic level 4 fish (Largemouth Bass) were harvested from Big Piney Reservoir and were analyzed for mercury tissue concentrations. Water column samples were also taken and analyzed for mercury concentrations. A bioaccumulation factor was developed based on the above samples (see Section 4.3.1 for details of the calculation). Samples were collected by the Maryland Department of Natural Resources (DNR) and the University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory (UMCES) and were analyzed by UMCES.

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 fish (trophiic level 4) can present a potential health risk to humans. The health risk to humans represented 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 methylmercury form. Mercury chemistry in the environment is complex and not totally understood. Mercury exhibits certain properties of a metal, specifically, persistence in the environment, in that it is not chemically broken down beyond the elemental mercury form (Hg^0) or its ionic forms (Hg^+ and Hg^{+2}). It 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 solution under anerobic 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 will bioaccumulate as it has a strong affinity for muscle tissue. It is effectively transferred through the food web, with tissue concentrations magnifying at each trophiic level. This process can result in high levels of mercury in organisms high on the food chain, despite nearly immeasurable quantities of mercury/methylmercury concentrations in the water column.

For public health purposes, the MDE has the responsibility to monitor and evaluate the contaminant levels in Maryland fish, shellfish and crabs, and to determine if contaminant levels are within the limits established as safe for human consumption. In fulfillment of this public

²Source: www.epa.gov/mercury/information.htm

health responsibility, MDE has issued a statewide fish consumption advisory for mercury in fish. This advisory provides guidelines (Table 2) 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 and impoundments.

These guidelines were developed, in part, to be protective for neurobehavioral effects during human fetal development and early childhood. An 8-ounce meal size is recommended for the general population. Recommended meal sizes for women of childbearing age and children (0-6 years) are 6 ounces and 3 ounces respectively. Levels of total mercury in fish tissue above 235 $\mu\text{g}/\text{kg}$ are an indication of impairment. When data for total mercury concentrations in fish tissue are not available, data for methylmercury concentrations are used alternately for impairment decisions.

**Table 2: Maryland Department of the Environment
Fish Consumption Guidelines**

Total mercury in fish tissue residue Range ($\mu\text{g}/\text{kg}$)	Recommended fish consumption meals per month (based on an 8 oz. meal size)
117 – 235	7 - 4
236 - 322	3
322 – 409	2
410 – 939	1
> 939	< 1

2.2.2 Mercury in Fish Tissue Data

Samples of fish were taken from Big Piney Reservoir. Trophic level 4 fish (largemouth bass) were targeted in the collection because they represent the top of the bioaccumulation food chain and provide a conservative estimate of the mercury dose associated with fish consumption from this reservoir. The fish fillets obtained during the sampling effort were analyzed for mercury concentrations and were measured for length and weighed. Appendix G lists the individual fish data. A statistical analysis of the individual fish samples is presented in Table 3.

**Table 3: Summary of Mercury in Fish Tissue Concentrations
from Big Piney Reservoir**

Trophic Level	Sample Count	Geometric mean Methylmercury Concentration ($\mu\text{g}/\text{kg}$)
4	15	582.1

2.2.3 Water Column Mercury Concentrations

Water column samples were taken from Big Piney Reservoir and were analyzed for total mercury and methylmercury concentrations using EPA Method 1631. Samples were analyzed for both constituents in both whole water and as dissolved (filtered). The geometric mean value of whole total mercury in the whole water column is 2.56 ng/L. The geometric mean value of dissolved total mercury in the water column concentration is 1.06 ng/L. The geometric mean value of whole methylmercury in the whole water column is 0.302 ng/L. The geometric mean value of dissolved methyl mercury in the water column concentration is 0.262 ng/L. Appendix G contains the individual data sets and a discussion of data reduction.

2.3 Water Quality Impairment

The Maryland water quality standards Surface Water Use Designation [Code of Maryland Regulations (COMAR) 26.08.02.07] for Big Piney Reservoir is Use III-P designation – *Natural Trout Waters and Public Water Supply*. The water quality impairment of Big Piney Reservoir being addressed by this TMDL analysis consists of a higher than acceptable level of mercury. Concentrations in the water are well below the threshold for concern in regard to drinking water. Maryland water quality standards, under the federal CWA, require that water quality support public health and welfare for this designated use. An existing public health fish consumption advisory for Big Piney Reservoir recommends significant limits on the consumption of fish from this impoundment. This is a violation of the State’s narrative water quality standards, because the designated use of “fishing” is not fully supported. This loss of use results in Big Piney Reservoir’s identification on Maryland’s 2002 303(d) list as impaired for mercury residue in fish tissue. Mercury concentrations in the water are well below the threshold for concern in regard to drinking water.

3.0 TARGETED WATER QUALITY GOAL

The objective of the TMDL established in this document is to reduce mercury loads to levels that are expected to result in meeting water quality criteria that support the Use III-P designation – *Natural Trout Water and Public Water Supply*. See COMAR 26.08.02.02 B (1). Specifically, limiting the mercury loads is intended to ensure that concentrations in fish tissue are consistent with the protection of human health.

- MDE considers the term “suitable for fishing” (See COMAR 26.08.02.02 B (1) (c)) or “fishable” as the ability for the general population to eat at least 4 meals per month of any single common recreational fish species from the given waterbody. This upper threshold value for fish tissue is 235 µg/kg for methylmercury.³

³ To determine if a waterbody is impaired, the contaminant concentration from a sample of fish fillets of any single common species of recreational fish is compared to the established threshold. Generally, the geometric mean of 10 trophic level 4 fish make up the sample. If the threshold is exceeded, the waterbody’s use is not met and the waterbody is considered impaired.

The fish tissue endpoint is designed to ensure that the general population can safely consume at least four meals per month. This is consistent with water quality standards, which must protect the overall population and do not have to be protective of more sensitive subpopulations. The risk assessment used by MDE to determine this concentration threshold incorporates the same risk level, Reference Dose and body weights, is consistent with the guidance adopted by the U.S. EPA for the protection of human health from methylmercury described in “Water Quality Criteria for the Protection of Human Health: Methylmercury” (EPA-823-R-01-001).

4.0 TOTAL MAXIMUM DAILY LOADS AND ALLOCATIONS

4.1 Overview

This section describes how the mercury TMDL and loading allocations were developed for Big Piney Reservoir. The second subsection describes the analysis framework for developing the AAWCC and the TMDL calculation. The third subsection describes the steps in the TMDL calculation and the fourth subsection describes the TMDL allocations. The fifth subsection addresses seasonal variations and critical conditions, and the sixth subsection explains the rationale for the margin of safety (MOS). Finally, in the seventh subsection, the pieces of the equation are combined in a summary accounting of the TMDL.

4.2 Analysis Framework

The computational framework used for this TMDL calculation is a refinement of the methodology described in “*Total Maximum Daily Load for Total Mercury in Fish Tissue Residue in Big Haynes Reservoir,*” which was developed and proposed by the EPA, Region 4 for the State of Georgia, dated August 30, 2001. Maryland has refined the method by using a fish tissue threshold for mercury that is consistent with its fish consumption advisory methods and more stringent than the EPA guidelines applied in Georgia. In addition, Maryland has estimated loads from air deposition and watershed sources using mass balance calculations.

The TMDL analysis sets a maximum allowable ambient water column concentration (AAWCC), which ensures that bioaccumulation of the total mercury concentration in fish tissue will remain below the threshold stated in Section 3.0. The AAWCC is computed using bioaccumulation factors based on site-specific fish tissue mercury concentration data and water column mercury concentration data. The TMDL is expressed in terms of an average annual load into the waterbody. A future allocation is also set aside, which may be used in the future if additional information indicates that it is necessary to provide an explicit allocation to point sources.

The TMDL analysis framework can be summarized in the following steps:

- (1) Determine the Biological Accumulation Factor (BAF) based on observed fish tissue data and observed water column concentrations.
- (2) Using the BAF, calculate a maximum AAWCC that will ensure the targeted water quality goal of a mean fish tissue concentration of methylmercury remains below 235 µg/kg.

- (3) Using a mass balance approach, estimate the TMDL that will result in the desired water quality target. This target consists of the AAWCC that is adjusted to account for particulate mercury, because the AAWCC is solely the dissolved component. (See Appendix H).

4.3 Total Maximum Daily Load Analysis

This section expands upon the three steps outlined immediately above.

4.3.1 Bioaccumulation Factor

A BAF is the ratio of the concentration of a chemical in fish tissue to the concentration of the chemical in the water column. As defined in Mercury Study Report to Congress (EPA 1997), the BAF is “The concentration of the methylmercury in fish divided by the concentration of total dissolved methylmercury in water.” When computing a BAF, MDE considered one of the three methods utilized in the Mercury Study report to Congress. Specifically this entails the direct estimation of BAF for trophic level 4 fish from site-specific criteria. The BAF calculated for this analysis is site specific, because it uses data from Big Piney Reservoir. More details are given in the U.S. EPA technical support document for BAFs (EPA-820-B-95-005, March 1995). Also see, the EPA Science Advisory Board report, EPA-SAB-EPED/DWC-93-005, December 1992.

A food chain can be described in terms of trophic levels, in which higher levels represent species that are higher on the food chain.

$$BAF = \{TL_4Fc_{(MeHg)} / Wc_{(MeHg)}\}$$

Where:

(MeHg) means the particular concentration is for methylmercury

TL₄Fc = Geometric mean of trophic level 4 fish tissue concentrations (µg/kg), from Table 3

Wc = Water column concentration (µg/L); from Appendix G, Table G5.

The BAF calculation for Big Piney Reservoir is expressed as:

$$BAF = \frac{582.1\mu g / kg}{0.000262\mu g / L}$$

$$BAF = 2,221,756L / kg$$

4.3.2 Maximum Allowable Ambient Water Column Concentration

The maximum AAWCC is the concentration in the water that ensures that bioaccumulation will not exceed a fish tissue concentration that serves as the water quality endpoint. The water quality endpoint, stated in Section 3.0 is an average total mercury fish tissue concentration of 235 µg/kg for any trophic level.

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The AAWCC uses the following equation from EPA guidelines (EPA, 2000):

$$AAWCC = \frac{\{(RfD - RSC) * BW * ConversionUnits\}}{(CR * BAF * FractionMeHg)}$$

Where:

RfD = 0.1 µg/kg/day MeHg	Combined consumption rate: fresh + saltwater fish
RSC = 0.027 µg/kg/day MeHg	Relative Source contribution (saltwater fish). This value is subtracted because the system under study is fresh water
BW = 70 kg	Body weight (average of males and females)
CR = 29.8 g/day	Consumption rate (4 meal/month) based on MD fish consumption advisory risk analysis
BAF= (L/kg)	Bioaccumulation Factor (site specific). See Section 4.3.1
Fraction MeHg	Ratio of dissolved methylmercury to dissolved total mercury in the water column (Appendix G)
Conversion units = 1,000,000 (ug/g)	To convert the AAWCC to units of ng/L

Therefore:

$$AAWCC = \frac{(0.1 - 0.027) * 70 * 1,000,000}{(29.8 * 2,221,756 * (0.262 / 1.06))}$$

$$AAWCC = 0.312ng / L \text{ Dissolved Total Mercury}$$

The fraction of methylmercury was calculated using the geometric mean values for dissolved concentrations for total mercury and methylmercury values (Tables G3 and G5). Because the AAWCC accounts only for the dissolved component of the total mercury concentration, it is necessary to estimate the particulate mercury component expected to be present under conditions of a TMDL. To this end, a total mercury component, which is used in the load calculation for the TMDL, is computed in Appendix H.

4.3.3 Total Maximum Daily Load Calculation

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The key finding in this overall analysis is the AAWCC, which is the water column concentration below which fish tissue concentrations will be protected to support human consumption. This section presents a computation of the estimated average annual load that corresponds to achieving the adjusted AAWCC (See Appendix H). This annual load constitutes the TMDL.

The computation used to estimate the average annual load is a straightforward mass balance calculation. The computational procedure assumes a constant direct atmospheric deposition of mercury to the surface of the lake, and a constant loading from the watershed that feeds the lake. The contribution from the watershed is a combination of atmospheric loads that wash off the landscape of the watershed and any other terrestrial sources. A Future Allocation is set aside for future use in the event future data indicates an explicit allocation is necessary for point sources.

Briefly, the calculation involves an estimation of current loads that are necessary to produce the observed water column concentration. This is done using mass balance calculations. After the current loads are determined, reductions are calculated by including a load reduction factor. These steps are described in more detail below with values that apply to Big Piney Reservoir.

Current Load: The calculation of the current total mercury load is performed in Appendix I. The current load includes the effect of direct atmospheric deposition to the surface of the reservoir, the nonpoint source load from the watershed, which includes atmospheric mercury that is deposited to the surface of the land and is passed through the watershed and any identified point sources.

Based on the mass balance estimates, the current loads are summarized as follows:

Load from direct Air Deposition to the reservoir =	0.0153 g/day (10.7%)
Load from NPS from the Surrounding Watershed* =	0.1274 g/day (89.3%)
Point Sources** =	<u>0.0 g/day (0.0%)</u>
Current Daily Load =	0.1427 g/day (100.0%)

* Much of this is from atmospheric deposition to the land.

** This watershed contains no point sources

Maximum Allowable Load: The maximum allowable load is calculated by adjusting the estimated current direct atmospheric load and watershed load downward until the target concentration is achieved (Appendix I). The target concentration is the adjusted AAWCC, which accounts for particulate mercury (See Appendix H). Once the TMDL is determined, a future allocation is determined by adjusting the atmospheric and watershed contributions downward, maintaining their relative proportions. The Future Allocation is determined on the basis of the potential need for a future point source allocation⁴.

The results of the TMDL computation are summarized as follows:

⁴ A program is under development to conduct periodic monitoring using a new analytical technique that will provide meaningful estimates of potential point source contributions.

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Load from direct Air Deposition to the reservoir =	0.0044 g/day (10.38%)
Load from NPS from the Surrounding Watershed* =	0.0364 g/day (86.62 %)
Future Allocation =	<u>0.0012 g/day (3.0%)</u>
Total Maximum Daily Load =	0.0420 g/day (100.0%)

* This is from atmospheric deposition to the land.

4.4 Total Maximum Daily Load Allocations

In a TMDL assessment, the total allowable load is divided and allocated to the various pollutant sources. The allocations described in this section demonstrate how the subject TMDL can be implemented to achieve water quality standards in Big Piney Reservoir. Specifically, these allocations show that the sum of mercury loadings to the Big Piney Reservoir from existing nonpoint sources can be maintained safely within the TMDLs established here.

The CWA and EPA regulations provide for flexibility in implementation of TMDLs, as long as the overall load is not exceeded. The allocations are generally classified as waste load allocation (WLA) for point sources, load allocation (LA) for nonpoint sources, and future allocation (FA). As future information becomes available, MDE expressly reserves the right to allocate this TMDL among different sources and land use categories in any manner that is reasonably calculated to achieve water quality standards. In particular, the Future Allocation may be used in the future if additional information indicates that it is necessary to provide an explicit allocation to point sources.

4.5 Seasonal Variations and Critical Conditions

Seasonal Variations: This TMDL is effectively represented as an AAWCC level that is designed to reduce mercury concentrations in fish, thus protecting human health by minimizing exposure through fish consumption. The analysis is based on long-term averages. Although many factors might vary over a given year, the effect is averaged out over several years during which fish accumulate mercury. An analysis of the length and weight of individual fish used in the BAF calculation (Table G1) indicates they were of legal (keepable) size and the average age was approximately five to six years (DNR, 2000). The averaging effect of long-term bioaccumulation is reflected in the analysis and supports the use of an average annual AAWCC and average annual load. Specifically, the fish tissue concentration at the time of sampling is the result of long-term accumulation in fish that are several years old. The bioaccumulation factor is, in turn, computed on the basis of this long-term accumulation. An AAWCC is then calculated based on the relationship between the BAF, water column mercury concentration ratios and risk parameters related to fish consumption. Finally, the average annual loading values for the waterbody are calculated to meet the AAWCC.

Critical Conditions: Critical conditions concerns do not arise in this analysis because acute conditions are not a concern at the observed concentrations and the allowable concentrations of mercury are based on human fish consumption over a long time period, which averages out critical events. Also, the TMDL is protective of human health from fish consumption at all times, so that any “critical conditions” within that time frame are considered. Finally, the TMDL

level established to be protective of human health is more conservative than the mercury levels to protect environmental resources, implying that critical conditions for environmental resources are also addressed by the previous logic that is applied to human health.

The annual average load is of primary significance because mercury bioaccumulation and the resulting risk to human health that results from mercury consumption is a long-term phenomenon. Therefore, shorter seasonal inputs are less meaningful than total annual loads over many years. The use of annual loads allows for integration of short-term or seasonal variability.

The reader should also note that, although this analysis presents a loading limit, the fish tissue concentration depends on mercury water column concentration, not on load. Thus, annual loads alone do not determine fish tissue accumulations; that is, if a fish is exposed to the same concentration of mercury, but more water or less water of the same concentration passes through the reservoir due to seasonal differences in rainfall, the fish tissue accumulation will be the same. This understanding is important when interpreting future information to evaluate the success of implementing controls to achieve the TMDL.

4.6 Margin of Safety

A margin of safety (MOS) is required as part of a TMDL in recognition of the fact that there are many uncertainties in scientific and technical understanding of water quality in natural systems. Specifically, knowledge is incomplete regarding the exact nature and magnitude of pollutant loads from sources and the specific impacts of those pollutants on the chemical and biological quality of complex, natural water bodies. The MOS is intended to account for such uncertainties in a manner that is conservative from the standpoint of environmental and human health protection.

Based on EPA guidance, the MOS can be achieved through one of two approaches (EPA, April 1991). One approach is to reserve a portion of the loading capacity as a separate term in the TMDL (i.e., $TMDL = WLA + LA + MOS$). The second approach is to incorporate the MOS as conservative assumptions in the design analysis. For purposes of this mercury TMDL methodology, Maryland has adopted margins of safety that make use of conservative assumptions, that is, a built-in MOS.

- (1) When computing the bioaccumulation factor (BAF) it is assumed that anglers consume only trophic level four fish, which results in a larger BAF. Trophic level four fish are near the top of the food chain, and thus consistently have the highest observed fish tissue concentrations due to bioaccumulation. Adopting the assumption that people eat only trophic level four fish represents a conservative assumption of exposure. This larger BAF is used in the denominator of the formula for computing the allowable ambient water column concentration (AAWCC), which makes the AAWCC tighter (a lower allowable water column concentration).
- (2) EPA's recommended threshold for mercury in fish tissue is for 300 $\mu\text{g}/\text{kg}$, but MDE is using a value of 235 $\mu\text{g}/\text{kg}$. This lower threshold is based on a risk analysis used

for Maryland's fish consumption procedures. The analysis assumes that some people consume more meals of fish over a given period of time than is assumed by EPA.

- (3) The AAWCC formula includes the computation of the maximum allowable mercury in fish tissue, based on human health risk principles. Subtracting the relative source contribution (RSC), associated with mercury contribution to a typical diet due to marine fish, has the effect of allowing a maximum fish tissue concentration of about 172 $\mu\text{g}/\text{kg}$, rather than 235 $\mu\text{g}/\text{kg}$. This is a conservative assumption.

Items (2) and (3) immediately above result in a combined MOS of about 43%. The loss of mercury from the waterbody through reduction and volatilization is not accounted for in the analysis. Therefore, credit for this phenomenon is taken as an additional margin of safety.

4.7 Summary of Total Maximum Daily Loads

The annual TMDL for mercury is calculated from the equation:

$$\text{TMDL} = \text{WLA} + \text{LA} + \text{FA} + \text{MOS}$$

Where: WLA = Waste Load Allocation

LA = Load Allocation

FA = Future Allocation

MOS = Margin of Safety

The TMDL for mercury (g/day) is presented below in Table 4.

Table 4: Summary of Mercury TMDL for Big Piney Reservoir

TMDL (g/yr)	Waste Load Allocation (g/yr)	Load Allocation (g/yr)	Future Allocation (g/yr)	Margin of Safety
15.34	0	14.88	0.46	Implicit (Approximately 43%)

On average, the TMDL will result in loads of approximately 0.042 g/day.

MDE reserves the right to update the TMDL calculation and the TMDL source allocations as additional information from currently active or future programs becomes available and is analyzed.

5.0 ASSURANCE OF IMPLEMENTATION

Big Piney Reservoir is located in a watershed in which the mercury impairment is dominated by nonpoint source mercury contributions (resulting from atmospheric deposition). The EPA considers coal-fired electric power generating plants to be the largest anthropogenic source of

mercury emissions in the nation. As such, the TMDL implementation provisions may differ from the implementation of TMDLs from other pollutants (nutrients and toxics - other than mercury). EPA Region 4 and EPA Region 6 have indicated that reductions in atmospheric contributions will be accomplished over time through existing and proposed Clean Air Act regulatory controls that will ensure significant reductions in mercury loading on a nationwide basis by reducing atmospheric emissions. However, they believe it is too early to estimate the reductions in mercury emissions that may result from the future regulation of electric power generating utilities. The EPA expects to see reduced emissions of mercury from this industry sector as a number of regulations are implemented to control sulfur dioxide emissions and nitrous oxide emissions, since some control technologies used to limit these pollutants collaterally reduce mercury emissions to some degree.

EPA has taken a number of actions to reduce mercury pollution, including regulations for industries that contribute significantly to mercury pollution. These actions, once fully implemented, are expected to reduce nationwide mercury emissions caused by human activities by about 50% over 1990 levels. Examples include:

- Municipal waste combustors. EPA issued final regulations on October 31, 1995. These regulations were expected (by 2000) to reduce mercury emissions from these facilities by about 90%, from 1990 levels;
- Medical waste incinerators. EPA issued emission standards on August 15, 1997. These were expected (by 2002) to reduce mercury emissions from these facilities by about 94%, from 1990 levels.⁵

In addition to controls on mercury air emissions, proper management of mercury containing productions and source reduction are critical components to reducing mercury in the waste stream and to the environment. To this end, the following activities are examples of actions taken within Maryland:

- About 11 counties in Maryland have instituted household hazardous waste collection programs, where wastes including mercury containing products can be collected for safe management and disposal;
- Effective October 1, 2002, there is a prohibition on the sale and distribution of mercury fever thermometers in Maryland except by prescription (with certain exceptions, such as hospitals);
- Effective October 1, 2003, primary and secondary schools cannot use or purchase elemental or chemical mercury. MDE is required to provide outreach to schools on the management, recycle and disposal of mercury products.⁶
- Effective November 1, 2002, MDE will be implementing EPA's Universal Waste Rule which encourages the collection and recycling of wastes including mercury containing thermostats, lamps, and other products.
- Maryland is part of EPA Region 3's "e-cycling" project, which encourages the

⁵Source: www.epa.gov/mercury/information.htm

⁶Source: www.mde.state.md.us/assets/document/Retailers_Manual_web_version.pdf

collection, refurbishment, and recycling of electronic devices. Four permanent sites in Maryland have been established for collection of computers, televisions, monitors, etc.

- Five sites in Maryland are partners and another MD company is a champion in the Hospitals for a Healthy Environment (H2E) program. Under this program, a Memorandum of Understanding was signed between USEPA and the American Hospital Association, calling for, among other things, virtual elimination of mercury-containing hospital wastes by the year 2005. As of November 1, 2002, the program has 338 partners representing 1021 health care facilities.⁷ The program's website, www.h2e-online.org/tools, provides additional tools to these facilities for waste management and pollution prevention.

As additional data and information are collected for the Big Piney watershed and as new legal requirements are imposed under the Clean Air Act and other environmental statutes, MDE will continue to evaluate the effectiveness of the regulatory and non-regulatory programs in achieving the water quality targets under this TMDL.

As part of Maryland's Watershed Cycling Strategy, follow-up monitoring and assessment will be conducted to evaluate the impairment status of Big Piney Reservoir. For public health purposes, the MDE has the responsibility to monitor and evaluate the contaminant levels in Maryland fish, shellfish and crabs, and to determine if contaminant levels are within limits established as safe for human consumption. The currently issued fish consumption advisories are one result of the execution of this responsibility.

MDE's website (<http://www.mde.state.us>) contains extensive information for consumers and businesses concerning reducing mercury in Maryland's environment. Information includes descriptions of mercury in the home and the environment, alternate products to mercury-containing products, mercury spill cleanup safety and mercury recycling resources.

⁷Source: www.h2e-online.org

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Appendix A

Mercury Air Deposition

Summary

Mercury air deposition data was utilized to quantify the contribution of nonpoint air sources to mercury loads in impaired water bodies. Air deposition data provided total annual loads of mercury to various water bodies.

Method

Five sites of the National Atmospheric Deposition Program – Mercury Deposition Network (NADP – MDN; <http://nadp.sws.uiuc.edu/mdn/>) were used to estimate mercury air deposition rates in Maryland: Maryland (Wye), Delaware (Lewes), and Pennsylvania (Valley Forge, Arendtsville, Holbrook). This network was instituted in 1995 by federal, state, non-governmental research organizations, and state agricultural experiment stations in order to monitor the amount of regional deposition of total mercury in precipitation. These sites spanned the western, northern, and central regions of Maryland (Figure A1). Data obtained from the network were converted to an annual basis ($\text{ug}/\text{m}^2\text{-wk}$) and then plotted as a frequency histogram. Plots and estimates of kurtosis and skewness revealed non-normally distributed data. Geometric means were therefore calculated for each site. An average of the geometric means was then taken ($8.43 \pm 1.26 \text{ ug}/\text{m}^2\text{-yr}$) in order to estimate the statewide wet deposition of mercury (in precipitation) per year (Table A1).

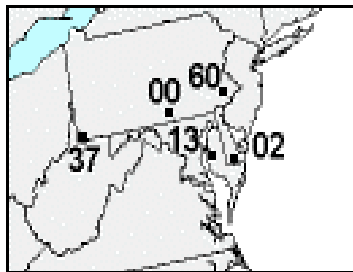


Figure A1: Mercury Deposition Network Monitoring Stations

Table A1: Wet Deposition of Total Mercury

Site	Location	Start Date	End Date	Geo Mean (ug/m ² -yr)
DE02	Lewes, DE	03/14/95	10/08/96	7.71
MD13	Wye, MD	10/03/95	10/08/96	8.10
PA60	Valley Forge, PA	11/23/99	06/26/01	10.48
PA00	Arendtsville, PA	12/12/00	06/26/01	8.63
PA37	Holbrook, PA	06/22/99	11/21/00	7.21
Average				8.43
Stdev				1.26

Estimates for the amount of wet mercury deposition (8.43 ug/m²-yr) were then applied to dry deposition estimates used in EPA-approved RELMAP air deposition analyses (<http://www.epa.gov/region4/water/tmdl/georgia/index.htm>). These analyses calculated the amount of mercury that is deposited from wet and dry sources in the United States using measured amounts of wet deposition and estimated proportions of dry deposition (RELMAP estimates; EPA, 1997).

Particulate, reactive gas (RGM; Hg²⁺), and elemental (Hg⁰) mercury were considered for final depositional estimates in Maryland. Distinction was not made between locally deposited mercury species (RGM; Hg²⁺) and those that deposit farther from source emitters (particulate and Hg⁰), since all forms of mercury are ultimately incorporated into the food web. Final calculations determined that approximately 12.52 ug/m²-yr of mercury is deposited in areas adjacent to Big Piney Reservoir (Table A2).

Table A2: Measured, Estimated, and Total Mercury Deposition

Total Wet Deposition in MD ($\mu\text{g}/\text{m}^2\text{-yr}$) ⁸	RELMAP wet deposition	$\mu\text{g}/\text{m}^2/\text{yr}$ ⁹	Hg Species Ratios (EPA, 1997) ¹⁰	Wet Deposition Total ($\mu\text{g}/\text{m}^2/\text{yr}$) ¹¹
8.43	Hg ²⁺ (RGM) from US	2.65	0.267	2.25
	Particulate Hg from US	1.96	0.197	1.66
	Hg ⁰ from US sources	0.18	0.018	0.15
	Hg ⁰ from global sources	5.14	0.518	4.36
	Total	9.93	1.000	8.43

RELMAP dry/wet deposition ratio	0.486 ¹²
---------------------------------	---------------------

Dry deposition (RELMAP estimate; $\mu\text{g}/\text{m}^2\text{-yr}$) ¹³	RELMAP dry deposition	$\mu\text{g}/\text{m}^2/\text{yr}$ ¹⁴	Hg Species Ratios (EPA, 1997) ¹⁵	Dry Deposition Total ($\mu\text{g}/\text{m}^2\text{-yr}$) ¹⁶
4.10	Hg ²⁺ (RGM) from US	4.10	0.98	4.02
	Particulate Hg from US	0.08	0.02	0.08
	Total	4.18	1.00	4.10

Total Deposition of Reactive Gas Mercury (Hg ²⁺ ; RGM; $\mu\text{g}/\text{m}^2\text{-yr}$)	6.27
Total Deposition of Particulate Mercury ($\mu\text{g}/\text{m}^2\text{-yr}$)	1.74
Total Deposition of Elemental Mercury ($\mu\text{g}/\text{m}^2\text{-yr}$)	4.52
Total Deposition of Mercury ($\mu\text{g}/\text{m}^2\text{-yr}$)	12.52

The wet deposition numbers are taken from the indicated monitoring data. The RELMAP modeled deposition numbers are used to estimate the wet/dry ratio, which is then used to determine dry deposition and then total deposition (wet + dry). The RELMAP estimates are from a national model, so extrapolating to a finer watershed scale is important, as there are differences in deposition rates within Maryland, which should be considered important. The calculated mercury deposition rate for Big Piney Reservoir (12.52 $\mu\text{g}/\text{m}^2\text{-yr}$) was multiplied by the waterbody area (Table A3) to generate annual mercury loadings directly deposited to the waterbody.

⁸ Average geomean from Table A1

⁹ Data from RELMAP model

¹⁰ Individual species divided by total RELMAP

¹¹ = footnote 8 X footnote 10

¹² Data from RELMAP model.

¹³ = footnote 8 x footnote 12

¹⁴ Data from RELMAP model.

¹⁵ Individual species divided by total RELMAP

¹⁶ = footnote 13 x footnote 15

Table A3: Mercury Deposition Estimates for a Select Waterbody

Lake/Impoundment	Area (km ²)	Direct Mercury Deposition to Waterbody (kg/year)
Big Piney Reservoir	0.4452	0.00557

Uncertainty in Mercury Air Deposition Estimates

Quantification of the deposition of mercury from the air relies on many factors that are not derived empirically or from Maryland data. Four of the five mercury deposition network sites used in the estimation of atmospheric mercury deposition were in states adjacent to Maryland (PA and DE). These sites may be influenced by site-specific conditions, and therefore may alter overall deposition means used in subsequent calculations. Extrapolation from wet deposition means relies on modeling factors and estimates proposed in Savannah River TMDLs (EPA, 2000). Specifically, they rely on older regional-scale LaGrangian model (Regional LaGrangian Model of Air Pollution; RELMAP) output that may not represent smaller scales (Maryland) accurately (EPA, 2001). Accuracies in scaling may be of particular importance when considering Maryland RELMAP isopleth model data on wet and dry deposition, since fine alterations in scale could change the wet: dry deposition ratio, and hence the overall estimates of total mercury deposition. Similarly, RELMAP modeling output is based on 1996 mercury emissions estimates and mercury speciation patterns that have not been rigorously investigated. Alteration of speciation ratios would change total depositional estimates directly.

Derivation of the total load relies in part on accurate estimation of the waterbody volume. Waterbody volumes were obtained from an inventory of Maryland dams and impoundments (PPRP, 1999). These were defined as the “volume of water stored below the normal operating pool elevation, excluding any flood storage” and the “impounding capacity in acre-feet, obtained from plans, design computations, or estimated”. Waterbody volume estimates, therefore, may not represent current conditions that have been changed because of subsequent impoundment infilling by sediment or dredging and channelization.

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Appendix B

Addendum For Toxics Methodology – MD 2002 303(d) List: Designated Use Impairments Based on Fish Tissue.

Background:

Section 101(a)(2) of the CWA establishes as a national goal "water quality which provides for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water, wherever attainable." These are commonly referred to as the "fishable/swimmable" goals of the Act. Section 303(c)(2)(A) requires water quality standards to protect the public health and welfare, enhance the quality of water, and serve the purposes of the Act (EPA 2000). EPA, along with the Department, has interpreted these regulations to mean that not only should waters of the State support thriving and diverse fish and shellfish populations, but when caught, may also be safely consumed. Some water bodies may have elevated levels of contaminants, especially in the sediment. Some of these contaminants (especially mercury and PCBs) tend to bioaccumulate to elevated levels in the tissues of game fish and "bottom-feeders" (largemouth bass and catfish, respectively). When tissue levels of a contaminant are sufficiently elevated to increase the risk of chronic health effects if the fish is consumed regularly, the State has the responsibility to issue a fish consumption advisory to protect public health. Fish consumption advisories are designed to protect the general population as well as sensitive populations (i.e. young children; women who are or may become pregnant). If consumption advisory is issued for a waterbody, its designated use may not be supported and that waterbody may be listed as impaired for the contaminant(s) responsible for the fish consumption advisory.

The Department of the Environment has defined "fishable" as the ability to eat AT LEAST 4 meals/month (general population level) for common recreational fish species from a given waterbody. The tissue level corresponding to this will be the upper threshold at the 4 meal/month level for a given contaminant. In addition to this, if the tissue concentration is within 5% of the threshold, the water body's designated use will be considered impaired. The 5% "safety factor" accounts for the uncertainty and spatial/temporal variability in monitoring data and sampling regimes. This safety factor is designed to protect and maintain the "fishable" designated use status of a waterbody. To determine if a waterbody is impaired, the appropriate measure of central tendency (i.e. geometric mean) for a contaminant from the fillet samples of common recreational fish species will be compared to the established threshold. If the threshold is exceeded, the water body's designated use is not met, and the waterbody is considered impaired.

Data Requirements:

The data required to list a waterbody as impaired are similar to the data requirements for the development of a fish consumption advisory. The same decision rules are used to test data adequacy, and spatial and temporal representation. Consumption advisories based on the minimum required samples that resulted in an impairment decision will be

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re-sampled prior to TMDL development to insure that the advisory was not due to a localized condition, and that the impairment is still temporally relevant. The data requirements for listing a waterbody are:

- a. The advisory is based on fish and shellfish tissue data. All available data will be used.
- b. The data are collected from the specific waterbody in question.
- c. A minimum of 5 fish from a given species (individual or composite analysis) for a given waterbody.
- d. 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 should only be used in conjunction with resident species, especially in the case of tidal rivers of the Chesapeake Bay.
- e. Contaminant thresholds used will reflect concentrations used to set consumption recommendations for the general population. The general population is defined as women beyond the years of childbirth (~45); and adult males.

In some instances, it may be inappropriate to consider certain fish and shellfish consumption advisories in making an impairment determination. For example, a State may have issued a statewide or regional warning, based on data from a subset of water bodies and species or a higher consumption value may have been used in determining the need for an advisory to protect a specific sensitive population compared to the value used in establishing water quality criteria for the protection of human health. In such instances, these types of advisories were not considered for making an impairment determination. This approach is consistent with EPA's current recommendations regarding impairment determinations using contaminant data from fish advisories.

Appendix C

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. Selected physical properties are listed in Table C1. Among the varied industrial and consumer uses of mercury are electrical apparatus, 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 a constituent of a number of antiseptics such as *mercurochrome*, *merthiolate* and *mercressin*. Mercury and all its compounds are toxic. Mercury fulminate, $\text{Hg}(\text{CNO})_2$, is used as a detonator for initiating the explosion of smokeless powder and various high explosives (TNT, dynamite). 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 C1: Physical Properties of Metallic Mercury

Atomic Number	80
Atomic Weight	200.59
Density	$13.5 \text{ g/cm}^3 @ 25^\circ\text{C}$
Melting Point	-39°C
Boiling Point	357°C
Water Solubility (molarity)	$3.0 \times 10^{-7} \text{ (mol/L) @ } 25^\circ\text{C}$
Water Solubility (mass basis)	$60 \text{ } \mu\text{g/L @ } 25^\circ\text{C}$

Source: Dean, 1992.

Mercury exists in three oxidation states: the metallic, uncharged state (Hg^0); the mercurous state (Hg^{+1}); and the mercuric state (Hg^{+2}). These states are separated by only a small oxidation potential, 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).

Mercury in natural waters may assume any of the three oxidation states. The predominate state is determined by the hydrogen ion concentration (described as pH) and the oxidation potential (Eh) 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, 1971, Gilmour and Henry 1991; Shimomora 1989). Ammonium, carbonate, bicarbonate and phosphate concentrations do not affect speciation (PPRP).

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In natural systems, pH is generally in the range of 5 to 8 and the Eh is typically less than 0.5 Volts. For these systems, HgS and metallic mercury are the most likely solids to be found in equilibrium with saturated solutions of mercury salts at moderate Cl^{-1} and S^{-2} concentrations. The predominate species in the corresponding solutions will be $\text{Hg}(\text{OH})_2$ and 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).

Methylated forms of mercury, CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$, are formed in both aerobic and anaerobic sediments through the action of bacteria. Methylated mercury is thought to be thermodynamically unstable in water; quantities of organic mercury found in surface waters are probably preserved through reaction barriers that prevent degradation. Methylation does not occur in the presence of moderate to high sulfide concentrations which immobilize the Hg^{+2} ion (PPRP).

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 fish (trophic level 4) can present a potential health risk to humans. The health risk to humans represented by the mercury content in consumed fish tissue is due the chemical, methylmercury. Typically, almost all of the mercury found in fish tissue (90 to 95%) is in the methylmercury form. Mercury chemistry in the environment is complex and not totally understood. Mercury has the properties of a metal, specifically, persistence in the environment because it is not chemically broken down beyond the elemental mercury form (Hg^0) or its ionic forms (Hg^+ and Hg^{+2}). It 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 solution under anerobic 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 will bioaccumulate as it has a strong affinity for fish muscle tissue. It is effectively transferred through the food web, with tissue concentrations magnifying at each trophic level. This process can result in high levels of methylmercury in organisms high on the food chain, despite nearly immeasurable quantities of mercury/methylmercury concentrations in the water column.

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Appendix D

Details of Mercury Source Assessment

Appendix D presents background information regarding potential sources of mercury.

Table D1: Industrial and Consumer Uses of Mercury

U. S. Mercury consumption (10 ³ kg) by end-use (based on Neme 1991)				
Use	1980	1985	1987	1989
Chlorine and Caustic Soda	326	234	310	380
Paint	298	168	198	191
Other Chemical Manufacturing Uses	104	74	78	58
Wiring and Switches	106	96	130	140
Batteries	958	950	532	250
Lighting and Other Electrical Uses	40	40	46	30
Dental Equipment/Instruments	174	128	118	126
Miscellaneous	28	20	34	36
Total	2,034	1,710	1,446	1,211
Sources: U.S. Department of the Interior (1983,1990,1991)				

In Maryland, the major sources of mercury air emissions are as follows: 43% attributed to power plants, 31% municipal waste combustors, 19% medical waste incinerators, 6% Portland Cement plants, and 1% other (e.g., landfills, oil-fired power plants, other industries).¹⁷

US industrial demand for mercury dropped 75% from 1988 to 1997. This drop can be attributed to actions including:

- Federal bans on mercury additives in paint and pesticides;
- Industry efforts to reduce mercury in batteries;
- Increasing state regulation of mercury emissions and mercury in products;
- State-mandated recycling programs; and
- Voluntary actions by industry.¹⁸

¹⁷www.mde.state.md.us/programs/landprograms/hazardous_waste/mercury/mercuryinfo.asp

¹⁸Source: www.epa.gov/mercury/information.htm

Table D2: Incineration Facilities

Major Municipal Solid Waste Incineration Facilities in Maryland			
Facility	Location	Total Waste Burned (kg/year)	Air Pollution Control Equipment
Waste Energy Partners	Edgewood	215 x 10 ⁶	ESP
Pulaski Highway	Baltimore	491 x 10 ⁶	ESP
Baltimore Refuse Energy System Co. (BRESKO)	Baltimore	1,281 x 10 ⁶	ESP

Electrostatic precipitators (ESP), which are widely used to control fine particulate matter, are ineffective at capturing gaseous emissions, including mercury vapor. The most efficient mercury controls include multi-stage wet scrubbers, high efficiency ESPs in series with wet scrubbers, activated carbon filters and removal of the waste stream prior to incineration.

Table D3: Maryland Estimated Mercury Emissions from Coal-burning Power Plants

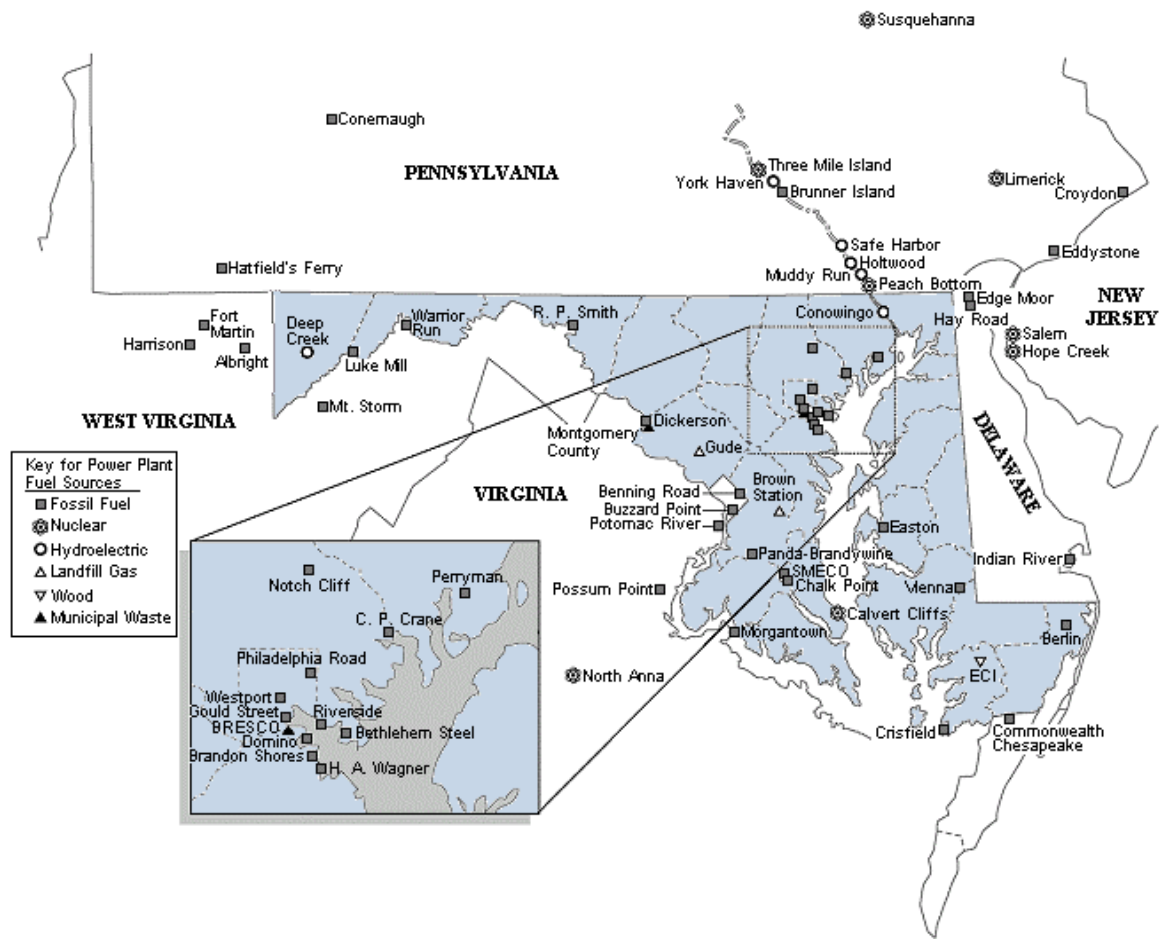
Plant	Parent Company	City	Estimated* Total Mercury Released 1998 (pounds)	Estimated** Mercury Air Pollution 1998 (pounds)
Brandon Shores	Baltimore Gas & Electric Co.	Baltimore, MD	604	489
Morgantown	Potomac Electric Power Co.	Newberg, MD	645	404
Chalk Point	Potomac Electric Power Co.	Aquasco, MD	549	302
Dickerson	Potomac Electric Power Co.	Dickerson, MD	483	290
H. A. Wagner	Baltimore Gas & Electric Co.	Baltimore, MD	221	149
C. P. Crane	Baltimore Gas & Electric Co.	Baltimore, MD	225	117
R. Paul Smith	Allegheny Power System, Inc.	Williamsport, MD	45	28
State Total			2,774	1,781

*Estimated mercury in coal is calculated using plant specific coal contamination and coal consumption data. Release includes disposal in ponds and landfills as well as reuse applications such as fertilizer.

** Total stack emissions are calculated by applying mercury released to plant specific modification factors.

Sources:

Environmental Working Group. Compiled from U. S. Department of Energy and U. S. Environmental Protection Agency databases. Plant ownership is attributed to the parent company of the plant as of January 1, 1999.



Source: Maryland Power Plant Research Program - Fact Book

Figure D1: Power Plant Locations In and Around Maryland

Appendix E

Risk Assessment

Fish consumption advisory thresholds were determined by utilizing human health risk assessment procedures presented in EPA (1997) and modifications as in MDE (in prep, 2002). These advisories recommend that a certain number of meals per month of a particular fish species not be exceeded in order to avoid long-term health effects from exposure to methylmercury.

Variables considered in the advisory risk assessment included: **meal frequency** (0, 1, 2, 4, 8, or unlimited meals per month), **meal size** (8 ounces for people 18-75 (GP) and women 18-45 (WOM) years of age, 3 ounces for children (CHD) 0-6 years of age), and **population weights** of 70 (GP), 64 (WOM), and 14.5 (CHD) kilograms. A **methylmercury reference dose** (RfD, 0.1ug/kg-day), based on neurological and developmental studies of infants chronically exposed to methylmercury through fish consumption, was also used in the risk analysis. These factors can be seen in Table E1

Table E1: Human Health Risk Assessment Parameters for MDE's Fish Consumption Advisories

RfD (ug/kg-day)	Body Weight (kg)	Meal Size (ounces/meal)	Fish Consumption Rate (kg/day)	Recommended Meal Frequency (meals/month)	Mercury Concentration in Fish Tissue (ppm)	
Men and Women 18 - 75 Years Old						
0.1	70	8	3.7	No Consumption	>	0.939
0.1	70	8	7.5	1	0.470	- 0.939
0.1	70	8	14.9	2	0.236	- 0.469
0.1	70	8	29.8	4	0.118	- 0.235
Women 18 - 45 Years Old						
0.1	64	8	3.7	No Consumption	>	0.858
0.1	64	8	7.5	1	0.430	- 0.858
0.1	64	8	14.9	2	0.216	- 0.429
0.1	64	8	29.8	4	0.108	- 0.215
Children 0 - 6 Years Old						
0.1	14.5	3	1.4	No Consumption	>	0.519
0.1	14.5	3	2.8	1	0.260	- 0.519
0.1	14.5	3	5.6	2	0.131	- 0.259
0.1	14.5	3	11.2	4	0.066	- 0.130

EPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories; Third Edition. Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency, Washington, D.C.

Appendix F

UMCES Procedures

Sample Collection:

Clean double-bagged 2L Teflon bottles, partially filled with dilute trace metal grade HCl, were used for water collection. Prior to sampling, each bottle was emptied of the HCl downstream from the sampling location. Next, the bottle was rinsed three times with reservoir water and filled with water collected approximately 6 to 12 inches below the surface. After being filled with sample-water, the bottle was immediately recapped, double-bagged and stored in a cooler for transport back to the laboratory.

Sample filtration and storage:

Approximately 0.5 L of sample from each bottle was filtered through an acid cleaned AquaPrep 600 in line filter (0.45 um) into an acid washed and sample rinsed 500 ml Teflon bottle for dissolved Hg and MeHg. All equipment used for filtering was acid washed between samples and rinsed with Q-water. Both unfiltered and filtered water samples were spiked with Optima HCl acid (to 0.5%) and stored in a refrigerator until analysis for HgT and MeHg was performed.

Total Mercury

Based on U.S. EPA, *Method 1631, mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*, October 2001.

Methylmercury

Bloom, NS (1992) Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. *Canadian Journal of Fisheries and Aquatic Sciences*, vol 46 1131-1140; Bloom, NS.

MeHg analysis

Water samples were distilled with additions of a 50% sulfuric acid solution and a 20% potassium chloride solution (Horvat et al., 1993). The MeHg in the distillate was derivitized with sodium tetraethylborate to convert it to volatile methyl-ethyl-mercury (Bloom, 1989). The volatile adduct was then purged from solution and collected onto a graphitic carbon trap. The MeHg was then thermally desorbed from the trap and analyzed by isothermal gas chromatography separation with CVAFS.

Total Hg analysis

BrCl was added to each sample at least 2 hours prior to analysis. Just prior to analysis, hydroxylamine hydrochloride was added to destroy any excess bromine in the sample. The samples were trapped by gold amalgamation after reduction with SnCl₂. The Hg

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was then thermally desorbed from the trap and analyzed by CVAFS. (Mason et al., 1997; 1983; Bloom, 1989).

Chemical form of mercury in edible fish and marine invertebrates
Canadian Journal of Fisheries and Aquatic Sciences, vol. 49, 1010-1017.

Appendix G

Individual Sample Data and Analysis

This appendix presents all of the data for fish tissue samples and water column samples. The data reduction steps are also described.

Table G1: Individual fish sample data for mercury residue in fish tissue from Big Piney Reservoir

Sample ID No.	Trophic Level	Species	Collection date	Methylmercury (µg/kg) wet weight	Length (mm)	Weight (gm)
BPI061801LMB1	4	Largemouth Bass	6/18/2001	263.5	305	398.6
BPI061801LMB2	4	Largemouth Bass	6/18/2001	401.7	305	404.8
BPI061801LMB3	4	Largemouth Bass	6/18/2001	441.6	305	358.5
BPI061801LMB4	4	Largemouth Bass	6/18/2001	653.0	350	541.5
BPI061801LMB5	4	Largemouth Bass	6/18/2001	577.4	315	423.8
BPI061801LMB6	4	Largemouth Bass	6/18/2001	783.0	380	849.8
BPI061801LMB7	4	Largemouth Bass	6/18/2001	895.8	400	962.0
BPI061801LMB8	4	Largemouth Bass	6/18/2001	546.9	370	669.2
BPI061801LMB9	4	Largemouth Bass	6/18/2001	815.6	370	775.7
BPI061801LMB10	4	Largemouth Bass	6/18/2001	557.6	385	982.8
BPI061801LMB11	4	Largemouth Bass	6/18/2001	967.5	465	1,536.5
BPI061801LMB12	4	Largemouth Bass	6/18/2001	434.6	410	1,001.7
BPI061801LMB13	4	Largemouth Bass	6/18/2001	675.5	420	1,028.8
BPI061801LMB14	4	Largemouth Bass	6/18/2001	443.8	415	872.2
BPI061801LMB15	4	Largemouth Bass	6/18/2001	770.6	408	900.0

An analysis of the length and weight of the fish used in the BAF calculation indicates that the fish were of legal (keepable) size and that the average age was approximately five to six years (MDDNR, 2000).

Water column samples were collected from the reservoir. Where possible, three samples were taken from just below the inflow, the middle, and just above the outfall of the reservoir (in some instances, access limitations prevented the collection of all three samples).

The analytical method used for these analyses (*U. S. EPA Method 1631*) has a minimum detection level of 0.5 ng/L. One nanogram per liter represents a detection level of one part per trillion. As all analytical methods have, *Method 1631* has an inherent variability of about +/- 15%. All the data was subject to laboratory quality assurance/quality control procedures, prior to being released to MDE (such as blanks, spiked samples, etc.). However, due to the sensitive nature of this test, there are cases in which the results from the same sample show a larger concentration of dissolved mercury than the total concentration. When this occurs, and the difference is within the inherent range of variability, the two values must be interpreted as being the same. To check this, a data reduction process was developed and employed as described below.

Water Column Data Reduction Process

The TMDL analysis requires that we aggregate a number of samples into a single value that represents an estimate of the central tendency of the data. This data reduction process also must account for any data that we suspect is not valid.

Performing a laboratory analysis for trace elements is a very sensitive undertaking. The potential error in the measurements for mercury in the water column is about 15 % in either direction (over or under estimation). This implies that two samples that are within 30% of each other cannot be considered different.

The measurement of whole concentrations (dissolved plus particulate) is less subject to error than measurements of dissolved concentrations. This is because measuring whole concentrations does not require a filtration step, which can introduce error. In cases where the dissolved values are significantly greater than the whole sample (20% or more), it has been advised that the dissolved sample not be used due to the potential contamination during the filtration process (Mason, 2002, personal communications).

The data reduction process described below addresses pairs of water column samples of total mercury representing whole samples and dissolved samples. It is outlined in the form of decision rules to address all of the different cases that can be confronted.

For each pair of results from a given sample, whole and dissolved:

- i. If the whole sample is more than 20% greater than the dissolved sample, keep both numbers as good, and interpret the difference as being the particulate fraction.
- ii. If the whole sample and dissolved are within 20% of each other, compute the arithmetic mean of the two numbers. Use this average value to represent both whole and dissolved values in future calculations.
- iii. If the dissolved number is more than 20% greater than the whole, discard the dissolved as being contaminated. Interpret the whole value as dissolved, and use this value to represent both whole and dissolved values in future calculations.

**Table G2: Water Column Total Mercury Concentration Data
from Big Piney Reservoir**

Sample Date	Sample Site	Total Mercury Concentration (Whole) ng/L	Total Mercury Concentration (Dissolved) ng/L	% Difference (whole-dissolved)/dissolved
8/02/02	Downstream of Inflow	1.70	0.593	187
8/02/02	Mid Reservoir	3.86	2.22	78
	Geometric Mean Value	2.56	1.06	145

In both cases the percentage differences are greater than 20 % and case i applies. The results of the data reduction process are presented in Table G3. The value of 2.56 ng/L represents the expected whole water column concentration for total mercury. The value of 1.06 ng/L represents the expected water column concentration of dissolved mercury. The difference represents the expected particulate fraction.

**Table G3: Data Reduction for Total Mercury Water Column Concentrations
for Big Piney Reservoir**

Sample Site	Total Mercury Concentration (Whole) ng/L	Total Mercury Concentration (Dissolved) ng/L
Downstream of inflow	1.70	0.593
Mid Reservoir	3.86	2.22
Geometric Mean Values	2.56	1.06

**Table G4: Water Column Methylmercury Concentration Data
from Big Piney Reservoir**

Sample Date	Sample Site	Methylmercury Concentration (Whole) ng/L	Methylmercury Concentration (Dissolved) ng/L	% Difference (whole-dissolved)/dissolved
8/02/02	Downstream of Inflow	0.352	0.265	33
8/02/02	Mid Reservoir	0.259	0.322	- 22
	Geometric Mean Value	0.302	0.292	3

Table G5 presents the reduced water column data for whole methylmercury and dissolved methylmercury. We check the percentage difference of each pair of samples presented in Table G4. For the Downstream sample the percentage difference is greater than 20 %

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(whole >dissolved) and thus the sample follows case i. For the Mid Reservoir sample the percentage difference is greater than 20 % (whole <dissolved) and thus the sample follows case iii. The value of 0.302 ng/L represents the expected whole water column concentration for methylmercury. The value of 0.262 ng/L represents the expected water column concentration of dissolved methylmercury. The difference represents the expected particulate fraction.

Table G5: Data Reduction for Dissolved Methylmercury Water Column Concentrations for Big Piney Reservoir

Sample Site	Methylmercury Concentration (Whole) ng/L	Methylmercury Concentration (Dissolved) ng/L
Downstream of inflow	0.352	0.265
Mid Reservoir	0.259	0.259
Geometric Mean Values	0.302	0.262

Appendix H

TMDL Target Concentration (AAWCC Value Adjustment)

The AAWCC initially calculated in Section 4.3.2 is just the dissolved part of the total mercury in the reservoir. However when we compute a total load to the reservoir we are assuming that both dissolved and particulate components are included in the load. That is, when we compute the TMDL via a mass balance calculation, we need the calculation target to be a whole value (dissolved + particulate). The dissolved component is the AAWCC; the particulate part is determined by the ratio of the dissolved and particulate that was observed for the existing data. Implied in this is the assumption that when the load is reduced, the ratio of dissolved to particulate total mercury remains constant. Therefore the formula for calculating the TMDL target concentration is expressed as:

$$\frac{\text{Observed whole total Hg value}}{\text{Observed dissolved total Hg value}} = \frac{X}{\text{AAWCC}}$$

Solving for X yields the TMDL target concentration:

$$\frac{2.56}{1.06} = \frac{X}{0.312}$$

$$X = 0.754 \text{ ng/L total mercury}$$

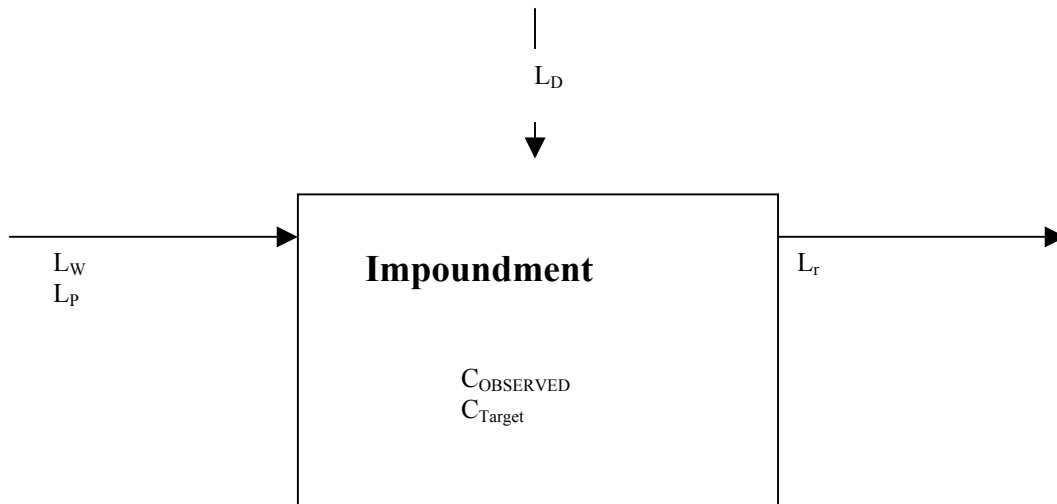
As explained, X – AAWCC equals the particulate fraction.

Appendix I

Steady State Mass Balance Calculations

This Appendix describes the mass balance calculations used to estimate the mercury loads into and out of the impoundment and is divided into four sections. The first section describes the mass balance equations. The second section describes parameters used, lists general definition of terms and identifies the location in the report to find data. The third and fourth sections show in detail the calculations for current loads and the total maximum daily loads, respectively.

Mass Balance Equations:



The assumptions for the Mercury TMDL calculation is that the system is in steady state and therefore the outflow load can be calculated from the impoundment discharge and a specified water column concentration. To calculate the current load, the observed water column concentration is used and to calculate the TMDL, the target water column concentration is used (see Appendix H for details on the target water column concentration). Therefore the following steady state mass balance equation can be used to determine current loads and future allocations.

$$\Sigma \text{ Load In} = \Sigma \text{ Load out}$$

The above equation can be further expanded to

$$L_p + L_D + L_W = L_r$$

It is important to note that if no point sources are present into the impoundment then L_p equals zero.

Definitions:**Point Source Information:**

Parameter	Description	Source
Q_p	Point source flow into the impoundment	Table 2
C_p	Mercury concentration into the impoundment, attributed to point sources	Section 2.1
L_p	Mercury load into the impoundment, attributed to point source loads	Calculated
Q_{fp}	Future permitted maximum point source flow into the impoundment	Table 2
C_{fp}	Future permitted point source Mercury concentration into the impoundment (Same as C_p)**	Section 2.1
L_{fp}	Future mercury load into the impoundment, due to anticipated increased point source flows	Calculated
% Time Active	Percent of time point source is active during one year period.	Section 2.1

Reservoir Information:

Parameter	Description	Source
Q_r	Average annual flow out of reservoir	Table 1
C_r	Observed reservoir water column total mercury concentration after data reduction	Appendix G
L_r	Current mercury load from reservoir	Calculated

Atmospheric Deposition:

Parameter	Description	Source
RSA	Reservoir surface area	Table 1
TDM	Total deposition of mercury	Appendix A
L_d	Mercury load due to direct atmospheric deposition to the impoundment	Calculated
L_{da}	Allowable mercury load due to direct atmospheric deposition to the impoundment	Calculated

* Point source contributions of mercury are currently unknown. All estimates are intentionally high to ensure that the future allocation developed in this TMDL is sufficient to address a future point source allocation if deemed appropriate.

** It is assumed that the concentration stays constant, although the point source flows may increase over time.

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Definitions (Continued):

Watershed:

Parameter	Description	Source
Lw	Existing mercury load from the watershed to the impoundment	Calculated
Lwa	Allowable mercury load from the watershed to the impoundment	Calculated

TMDL Calculation:

Parameter	Description	Source
	Corrected Water Column Concentration Target	Appendix H
Fr	TMDL coefficient is the factor by which the atmospheric deposition and watershed loads must be multiplied by to determine the allowable loads	Calculated
1-Fr	The percent reduction required from the atmospheric deposition and watershed loads.	Calculated
FA	The future allocation, which may be used to address point sources if warranted by future information	Calculated
LA	The load allocation is the sum of the atmospheric deposition load and the watershed load after the TMDL reduction factor (Fr) is applied $LA=Fr*(Ld+Lw)$	Calculated

Current Load Calculation

Location: Big Piney Reservoir

Point Source Contribution

Average Annual

%time active= n/a

Qp= n/a MGD $\times (3.785\text{l/gal}) \times (1\text{e}6\text{gal/1MGal}) \times (\% \text{time}) =$ n/a l/d

Note: Qp accounts for percent of time active

Cp= n/a ng/l

Lp= 0.000000 g/day = Qp[l/d] * Cp[ng/l] * (1e-9g/ng)

Permit Maximum

%time active= n/a

Qfp= n/a MGD $\times (3.785\text{l/gal}) \times (1\text{e}6\text{gal/1MGal}) \times (\% \text{time}) =$ n/a l/d

Note: Qp accounts for percent of time active

Cfp= n/a ng/l

Lfp= n/a g/day = Qfp[l/d] * Cfp[ng/l] * (1e-9g/ng)

Reservoir Information

Qr= 0.645 m³/s $\times (1000\text{l/m}^3) \times (86400\text{sec/1day}) =$ 55,728,000 l/d

Cr= 2.56 ng/l

Lr= 0.1427 g/d = Qr[l/d] * Cr[ng/l] * (1e-9g/ng)

Atmospheric Deposition

RSA= 0.4452 km² =Reservoir Surface Area

TDM= 12.52 ug/m²/yr =Total Deposition of Mercury

Ld= 0.005574 kg/yr =RSA*TDM*((1000m/1km)²)*(1g/1e6ug)*(1kg/1000g)

0.0153 g/d =Ld*(1000g/kg)*(1yr/365day)

Watershed

Lw=Lr-Ld-Lp

Lw= 0.1274 g/d

Summary-Current Daily Total Load

Lp= 0.000000 g/d (0.0000%)

Ld= 0.015271 g/d (10.7042%)

Lw= 0.127393 g/d (89.2958%)

Ld+Lw+Lp= 0.142664 g/d

Calculation of the Maximum Allowable Load

TMDL Calculation

Corrected Water Column Conc. Target= 0.754 ng/l
 Reservoir Flow (Qr)= 55,728,000 l/d
 $TMDL=(Qr)[l/d]*(Ct)[ng/l]*[1e-9g/ng]= 0.0420 \text{ g/d}$ Annual TMDL=0.042g*365= 15.34 g/yr

Future Allocation

Future Point Source Contribution = 0.0000% =Lfp/TMDL Lfp= 0.000000 g/d
 Total Future Allocation w/ ps= 3.00% FA= 0.001261 g/d
 Note: Total Future Allocation includes max permit point source Future Allocation=TMDL*(%contribution)

TMDL Reduction Factor

$TMDL=(Lw+Ld)*Fr+Lf$
 $Fr=(TMDL-Lf)/(Lw+Ld)$
 Fr= 0.2857 % Reduction=(1-Fr)= 71.43%

TMDL Summary

					% Contribution
FA(TMDL*%FA)=	0.04202	g/d x	3.00%	=	0.001261 g/d (3.00%)
Lda (TMDL*Fr)=	0.01527	g/d x	0.2857	=	0.004363 g/d (10.38%)
Lwa (TMDL*Fr)=	0.12739	g/d x	0.2857	=	0.036396 g/d (86.62%)
Check:	Sum=	0.042019	g/d =		0.0420 g/d TMDL
LA=	0.04076 g/d (Ld+Lw)				14.8768 g/yr
FA=	0.00126 g/d (Lf)				0.46011 g/yr

Notes: =inputs